Thesis for the Degree of Doctor of Philosophy

Application of Aluminum based coagulants for the Treatment of Turbidity and Natural organic matter in Surface water and the Treatment of Phosphorus in Sewage effluent

by

Thuy Khanh Trinh

Department of Environmental Engineering

The Graduate School

Pukyong National University

February 2012

Application of Aluminum based coagulants for the Treatment of Turbidity and Natural organic matter in Surface water and the Treatment of Phosphorus in Sewage effluent

(하천수 중 NOM과 하수방류수 중 인 처리를
위한 알루미늄계 응집제의 적용)

Advisor: Professor Lim Seok Kang

by

Thuy Khanh Trinh

A thesis submitted in partial fulfillment of the requirements
for the degree of

Doctor of Philosophy

in Department of Environmental Engineering,
The Graduate School, Pukyong National University

February 2012

Application of Aluminum based coagulants for the Treatment of Turbidity and Natural organic matter in Surface water and the Treatment of Phosphorus in Sewage effluent

A dissertation

by

Thuy Khanh Trinh

Approved by:

Byunghun Lee

(Chairman) **Professor BYUNG HUN LEE**

Seok Jun Yeo

(Member) **Professor SEOK JUN YEO**

Kim, Sangdan

(Member) **Professor SANG DAN KIM**

(Member) **Dr. SEUNG WOO HAN**

Lim Seok Kang

(Member) **Professor LIM SEOK KANG**

February 2012

Application of Aluminum based coagulants for the Treatment of Turbidity and Natural organic matter in Surface water and the Treatment of Phosphorus in Sewage effluent

Thuy Khanh Trinh

Department of Environmental Engineering, The Graduate School,

Pukyong National University

Abstract

Using aluminium based coagulants for the removal of natural organic matter and turbidity from surface water and phosphorus from sewage effluent were investigated. Conventional Al salts, such as alum and $AlCl_3$, and Polyaluminum Chlorides (PACl) with different *r* (*r* = [OH]/[Al]) values were prepared in laboratory. Based on the difference in reaction kinetics of Al species and ferron reagent, the hydrolytic Al species in aluminum based coagulants were classified as fast reacting monomeric Al_a, slow reacting polymeric Al_b, and very slow/ or non reacting colloidal/precipitate Al_c. The results showed that the higher the *r* value of PACl, the lower the Al_a and the higher the Al_b and Al_c obtained. The characteristics of raw waters were analysed before performing jar tests. Various fractions of dissolved organic matter (DOM) in The Nakdong River water (Busan, Korea), such as hydrophobic acid, hydrophilic acid, and transphilic organic were isolated and coagulation behavior of each fraction was investigated. Also, phosphorus in sewage effluent from Nambu Sewage Treatment Plants was classified as organic-, condensed-, and ortho-P.

Preformed monomeric Al_a is the most unstable species and quickly transformed to other Al species while preformed Al_b and Al_c were relatively stable during coagulation. Performance of the coagulants was controlled not only by preformed species but also by those forming in situ during coagulation. The presence of Al species formed in situ strongly depends on coagulant dose and coagulation pH. At neutral and basic pHs, PACls containing more stable preformed Al_b were more efficient for turbidity and organic matter removal. At slightly acidic pH, predominant Al_a coagulants were more efficient since more Al_b was formed in situ at this condition. Experiments with isolated hydrophilic acids, humic acids, and fulvic acids also indicated Al_b was effective for removal of hydrophilic acids, the organic fraction that is most difficult to coagulate. Al_b (preformed and in situ formed), therefore was effective for removal of turbidity and NOM. However, at high Al doses and high pH, where Al_c was the predominant species formed in situ, the superior performance of Al_b in removing of turbidity disappeared. Due to its bulky structure which is effective in sweep flocs mechanism, Al_c is the most effective species for turbidity removal.

Experiments conducted with sewage effluent showed that phosphorus removal was correlated well with the content of Al_a in coagulants. Positive effects of Al_a for the removal of P might be due to high ability of monomeric Al in forming the $Al(OH)_x(PO_4^{3-})_{3-x}$ precipitates and in adsorption of phosphates into aluminum hydroxide precipitates that are formed predominantly in hydrolysis process of Al_a coagulants. Al_b, although has been known as the most effective species in removal of organic matter, did not show any superior performance in P removal. Al_c (preformed and in situ formed) might be favorable for adsorption of P and this species also showed a positive effect on removal of suspended P due to its superior performance in removal of turbidity from water. The residual P concentrations obtained were strongly depended on the coagulant type used, or the contents of Al_a, Al_b, and Al_c in the coagulants.

Results obtained from the study could be used for making an appropriate coagulant for a preferential aim of coagulation. Prehydrolyzed degree of PACl (*r* value) used should be determined according to a specific water characteristic and a target substance that need to be removed during coagulation.

CONTENTS

TABLES

FIGURES

Chapter 1

INTRODUCTION

Coagulation-flocculation has played, and will still play an important role, directly or indirectly, in the control of particulates, microorganisms, natural organic matter (NOM), synthetic organic carbon, precursors of disinfection byproducts (DBPs), some inorganic ions and metals, and ultimately, in the control of drinking water quality (Jiang, 2001). Although many advance treatment technologies have been developed recently, such as membrane, reverse osmosis…, coagulation is in of significance as a necessary pretreatment process to achieve high effectiveness of the treatment.

Coagulation using metal salts is also known as a very effective treatment process for removal of phosphorus (P) from wastewater. P is a limiting nutrient of eutrophication process and its presence, although with a low concentration of 0.05 mg/L (Manahan, 2001), may cause excessive growth of algal and nuisance aquatic plants in surface water. A significantly reducing of P load discharged into a receiving water body can control the eutrophication process (Chutter, 1990a; Dillon and Molot, 1996a). An importance source of phosphorus disposal into surface water comes from municipal wastewater and therefore, control of P discharge from wastewater treatment plants is necessary. The wastewater treatment plants must often meet effluent P discharge limitation. Chemical techniques using metal salts in coagulation process are reliable and well-established processes for achieving very low residual phosphorus concentration in wastewater treatment plant effluents.

Along with turbidity, removal of NOM is an important objective in coagulation process because it effect on treatment efficiency and finished water quality. For instance, NOM can decrease effectiveness of activated carbon, increase coagulant doses, and is an essential factor in the formation of disinfection by-products. Natural organic matter can be characterized by a number of different ways including separation by size, molecular weight (MW) and polarity. Size fractions can be defined as particulate (> 0.45 μm), dissolved (< 0.45 μm) and colloidal (1 nm to 1 μm) where the colloidal fraction spans the dissolved and particulate definitions. The dissolved organic carbon (DOC) fraction can be further characterized in terms of polarity (negative charge). The DOC fractions in order of increasing polarity are defined as hydrophobic (typically the largest DOC fraction for natural waters), transphilic and hydrophilic. Generally, hydrophobic DOC has the highest MW followed by followed by transphilic and hydrophilic DOC fractions. While most DOC exhibits polar characteristics, there is a higher density of polar groups on smaller hydrophilic compounds compared to larger hydrophobic compounds. Because of the complexity of NOM manner, coagulation for effectively removal of NOM is a challenge.

Al salts has long been used as coagulants in water treatment. When added into water, ion Al^{3+} rapidly undergoes a series of hydrolysis reactions in an uncontrolled manner to form a range of hydrolytic Al species, which is strong dependent on the nature of water, the coagulation pH, and the dose of coagulants. These Al hydrolytic species help to aggregate various aquatic particles into larger flocs and then these flocs are settled, filtered and removed from bulk water in subsequent processes. The Al hydrolytic products, but not coagulant itself, is responsible for the coagulation performance. Attention has been paid in recent years to preparing pre-hydrolysed Al coagulants, with Al hydrolytic species is controlled in manufacturing process. By this way, the coagulant chemistry can be controlled and the preferred solution conditions for the formation of the desired coagulant species can be maintained. These have been shown to perform better in some cases, in comparison with conventional coagulants such as alum. The superior performance of pre-polymerised coagulants is attributed to their wider working pH range, a lower sensitivity to low water temperature, lower doses required to achieve the equivalent treatment efficiency, and lower residual metal-ion concentrations.

