

การเตรียมพอลิอะลูมิเนียมคลอไรด์และพอลิอะลูมิเนียมซิลิเกตคลอไรด์จากกากตะกอนของ  
กระบวนการผลิตเรซินที่มีคาร์บอน 5 อะตอม

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PREPARATION OF POLY(ALUMINIUM CHLORIDE) AND  
POLY(ALUMINIUM SILICATE CHLORIDE) FROM SLUDGE OF  
C5 RESIN PROCESS

Mr. Sookhasart Jareronpol

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

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Thesis Title                    PREPARATION OF POLY(ALUMINIUM CHLORIDE)  
   AND POLY(ALUMINIUM SILICATE CHLORIDE)  
   FROM SLUDGE OF C5 RESIN PROCESS

By                                    Mr. Sookhasart Jareronpol

Field of Study                    Petrochemistry and Polymer Science

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สุทธศาสตร์ เจริญผล : การเตรียมพอลิอะลูมิเนียมคลอไรด์และพอลิอะลูมิเนียมซิลิเกตคอลลอยด์จากกากตะกอนของกระบวนการผลิตเรซินที่มีคาร์บอน 5 อะตอม. (PREPARATION OF POLY(ALUMINIUM CHLORIDE) AND POLY(ALUMINIUM SILICATE CHLORIDE) FROM SLUDGE OF C5 RESIN) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร. ศุภวรรณ ตันตยานนท์, 57 หน้า.

ในกระบวนการผลิตเรซินที่มีคาร์บอน 5 อะตอม จะเกิดกากตะกอนของเสียที่ประกอบไปด้วยอะลูมิเนียมไฮดรอกไซด์ ซึ่งในปัจจุบันได้ทำการกำจัดโดยการฝังกลบ ในงานวิจัยครั้งนี้จึงได้นำกากตะกอนดังกล่าวมาใช้เป็นสารตั้งต้นในการสังเคราะห์พอลิอะลูมิเนียมคลอไรด์ ซึ่งมีการควบคุมอัตราส่วนของไฮดรอกไซด์ต่ออะลูมิเนียมอยู่ในช่วง 0-3 และพอลิอะลูมิเนียมซิลิเกตคอลลอยด์ ซึ่งอัตราส่วนของซิลิคอนต่ออะลูมิเนียมอยู่ในช่วง 5-20 โดยวิธีแอซิดไฮโดรไลซิส กากตะกอนที่อบแห้งพบปริมาณอะลูมินา 43.95 เปอร์เซ็นต์โดยน้ำหนัก และมีปริมาณอะลูมิเนียม 23.26 เปอร์เซ็นต์โดยน้ำหนัก ได้ศึกษาลักษณะทางกายภาพของพอลิอะลูมิเนียมคลอไรด์ และพอลิอะลูมิเนียมซิลิเกตคอลลอยด์ โดยเทคนิคเอกซเรย์ดิฟแฟรกชัน, ฟลูออโรกราฟ, สฟอรัมอินฟราเรดสเปกโทรสโกปีและการกระจายตัวของพอลิเมอร์ที่เกิดขึ้นด้วยเทคนิคเพอรอน ทดสอบประสิทธิภาพของสารที่ช่วยในการตกตะกอนที่สังเคราะห์ได้ โดยใช้วิธีจาร์เทสกับน้ำตัวอย่างที่มาจากแม่น้ำระยอง เพื่อวัดค่าความขุ่นของน้ำตัวอย่าง, ความเป็นกรด-ด่าง และเวลาในการตกตะกอน พอลิอะลูมิเนียมคลอไรด์ที่มีอัตราส่วนของไฮดรอกไซด์ต่ออะลูมิเนียม 2.5:1 มีประสิทธิภาพในการเป็นสารช่วยการตกตะกอนดีที่สุดในที่มีอัตราส่วนอื่นๆ และให้ผลการทดลองใกล้เคียงกับพอลิอะลูมิเนียมคลอไรด์ที่จำหน่ายทั่วไป ส่วนพอลิอะลูมิเนียมซิลิเกตคอลลอยด์ที่มีอัตราส่วนของซิลิคอนต่ออะลูมิเนียมอยู่ในช่วง 20:1 ให้ประสิทธิภาพสูงสุดเมื่อเทียบกับพอลิอะลูมิเนียมคลอไรด์ที่จำหน่ายทั่วไป

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต.....

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## 5273413123 : PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS : POLY(ALUMINIUM CHLORIDE)/POLY(ALUMINIUM SILICATE CHLORIDE)/ COAGULANT/WASTEWATER TREATMENT

SOOKHASART JARERONPOL: PREPARATION OF POLY (ALUMINIUM CHLORIDE) AND POLY(ALUMINIUM SILICATE CHLORIDE) FROM SLUDGE OF C5 RESIN. ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 57 pp.

Sludge containing aluminium hydroxide generated in the C<sub>5</sub> resin processing, was currently disposed by landfill. In this research, this sludge was used as the raw material for synthesizing poly(aluminium chloride) or PAC. PACs with different OH/Al molar ratios (n= 0-3) and poly(aluminium silicate chloride) or PASiC. PASiC with different Si/Al molar ratios (n= 5-20) were prepared by acid hydrolysis method. The dried sludge contained Al<sub>2</sub>O<sub>3</sub> 43.95 % (w/w) or aluminium content 23.26 % (w/w). The products were characterized by x-ray diffraction spectroscopy, fourier transform infrared spectroscopy, and aluminium species distribution using the ferron technique. The performance of synthesized coagulants was investigated by jar test with water sample from rayong river and was monitored with turbidity, pH and time of coagulation. The PAC with OH/Al molar ratios (2.5:1) exhibited to be the best of all PACs and gave similar results of comercial PAC and the PASiC with Si/Al molar ratios (1:20) gave high performance more than comercial PAC.

Field of Study : Petrochemistry and Polymer Science Student's Signature.....

Academic Year : 2011..... Advisor's Signature .....

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## LIST OF ABBREVIATIONS

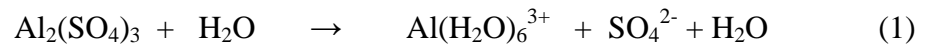
°C	:	degree Celsius
mg	:	milligram (s)
g	:	gram (s)
ppm	:	parts per million
mL	:	milliliter (s)
mm	:	millimeter
cm	:	centimeter
cm <sup>-1</sup>	:	unit of wavenumber (IR)
% w/w	:	percent weight by weight
% w/v	:	percent weight by volume
FT-IR	:	Fourier transform infrared spectrophotometry
XRF	:	X-ray fluorescence spectrometry
XRD	:	X-ray diffraction
PAC	:	poly(aluminium chloride)
PASiC	:	poly(aluminium silicate chloride)

# CHAPTER I

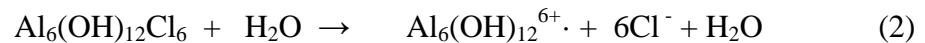
## INTRODUCTION

### 1.1 Background

The almost the coagulant used for water treatment is Alum (aluminum sulfate),  $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$  that were predominantly inorganic salts and has been proven to be an effective coagulant for the removal of contaminants, turbidity and color. Many research efforts have been devoted to improve the efficiency of coagulant, and essential treatment technique in water and wastewater treatment facilities with various applications, including removal of colloids, suspended matter, organic compounds and metal ions.



Nowadays, aluminum salts were developed to polymeric aluminium salts. Poly(aluminum chloride), PAC may be produced by adding hydroxide to chloride and empirical formula of  $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$  ( $0 < m < 3n$ ) is achieved. The positively removal and adsorb anionic substances[1]. Moreover, with the increase of pH value, the aluminium ion begins to hydrolyze, forming various products [2].



The preparation of polymeric aluminium salts involve the production of two aluminium solutions [3-5]. The primary solution is aluminium chloride and is produced through the processing of an aluminium containing raw material under vigorous condition with concentrated hydrochloric acid. The secondary solution is sodium aluminate and can be prepared by the dissolution of aluminium in a sodium hydroxide [3].

In process of C<sub>5</sub> resins with a capacity of 22,000 tons per year in one company in Thailand, the semi-sludge containing aluminium hydroxide, Al(OH)<sub>3</sub> approximately 770 tons per year has been generated as shown as in figure 1.1. It has been disposed by landfill, costed around 847,000 Baht or USD 25,000 each year and would gradually cause the damage to the environment. This research aims to transform this sludge into poly(aluminium chloride) which can be used as the coagulant in the water treatment process.



**Figure1.1** The semi-sludge containing aluminium hydroxide, Al(OH)<sub>3</sub>.

Poly(aluminium chloride), PAC, is an aluminium salt with the chemical formula of Al<sub>n</sub>(OH)<sub>m</sub>Cl<sub>(3n-m)</sub>; 0 <m> 3n. In general poly(aluminium chloride) is prepared from the reaction of aluminium metal or aluminium chloride (AlCl<sub>3</sub>.6H<sub>2</sub>O) with sodium hydroxide via the titration [1-2], and the electrochemical method [4]. Poly(aluminium chloride) generated from the dewatered sludge of aluminium pickling baths has also been reported containing either aluminium hydroxide and aluminium sulphate has also been reported to by reacting with hydrochloric acid under high pressure and temperature .

In many years, the research in the coagulation–flocculation field has focused mainly to improve coagulation reagents, with the introduction in the structure of pre-

polymerized coagulants (such as PAC) of other components, either organic or inorganic.

The new coagulant agent is poly(aluminium silicate chloride), PASiC [3]. The preparation was polymerized silica addition into PAC with silicic acid solution, as from different Si/Al and OH/Al molar ratios various products can be derived. Their properties were intensively examined and had proved to be more efficient in lower dosages and in wider pH, temperature and colloids concentration ranges, than the conventional simpler products, leading to cost and operative more effective treatment.

In this case, the product was rather an inorganic metal-polysilicate flocculant (silica was the main component) than a pre-polymerized inorganic coagulant. The method was increased molecular weight and the respective stability and coagulation performance.

## **1.2 Objective of this research**

Preparation of poly(aluminium chloride), (PAC) and poly(aluminium silicate chloride), (PASIc) from semi-solid sludge from C<sub>5</sub> resin process and compared efficiency of coagulant between poly(aluminium chloride), poly(aluminium silicate chloride) and poly(aluminium chloride) commercial grade.

## **1.3 Scope of this research**

Synthesis poly(aluminium chloride), (PAC) [1-2] and poly(aluminium silicate chloride), (PASIc) [3] with different OH/Al molar ratios (n= 0, 1, 2, 3) and Si/Al molar ratios (n= 5, 10, 20) were prepared by acid hydrolysis method. The product was characterized by x-ray diffraction spectroscopy, fourier transform infrared spectroscopy, and aluminium species distribution with the ferron technique, percentage of basicity, percentage of alumina (Al<sub>2</sub>O<sub>3</sub>) content and efficiency of coagulant to water sample with jar test, turbidity, chemical oxygen demand and pH



## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Coagulants [6]

Coagulation can be accomplished through the addition of inorganic salts of aluminum which neutralize the charge on the particles causing raw water turbidity, and also hydrolyze to form insoluble precipitates, which adsorb particles.

The coagulant chemicals have two types, one is the inorganic coagulants and another is polymeric coagulant or coagulant polyelectrolytes.

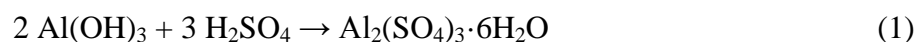
##### 2.1.1 Inorganic coagulants

Primary coagulants neutralize the electrical charges of particles in the water which causes the particles to clump together such as aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$ ), ferrous sulfate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ), ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ ), ferric chloride ( $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ). They are acid salts, pH less than 7 and treated water by hydrolysis. Depend on initial raw water alkalinity and pH. Fe and  $\text{Al}(\text{OH})_3$  flocs are the best precipitated at pH levels that minimize the coagulant solubility.

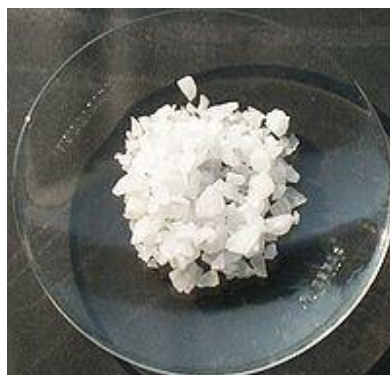
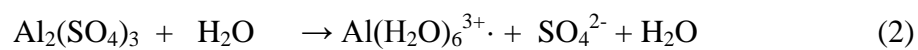
The optimum pH for hydroxide floc formation. Also, aluminum sulfate was good coagulant at pH 6.0 to 7.0. and ferrous sulfate was coagulant can be used successfully over the much broader pH range of 5.0 to 11.0

##### 2.1.1.1 Aluminum sulfate, alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$ ) [7]

Aluminium sulfate or alum used as a flocculating agent in the drinking water purifier, waste water treatment process, and in paper industries. Aluminium sulfate may be made by adding aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , into sulfuric acid,  $\text{H}_2\text{SO}_4$ :



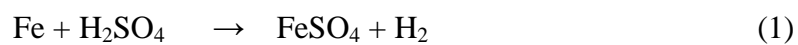
Alum can be used in liquid form with a concentration of 8.3%, or in dry form with a concentration of 17% as shown as in figure 2.1. When alum is dissolved in water, it reacts with the water and results in positively charged ions. The ions can have charges as +3.



**Figure 2.1** Aluminum sulfate , alum.

#### 2.1.1.2 Ferrous sulfate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) [8]

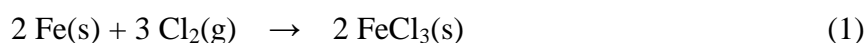
Ferrous sulfate is added in water to give the same complex  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , that has octahedral molecular geometry and is paramagnetic. This treatment produces large quantities of iron (II) sulfate as a by-product.