Hydrolysis process to form hydrolyzed Al species is a very importance manner of Al based coagulants. Because of hydrolysis, the simple Al^{3+} ions do not exist in solutions around neutral pH and a range of hydrolysis products are responsible for the destabilisation/coagulation to remove impurities in water. Conventional coagulants, when added into water, are quickly hydrolyzed to form a series of hydrolysis products and frequently very rapid precipitation. The hydrolysis process is affected by many factors, such as pH, alkalinity, temperature, raw water compositions and consequently, the formed hydrolysis products are uncontrolled. Pre-polymerised Al coagulants with preformed Al species were developed to overcome this weak-point. Instead of controlling Al species forming in hydrolysis of coagulation-flocculation, that is very difficult, the Al species was controlled in preparation-manufacturing and pre-formed Al species are considered as stable species during coagulation/ flocculation.

Preformed polymeric Al coagulants have been shown to improve some of the coagulation performance compared to conventional coagulant (Edzwald, 1993; Matsui et al., 1998). The superior performance of pre-polymerised coagulants is attributed to their wider working pH range, a lower sensitivity to low water temperature, lower doses required to achieve the equivalent treatment efficiency, and lower residual metal-ion concentrations. Additionally, pre-polymerised coagulants have become increasingly used in water treatment due to their wider availability and reduction in cost (Sinha et al., 2004). It is believed that the superior of PACl is due to high positive charge and strong binding ability of preformed Al_{13} and this Al species were claimed as the most active species responsible for coagulation (Duan and Gregory, 2003; Van Benschoten and Edzwald, 1990). However, polymeric Al coagulants have not always shown the superior performance to traditional coagulants. Work of two researchers (Hu et al., 2006; Yan et al., 2008) demonstrated that traditional Al salt $AlCl_3$ was more effective than PACl in removing DOC and UV_{254}. Therefore, although high basicity PACl is generally considered as more effective coagulant in water treatment, the traditional coagulants also show effective removal in some circumstances. For phosphorus, although the removal using PACl has been carried out by a number of researchers (Boisvert et al., 1997a; Gillberg, 1996; Ratnaweera, 1992), their results showed considerable uncertainty about the precise mechanisms and overall performance of P removal (Jiang, 1998). The objective of this research was to develop a better understanding of the relationship between raw water characteristics, focus on NOM in surface water and phosphorus in sewage effluent, in considering of the relationship between Al species such as Al_a, Al_b, and Al_c species and removal performance. This research used batch jar test experiments to investigate coagulation performance. The main experimental variables were raw water manner, coagulant type with different Al species, coagulation pH, and coagulation dose. Specific component of this research were:

1. Coagulants (prepared in laboratory and commercial coagulants) were analysed in terms of various Al species of monomeric Al_a, polymeric Al_b, and precipitate/colloidal Al_c using ferron assay.

2. Raw waters were characterized by pH, alkalinity, dissolved organic

carbon (DOC), concentration, ultraviolet absorbance at 254 nm (UV_{254}), specific UV_{254} absorbance (SUVA), DOM (Dissolved Organic Matter) fractions as hydrophobic fulvic acids, hydrophobic humic acids, and hydrophilic acids, and average molecular weight ultra-filtration of DOM. Fractionation through XAD-8 and XAD-4 resin column was used to fractionate and isolate DOM. For sewage effluent, the various P species was analysed.

3. Coagulation performance of Al species was evaluated in terms of turbidity removal, U_{V254} and DOC removal. For sewage effluent, different phosphorus forms such as total, reactive, suspended, condensed, and organic P were measured.

4. Interaction between Al species and their coagulation performance of isolated organics such as fulvic acids, humic acids, and hydrophilic acids was investigated. Also, coagulation performance of an Al species with respect to a phosphorus fraction was considered.

5. Effects of coagulation pH and coagulant dose on coagulation of surface water and sewage effluent were investigated, focused on the behaviors of Al species at different conditions of dose and pH to understand the removal mechanisms.

A literature review on hydrolytic Al species, coagulation-flocculation for treatment of surface water and sewage effluent is presented in Chapter 2.

Chapter 3 describes the methods and materials used in the study. Chapter 4 presents the results of preparation and characterization of coagulants. The information in Chapter 5 is results of characterizing DOM and coagulation for treatment of surface water. Chapter 6 presents results of coagulation for removal of phosphorus. Chapter 7 summarizes the key findings of this research.

Chapter 2

LITERATURE REVIEW

This chapter provides background and a review of literature regarding the interaction between coagulants and coagulation-flocculation process. First, the hydrolysis process of Al-based coagulants and factors affect formed Al hydrolysis products are indentified. Second, the mechanisms of coagulation-flocculation are addressed and finally, relationships between water source quality, Al hydrolysis species, and coagulation performance are documented.

2.1. Chemistry of Al based coagulant

Water treatment using aluminum salts is closely related to the hydrolysis of aluminum ion when aluminum based coagulant is added into water. When the metal salt coagulants dosed into water, the metal ion in its structure such as Al^{3+} undergoes hydrolysis, polymerization, and precipitation process to form a range of various meta-stable and transient species existing in bulk solution. Studies on hydrolysis and coagulation mechanisms showed that it is not the coagulant itself, but these hydrolysis species (generated in situ), are responsible for the performance of coagulation process (Hu et al., 2006; Jiang, 2001; Shi et al., 2007). This part focuses on the hydrolysis process of aluminum, including hydrolysis products formed, aggregation and precipitation of these Al species, methods of speciation, and factors affect distribution of Al species in hydrolytic polymeric Al solution.

2.1.1. Mononuclear Hydrolytic Aluminum Species

Aluminium presents itself in a normal environment as the Al^{3+} cation. The aluminium cation takes six ligands into the inner coordination sphere, forming an octahedral complex in water (Fig. 2.1). This structure has been confirmed 40 years ago using proton nuclear magnetic resonance (^1H NMR) method (Fratiello et al., 1968).

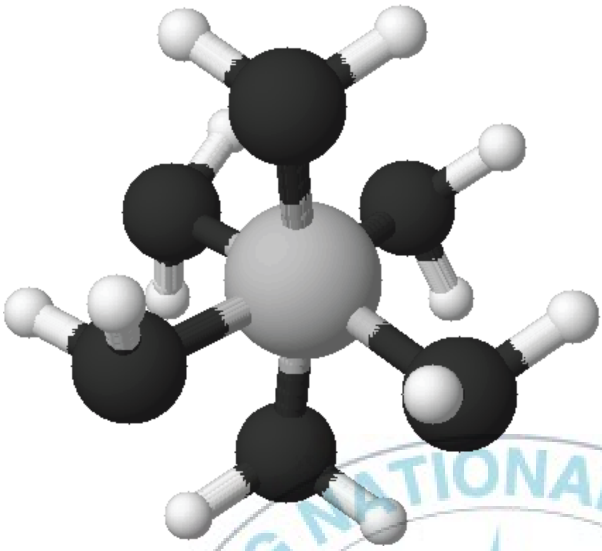


Fig. 2.1. Aluminium cation, $Al(OH_2)_6^{3+}$.

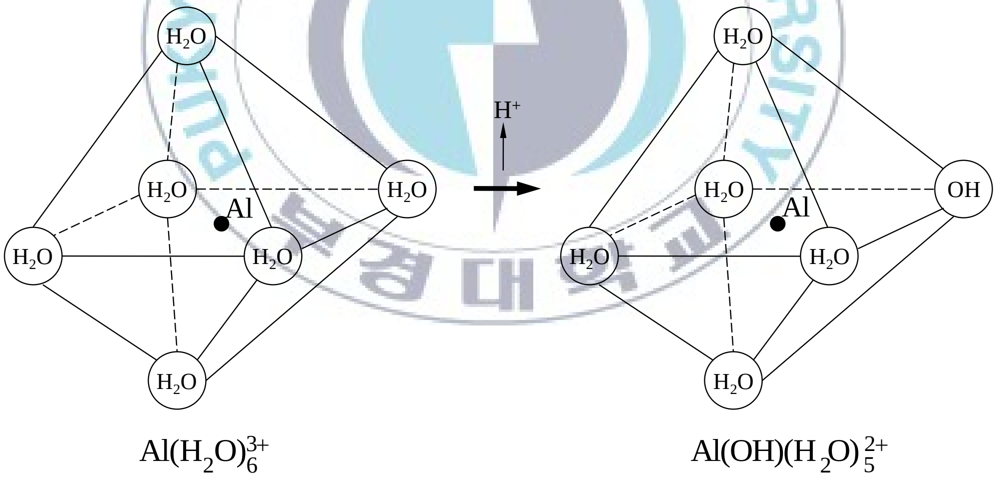


Fig. 2.2. Deprotonation of the aquo aluminum ion-initial step in aluminum hydrolysis (Letterman, 1991).

Owing to the high charge on the metal ion, water molecules are polarized and this can lead to a loss of one or more protons, depending on the solution pH (Fig. 2.2). The water molecules in the hydration shell are progressively replaced by hydroxyl ions, giving a lower positive charge, according to the following sequence:

$$\mathrm{Al(H_2O)_6^{3+} \rightleftharpoons Al(OH)(H_2O)_5^{2+} \rightleftharpoons Al(OH)_2(H_2O)_4^{+} \rightleftharpoons Al(OH)_3(H_2O)_3^{0} \rightleftharpoons Al(OH)_4^{-}}$$

$$\xrightarrow{\text{Increasing pH}}$$

However, this scheme is oversimplified. In addition to mononuclear Al dimeric, trimeric and polynuclear Al species can form in Al hydrolysis. Polynuclear hydrolysis products will be discussed in the following part.

The hydrolytic reactions of mononuclear Al solutions can be described by four stage equilibrium reaction:

In dilute acidic solution:

$$\mathrm{Al(H_2O)_6^{3+} + H_2O \rightleftharpoons Al(OH)(H_2O)_5^{2+} + H_3O^{+};} \qquad K_{1,1} \qquad (2.1)$$

$$\mathrm{Al(OH)(H_2O)_5^{2+} + H_2O \rightleftharpoons Al(OH)_2(H_2O)_4^{+} + H_3O^{+};} \qquad K_{1,2} \qquad (2.2)$$

$$\mathrm{Al(OH)_2(H_2O)_4^{+} + H_2O \rightleftharpoons Al(OH)_3(H_2O)_3^{0} + H_3O^{+};} \qquad K_{1,3} \qquad (2.3)$$

At higher pH values, a fourth-stage hydrolysis reaction described the formation of aluminate anion:

$$\mathrm{Al(OH)_3(H_2O)_3^{0} + H_2O \rightleftharpoons Al(OH)_4^{-} + H_3O^{+};} \qquad K_{1,4} \qquad (2.4)$$

The solubility of the amorphous Al(III) hydroxide species is governed by the reaction:

$$Al(OH)_3{}_{(amorph.)} + 3H^+ \rightleftharpoons Al^{3+} + 3H_3O^+; \qquad K_{so} \tag{2.5}$$

where $K_{x,y}$ are the stepwise equilibrium hydrolysis constants for the respective reactions. The overall formation constants (β) for these reactions, and also for the formation of a polynuclear hydroxoaluminium complex of the general form

$$xAl^{3+} + yH_2O \rightleftharpoons Al_x(OH)_y^{(3x-y)+} + yH^+ \tag{2.6}$$

can be expressed as

$$\beta_{x,y} = \frac{(Al_x(OH)_y^{(3x-y)+})(H^+)^y}{(Al^{3+})^x} \tag{2.7}$$

Because different investigators use different technique and methods to evaluate thermodynamic constants, the solubility constants $\beta_{x,y}$ for Al species has been determined with a certain degree of unanimity in the literature. Table 2.1 shows the solubility constants at infinite dilute and 25°C, which are believed are the most authoritative values (Bertsch and Parker, 1996).

Table 2.1. Aluminium hydrolysis and solubility constants at infinite dilute and 25^{o}C

Reaction	Log β	Reference
$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$	− 4.95	(Driscoll and Schecher, 1990)
$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$	− 10.10	(Cambier and Sposito, 1991)
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3^o(aq) + 3H^+$	− 16.80	(Cambier and Sposito, 1991)
$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+$	− 22.87	(Hargrove, 1986)
$Al(OH)_{3(am)} + 3H_3O \rightleftharpoons Al^{3+} + 3H_2O$	+ 10.80	(Nordstrom and May, 1996)
$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3(s)$	+ 33.00	(Faust and Aly, 1998a)
$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_{3(gibbsite)} + 3H^+$	− 7.74	(Anderson et al., 1982)

Note: Waters of hydration are omitted for simplicity

Although the most stable solids are crystalline forms of aluminum hydroxides, e.g. gibbsite, this form usually is formed very slowly (typically weeks or months). In the context of coagulation mechanisms, it is more relevant to consider the solubility of the amorphous $Al(OH)_3$, that is fresh precipitates. The fresh solid precipitation is usually considered to be the amorphous $Al(OH)_3$, which is amphoteric. It dissolves in a basic solution having excess of hydroxo-ions as aluminate-anion, or in acidic solutions as a cationic mono- or dihydroxo-complex.

Fig. 2.3 shows aluminum speciation diagram produced by MineQL+ program using data in Table 2.1. When pH is below 3, Al_{3+} is the dominant species. At pH value higher than 3, Al^{3+} is hydrolysed and hydrolysis products formed are $Al(OH)^{2+}$, $Al(OH)_2^+$, and finally $Al(OH)_4^-$. The complex $Al(OH)^{2+}$ is predominant present at the pH range of 4 to 5. Above pH 8, $Al(OH)_4^-$ is the dominating species. Trihydroxo-Al complex $Al(OH)_3^o(aq)$ is not a significant species in acidic pH and also in basic pH. Fig. 2.4 shows concentrations of various species in equilibrium with amorphous $Al(OH)_3(s)$ precipitate. Aluminum is the least soluble within a pH range of 5.7 to 6.2. Below a pH of 5.7, freshly precipitated $Al(OH)_3(am)$ is quite soluble and other species can predominate.

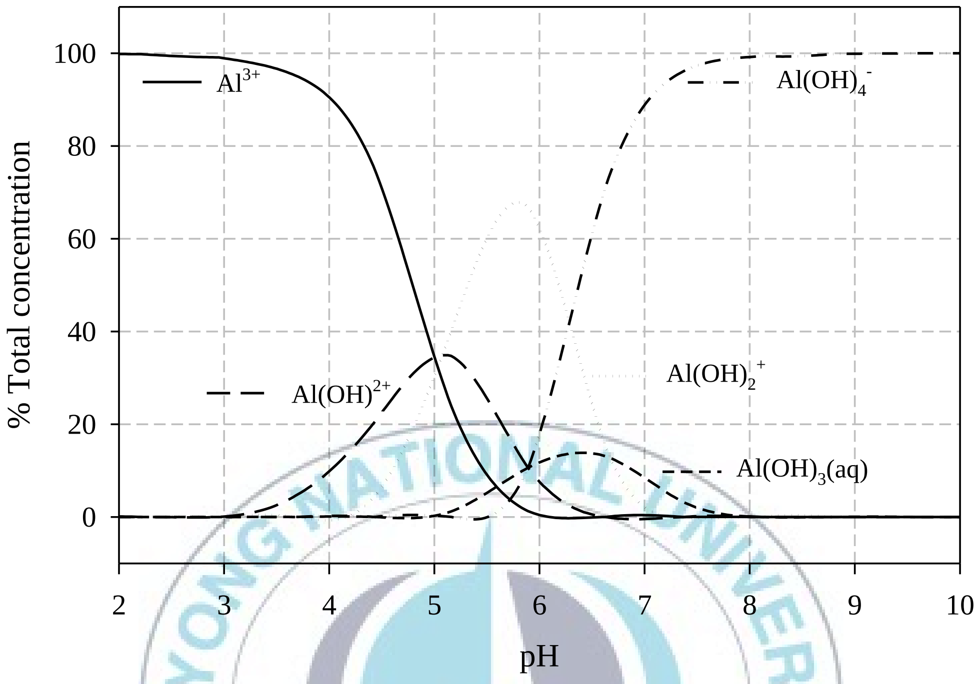


Fig. 2.3. Distribution of aluminum species in equilibrium with amorphous $Al(OH)_3$(am) produced by MineQL$^+$ program, using thermochemical data in Table 2.1, without crystalline solids and without ion strength correction, Al concentration of 10^{-9} M.