**Figure 2.2** Ferrous sulfate.

### 2.1.1.3 Ferric chloride ( $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ ) [9]

Iron(III) chloride or ferric chloride ( $\text{FeCl}_3$ ). was dark green, but by transmitted light they appear purple-red. When ferric chloride dissolved in water undergoes hydrolysis and gives off heat in an exothermic reaction. The resulting brown, acidic, and corrosive solution is used as a flocculent in waste water treatment and drinking water process. Iron (III) chloride may be prepared by union of the elements:



**Figure 2.3** Ferric chloride.

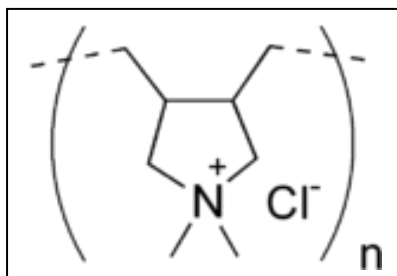
### 2.1.2 Polymeric coagulants [9]

They are strong positive charge and typically have molecular weights less than 400,000. When primary coagulants were used, they adsorb on particle surfaces, reducing the repelling negative charges. These polymers may also bridge, to some extent, from one particle to another but are not particularly effective flocculants. The use of polymeric coagulants permit water clarification without the precipitation of additional hydroxide solids formed by inorganic coagulants. Suspended matter in sample water is removed by various methods to provide a water suitable for domestic purposes and industrial requirements. Removal is generally accomplished by coagulation, flocculation, and sedimentation. The combination of three processes

is referred to as conventional clarification that coagulation is the process of destabilization by charge neutralization. Coagulation is necessary for the removal of the colloidal-sized suspended matter such as polydiallyldimethylammonium chloride (polyDADMAC)

#### 2.1.2.1 Polydiallyldimethylammonium chloride (polyDADMAC) [10]

PolyDADMAC is a homopolymer of diallyldimethylammonium chloride (DADMAC) that is usually delivered as a liquid concentrate having a solids level in the range of 10 to 50%. It is a high charge density cationic polymer. However, PolyDADMAC is used in waste water treatment process as a primary organic coagulant which neutralizes negatively charged colloidal material when compared with inorganic coagulants and used coagulant in water purification. It is effective in coagulating and flocculating inorganic and organic particles.



**Figure 2.4** Chemical structure of polyDADMAC.

## 2.2 Flocculants or coagulant aids [11]

Flocculation can be enhanced by the addition of high molecular weight that is water soluble organic polymers. They increase floc size by charged site binding and by molecular bridging.

Flocculant increased density to slow-settling flocs and toughness to the flocs so that they will not break up during the mixing and settling processes such as cationic polymer, anionic polymer, nonionic polymer, etc. Three flocculants groups are currently used;

### 2.2.1 Mineral flocculants [12]

They are colloidal substances. Adsorption and charge neutralization play some part in the flocculation mechanism, such as activated silica, certain colloidal clays, etc. Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), or slaked lime, is an inorganic compound with the chemical formula  $\text{Ca}(\text{OH})_2$ . It is a colorless crystal or white powder and is obtained when calcium oxide. Calcium hydroxide is used in many applications, including food preparation. When heated to  $512\text{ }^\circ\text{C}$ , the partial pressure of water in equilibrium with calcium hydroxide reaches 101 kPa, which decomposes calcium hydroxide into calcium oxide and water.



A suspension of fine calcium hydroxide particles in water is called milk of lime. The solution is called lime water and is a medium strength base that reacts with acids and attacks many metals. Lime water turns milky in the presence of carbon dioxide due to formation of calcium carbonate:



Calcium hydroxide adopts a polymeric structure, Strong hydrogen bonds exist between the layers. Calcium hydroxide is produced commercially by treating lime with water:



In laboratory, it can be prepared by mixing an aqueous solutions, of calcium chloride and sodium hydroxide. The mineral form, portlandite, is relatively rare but can be found in some volcanic, plutonic, and metamorphic rocks. This application is enabled by the low cost and non-toxicity of calcium hydroxide. It is also used in fresh water treatment for raising the pH of the water so that the pipes will not corrode where the base water is acidic because it is self-regulating and does not raise the pH too much.



**Figure 2.5** Calcium hydroxide.

### **2.2.2 Natural flocculants [13]**

They are 3 types of water soluble as anionic, cationic or nonionic polymers. Nonionic polymers adsorb on the suspended particles. The most common natural flocculants are the starch derivatives that can be natural starches, anionic oxidized starches or amine treated cationic starches. The use of this class of products has decreased in water treatment but remains important in the paper industry, the polysaccharides: usually guar gums and mostly used in acid medium, the alginates: anionic and used in potable water treatment.

### **2.2.3 Synthetic flocculants [14]**

The commonest polymers are a nonionic polymer that dependent upon polyacrylamide. Their effect is owing to bridging between particles by polymer chains. Co-polymerizing acrylamide and acrylic acid can produce anionic character polymers. All acrylamide based polymers have a specific amount of ionic monomer giving a certain degree of ionic character. They have a specific average molecular weight. For each suspension, a certain degree of anionic, cationic or nonionic character is beneficial. Usually, the intrinsic flocculating power increases with the molecular weight. They are mostly such as Polyethylene-imines, Polyamides-amines, Polyamines, Polyethylene-oxide, Sulfonated compounds.

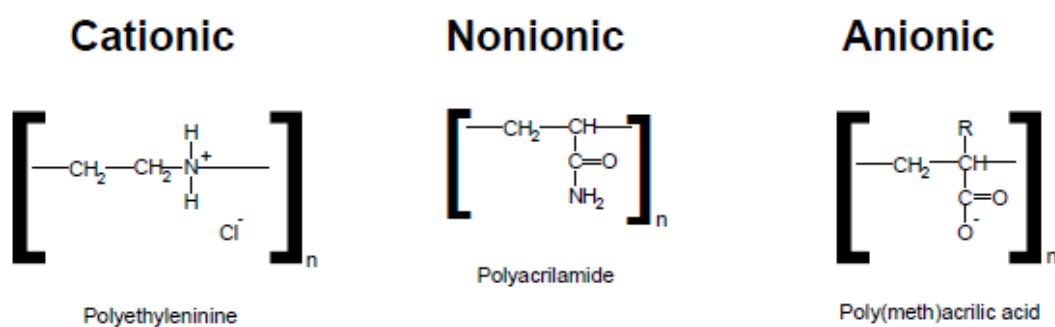
Polyacrylamide or poly(1-carbamoylethylene) is a polymer  $(-\text{CH}_2\text{CHCONH}_2-)$  formed from acrylamide subunits. It can be synthesized as a simple linear-chain

structure or cross-linked, typically using *N,N'*-methylenebisacrylamide. Polyacrylamide is not toxic. It is highly water-absorbent, forming a soft gel when hydrated, used in such applications as polyacrylamide gel electrophoresis.

The ionic form of polyacrylamide has found an important role in the potable water treatment process. Trivalent metal salts like  $\text{FeCl}_3$  and  $\text{AlCl}_3$  are bridged by the long chains of polyacrylamide. This results in significant enhancement of the flocculation rate. This allows water treatment process to greatly improve the removal of total organic content (TOC) from waste water.



**Figure 2.6** Polyacrylamide.



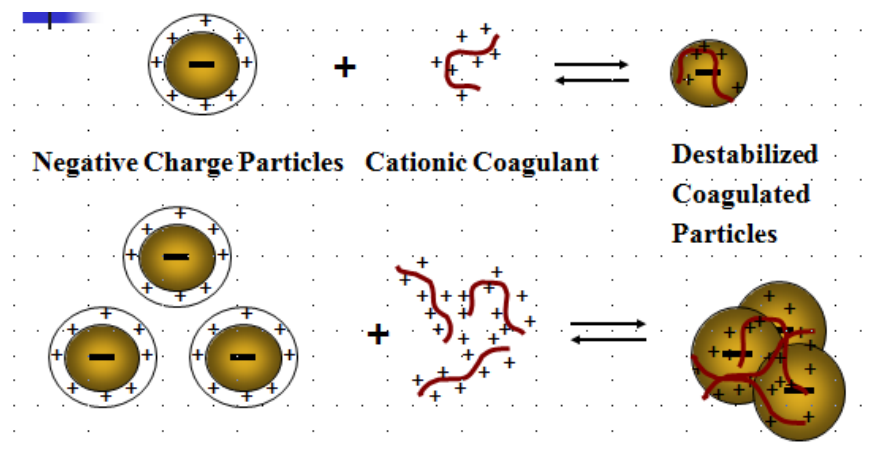
**Figure 2.7** Chemical structure of polymeric coagulant.

## 2.3 Steps of Clarification [11]

Finely divided particles suspended in surface water repel each other because most of the surfaces are anionic matter. The following steps in clarification are necessary for particle agglomeration:

### 2.3.1 Coagulation

Coagulation can be accomplished through the addition of inorganic salts of Al or Fe. These inorganic salts neutralize the charge on the particles causing raw water turbidity, and also hydrolyze to form insoluble precipitates, which entrap particles as shown as in figure 2.5.



**Figure 2.8** Coagulant mechanism.



### 2.3.2 Flocculation

Flocculation, the agglomeration of small into large particles, can be enhanced by the addition of high molecular weight, water soluble organic polymers. These polymers increase floc size by charged site binding and by molecular bridging. Therefore, coagulation involves neutralizing charged particles to destabilize suspended matters. In clarification processes, a flocculation step then follows. Flocculation starts when neutralized matters begin to collide and fuse to form larger particles. This process can occur naturally or can be enhanced by the addition of polymeric flocculant aids. The efficiency of primary coagulant polyelectrolytes depends up on the nature of the turbidity particles to be coagulated, the amount of turbidity present, and the mixing or reaction energies available during coagulation, more turbulence or mixing is required to achieve maximum charge neutralization. A polymeric coagulant is then added to the coagulation process. The clarification to achieve improved settling rates of precipitates and clearly.

### 2.3.3 Color Reduction

Frequently, the objective of clarification is reduce color. Color in raw water materials can cause various problems, such as objectionable taste, increased microbiological content.

The most organic color in surface waters is colloidal and negatively charged. Chemically, color-producing compounds are classified as humic and fulvic acids. Color can be removed by chlorination and coagulation with Al or Fe salts or organic polymeric. Chlorine oxidizes color compounds, while the inorganic coagulants can physically remove many types of organic color by neutralization of surface charges. Additional color removal is achieved by chemical interaction with Al or Fe hydrolysis products. Highly charged cationic polymeric can also be used to coagulate some types of color particles.

Coagulation for reduced color is normally carried out at pH 4.5 to 5.5. Optimum pH for turbidity removal is usually much higher than that for color reduction. The presence of  $\text{SO}_4^{2-}$  can interfere with coagulation for color reduction,

whereas calcium and magnesium ions can improve the process and broaden the pH range in which color may be reduced effectively.

## **2.4 The effectiveness of a coagulant**

### **2.4.1 pH**

Water with a color will coagulate better at low pH (4.4-6).

### **2.4.2 Alkalinity**

It is needed to provide anions, such as hydroxide for forming insoluble compounds to precipitate them. It could be naturally present in the water or needed to be added as hydroxides, carbonates, or bicarbonates.

### **2.4.3 Temperature**

The faster the reaction, and the more effective is the coagulation. Winter temperature will slow down the reaction rate, which can be helped by an extended detention time.

### **2.4.4 Time**

It is an important factor. Mixing and detention times are very important to coagulation.

### **2.4.5 Velocity**

The higher velocity causes the breaking of floc particles, and lower velocity will let them settle in the flocculation basins.

### **2.4.6 Zeta potential**

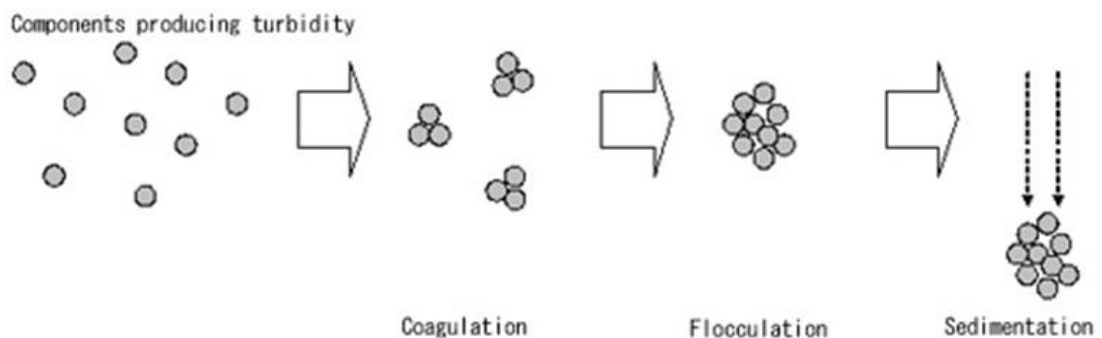
It is the charge at the boundary of the colloidal turbidity particle and the surrounding water. The higher the charge the more is the repulsion between the turbidity particles, less the coagulation, and vice versa. Higher zeta potential requires the higher coagulant dose. An effective coagulation is aimed at reducing zeta potential charge to almost 0.

## 2.5 Types of Solid-liquid Separation

Water purification processes are classified into some methods based on the fundamental principle of each purification process. Among them, the process to separate the components producing turbidity in water from water is solid-liquid separation. In the presence of less soluble components in water, high quality treated water can be obtained by separating the components producing turbidity properly. The solid-liquid separation includes sedimentation and filtration.

### 2.5.1 Sedimentation

Sedimentation is the method to precipitate the particles producing turbidity in water. Large particles can be separated by natural sedimentation, while smaller particles are difficult to precipitate naturally because they suspend stably in water. Due to this, sedimentation treatment is conducted after coagulation-flocculation pretreatment for particle enlargement as shown as in Figure 2.6.



**Figure 2.9** Diagram of coagulation-sedimentation.

## 2.5.2 Filtration

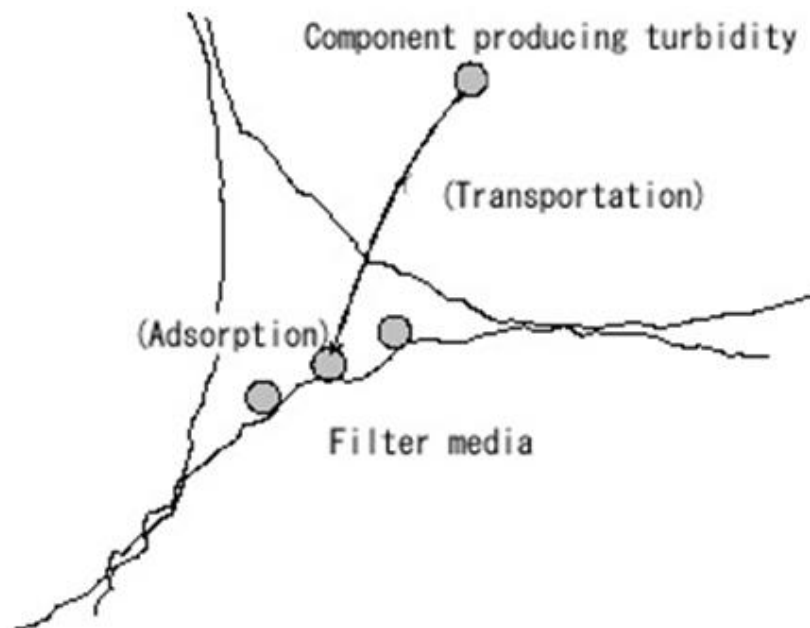
Filtration is the method to stay the components producing turbidity in filter beds composed of filter media such as sand. Filtration is classified into slow and rapid filtrations.