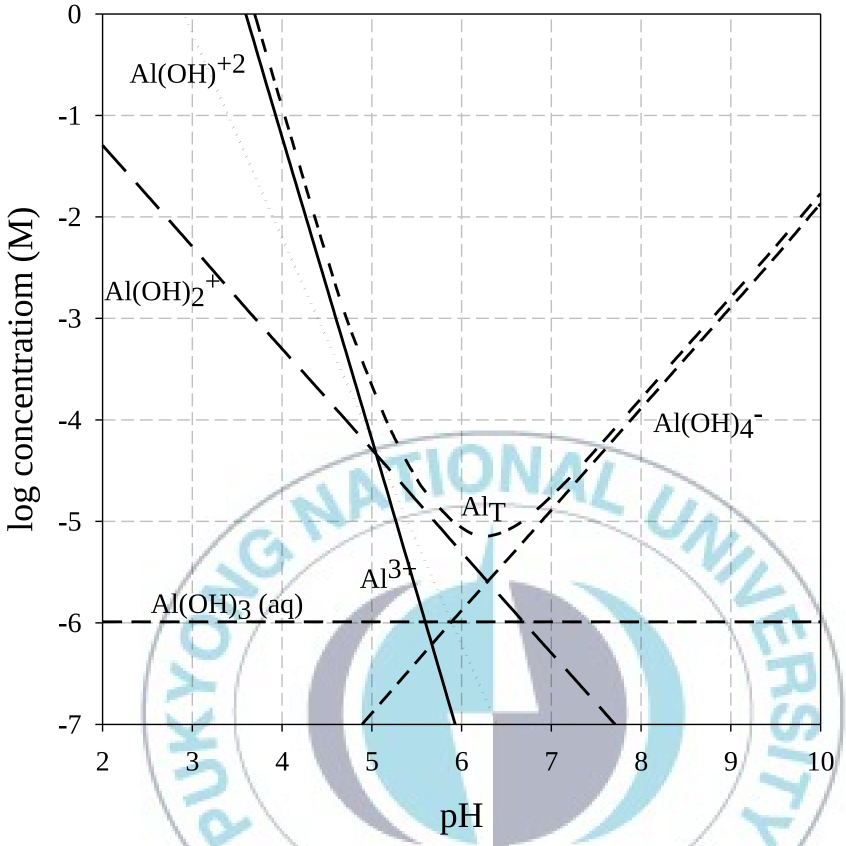


Fig. 2.4. Concentration of Al monomeric hydrolysis products in equilibrium with $Al(OH)_3$(am), produced by MineQL$^+$ program, using thermochemical data in Table 2.1, without crystalline solids and ionic strength corrections, Al concentration of 10^{-9} M.

2.1.2. Polynuclear Hydrolytic Aluminium Species

Brosset (Brosset, 1952) outlined a large number of polynuclear Al(III) hydrolysis species which could form as a function of an increasing of *r* ratio:

$$
\begin{array}{l}
Al^{3+} + Al^{3+} + 3H_2O \rightleftharpoons Al_2(OH)_3^{3+} + 3H^+ \\
Al_2(OH)_3^{3+} + Al^{3+} + 3H_2O \rightleftharpoons Al_3(OH)_6^{3+} + 3H^+ \\
\qquad\qquad -- -- -- -- -- \\
Al_{n-1}(OH)_{3(n-2)}^{3+} + Al^{3+} + 3H_2O \rightleftharpoons Al_n(OH)_{3(n-1)}^{3+} + 3H^+ \\
\qquad\qquad -- -- -- -- -- \\
\qquad\quad \text{(iso electric point)} \\
\qquad\qquad -- -- -- -- -- \\
Al_n(OH)_{3n+1}^{-} + H_2O \rightleftharpoons Al_{n-1}(OH)_{3(n-1)}^{0} + Al(OH)_4^{-} + H^+ \\
\qquad\qquad -- -- -- -- -- \\
Al_3(OH)_{10}^{-} + H_2O \rightleftharpoons Al_2(OH)_7^{-} + Al(OH)_4^{-} + H^+ \\
Al_2(OH)_7^{-} + H_2O \rightleftharpoons Al(OH)_4^{-} + Al(OH)_4^{-} + H^+
\end{array}
\qquad (2.8)
$$

Fig. 2.5 shows the hydrolysis schematic of Al from mono nuclear species to polynuclear Al species and finally aluminate ion at high pH.

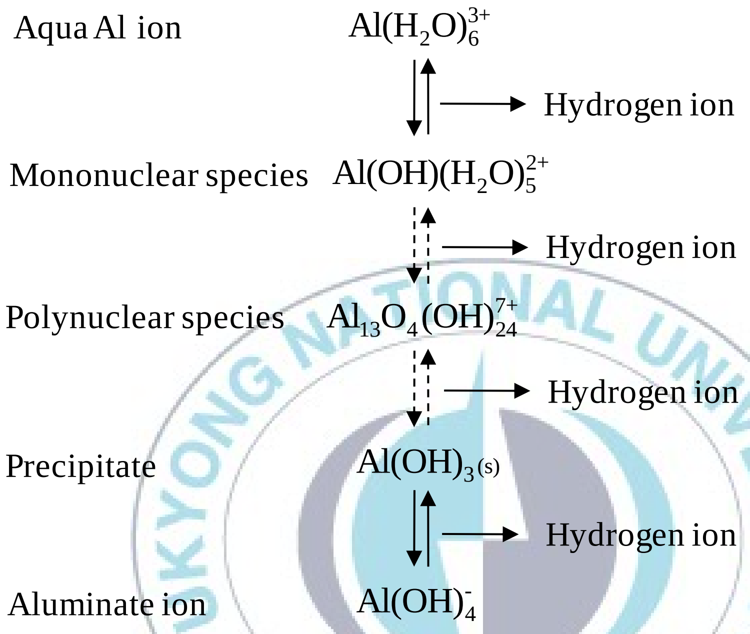


Fig. 2.5. Aluminum hydrolysis products. The dash lines are used to denote an unknown sequence of reactions (Letterman, 1981).

Some polynuclear species which had convincing experimental support, albeit usually indirect, were proposed: $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^+$, $Al_3(OH)_8^+$, $Al_3(OH)_4^{5+}$, $Al_8(OH)_{20}(H_2O)_x^{4+}$, those of the "core-link" or "gibbsite fragment" model, $Al_6(OH)_{12}(H_2O)_{12}^{6+}$ through $Al_{54}(OH)_{144}(H_2O)_{36}^{18+}$, and the $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ species and its larger congeners (Bertsch and Parker, 1996). However, regardless of a great deal of literatures, the chemistry composition in hydrolyzed Al solution is not completely determined yet.

Only eleven Al species have been crystallized and identified in hydrolyzed Al solutions up to now. These species include: five monomers Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^0(aq)$, and $Al(OH)_4^-$; dimers $Al_2(OH)_2^{4+}$; trimers $Al_3(OH)_4^{5+}$; two Keggin polymers $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (ε-Al_{13}), $Al_{30}O_8(OH)_{56}(H_2O)_{24}^{18+}$ (δ-Al_{13}); and two flat polymers $Al_{13}(OH)_{24}(H_2O)_{24}^{15+}$ and $Al_8(OH)_{14}(H_2O)_{18}^{10+}$ (Baes and Mesmer, 1976; Bertsch and Parker, 1996; Casey et al., 2005; Casey et al., 2001; Jolivet et al., 2000; Seichter et al., 1998).

Traditionally, the most popular hydrolysis polynucleation model among geochemists is the "core link" or hexameric ring scheme with the basic unit for Al polynuclear formation is either $Al_6(OH)_{12}(H_2O)_{12}^{6+}$ (single ring, Fig. 2.6) or $Al_{10}(OH)_{22}(H_2O)_{16}^{8+}$ (double ring). A series of "Core-link" polymeric Al species, such as $Al(Al_2(OH)_5)_n^{3+n}$ was first suggested by Brosset in 1954 (Brosset et al., 1954). The model afterward was introduced and improved by Hsu (Hsu, 1989a; Hsu and Bates, 1964), Hem (Bersillon et al., 1978; Hem and Roberson, 1967, 1990; Smith and Hem, 1972). The basic premise for this model is that the hexanuclear species condense in a bidimensional pattern to form larger and larger polynuclears having the basic structural features of the trihydroxide mineral phases, such as gibbsite (Fig. 2.7). It was found that in gibbsite crystal produced as a result of neutralization of Al(III) solutions and the model follows the crystallographic law of gibbsite. This model can not only interpreter the existence of various polymeric Al species, but also explains how the monomeric Al and polymeric Al are converted into $Al(OH)_3(am)$. Although there is no direct evidence supporting the existence of these transient species, the "core-link" model has been coexisting with the "Cage-like" Keggin-Al_{13} model, which is discussed in the next paragraph.

Fig. 2.6. Representation of the hexanuclear $Al_6(OH)_{12}(H_2O)_{12}^{6+}$ Al species - basic structure of the "core-link" or "gibbsite fragment" model (Schutz et al., 1987).

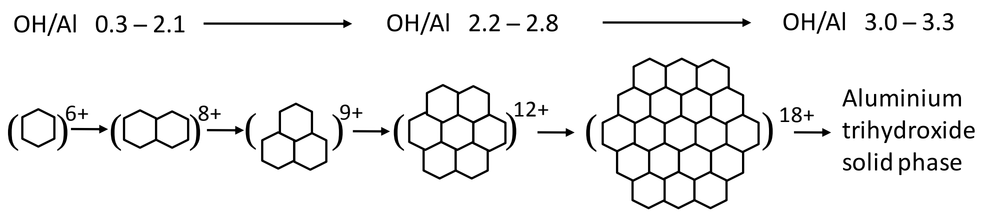


Fig. 2.7. The polymerization of Al^{3+} via coalescence of the hexamer units according to the "gibbsite-fragment" model (Hsu, 1989b).

The "Cage-like" Keggin-Al_{13} model was more recently proposed by researchers who believe that the polymeric species are formed with unit cells of the tricadimeric Al_{13} polynuclear species, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (Fig. 2.8) (note that the charge of Al_{13} polynuclear has been reported to range from 3^+ to 7^+ (Bottero et al., 1980). The work of Akitt (Akitt, 1990; Akitt and Elders, 1985; Akitt and Farthing, 1978; Akitt et al., 1972), Bottero (Bottero et al., 1987a; Bottero and Bersillon, 1989; Bottero et al., 1988; Bottero et al., 1982), Bertsch (Bertsch, 1987; Bertsch et al., 1986a; Bertsch et al., 1986b; Bertsch and Parker, 1996; Bertsch et al., 1986c; Parker and Bertsch, 1992a, b) has been proving the existence of this species. Nowadays, the existence of Al_{13} is undoubtable and the study of Al_{13} mainly focuses on how to purify this species in hydrolyzed Al solution containing various Al species. This model includes Al_{13} and larger condensed units of this basic structure, usually in combination with a minimum of other species, such as the dimer and/or the trimer. The polynuclear species of Al^{3+} in the "Cage-like" model can be identified instrumentally, such as ^{27}Al-NMR (Akitt et al., 1972) and small angle X-ray (Bottero et al., 1982) methods. Therefore, this model has gained more approval and become the main viewpoint in the chemistry of flocculants. However, it can only monitor four highly symmetric Al species by ^{27}Al-NMR studies, whose chemical shifts follow as: 1) hexaaqua Al^{3+} and monomer at 0 ppm: $Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{2+}$ and $Al(OH)(H_2O)_4^{1+}$; 2) dimer and few trimer at 3–5 ppm: $Al_2(OH)_2(H_2O)_8^{4+}$ and $Al_3(OH)_4(H_2O)_{10}^{5+}$; 3) the tricadimer ($\varepsilon$-$Al_{13}$) at 62.5 ppm: $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and the δ-Al_{13} polymer at 70 ppm: $Al_{30}O_8(OH)_{56}(H_2O)_{24}^{18+}$; and 4) the $Al(OH)_4^-$ anion assigned at 80 ppm. A lot of polymeric Al species can't be detected by ^{27}Al-NMR, so those species that can't be detected directly by experiments may also exist. Those species that are detected by ^{27}Al-NMR are only the species of certain stage of the hydrolysis–polymerization of Al^{3+}. ^{27}Al-NMR spectrum sometimes make the peak base greatly wider without confirming their forms (Bi et al., 2004).

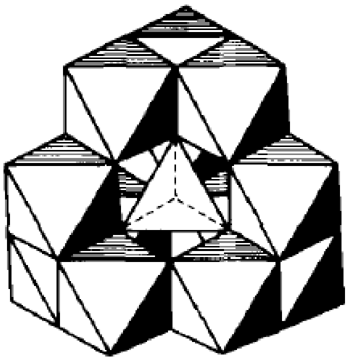


Fig. 2.8. Representation of the tricadimeric $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ Al_{13} polynuclear species - basic structure of the “Keggin-Al_{13} model (Bertsch and Parker, 1996; Schutz et al., 1987).

2.1.3. Aggregation and Precipitation of Al Species

Nucleation of Al mononuclear and polynuclear species into colloidal or other solid phases is an important phenomenon utilized in physicochemical treatment of water and wastewaters (De Hek et al., 1978; Letterman and Iyer, 1985; Snodgrass et al., 1984). (Bertsch and Parker, 1996) proposed reaction pathways for formation of trihydroxide mineral phase, as shown in Fig. 2.9. Reaction pathway 1 proceeds when solution is super saturation by diluting or when the samples are neutralized very rapidly. Under these conditions, little or no Al_{13} form and transform to nuclei is rapid. Reaction pathway 2 and 3 both involve the formation of Al_{13}. Al_{13} formed in hydrolysis can be present either as a soluble species (Pathway II) or can form aggregates through anion bridging mechanisms (outer-sphere associations). The researchers believe that this aggregation mechanism (pathway III) can account for the Al_c fraction in partially neutralized solutions as measured by spectrophotometric kinetic methods.

Pathway 2 happens when conditions favor formation of significant quantities of Al_{13} and aggregated Al_{13} unit ($[Al_{13}]_n$) (Rx path III) are not formed during neutralization. Dissociation of Al_{13} units to mononuclear species (pathway IIa) or transform to condensed aggregates (pathway IIb) is very slow and the Al_{13} exhibit long-term meta-stability (months to years). In case of ($[Al_{13}]_n$) units are formed during the initial hydrolysis, the disappearance of Al_{13} through deposition on these nuclei is fast (weeks to months) (pathway IIc). The transformation from $[Al_{13}]_n$ to poorly ordered solid phase is highly depend on the neutralization conditions, the nature and the concentration of anion which act to neutralize the charge on the Al_{13} unit and facilitate bridging.

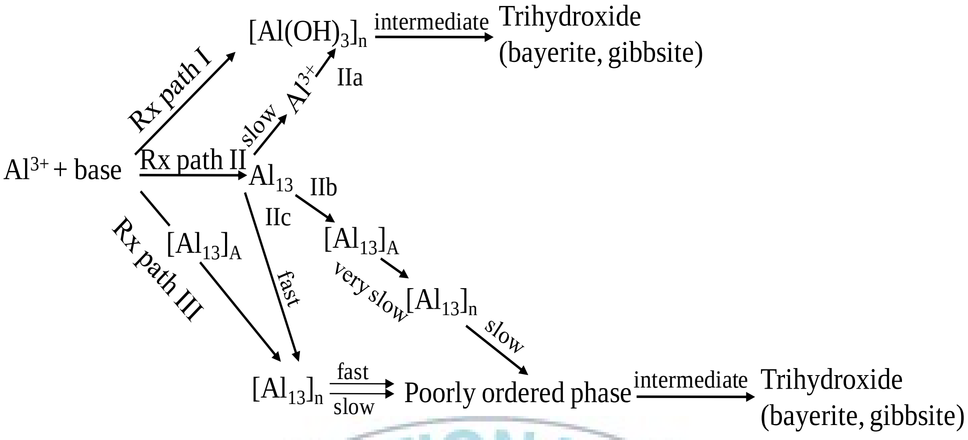


Fig. 2.9. Proposed reaction pathways (Rx path) for trihydroxide mineral phase formation from hydrolyzed aluminum solutions, demonstrating the role of Al_{13} in controlling relative reaction kinetics. The subscript “n” indicates nuclei of precipitated Al. “A”denotes outer-sphere aggregates of Al_{13} units.