### 2.5.2.1 Slow filtration

Slow filtration is the method to stay the components producing turbidity on biological membranes produced on the filter bed surface, oxidize inorganic substances and remove biodegradation substances by decomposition.

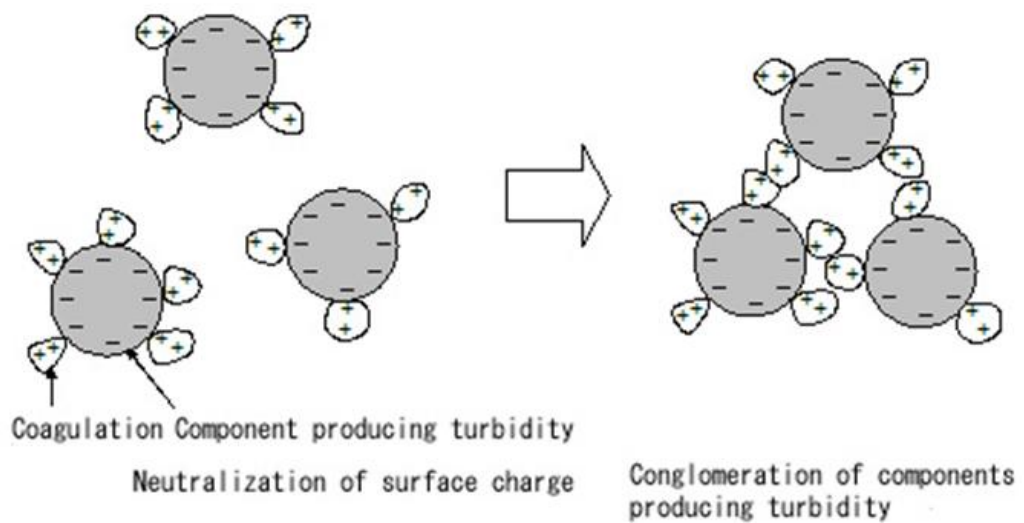
### 2.5.2.2 Rapid filtration

Rapid filtration is the method to remove by adsorbing the components producing turbidity transported into filter beds to the particle surfaces of filter media as shown as in Figure 2.7.



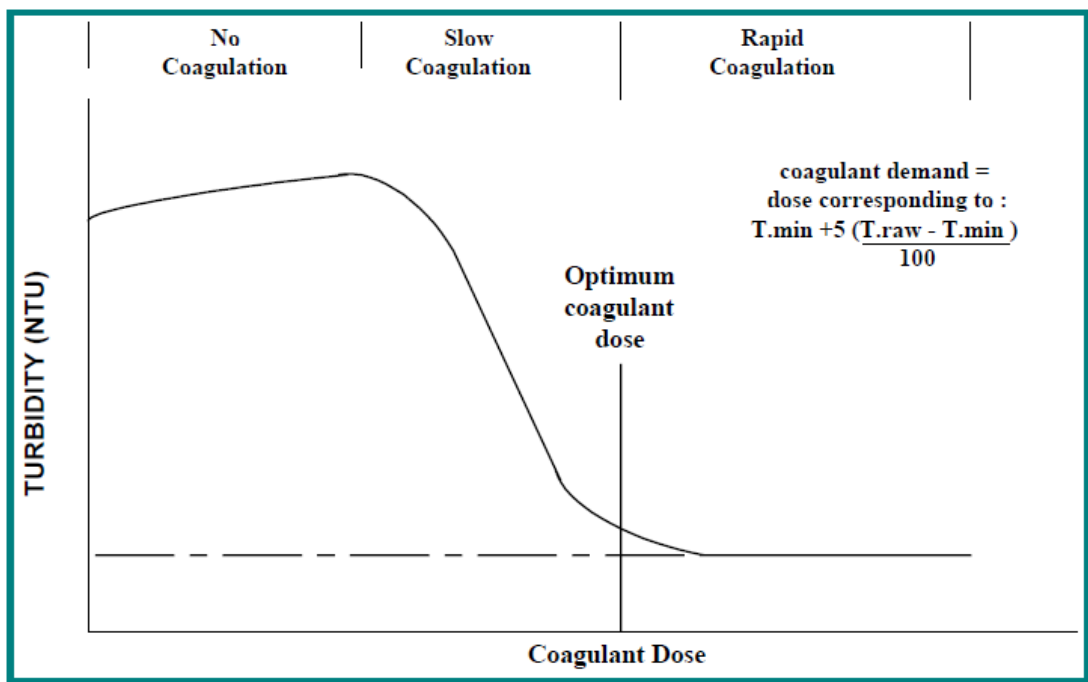
**Figure 2.10** Diagram of filtration .

It is the method based on coagulation of the components producing turbidity and filter media particles. As mentioned above, coagulation process is vital for sedimentation and rapid filtration treatment. Coagulation indicates the process that a coagulant neutralizes the surface charge of the components producing turbidity suspending stably in water. This is done by electrical repulsion. At the same time, the components producing turbidity are conglomerated as shown as in Figure 2.8.



**Figure 2.11** Diagram of coagulation.

The coagulation tests is needed to determine the optimum coagulant dose and pH. Initially, no pH, adjustment is applied to the water and the coagulant dose is varied over a suitable range. A coagulation curve is plotted from which the coagulant demand can be determined as shown as in Figure 2.9.



**Figure 2.12** Typical coagulation curve.

## 2.6 Literature reviews

A.I. Zouboulis *et al.* [1] studied the preparation of polyaluminium chloride (PAC) by using granular aluminium metal instead of using  $\text{Al}_2\text{O}_3$  or a mineral containing. Furthermore, we assessed the  $\text{PAC}_{\text{lab}}$  for the treatment of polluted tap water and waste water samples and compared it with the action of a commercially accessible PAC solution. We used Photometric Dispersion Analyzer instrument (PDA) to analyze the coagulation-flocculation kinetics. Then the growth rates of floc between the two coagulants were compared. We have found that PAC can be alternatively generated under gentle condition. PAC also shows better properties than the commercial PAC. Compared with commercially obtainable PAC-18,  $\text{PAC}_{\text{lab}}$  exhibits ameliorated properties, with the same Al content (~9% w/w), but slightly higher basicity and  $\text{Al}_{13}$  content. Furthermore, the result reveals that  $\text{PAC}_{\text{lab}}$  increases that floc size and growth and stimulates the procedure of particle aggregation. The process mentioned before has advantages in terms of energy and time saved during the production of PAC which might result in the lower expense of operation and compensate for the high expense of metallic Al, which is utilized as raw material. A variety of aluminium by-products might be utilized for PAC manufacture after the proper treatment and the cost efficiency option would be ameliorated.

Yun-Hwei Shen *et al.* [2] studied synthesis and speciation of polyaluminium chloride (PAC) in waste water treatment that was investigated using a colorimetric technic which was possible to produce stable preparations of PAC solutions in which a relatively stable cationic polymer predominated. Some important parameters such as OH, mixing intensity, injection rate of NaOH and aging were identified in this study. PAC was prepared by titration of aluminium solution by NaOH solutions that the major independent variables were concentrations, rate of titration, mixing intensity, and counter-ion composition. After addition of the ferron reagent, the coagulant species were determined using color development. First, it was probable to produce stable, clear preparations of partially neutralized aluminium chloride (PAC) in which “polymeric” materials comprised a majority.

These polymeric species have a similar appearance to aluminium species frequently described as  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  and written as  $\text{Al}_{13}$  according to the reaction rate constant with ferron test. Second, the mode of preparation has a dramatic effect on the composition of PAC. Some significant parameters such as concentrations (both  $[\text{Al}]$  and  $[\text{OH}^-]$ ), mixing intensity, base injection method and aging were identified in this study. In general, a continuously linear increase in polymeric concentration is observed with increasing  $[\text{OH}^-]$  added until a molar ratio ( $[\text{OH}^-]/[\text{Al}]$ ) of 2.5 is reached. Lowering the Al concentration or inadequate mixing both caused a reduction in the formation of polymeric material that was similar to  $\text{Al}_{13}$ .

N.D. Tzoupanos *et al.* [3] studied in coagulation–flocculation field has focused mainly in understanding the behavior and chemistry of pre-polymerized coagulants and the improvement of their properties. A possible way to increase the efficiency of PAC is claimed to be the incorporation of silica in its structure, in the form of polysilicates. The new-product is called poly(aluminium silicate chloride) (PASiC) and is supposed to be more effective than PAC, when applied in the coagulation–flocculation process. The purpose of this study was the synthesis and characterization of many possible derivatives of polyaluminium silicate chloride, based on different basicity (OH/Al molar ratio), silica content (Al/Si molar ratio) and preparation method (co-polymerization or composite polymerization). Their properties were mainly evaluated by means of polymerization degree and aluminium species distribution employing either the ferron technique or the  $^{27}\text{Al}$  NMR method, in order to evaluate the impact of silica addition in the new coagulants.

Guangjie Lu *et al.* [4] studied factors of the electrochemistry and the chemistry of the aqueous solution (affecting the formation of the most effective species of PAC) and presented a new electrolytic method for the synthesis of PAC (polyaluminum chloride). The ECR (electrochemical reactor) used aluminum sheets as anode and  $\text{AlCl}_3$  aqueous solution as electrolyte. This method adopted low voltage and high electric current intensity during electrolysis. The liquid



product of PAC, in which the most effective species,  $Al_b$  (The polymeric Al component estimated by the ferron method), was above 70% by weight of the total aluminum with a basicity,  $B$  ( $OH/Al$  molar ratios) = 2.4, was successfully generated. The results measured by the ferron method and  $^{27}Al$  NMR method showed that the  $Al_b$  or  $Al_{13}$  content of the E-PAC (PAC prepared by electrolysis) were obviously higher than that of the general PAC and other coagulants. The electrolytic method can provide the best conditions to generate more  $Al_{13}$ , and get the PAC which contains the highest  $Al_{13}$  content and the experimental data showed that the Al speciation of all kinds of coagulants solution were much different, and the E-PAC has much higher  $Al_{13}$  content than the other coagulants. In actual industrial processes for PAC preparation, the product prepared by the method is the best in quality. The electrolytic synthesis method of PAC is expected to have a good future because the process is simple and easily controlled.

Dongsheng Wang et al. [5] studied the coagulation behavior of polyaluminum chloride (PAC) with various basicities ( $B = OH/Al$  values) was investigated under different alkalinities. Jar tests were used to evaluate the coagulation efficiencies, including zeta potentials, residual turbidities (RT) and pH values. An optical monitoring technique of photometric dispersion analyzer (PDA) was utilized to observe the coagulation dynamics. The experimental results show that the traditional coagulant such as alum evolves a rapid hydrolysis after dosing and the in situ formed hydrolysis products can destabilize the kaolin particles by precipitation charge neutralization (PCN) that is the main mechanism for turbidity removal in this case. The preformed polymeric species contained in PACs are fairly stable and highly positively charged and these species can be adsorbed on partial surfaces of clay particles and experience aggregation and rearrangement to form electrostatic patches. Increasing alkalinity extends both PCN and EPC zones. Under the low alkalinity, EPC with high  $Al_b$  contained in PACs works better than PCN coagulation; increased alkalinity improves the efficiency of traditional coagulant due to sweep flocculation. Under the higher alkalinity, more coagulant is required to achieve complete charge neutralization. The stoichiometric

relationships between the dosage and alkalinity are different depending on the  $B$  values of PACls

J.Wang *et al.* [6] studied the characteristic of aggregates pre-coagulated by inorganic monomer alum, polymer aluminium chlorohydrate(ACH) and polyaluminium chloride(PACl) coagulants impose major impact on the removal of humic acids (HAs) and the reduction of microfiltration (MF) membrane fouling. The fractal dimension of flocs formed by ACH and PACl is higher than that by monomer alum, indicating Keggin structure produced by polymer coagulants is much more compact compared with hexameric ring structure of alum hydrolysis species. Correspondingly, cake layer specific resistance is far higher and the MF membrane flux deteriorates much more severely when pre-coagulated by ACH and PACl than by alum. removal efficiency, and produce lower cake layer specific resistance and higher membrane filterability for pre-coagulation–MF hybrid process.

The minimum dose of alum, PACl and ACH calculated as Al was 1.7, 2.6 and 3.4 mg/L, respectively for HAs removal effectively. But if calculated as coagulant dose, the polymer PACl and ACH was far less than monomer alum. It is consistent with polymer coagulants save dosage to remove organics not only for conventional treatment but also for pre-coagulation–MF hybrid process.

B.S. Lartiges *et al.* [7] reported the coagulation of combined sewer overflow (CSO) was investigated by jar-testing with a ferric chloride solution (CLARFER) and a polyaluminium chloride. Jar-tests showed that an efficient turbidity removal can be achieved with both coagulants, though lower optimum dosages and higher re-stabilization concentrations were obtained with the aluminumbased coagulant. The removal behaviors can be explained by a selective aggregation of heavy metal carriers present in CSO and a specific interaction between hydrolyzed coagulant species and soluble metals. The stoichiometric relationships were established between optimal coagulant concentration, range of optimal dosing, and CSO conductivity. thus providing useful guidelines to adjust the coagulant demand during the course of CSO events.