2.1.4. Al Speciation Methods

2.1.4.1. Potentiometric Titration

The method of potential metric titration has been used for more than 70 years and it is the key method in most investigations of aqueous aluminum chemistry. Because of the lack of a suitably reversible electrode for aluminum, ion activities of this ion cannot be measured directly by ion-selective electrodes. Hydrolysis of Al^{3+} is investigated through application of readily available ion-selective electrodes for measuring pH values and F^- ion activities in studies of aluminum fluoride complexes. The data achieved is usually handled by software that calculate the best fit of the titration curve for a suggested speciation as well as gives β value of the selected species.

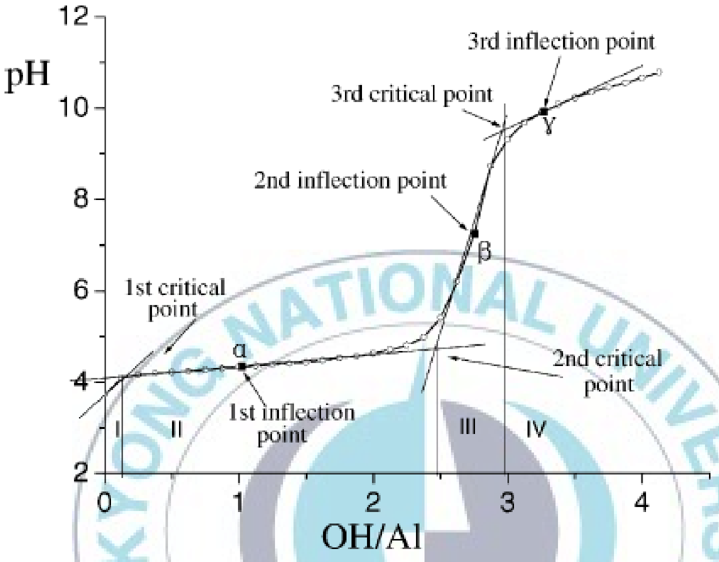


Fig. 2.10. The base titration curve (pH vs. OH/Al) and the fractionation of polynuclear Al under the moderate low rate of base addition (four districts/six characteristic points). Titration rate = 0.8 ml/min, $AlCl_3 = 5 \times 10^{-3}$ M, NaOH = 0.01 M, ionic strength I = 2×10^{-2} M.

Fig. 2.10 illustrates the potentiometric titration experimental method to interpreter fractionation of polynuclear Al. In district I ($r < 0.2$, pH =4.1), the main Al species are Al^{3+}. The main Al species are small/middle polymeric Al exists in district II ($0.2 < r < 2.5$, $4.1 < \text{pH} < 4.6$). District III ($2.5 < r < 3.0$) with the main Al species are large polymeric Al and sol/gel $Al(OH)_3$. District IV ($r > 3.0$, pH = 9.6) is district of the gel Al_c and then monomeric $Al(OH)_4^-$.

2.1.4.2. The ^{27}Al NMR

^{27}Al NMR, along with Al-Ferron complexation timed spectrophotometry, are the two main methods used in the study of Al(III) hydrolysis and formation of polymeric species. ^{27}Al NMR method was founded on 1969 by (Akitt et al., 1969a, b) and it has been widely used, in combination with other data, as a method that provide direct evidence for the existence of a number of Al polynuclear species in a wide range of hydrolyzed Al solution. There are usually three major signals, such as monomeric ions at 0 ppm, Keggin cation $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ at 62.5 ppm, and the $Al(OH)_4^-$ at 80 ppm. However, a number of additional resonances in ^{27}Al NMR spectra of hydrolyzed Al solutions have been reported and summarized in Table 2.2. In 1991, (Fu et al., 1991) used ^{27}Al NMR spectroscopic kinetic studies to identify three new polyoxoaluminum cations formed by transformation of Al_{13}, which we denoted as Al_{P1}, Al_{P2}, Al_{P3}. They have resonances corresponding to tetrahedrally coordinated Al at 64.5, 70.2, and 75.6 ppm, respectively, and octahedral resonances at about 10 ppm. Although being considered as a powerful method to provide direct evidence for polynuclear species and the changes of their relative concentrations during the hydrolysis (Akitt and Farthing, 1981; Bottero et al., 1982), the method is rather slow and it requires relatively concentrated solutions, for example Al_{13} cannot be detected in solutions of Al concentration < 0.1 M (Zhou et al., 2006b). Moreover, this method cannot detect unsymmetrical aluminum–units, such as five coordinated aluminum hydroxide (Swaddle et al., 2005) and therefore, have been unable to provide unequivocal evidence for all of the polynuclear species that may be present (Bertsch and Parker, 1996).

Table 2.2. ^{27}Al NMR-resonances observed in hydrolyzed Al solutions and their assignments

Chemical shift (δ), ppm	Assignment	Reference
Octahedral coordination		
~ 0[a]	Monomer: $Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{5+}$, $Al(OH)_2(H_2O)_4^{+}$	(Akitt et al., 1989)
~ 3–4	Oligomer: $Al_2(OH)_2^{4+}$, $Al_2(OH)_5^{+}$; $Al_3(OH)_8^{+}$	(Akitt et al., 1989)
~ 8–12	Al_{13} or Al_{P1}[b] Al_{P2}[b], Al_{P3}[b]	(Fu et al., 1991)
Tetrahedral coordination		
~ 63	Al_{13}	(Fu et al., 1991)
~ 65	Al_{P1}[b]	(Fu et al., 1991)
~ 70	Al_{P2}[b]	(Fu et al., 1991)
~ 75	Al_{P3}[b]	(Fu et al., 1991)

[a] The chemical shift of the $Al(H_2O)_6^{3+}$ species in influenced slightly by salt used and by the pH of solution, which broadens and shifts the peak position due to exchange with the $Al(OH)(H_2O)_5^{2+}$.

[b] "Al^{13}-like" polynuclears, most likely condensation products of Al_{13}.

An example of ^{27}Al NMR spectrum is illustrated in Fig. 2.11. The ^{27}Al NMR spectrum of a solution containing Al_{13} Ke-J and monomers heated at 130°C, during 15 h, presents five signals in the AlO_4 chemical shift range: 63, 64.5, 70, 76 and 81 ppm (Fig. 2.11b). Al_{13} Ke-J (63 ppm) and Al_{30} Kd-T (70 ppm) were unambiguously assigned. As suggested in the literature, the signals at 64.5 and 76 ppm correspond to Keggin aluminum polycations having a central AlO_4 in a shell of AlO_6. A new signal, of very low intensity, appears at 81 ppm. At 80 ppm one finds the $Al(OH)_4^-$ signal, but this species does not exist at pH 3.7. The signal at 81 ppm must, therefore, be assigned to another Keggin polycation (Allouche and Taulelle, 2003).

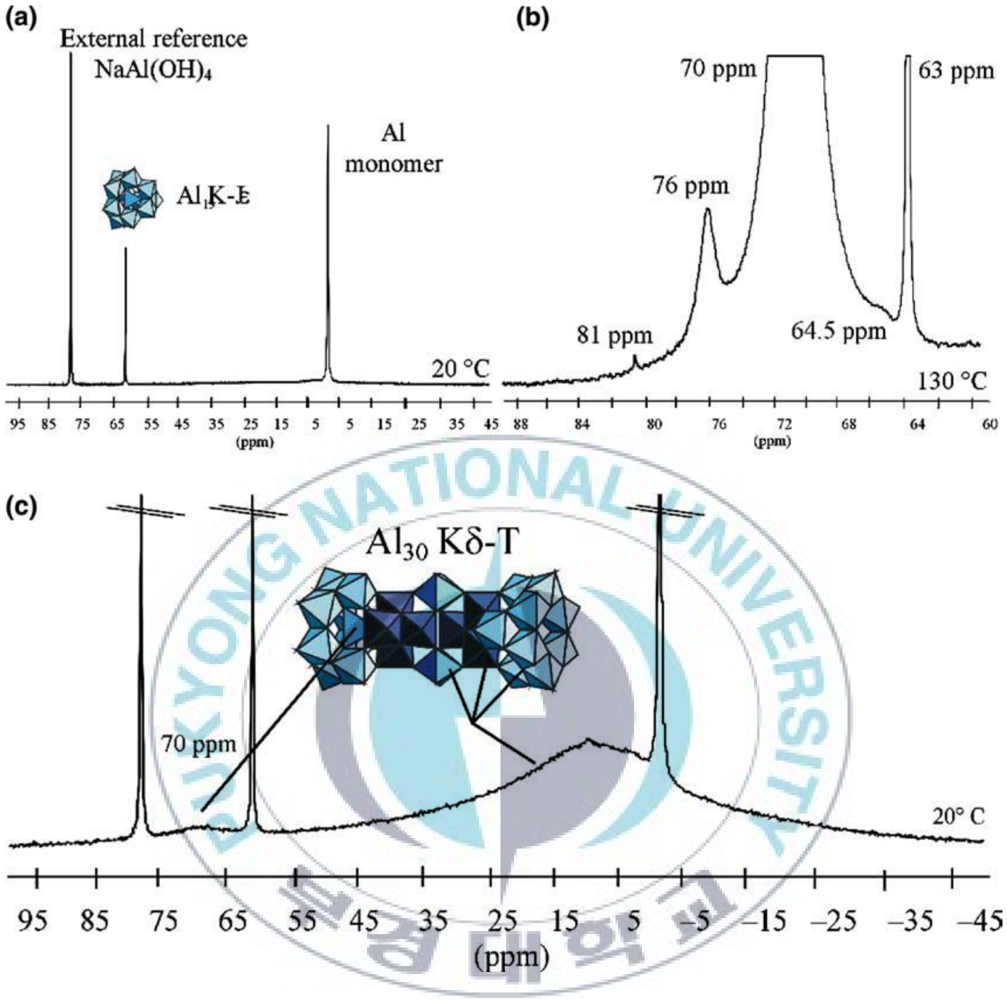


Fig. 2.11. Referenced ^{27}Al NMR spectrum, at 20^{o}C of (a) freshly hydrolyzed aluminum solution (r = 2:46) containing monomers and Al_{13} Ke-J; (b) Expansion of the AlO_4 chemical shift range of a hydrolyzed solution (r = 2.46), after 12h at 130^{o}C; and (c) ^{27}Al NMR spectrum of an aged (6 months) hydrolyzed solution (r = 2.46), containing initially Al_{13} Ke-J and monomers (Allouche and Taulelle, 2003).

2.1.4.3. The Spectrophotometric Ferron Method

Kinetically based spectrophotometric methods have been utilized for many years in attempt to quantify the various Al species. The kinetic methods based on the interaction of Al with a complexing agent, such as 8-quinolinolate (Okura et al., 1962) and ferron (Smith, 1971). In preparing of aluminum coagulant for water treatment, the Al species are mainly obtained by the Ferron method because of its simplicity, level of precision, and moderate reaction rate of ferron with Al (Åström and Corin, 2000).

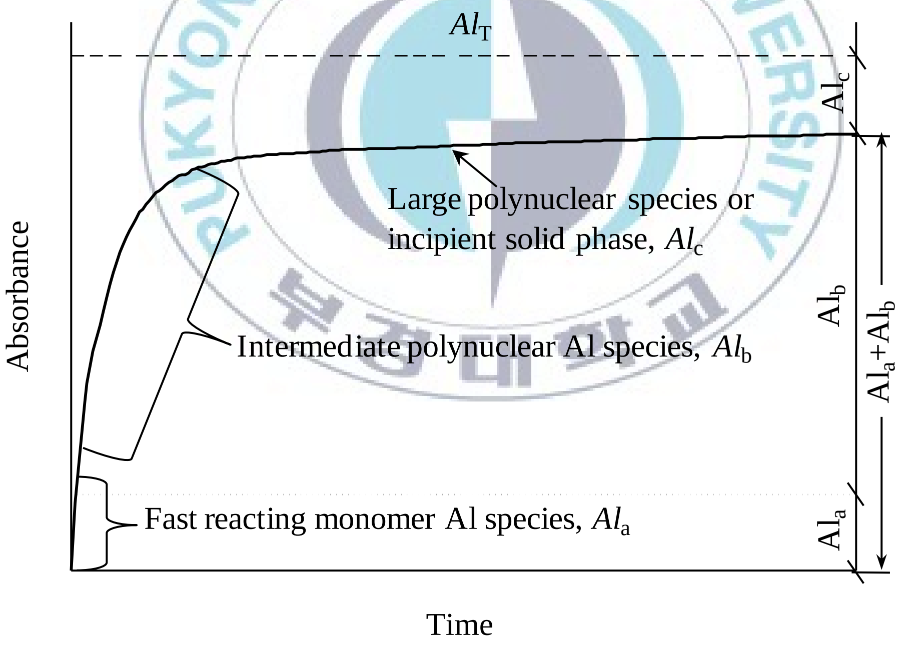
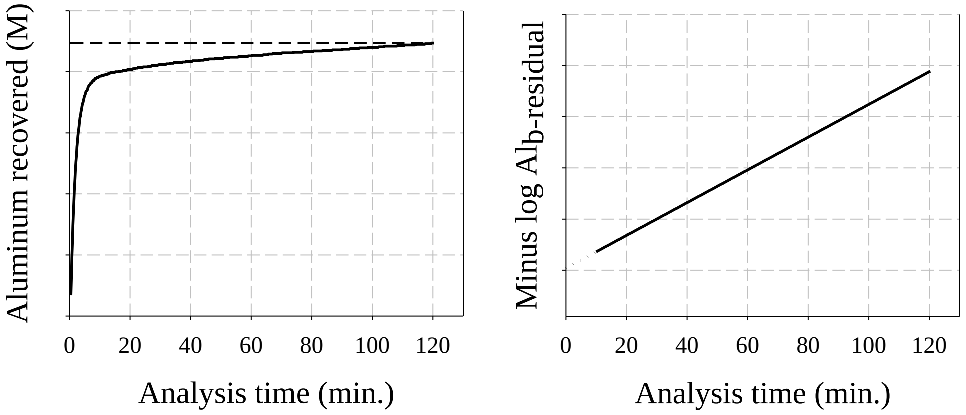


Fig. 2.12. Common interpretation of the ferron-Al reaction.

Ferron method was first found by Smith in 1971 (Smith, 1971; Smith and Hem, 1972) and since then, it have been continuously modified. Common interpretation of the ferron-Al reaction is shown in Fig. 2.1. Smith and Hem identified three forms of Al in partially neutralized solutions that exhibited differential reaction kinetics with ferron: Al reacting instantaneously with ferron was mononuclear (Al_a), while intermediate polynuclear Al species (Al_b) displayed pseudo-first-order reaction kinetics with ferron, and that the Al fraction having a virtually imperceptible reaction rate with ferron was composed of very large polynuclear species or incipient solid phase (Al_c). Estimation of Al species was summarized as follow: Concentration of aluminum recovered which was calculated from absorbance of Al-ferron complexes at 370 nm was plotted as a function of analysis time and from this curve, three types of aluminum was measured. Total quantity of Al_a + Al_b was determined by extrapolating the essentially straight portions of the curve (Al_c section) back to zero time (Fig. 2.13 a). Minus log $Al_{b\text{-residual}}$ was plotted as a function of analysis time (concentration of $Al_{b\text{-residual}}$ was determined by subtracting data points on aluminum recovered-analysis time curve from the values of the extrapolated (dotted line) at the same analysis). Al_b was obtained by extrapolating the minus log $Al_{b\text{-residual}}$ – analysis time line from the zero time, and Al_a was calculated from the difference between ($Al_a + Al_b$) and Al_b values (Fig. 2.13b).



a) b)

Fig. 2.13. Graphically determination of Al species, according to Smith, 1972.

After that, in 1980, (Bersillon et al., 1980) developed a speciation scheme to differentiate Al species, where they employed (1) a modification of the ferron procedure to estimate mononuclear Al, (2) a kinetically controlled selective adsorption procedure for the estimation of “low” polynuclear Al species, and (3) a precipitation step using Na_2SO_4 to estimate “medium” and “high” hydroxo-Al polynuclear species. However, in 1986, (Bertsch et al., 1986b), using ^{27}Al NMR, have cast a doubt on such indirect methods, since they found that a single polynuclear species displayed differential precipitation kinetics with added sulfate and be differentially adsorbed by a cation-exchange resin.