Jiuhui Qu *et al.* [8] studied the role of aluminum speciation incoagulation–flocculation of humic acid (HA) by polyaluminum chloride (PAC) with high content of  $Al_{13}$  which was investigated by using  $^{27}Al$  NMR spectroscopy, solid-state  $^{27}Al$  NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and Al-Ferron method. The mechanism of HA removal is directly related to the form of aluminum in solution. In the coagulation process, the  $Al_{13}$  polymers are the dominant species in acidic pH and some of them change to Al precipitates at higher pH. The results of ESI-MS and Al-Ferron method show that  $Al_{13}$  polymers are stable in dilute solution at pH 4–6 and some of them change to Al precipitates when the pH higher than 6.5. The aluminum speciation directly influences the mechanism of HA removal. The maximum removal of the HA is found to occur in the pH range from 5 to 6 that it can be concluded that charge neutralization is the main mechanism of coagulation at slightly acidic pH because the positively polymers are very effective in charge neutralizing with the HA molecules, while adsorption and sweep coagulation of HA by amorphous  $Al(OH)_3(s)$  play an important role at pH > 6.0 or over dosing.

Seung Han Woo *et al.* [9] studied the effectiveness of chitosan (CS), a polycationic biodegradable polymer, as a coagulant was compared to polyacrylamide (PAA) and polyaluminium chloride (PAC) for the coagulation of a soil suspension. The effect of surfactants in the coagulation process was investigated such as Triton X-100 (TX-100), a non-ionic surfactant, sodium dodecyl sulfate (SDS), and an anionic surfactant. CS removed 86% and 63% of the suspended soil in the presence of TX-100 and SDS respectively, after 30 min at a pH of 6. The results prove that coagulation in the presence of TX-100 is more effective than with SDS. The soil coagulation process was found to decrease with an increase in the pH of the suspension, and maximum coagulation was achieved with an acidic pH. The effects of commercial coagulants on coagulation in soil suspensions were investigated in the presence of nonionic and anionic surfactants. Many of cases, nonionic surfactants are used for soil washing due to their biodegradability, low cost, and washing efficiency.

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Equipments and apparatus**

##### **3.1.1 X-ray fluorescence spectrometer (XRF)**

Aluminium content in dried sludge (%w/w), before digestion, was analyzed with wavelength dispersive X-ray fluorescence spectrometer (Philips PW2400). It was also determined in the form of  $\text{Al}_2\text{O}_3$ .

##### **3.1.2 Flame atomic absorption spectrophotometer (AAS)**

Aluminium content in dried sludge (%w/w), after digestion, was analyzed with  $\text{N}_2\text{O-C}_2\text{H}_2$  Flame atomic absorption spectrophotometer using AAS(Varian AA280FS)

##### **3.1.3 Fourier transform infrared spectroscopy (FTIR)**

Dried sludge and each type of PAC 1 mg was well ground and mixed with 200 mg KBr to obtain the KBr disk sample. The FTIR spectra of these samples were recorded in the range of  $4000 - 400 \text{ cm}^{-1}$  using FT-IR spectrometer (Perkin-Elmer, Spectrum One).

##### **3.1.4 X-ray diffraction spectroscopy (XRD)**

Each PAC was determined in terms of crystalline phases with  $\text{Cu K}\alpha$  Radiation in the range  $5-80^\circ$  scale  $2\theta$  at scan rate  $2^\circ.\text{min}^{-1}$  using X-ray diffractometer (Siemens D-500).

#### **3.2 Chemicals**

All chemicals used were analytical reagent grade;

1. Hydrochloric acid,  $\text{HCl}$  (37%, Merck)
2. Sodium hydroxide pellets,  $\text{NaOH}$  (min 85.5%, Carlo Erba )
3. Zinc chloride,  $\text{ZnCl}_2$  (95%, Ajax Finechem)
4. Silicic acid,  $\text{SiO}_2.x\text{H}_2\text{O}$  (99%, Sigma-Aldrich)
5. Sodium acetate,  $\text{CH}_3\text{COONa}$  (99%, Merck)

6. Ferron reagent (8-hydroxy-7-iodoquinoline-5-sulphonic acid),  $C_9H_6INO_4S$  (99%, Sigma-Aldrich)
7. Demineralized water.

### **3.3 Chemical analysis of sludge**

#### **3.3.1 Determination of the moisture content**

The semi-solid sludge was sliced into a thin sheet and weighed, and then dried at 105 °C for 4 hrs. The average weight of 10 sheets before and after drying was obtained. The moisture content of the semi-solid sludge was thus determined.

#### **3.3.2 Determination of aluminium content**

Aluminium content in dried sludge (% w/w), before digestion, was determined in the form of  $Al_2O_3$  using XRF (Philips PW2400).

Aluminium content in dried sludge (% w/w), after digestion, was analyzed with  $N_2O-C_2H_2$  Flame Atomic Absorption Spectrophotometry using AAS (Varian AA280FS)

### **3.4 Preparation of poly(aluminium chloride), PAC and poly(aluminium silicate chloride), PAsiC.**

#### **3.4.1 Preparation of poly(aluminium chloride), PAC [1-2]**

The aluminium solution,  $0.1 \text{ mol.L}^{-1}$ , was prepared from the dried sludge 20 g in 37% HCl 200 mL at 80 °C and the required amount of demineralized water. Then the given volume of 20% NaOH was added drop-wise at the rate  $0.5 \text{ mL.min}^{-1}$  at 80 °C, into 1,000 mL of  $0.1 \text{ mol.L}^{-1}$  aluminium solution from the burette with continuous stirring at 1,500 rpm. The amount of 20% NaOH was varied, i.e., 0, 20, 30, 40, 50, 60 mL. The mixture was kept stirring for 8 hrs and then dried in the oven at 105 °C for 10 hrs. The white solid with different OH/Al molar ratio was obtained as exhibited in Table 3.1.

**Table 3.1** Empirical formula of PAC and calculated OH/Al molar ratio ( $n = 1$ ,  $m = 0-3$ )

OH/Al molar ratio	20% NaOH (mL)	Empirical formula $Al_n(OH)_mCl_{3n-m}$	Symbol
0	0	$AlCl_3$	$PAC_0$
1.0	20	$Al(OH)Cl_2$	$PAC_1$
1.5	30	$Al(OH)_{1.5}Cl_{1.5}$	$PAC_{1.5}$
2.0	40	$Al(OH)_2Cl$	$PAC_2$
2.5	50	$Al(OH)_{2.5}Cl_{0.5}$	$PAC_{2.5}$
3.0	60	$Al(OH)_3$	$PAC_3$

### 3.4.2 Preparation of poly(aluminium silicate chloride), PASiC [3]

The aluminium solution,  $0.1 \text{ mol.L}^{-1}$ , was prepared from the dried sludge 20 g in 37% HCl 200 mL at  $80 \text{ }^\circ\text{C}$  and the required amount of demineralized water. Then the given volume of 20% NaOH was added drop-wise at the rate  $0.5 \text{ mL.min}^{-1}$  at  $80 \text{ }^\circ\text{C}$ , into 1,000 mL of  $0.1 \text{ mol.L}^{-1}$  aluminium solution from the burette with continuous stirring at 1,500 rpm. The amount of 20% NaOH was 40 mL. The mixture was kept stirring for 8 hrs and then dried in the oven at  $105 \text{ }^\circ\text{C}$  for 10 hrs. The white solid with OH/Al molar ratio  $n = 2$  was obtained. The amount of 0.5 M  $SiO_2$  was varied, i.e., 40, 20, 10 mL. with Al/Si molar ratio  $n = 5, 10, 20$  as exhibited in Table 3.2.

**Table 3.2 :** Empirical formula of PASiC and calculated OH/Al and Si/Al molar ratio (n = 1, m = 2 and o = 5-20)

OH/Al molar ratio	Al/Si molar ratio	20% NaOH (mL)	Empirical formula $Al_n(OH)_mSi_oCl_{3n-m}$	Symbol
2	5	40	$Al(OH)_2Si_5Cl$	PASiC <sub>2/5</sub>
2	10	20	$Al(OH)_2Si_{10}Cl$	PASiC <sub>2/10</sub>
2	20	10	$Al(OH)_2Si_{20}Cl$	PASiC <sub>2/20</sub>

### 3.5 Characterization of poly(aluminium chloride), PAC and poly(aluminium silicate chloride), PASiC

#### 3.5.1 X-ray diffraction spectroscopy (XRD)

Each PAC and PASiC were determined formula structure in terms of crystalline phases with Cu K $\alpha$  Radiation in the range 5-80° scale 2 $\theta$  at scan rate 2°.min<sup>-1</sup>.

#### 3.5.2 Fourier transform infrared spectroscopy (FTIR)

Each PAC and PASiC 1 mg were well ground and mixed with 200 mg KBr to obtain the KBr disk sample. The FTIR spectra of these samples were recorded in the range of 4000 - 400 cm<sup>-1</sup>. It were determined Functional group of PAC and PASiC.

#### 3.5.3 Aluminium species distribution with the ferron technique

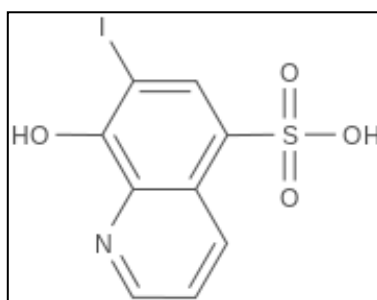
The ferron reagents were prepared according to Zhou,W., et al [5]. This method is described in Al(III) reacts with Ferron reagent to form Al-Ferron complex at pH 5,  $\lambda_{max} = 370$  nm. A Hitachi, U-2000 spectrophotometer was used to measure the Al-Ferron kinetics. The main procedure was as follows ;

Reagent A : (0.2% 8-hydroxy-7-iodo-5-quinoline sulfonic acid) under rapid stirring, 1.05 g 8-hydroxy-7-iodo-5-quinoline sulfonic acid was dissolved in 500 mL boiling distilled water and cooled to room temperature.

Reagent B : (35%, w/v  $\text{CH}_3\text{COONa}$ ): 70 g sodium acetate was dissolved in 200 mL of distilled water.

Reagent C : (10%, w/v Hydroxylamine HCl): 20 g  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 8 mL HCl (1:1 v/v) was mixed with 192 mL of distilled water.

The mixture of reagents A, B, and C was diluted to 1,000 mL and stored at 5-12 °C. After equilibration for 1 week, the experimental Ferron (with pH of 5.2) can be used within 1 month. recorded from 40 to 7200 s at a sample interval of 20 sec. For each sample, 30 mL of each  $0.1 \text{ mol}\cdot\text{L}^{-1}$  PAC solution, as prepared in section 2.3.1, was diluted to 100 mL followed by the addition of 10 mL mixed Ferron reagent. Reaction time was recorded immediately and the mixture was shaken to homogeneity. The reacting sample was then quickly added to a 10 mm-path quartz cell rinsed twice with the mixture before being placed into the spectrophotometer (Hitachi, U-2000). This process required less than 40 s. The absorbance at 370 nm was immediately recorded from 1 to 120 minutes.



**Figure 3.1** Chemical structure of 8-hydroxy-7-iodo-5-quinoline sulfonic acid .

Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) as shown in figure 3.4 is a dibasic acid ( $\text{H}_2\text{A}$ ) which dissociates to  $\text{HA}^-$  and  $\text{A}^{2-}$  with increased pH. The results show that only  $\text{HA}^-$ , which is the predominant species around pH 5, is reactive with Al. The Al-ferron complex yields an absorption maximum at 370 nm.  $\text{H}_2\text{A}$  and  $\text{A}^{2-}$  are not reactive with Al, while they both yield a strong absorption background near 370 nm. The variation in the distribution of various ferron species in solution accounts for



the acidity effect on Al determination. Based on the above information, the color-developing reagent was prepared by mixing ferron, sodium acetate, and acetic acid together. This recommended reagent have pH 5.2. The addition of hydroxylamine gradually alters ferron to a different chemical species. This hydroxylamine-modified species also reacts with Al and yields an absorption maximum at 370 nm.

#### **3.5.4 Percentage of alumina (% Al<sub>2</sub>O<sub>3</sub>)**

% Al<sub>2</sub>O<sub>3</sub> in PACsand PASiC<sub>s</sub> were determined by titrated with zinc chloride 0.02 M ;

- Weight  $2 \pm 0.20$  g of PACs and PASiCs in the 100 ml flask and add water to an extent.
- Pipette 20 ml into the erlenmeyer.
- Add 2 ml of HNO<sub>3</sub> (1:12). Boil for 1 minute on the heater.
- After cooling add 20 ml of 0.05 M EDTA and 2 ml of 2 M CH<sub>3</sub>COONa.
- Bring to a boil for 2 minutes on the water heater.
- After cooling add 10 ml of 2 M CH<sub>3</sub>COONa, then add 2-3 drops of xylenol orange indicator.
- Zinc chloride titration with 0.02 M (S ml), the titration end point is marked by a color change from yellow to red purple.
- Perform a blank with distilled water sample.

### **3.6 Performance of poly(aluminium chloride), PAC and poly(aluminium silicate chloride), PASiC**

#### **3.6.1 pH**

Determination of pH of PAC, PASiC solution and water sample using pH meter (TOA-65) by ASTM D5464-07

#### **3.6.2 Jar tester**

A water sample is placed in a beaker and magnetically stirred. The pH must be adjusted to adesired valued (typically 6) A known amount of coagulant is added and the agitation is maintained at a high value for 1 minute to promote coagulation. Then

the sample is agitated slowly for 3 minutes to promote flocculation. New additions are made until a visible floc is obtained. Using this concentration of coagulant the coagulation experiment is now repeated at different pH values using a longer flocculation time (typically about 10 to 40 minutes), followed by settling with no agitation (15-60 minutes) ASTM D2035-80.

- Pour 500 mL water sample into 6 beaker glass.
- Start the stirrer at 150 rpm and inject the coagulant for various dosage for 3 mins.
- Reduce the speed stirrer to slow mixing at 50 rpm keep mixing for 10-40 mins.
- Observe the floc size formed and settle the particles for 15-60 min.
- Measure the clear water parameters (Turbidity, pH, Color, etc).

### **3.6.3 Turbidity**

Clarified water samples from jar test were determined turbidity using turbidimeter ASTM D1889-00

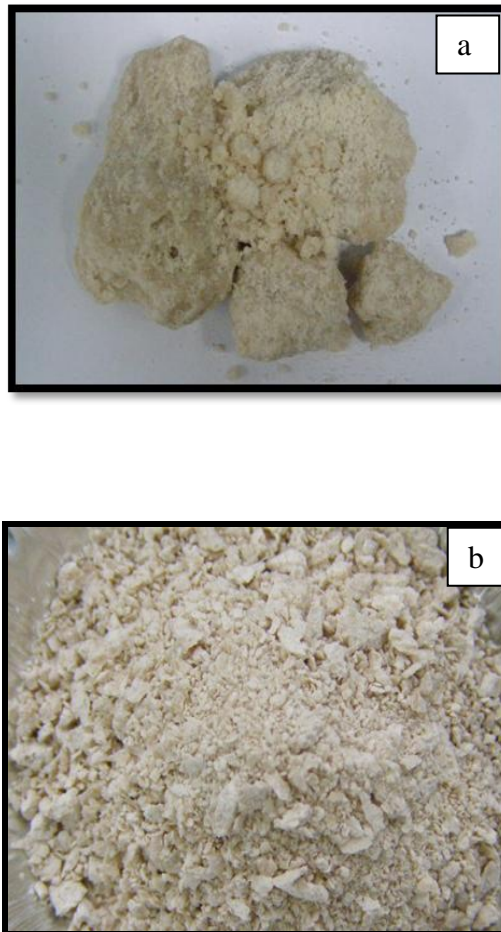
## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Chemical analysis of sludge

##### 4.1.1 Determination of the moisture content

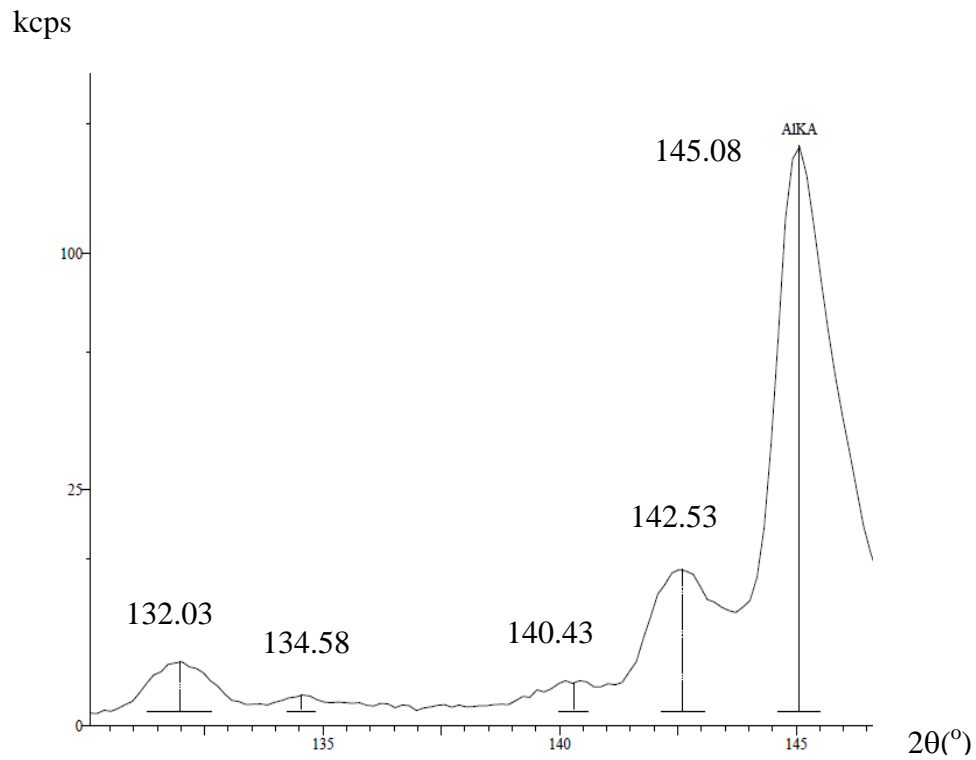
The semi-solid sludge was sliced into a thin sheet and weighed, and then dried at 105 °C for 4 hrs. The average weight of 20 sheets before and after drying was obtained. The moisture content of the semi-solid sludge was thus determined  $80.96 \pm 0.25$  (%), deviation within 0.31%.



**Figure 4.1** Semi-solid sludge (a), semi-solid sludge after drying at 105 °C for 2 hrs (b).

#### 4.1.2 X-ray fluorescence spectrometer (XRF) analysis

Determination was percentage of alumina ( $\text{Al}_2\text{O}_3$ ) in dried sludge, according to its XRF pattern, the appearance of the characteristic of alumina ( $\text{Al}_2\text{O}_3$ ), at  $132.03^\circ$ ,  $134.58^\circ$ ,  $140.43^\circ$ ,  $142.53^\circ$  and  $145.08^\circ$   $2\theta$ , as shown in Figure 4.2.



**Figure 4.2** XRF spectrum of  $\text{Al}_2\text{O}_3$  in dried sludge.

This indicated the presence of  $\text{Al}_2\text{O}_3$  in the dried sludge. This result revealed that the dried sludge contained  $\text{Al}_2\text{O}_3$  43.95 % (w/w) or aluminium content 23.26 % (w/w). In addition, some other element oxides in dried sludge were found, i.e.,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  as exhibited in Table 4.1.

**Table 4.1** Element oxide content in dried sludge (% w/w)

Percentage of element oxide content in dried sludge <sup>*,**</sup>				
$\text{Al}_2\text{O}_3$	$\text{SO}_3$	$\text{Na}_2\text{O}$	$\text{SiO}_2$	$\text{Fe}_2\text{O}_3$
$43.95 \pm 0.09$	$15.68 \pm 0.09$	$8.65 \pm 0.05$	$0.35 \pm 0.03$	$0.11 \pm 0.02$
$\text{CaO}$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{ZnO}$	-
$0.09 \pm 0.02$	$0.06 \pm 0.01$	$0.04 \pm 0.01$	$0.02 \pm 0.01$	-

\*Element content by theoretical formula method, “fundamental parameter calculation”

\*\*Deviation within 0.25% .

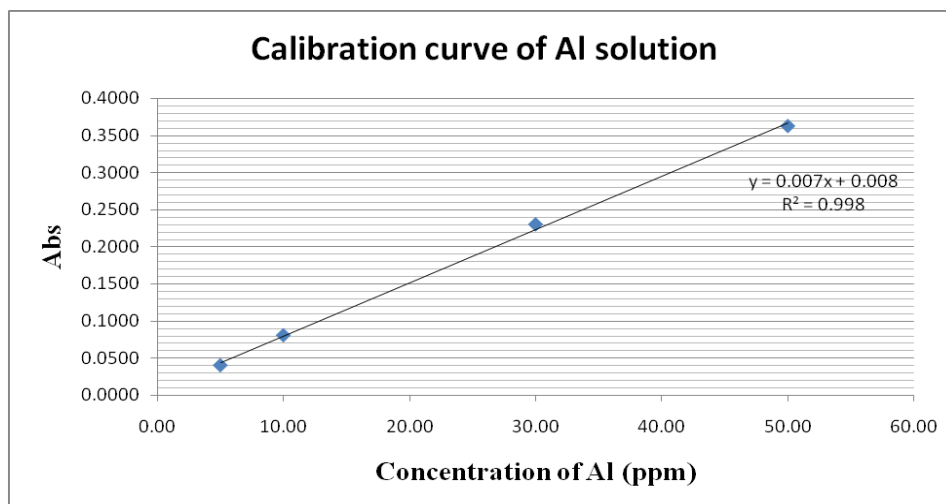
#### 4.1.3 Determination of aluminium content

Dried sludge was digested with conc. HCl, yellow solution. Bring aluminium solution was analyzed using AAS. Calibration curve was used standard Al solution 5, 10, 30 and 50 ppm. The aluminium content of the dried sludge was thus determined 3.56 ppm., deviation within 4.11 %.

**Table 4.2** Aluminium content in aluminium solution ( $\text{mg.L}^{-1}$ , ppm)

Al solution	Absorbance	Concentration(ppm)	%RSD
Standard 5 ppm	0.0402	5.000	0.7
Standard 10 ppm	0.0807	10.000	0.4
Standard 30 ppm	0.2305	30.000	0.4
Standard 50 ppm	0.3633	50.000	0.2
Sample	0.0329	3.557	4.11

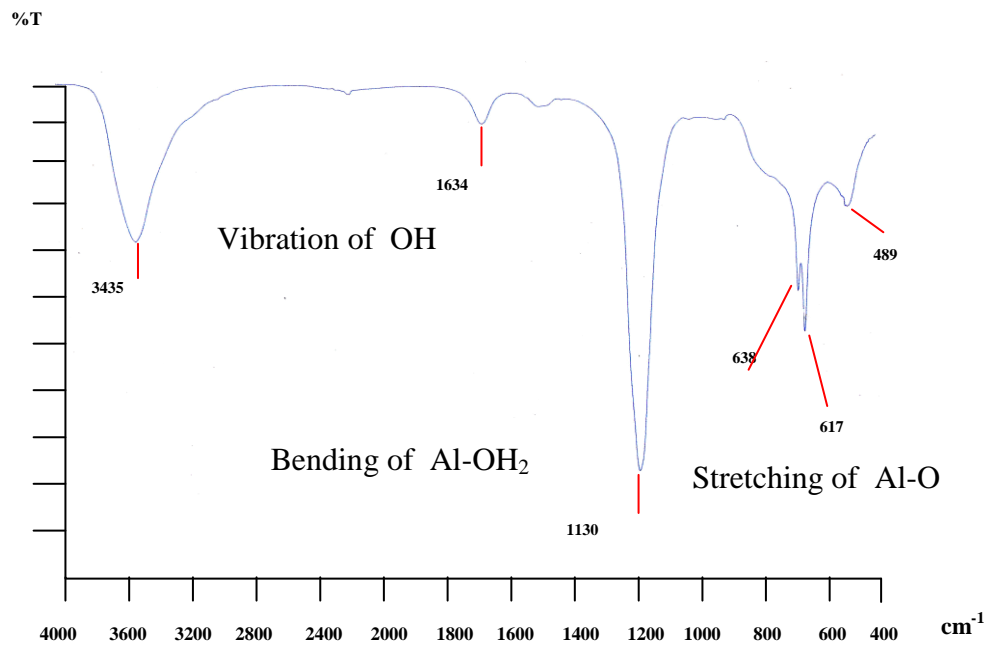
After the acid hydrolysis of the dried sludge, the aluminium content of the aluminium solution was determined by AAS.



**Figure 4.3** Calibration curve of aluminium solution.

#### 4.1.4 FT-IR analysis

This was confirmed by the appearance of the absorption bands at  $3435\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  which are associated with OH-vibration. The absorption bands at  $1130\text{ cm}^{-1}$  is assigned to the bending vibrations of  $\text{Al-OH}_2$  and the absorption band at  $638\text{ cm}^{-1}$  is assigned to the symmetric stretching of Al-O bond [3] as shown in Figure 4.4. The FT-IR spectrum of the dried sludge showed that the presence of aluminium in the sludge was in the form of aluminium hydroxide.



**Figure 4.4** FT-IR spectrum of aluminium hydroxide  $\text{Al(OH)}_3$  in dried sludge.

## 4.2 Preparation of poly(aluminium chloride), PAC

PAC was prepared as described in section 3.2. The addition of NaOH at various amount into the aluminium solution from sludge would lead to the formation of different types of PAC,  $\text{OH/Al} = 0-3$ , mole of Al was 1 ( $n=1$ ). Formula of PAC was  $n=1$  then  $\text{OH/Al}$  molar ratio increase effect to pH value increase too, because of OH in PAC increase, pH of  $\text{OH/Al} = 3 > 2.5 > 2 > 1.5 > 1 > 0$  or  $\text{PAC}_3 > \text{PAC}_{2.5} > \text{PAC}_2 > \text{PAC}_{1.5} > \text{PAC}_1 > \text{PAC}_0$  as proposed in Table 4.4.

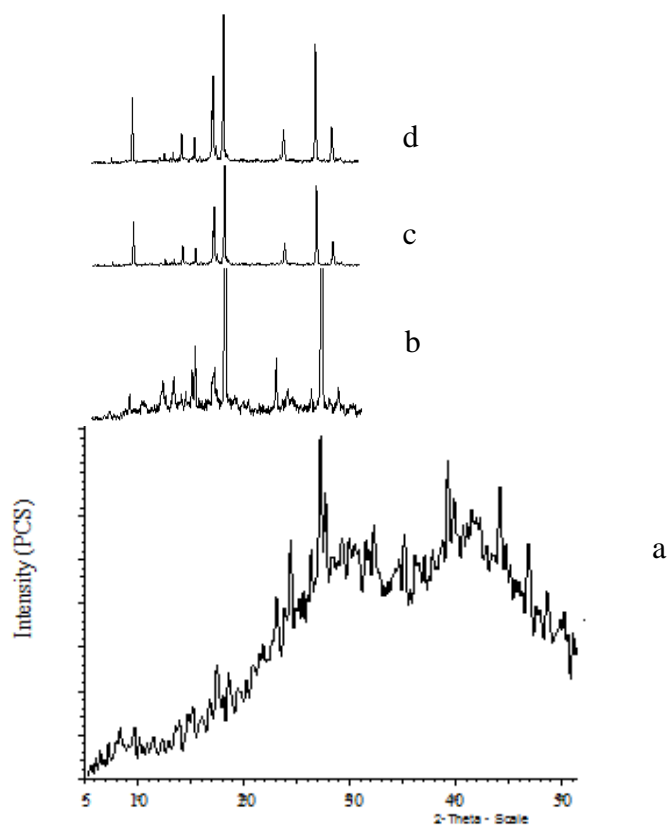
**Table 4.3** pH of Poly(aluminium chloride), PAC

Sample	pH
PAC <sub>0</sub>	2.71
PAC <sub>1</sub>	3.37
PAC <sub>1.5</sub>	3.45
PAC <sub>2</sub>	3.72
PAC <sub>2.5</sub>	4.12
PAC <sub>3</sub>	9.70

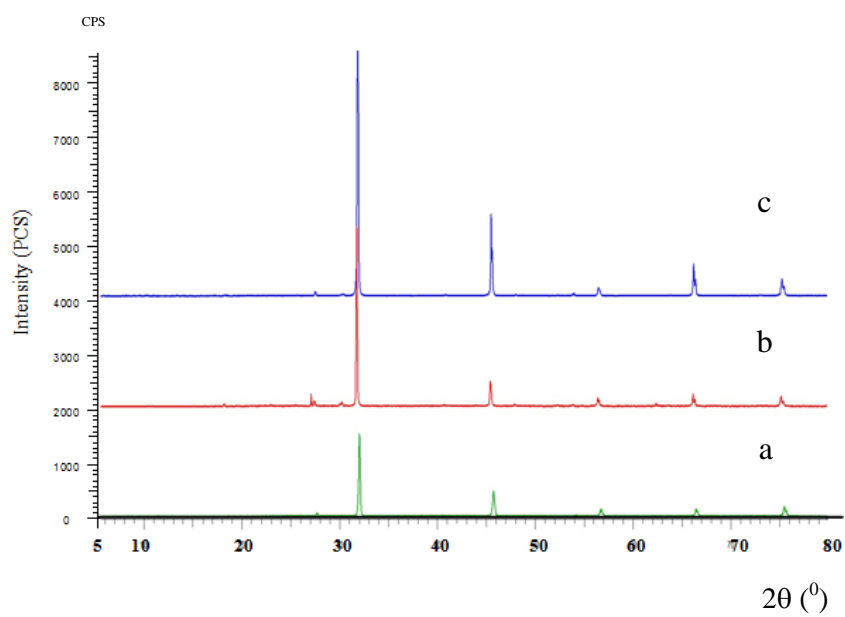
#### 4.2.1 XRD analysis

PAC<sub>1</sub>, PAC<sub>2</sub> and PAC<sub>2.5</sub> were characterized by XRD as exhibited in Figure 4.5. The appearance of the peaks at 15°, 17°, 24°, 26°, 28°, 35°, 39° and 44° 2θ which are indexed as [110], [012], [202], [300], [111], [024], [321] and [134] were assigned to aluminium chloride hexahydrate (AlCl<sub>3</sub>.6H<sub>2</sub>O) which is comparable to the commercial PAC. It should be, however, pointed out that sodium chloride was also formed as the co-product in a large amount. This can be seen in the XRD patterns (Figure 4.6) at the peaks at 27°, 32°, 45.5°, 56.5°, 66°, 75° 2θ. which are indexed as [110], [131], [220], [222], [400], [024], [420]. It was observed that the amount of NaCl in the material increased with the increasing amount of sodium hydroxide added to the aluminium solution, or the higher OH/Al molar ratio, PAC<sub>2.5</sub> > PAC<sub>2</sub> > PAC<sub>1</sub> as shown as Figure 4.6.





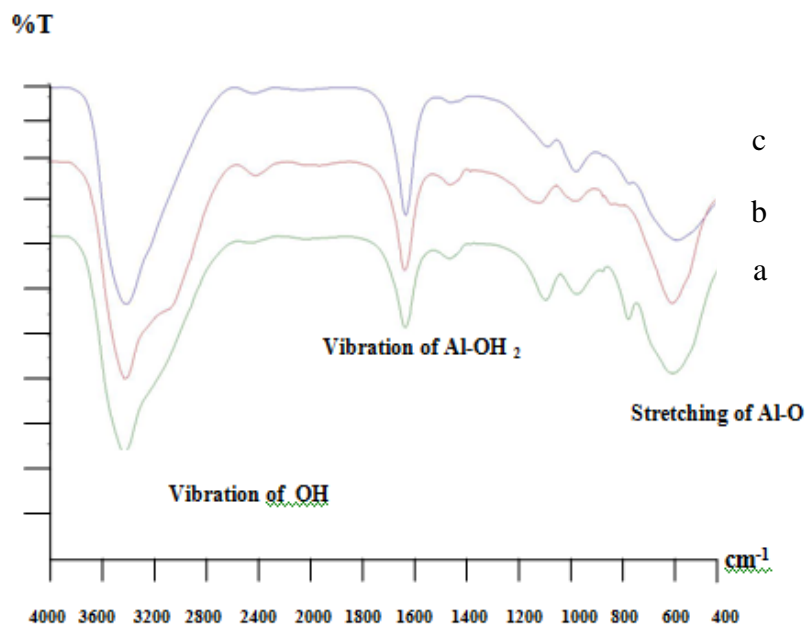
**Figure 4.5** XRD patterns of commercial PAC (a), PAC<sub>1</sub>(b), PAC<sub>2</sub>(c) and PAC<sub>2.5</sub>(d)



**Figure 4.6** XRD patterns of PAC<sub>1</sub>(a), PAC<sub>2</sub>(b) and PAC<sub>2.5</sub>(c).

#### 4.2.2 FT-IR analysis

The structure of PAC was confirmed by its FT-IR spectrum, as revealed in Figure 4.7.



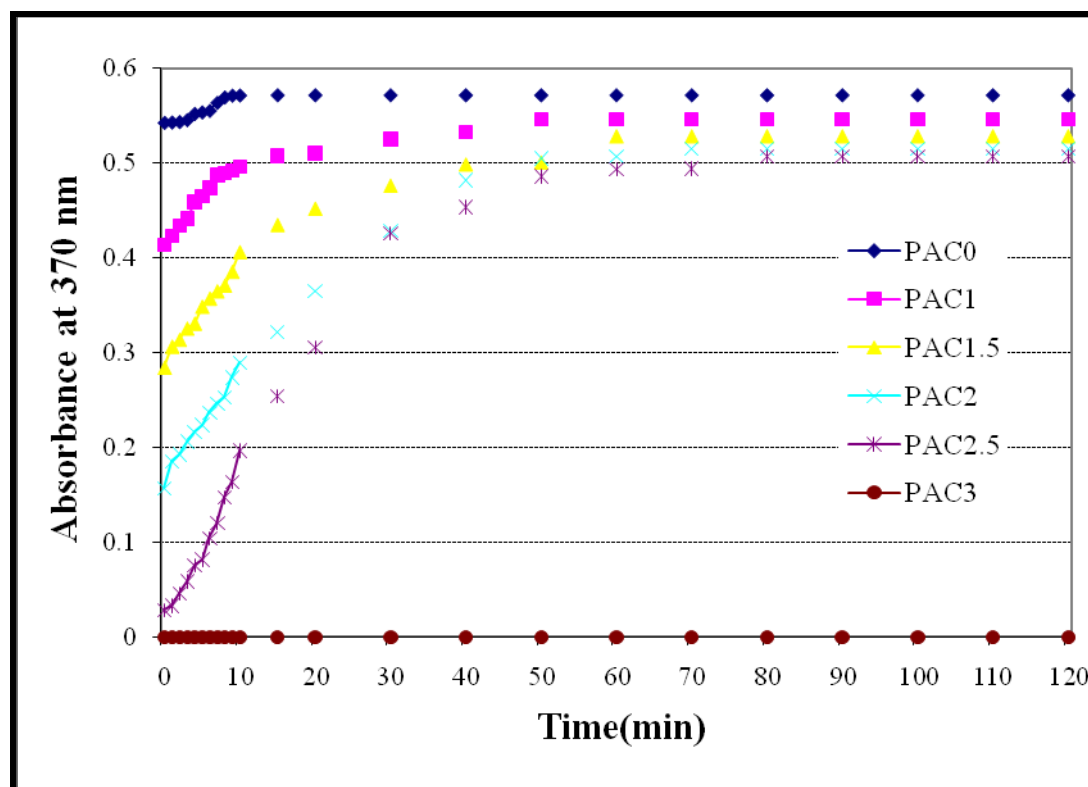
**Figure 4.7** FT-IR spectrums of PAC<sub>2.5</sub>(a), PAC<sub>2</sub>(b), PAC<sub>1</sub>(c).

The absorption bands at  $3428\text{ cm}^{-1}$  and  $1636\text{ cm}^{-1}$  were associated with OH-vibration. The bands at  $1120\text{ cm}^{-1}$  and  $984\text{ cm}^{-1}$  were assigned to the bending vibrations of Al-OH<sub>2</sub> and the band at  $610\text{ cm}^{-1}$  is assigned to the symmetric stretching of Al-O bond [3]. Furthermore, it should be noted that the absorption band at  $3428\text{ cm}^{-1}$  of each PAC was broader in the following order, PAC<sub>2.5</sub> > PAC<sub>2</sub> > PAC<sub>1</sub>. This observation was consisted with the formation of PAC.

#### 4.2.3 Ferron's test

Al-Ferron complexation timed spectrophotometry is the commonly used method of determining and measuring Al (III) speciation [5]. This technic can detect low Al concentrations ( $10^{-5}\text{ M}$ ) using simple apparatus at low cost, and as a kinetic

spectrophotometric technique, the ferron method can distinguish various forms of Al by their different rates of reaction with the ferron reagent.



**Figure 4.8** Al-Ferron kinetics curves of PACS.

Interestingly, PAC<sub>0</sub>, PAC<sub>1</sub>, PAC<sub>1.5</sub>, PAC<sub>2</sub>, PAC<sub>2.5</sub> and PAC<sub>3</sub> prepared in this work readily formed complexes with the ferron reagent, but at different rate of reaction as shown in Figure 4.8. The shapes of the Al-Ferron kinetics curves are all similar, which rise in the first 10 minutes then slowly become almost flat. However, it can be clearly observed that PAC<sub>0</sub> reacts more rapidly with ferron reagent than all PACs. PAC<sub>0</sub> was formed completable complex with ferron reagent at 15 min, absorbance 0.5712, PAC<sub>1</sub> was formed completable complex with ferron reagent at 50 min, absorbance 0.5452, PAC<sub>1.5</sub> was formed completable complex with ferron reagent at 60 min, absorbance 0.5289, PAC<sub>2</sub> was formed completable complex with ferron reagent at 70 min, absorbance 0.5153, PAC<sub>2.5</sub> was formed completable complex with ferron reagent at 80 min, absorbance 0.5068 and PAC<sub>3</sub> can not form

complex with ferron reagent. Rate of Al-Ferron kinetics was  $PAC_0 > PAC_1 > PAC_{1.5} > PAC_2 > PAC_{2.5} > PAC_3$ , because of  $PAC_0$  was monomeric but  $PAC_1$ ,  $PAC_{1.5}$ ,  $PAC_2$  and  $PAC_{2.5}$  were polymeric.  $PAC_{2.5}$  was the most polymeric, the results shown in Figure 4.8 has confirmed the formation of poly(aluminium chloride) in this work.

### 4.3 Preparation of poly(aluminium silicate chloride), PASiC

PAC was prepared as described in section 3.2. The addition of NaOH at various amount into the aluminium solution from sludge would lead to the formation of  $PAC = 2$ , and varied Si/Al molar ratio = 5, 10, 20 ( $PASiC_{2/5}$ ,  $PASiC_{2/10}$ ,  $PASiC_{2/20}$ ) with co-polymerization method and formula of PASiC was Si/Al molar ratio increase effect to pH value decrease too, because of silicic acid in PAC increase, pH of Si/Al = 5 > 10 > 20 or  $PASiC_5 > PASiC_{10} > PASiC_{20}$  as proposed in Table 4.5.

**Table 4.4** pH of poly(aluminium silicate chloride), PASiC

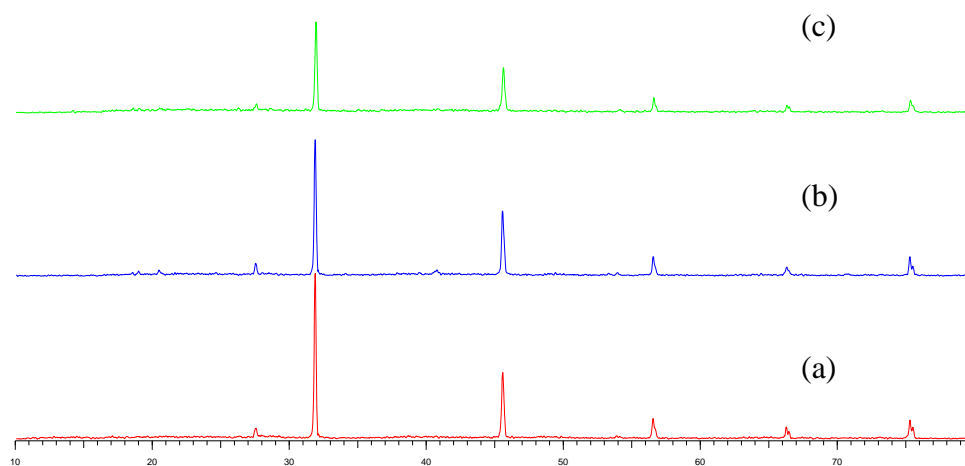
Sample	pH
$PASiC_{2/5}$	4.42
$PASiC_{2/10}$	4.34
$PASiC_{2/20}$	4.19

#### 4.3.1 XRD analysis

PASiC was characterized by XRD as exhibited in Figure 4.10. The XRD pattern of  $PASiC_{2/10}$  is displayed. The crystalline form of dried solids is obvious from the nature of the peaks. Three compounds could be identified, according to the instruments database: sodium chloride (NaCl), aluminium chloride ( $AlCl_3 \cdot 6H_2O$ ).  $PAC_1$ ,  $PAC_2$  and  $PAC_{2.5}$  were characterized by XRD as exhibited in Figure 4.5.

The appearance of the peaks at  $15^\circ$ ,  $17^\circ$ ,  $24^\circ$ ,  $26^\circ$ ,  $28^\circ$ ,  $35^\circ$ ,  $39^\circ$  and  $44^\circ$   $2\theta$  which are indexed as [110], [012], [202], [300], [111], [024], [321] and [134] were assigned to aluminium chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) which is comparable to the commercial PAC. It should be, however, pointed out that sodium chloride was also formed as the co-product in a large amount. This can be seen in the XRD patterns (Figure 4.6) at the peaks at  $27^\circ$ ,  $32^\circ$ ,  $45.5^\circ$ ,  $56.5^\circ$ ,  $66^\circ$ ,  $75^\circ$   $2\theta$ . which are indexed as [110], [131], [220], [222], [400], [024], [420]. It was observed that the amount of NaCl in the material increased with the increasing amount of sodium hydroxide added to the aluminium solution, or the higher Si/Al molar ratio,  $\text{PASiC}_{2/20} > \text{PASiC}_{2/10} > \text{PASiC}_{2/5}$  as shown as Figure 4.6.

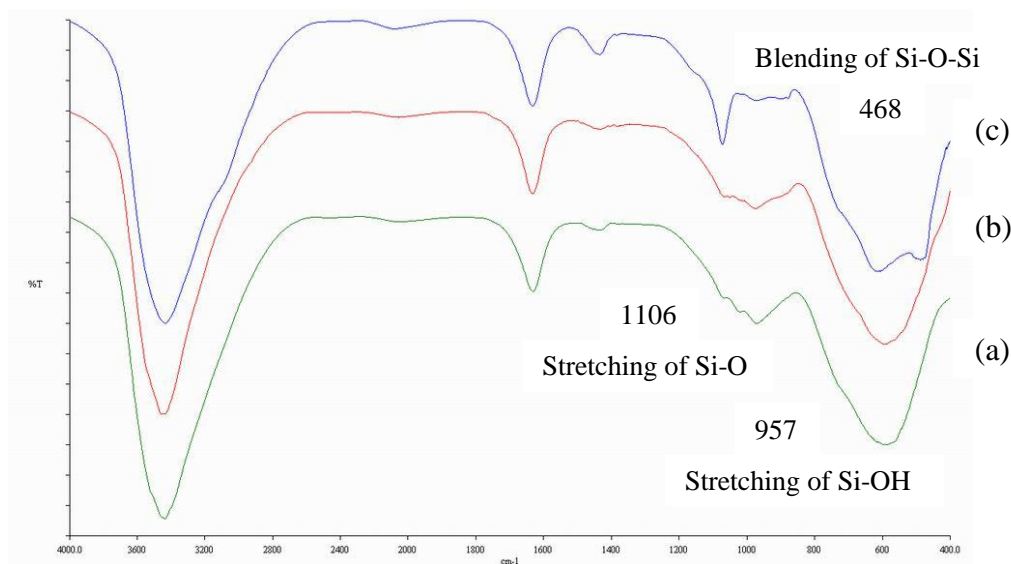
It should be, however, pointed out that sodium chloride was also formed as the co-product in a large amount.



**Figure 4.9** XRD patterns of  $\text{PASiC}_{2/5}$  (a),  $\text{PASiC}_{2/10}$  (b) and  $\text{PASiC}_{2/20}$  (c).

### 4.3.2 FT-IR analysis

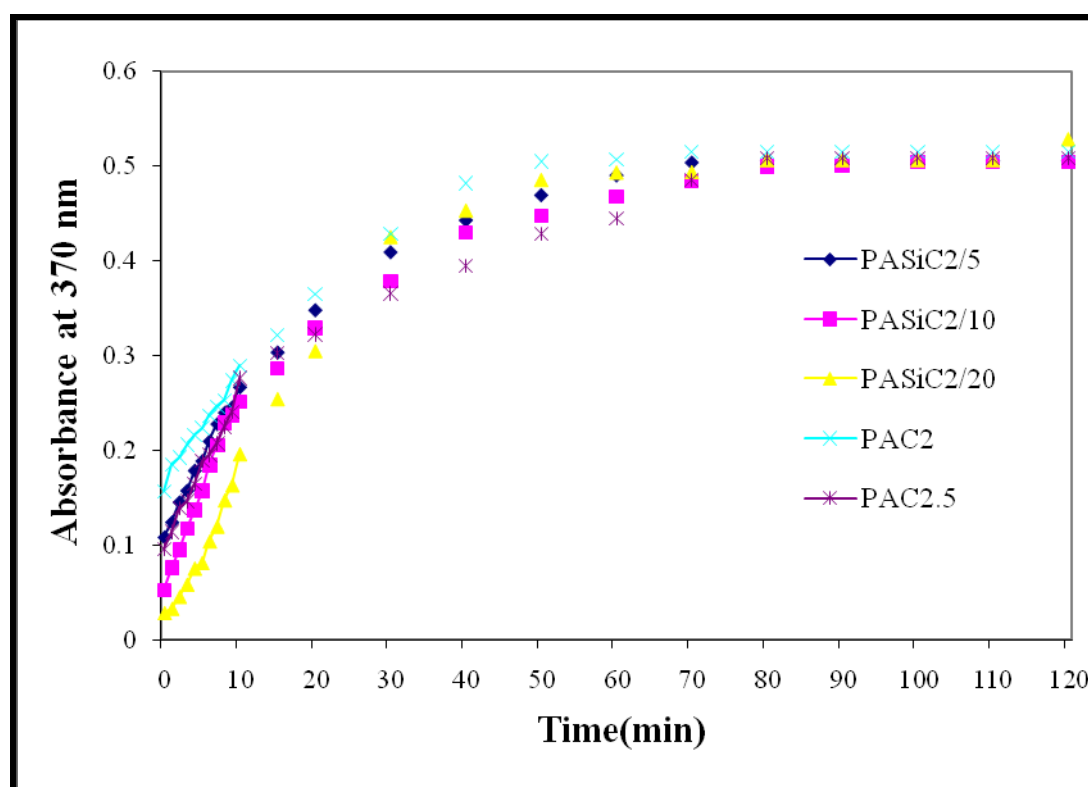
The structure of PASiC was confirmed by its FT-IR spectrum, KBr method, as revealed in Figure 4.10. The FTIR spectra of the examined reagents. In the case of PACI 2, the bands appearing at  $3400\text{ cm}^{-1}$  and  $1634\text{ cm}^{-1}$  are associated with OH vibrations. Specifically, the band at  $3400\text{ cm}^{-1}$  is assigned to  $\text{-OH}$  stretching vibration of hydroxyls and the band at  $1634\text{ cm}^{-1}$  to the bending vibration of water molecules in the structure of Al polycations. The bands at the low wavenumber, i.e  $468\text{ cm}^{-1}$  are associated with the blending vibrations of Si-O-Si bonds. The band at  $957\text{ cm}^{-1}$  is associated with stretching vibrations in silanol groups. The new band at  $1106\text{ cm}^{-1}$  was assigned to Si-O stretching. Observing the IR spectra in fig it can be seen that with increasing silica content the major change, due to polysilicate addition, appear at the region  $700\text{-}1200\text{ cm}^{-1}$



**Figure. 4.10** FT-IR spectra of PASiC  $_{2/20}$  (a), PASiC  $_{2/10}$  (b) and PASiC  $_{2/5}$  (c).

### 4.3.3 Ferron's test

Al-Ferron complexation timed spectrophotometry is the commonly used method of determining and measuring Al (III) speciation . This technic can detect low Al concentrations ( $10^{-5} M$ ) using simple apparatus at low cost, and as a kinetic spectrophotometric technique, the ferron method can distinguish various forms of Al by their different rates of reaction with the ferron reagent.



**Figure 4.11** Al-Ferron reaction kinetics PAC<sub>2</sub>, PAC<sub>2.5</sub>, PASiC<sub>2/5</sub>, PASiC<sub>2/10</sub>, PASiC<sub>2/20</sub>.

Interestingly, PAC<sub>2</sub>, PAC<sub>2.5</sub>, PASiC<sub>2/5</sub>, PAC<sub>2/10</sub> and PAC<sub>2/20</sub> prepared in this work readily formed complexes with the ferron reagent, but at different rate of reaction as shown in Figure 4.11. The shapes of the Al-Ferron kinetics curves are all similar, which rise in the first 10 minutes then slowly become almost flat. However, it can be clearly observed that PAC<sub>2</sub> reacts more rapidly with ferron reagent than all PACs. PAC<sub>2</sub> was formed complex with ferron reagent at 70 min, absorbance 0.5153, PAC<sub>2.5</sub>

was formed complex with ferron reagent at 80 min, absorbance 0.5086, PAC<sub>2/5</sub> was formed complex with ferron reagent at 80 min, absorbance 0.5048, PAC<sub>2/10</sub> was formed completable complex with ferron reagent at 100 min, absorbance 0.5033, PAC<sub>2/20</sub> was formed completable complex with ferron reagent at 110 min, absorbance 0.5068 Rate of Al-Ferron kinetics was  $PAC_2 > PAC_{2.5} \geq PASiC_{2/5} > PASiC_{2/10} > PASiC_{2/20}$ , because of PASiC<sub>2/20</sub> was higher positive charge than PAC<sub>2</sub>, PAC<sub>2.5</sub>, PASiC<sub>2/5</sub> and PASiC<sub>2/10</sub>. PASiC<sub>2/20</sub> was the most polymeric. PAC<sub>2.5</sub> was the most polymeric, the results shown in Figure 4.11 has confirmed the formation of poly(aluminium chloride) and poly(aluminium silicate chloride) in this work.

#### 4.3.4 Percentage of alumina (% Al<sub>2</sub>O<sub>3</sub>)

% Al<sub>2</sub>O<sub>3</sub> content in PACs and PASiC<sub>5</sub> were determined by titrated with zinc chloride 0.02 M and using xylenol orange indicator. Al<sub>2</sub>O<sub>3</sub> was active agent for any type of aluminium salt coagulant, PAC<sub>com</sub> was the most of % Al<sub>2</sub>O<sub>3</sub> content, PAC<sub>0</sub> was not detect % Al<sub>2</sub>O<sub>3</sub>



**Table 4.5** % Al<sub>2</sub>O<sub>3</sub> content in PACs , PASiC<sub>S</sub> and PAC<sub>com</sub>

Sample	%Al <sub>2</sub> O <sub>3</sub>
PAC <sub>0</sub>	<i>n.d.</i>
PAC <sub>1</sub>	5.3
PAC <sub>1.5</sub>	6.5
PAC <sub>2</sub>	7.6
PAC <sub>2.5</sub>	8.8
PAC <sub>3</sub>	0.7
PASiC <sub>2/5</sub>	7.8
PASiC <sub>2/10</sub>	8.0
PASiC <sub>2/20</sub>	8.1
PAC <sub>com</sub>	16.7

#### 4.4 Performance of poly(aluminium chloride), PAC and poly(aluminium silicate chloride), PASiC.

##### 4.4.1 Jar test

Water sample : Rayong river

**Table 4.6** Comparison performance of coagulant

Coagulant	Amount (%)	Turbidity (NTU)	Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	pH	COD (ppm)
Rayong river	-	85	520	7.14	98
PAC <sub>0</sub>	10	68	530	7.09	83
PAC <sub>1</sub>	10	54	519	7.17	78
PAC <sub>1.5</sub>	10	31	515	7.20	75
PAC <sub>2</sub>	10	12	517	7.21	62
PAC <sub>2.5</sub>	10	10	523	7.23	60
PASiC <sub>2/5</sub>	10	14	518	7.38	61
PASiC <sub>2/10</sub>	10	8	520	7.32	58
PASiC <sub>2/20</sub>	10	7	522	7.32	55
PAC <sub>ref</sub>	10	11	528	7.12	64

The resistance of the prepared coagulation reagents to the possible decomposition or change of the components with aging was examined by conducting periodic measurements of turbidity, pH, and visual observations.

The introduction of polymerized silica resulted in an increase of the products turbidity, as compared with the PAC sample, due to the alumino-silicate complexes formed. From Figure 4.13a it can be seen that this increase becomes more intense with increasing OH/Al and Al/Si molar ratios. The increase of macromolecular compounds, when increasing the polymerization degree and the silica content, as. The highest values were observed for the coagulants with OH/Al 2.0, but the respective data were excluded.

## CHAPTER V

### CONCLUSION

PAC with various OH/Al molar ratios were successfully prepared from the semi-solid sludge under mild condition in an open system. However, it should be noted that the aluminium solution contained aluminium 3.6% were used, while the aluminium content in the dried sludge was found to be 23.26%. This is due to the limitation of acid hydrolysis of aluminium. The alternative method of PAC preparation from this sludge has been further studied.

The aforementioned procedure has the benefits of energy and time saving during the manufacture of PAC, resulting in lower operating cost, which may compensate for the higher cost of metallic Al, used as raw material. Considering that various aluminium by-products could be used for PAC production after the appropriate treatment, the cost effectiveness option could be further improved. Finally, if the described procedure takes place in industrial scale, further improvement of the final product and refining of the method may be feasible, due to the appropriate equipment used.

The introduction of silica into poly(aluminium chloride) alters at a certain degree the composition and characteristics of the new composite coagulant agents. One of the most important effects of silica addition is the reduction of the most effective Al specie when the content of silica is relatively high. The interaction of monomeric  $Al^+$  species with polysilicates, which leads to the formation of aluminosilicates, is responsible for this reduction, as shown by IR . As a consequence, the larger polymeric Al species fraction increases, and the appearance of the new products becomes more turbid, than PAC.

Poly(aluminium silicate chloride) has proved to be an efficient coagulant for water or wastewater treatment, and in several cases even better than PAC, as stated in the respective literature. The formation of aluminosilicates, as shown in this study, probably plays a crucial role in the increase of the composite coagulants efficiency. On the other side, these complexes are responsible for the lower stability of poly(aluminium silicate chloride), as compared to polyaluminium chloride, and due to

their decomposition, the characteristics of the composite coagulant change with time, with consequences to its coagulation performance.

### **Suggestion of work**

Further research is needed in order to improve the stability of poly(aluminium chloride) and poly(aluminium silicate chloride) to enable it to be more competitive against the widely used conventional, or simple pre-polymerized coagulants. May be, we were increased mole ratio of aluminium in PAC and PASiC. High mole ratio of aluminium was effected to positive charge in PAC and PASiC.

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## **APPENDIX**

## APPENDIX

**Table A-1** Type of coagulant chemical

Chemical Name	Chemical Formula	Primary Coagulant	Coagulant Aid
Aluminum sulfate (Alum)	$\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$	<b>X</b>	
Ferrous sulfate	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	<b>X</b>	
Ferric sulfate	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$	<b>X</b>	
Ferric chloride	$\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$	<b>X</b>	
Cationic polymer	Various	<b>X</b>	<b>X</b>
Calcium hydroxide (Lime)	$\text{Ca}(\text{OH})_2$	<b>X*</b>	<b>X</b>
Calcium oxide (Quicklime)	$\text{CaO}$	<b>X*</b>	<b>X</b>
Sodium aluminate	$\text{Na}_2\text{Al}_2\text{O}_4$	<b>X*</b>	<b>X</b>
Bentonite	Clay		<b>X</b>
Calcium carbonate	$\text{CaCO}_3$		<b>X</b>
Sodium silicate	$\text{Na}_2\text{SiO}_3$		<b>X</b>
Anionic polymer	Various		<b>X</b>
Nonionic polymer	Various		<b>X</b>

\*Used as a primary coagulant only in water softening processes.



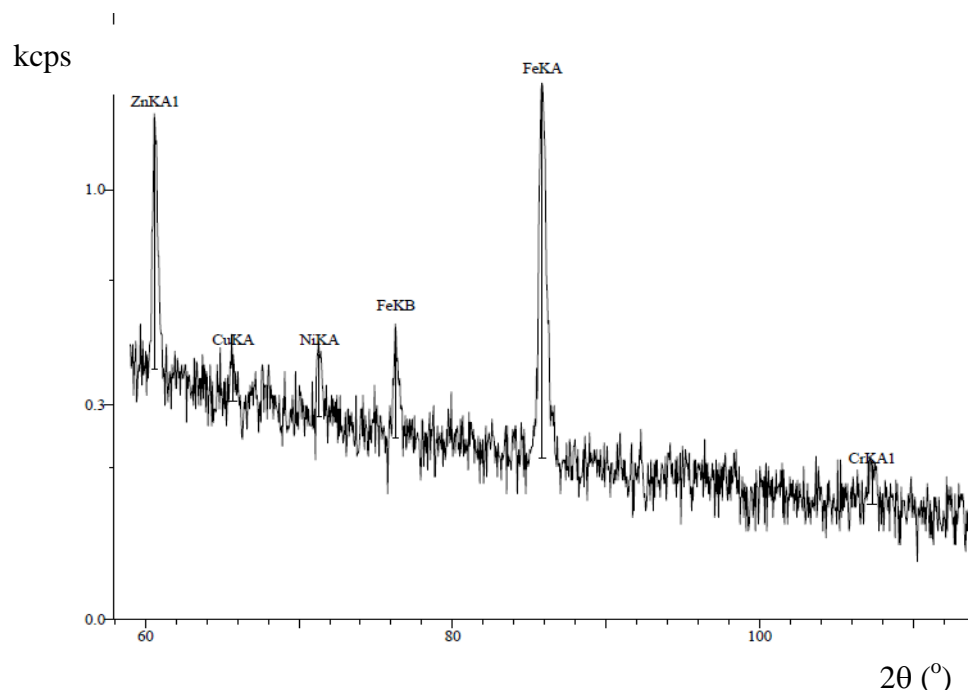
The semi-solid sludge was sliced into a thin sheet and weighed, and then dried at 105°C for 4 hrs. The average weight of 10 sheets before and after drying was obtained. The moisture content of the semi-solid sludge was thus determined as shown in table A-2

**Table A-2** Percentage of moisture content in semi–solid sludge

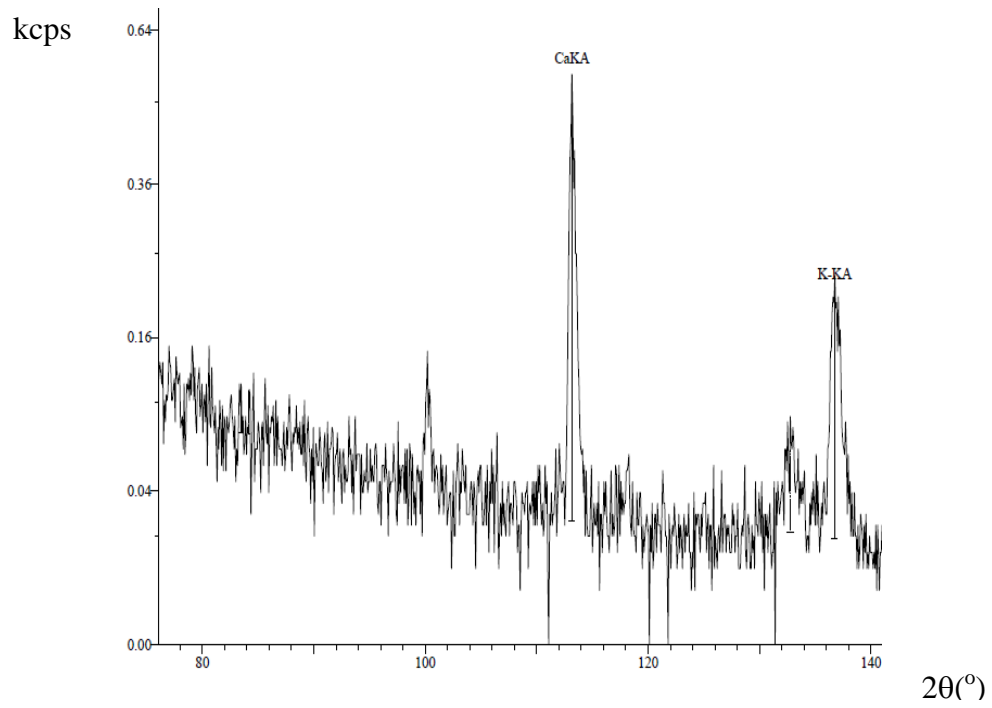
No.	Weight (g)				Moisture,%
	Sludge+Al cup (X1)	Al cup (A)	Sludge (X1-A)	Sludge+Al cup after drying (X2)	
1	6.5052	1.4794	5.0258	2.4248	81.19
2	6.5062	1.4718	5.0344	2.4165	81.24
3	6.4770	1.4714	5.0056	2.4087	81.27
4	6.5182	1.4783	5.0399	2.4314	81.09
5	6.5189	1.4787	5.0402	2.4535	80.66
6	6.4954	1.4885	5.0069	2.4503	80.79
7	6.5041	1.4867	5.0174	2.4298	81.20
8	6.5278	1.4893	5.0385	2.4352	81.23
9	6.4986	1.4765	5.0221	2.4288	81.04
10	6.5045	1.4855	5.0190	2.4359	81.06
11	6.5126	1.4888	5.0238	2.4296	81.27
12	6.4998	1.4754	5.0244	2.4324	80.95
13	6.4949	1.4879	5.0070	2.4295	81.19
14	6.5028	1.4886	5.0142	2.4474	80.88
15	6.4963	1.4672	5.0291	2.4298	80.86
16	6.4702	1.4654	5.0048	2.4352	80.62
17	6.5295	1.4776	5.0519	2.4429	80.89
18	6.4861	1.4734	5.0127	2.4427	80.66
19	6.5046	1.4748	5.0298	2.4497	80.62
20	6.4872	1.4761	5.0111	2.4509	80.55
	<b>Average</b>				<b>80.96</b>
	<b>SD</b>				<b>0.25</b>
	<b>%RSD</b>				<b>0.31</b>

$$\% \text{ Moisture} = 100 - \left( \frac{\text{Sludge weight after drying (g)} \times 100}{\text{Sludge weight (g)}} \right)$$

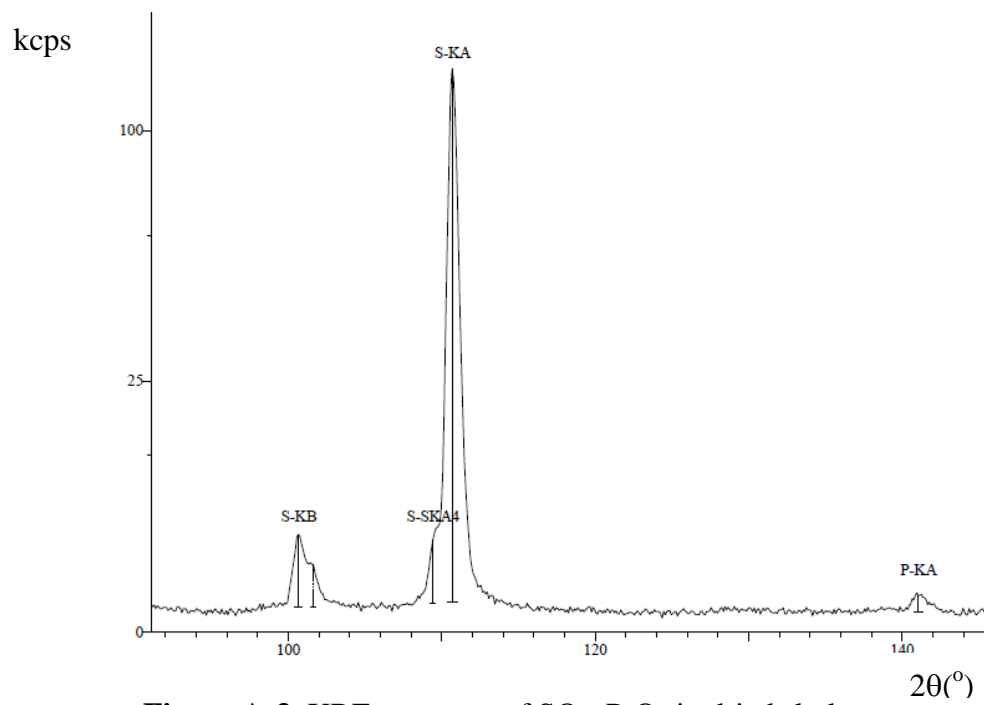
This indicated the presence of  $\text{Al}_2\text{O}_3$  in the dried sludge. In addition, some other element oxides in dried sludge were found, i.e.,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  as shown in Figure A-1 – 5 and amount of element oxide content in dried sludge as shown in table A-3



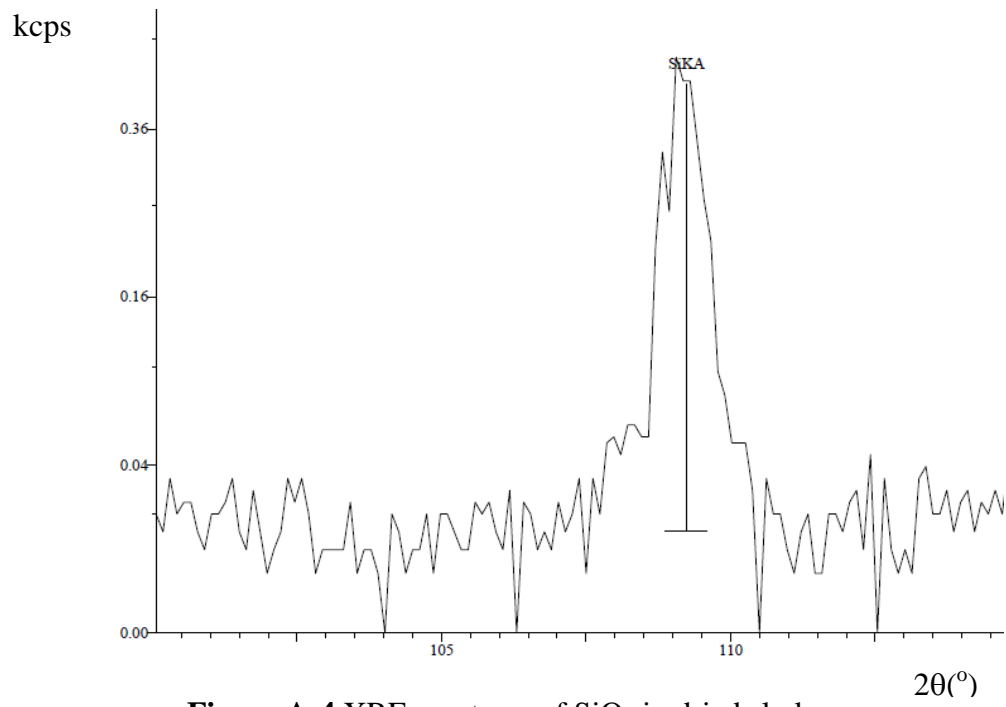
**Figure A-1** XRF spectrum of  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$  in dried sludge



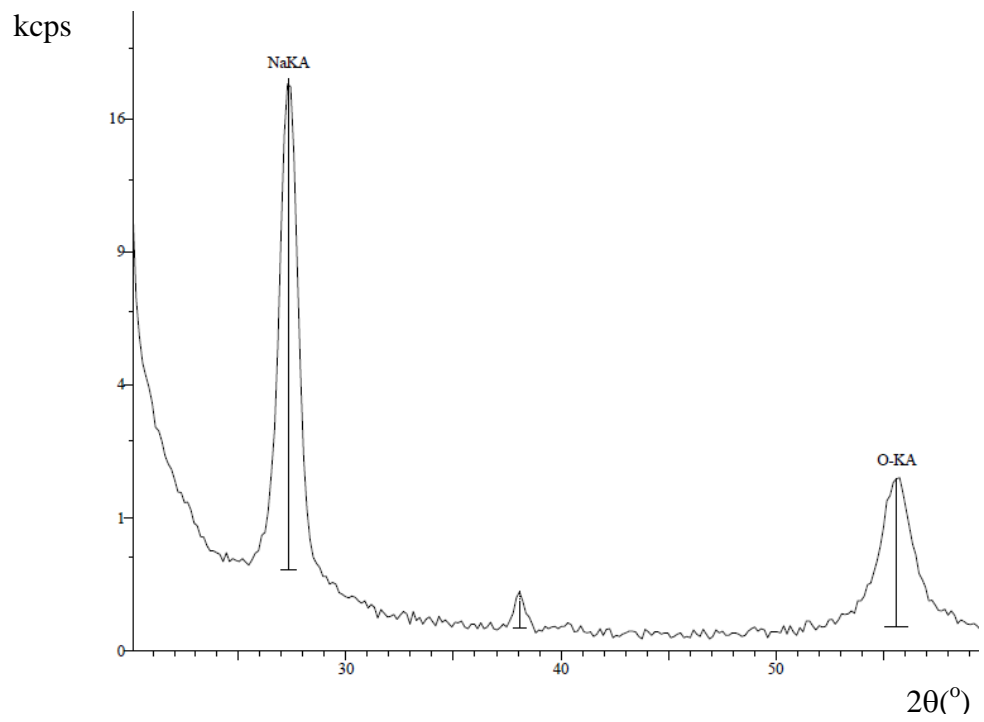
**Figure A-2** XRF spectrum of CaO, K<sub>2</sub>O in dried sludge



**Figure A-3** XRF spectrum of SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> in dried sludge



**Figure A-4** XRF spectrum of SiO<sub>2</sub> in dried sludge



**Figure A-5** XRF spectrum of Na<sub>2</sub>O in dried sludge

**Table A-3** Amount of aluminium oxide or alumina in dried sludge by XRF

No	Percentage of element oxide content in dried sludge*								
	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	Na <sub>2</sub> O	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	ZnO
1	43.91	15.65	8.65	0.35	0.11	0.09	0.06	0.04	0.02
2	43.89	15.61	8.60	0.32	0.10	0.08	0.05	0.03	0.03
3	44.06	15.79	8.69	0.38	0.13	0.11	0.07	0.05	0.02
<b>Avg</b>	<b>43.95</b>	<b>15.68</b>	<b>8.65</b>	<b>0.35</b>	<b>0.11</b>	<b>0.09</b>	<b>0.06</b>	<b>0.04</b>	<b>0.02</b>
SD	0.09	0.09	0.05	0.03	0.02	0.02	0.01	0.01	0.01
%RSD	0.002	0.006	0.005	0.086	0.135	0.164	0.167	0.250	0.247

\*Element content by theoretical formulas method, “fundamental parameter calculation”

## VITA

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