The developments of spectrophotometer which permit continuous monitoring the change in absorbance of ferron-Al complexes during a long time of reaction have given a lot of support to ferron method. Jardine and

Zelany (Jardine and Zelazny, 1986) conducted an investigation using such data, in which, interactions of monomeric Al and small polymeric Al with ferron were described as a binary species first-order rate function while ferron reactions at longer times were related to the decomposition of large polymeric Al, which were described by pseudo first-order kinetics. The authors proposed that this approach allowed more accurate quantification of the Al fractions present, and can be extended to accommodate several distinct fractions with overlapping reactions, as long as the rate constants are sufficiently different. The calculation was summarized as follow: The initial 250 sec of reaction were continuously recorded and the observed data was fitted to the two species first-order rate (Eq. 2.9). The model fitting using a nonlinear least square inversion technique provided the model fitted parameters, such as rates of monomer (k_a), the rate of small polymer (k_b) reactions with ferron as well as the mole fraction of monomeric species present (f_a, $f_a = (A_0)/(A_0 + B_0)$). Absorbance increases at times longer than 300sec was correspond to a tertiary reaction that was described by pseudo first-order kinetics and they said “most likely this portion of the reaction is related to the interaction of ferron with large polymers”. The data was plotted as $-\log(Al_\infty - Al_t)$ vs. t plot and from the plot, the rate constant of the reaction, k_c, were determined.

$$\frac{(C_\infty - C_t)}{C_\infty} = (e^{-k_a t} - e^{-k_b t})(\frac{A_0}{A_0 + B_0}) + e^{-k_b t} \qquad (2.9)$$

(Parker and Bertsch, 1992b) conducted an investigation testing the correspondence between Al_{13} ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$) determined by ^{27}Al NMR and polynuclear Al fraction that exhibits a moderate reaction rate with the spectrophotometric ferron reagent (Al_b). In their study, the composition of working ferron reagent and the procedure of spectrophotometric analysis was carefully introduced and since then, it has been cited as an importance reference in most of studies using ferron to investigate Al species in hydrolyzed Al solution. It is important to maintain a wide ferron: Al molar ratio (i.e > 50), such that the kinetics of ferron-Al reaction can be analyzed in terms of pseudo-*n*th-order reactions with respect to Al alone. The preparation of working ferron solution and measuring procedures are briefly summarized as following:

Three stock solutions described previously by Jardine and Zelany (Jardine and Zelazny, 1986), except that Parker and Bertsch employed twice the o-phenanthroline concentration:

- Solution A: 500 mL of 2.85×10^{-3}M ferron and 5.04×10^{-4} M o-phenanthroline
- Solution B: 200 mL of 4.3M sodium acetate
- Solution C: 200 mL of 100g/L $NH_2OH.HCl$ and 40mL/L concentrated HCl

Three stocks were filtered and combined to yield the mixed, working ferron reagent with the following composition: 1.58 M ferron; 0.28 mm o-phenanthroline; 0.95M sodium acetate; 0.32M $NH_2OH.HCl$; 0.11 M HCl; with the final pH of 5.2 – 5.4.

The procedure to measure Al-ferron reaction depends on Al_T ($Al_T = Al_a + Al_b + Al_c$) in Al solution and summarized in Table 2.3.

Table 2.3. Al_T dependence of spectrophotometric measuring procedure

Al_T	Spectrophotometric measuring
$\leq 1\times10^{-4}$ M	Sample was directly pipeted into a cuvette and within 3s of injection, the kinetics scan was initiated.
$= 5\times10^{-4}$ M	Mix ferron reagent and sample in a beaker, withdraw a sub-sample and transfer to a cuvette in the spectrophotometer.
$\geq 5\times10^{-4}$ M	Dilute to 1×10^{-4} M and the assay was initiated within ≤ 5 min.

Absorbance increases after 30 min were negligible Fig. 2.14, and the Al reacted at 30 min was assumed to represent [$Al_a + Al_b$]. The quantity [Al_c] was computed as the difference between [Al_T] and [$Al_a + Al_b$]. Ferron – Al_b reaction was analyzed based on Eq. 2.10:

$$\log[Al]_{un} = \log[Al_b] - (k_b / 2.303)t \tag{2.10}$$

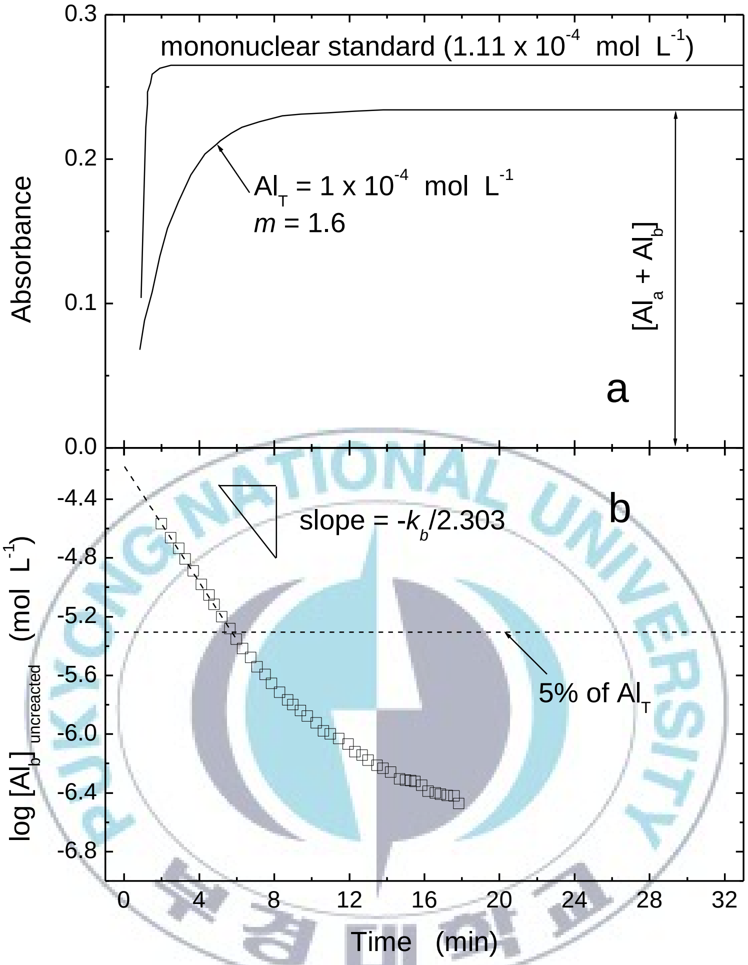


Fig. 2.14. Typical kinetics of ferron-Al reactions at 25°C with $\text{ferron}_T = 1.20 \times 10^{-3}$ M. (a) Raw absorbance vs. time plot for an acidified, mononuclear standard, and for a partially neutralized sample. (b) Linearized, first-order plot for selected data points for the sample. Solid line represents the data segment (2 – 6 min) fit to Eq. 2.10 by linear regression; the dashed extension shows the extrapolation to t=0 for calculation of $[Al_b]$. The horizontal dashed line represents 5% of Al_T, and illustrates that deviations from linearity usually occur only when reaction is nearly complete (Parker and Bertsch, 1992b).

2.1.5. Preparation Conditions Affecting the Distribution of Al Species in PACl

The speciation resulting from Al(III) hydrolysis is that of monomeric Al, polymeric Al, and colloidal/precipitated Al. Literature revealed that distribution of Al species (monomeric Al_a, polymeric Al_b, and colloidal/precipitated Al_c) in hydrolytic polymeric Al solution is dependent on factors such as:

- ✓ r = [OH]/[Al] ratio
- ✓ Type and concentration of added base
- ✓ Total Al(III) concentration
- ✓ Mode of base addition (slow, fast, dropwise, pulse)
- ✓ Base injection rate
- ✓ Mixing conditions (speed of mixing, impeller type)

2.1.5.1. *r* value

Generally, monomers decrease along with increase of the *r* value and the higher the *r* value, the higher the polymers and colloids/ precipitates would be. It is well known that Al_b or Al_{13} is the most effective species for charge neutralization and particle bridging actions in coagulation and flocculation processes (Bertsch et al., 1989; Bottero et al., 1987b; Shi et al., 2007b; Tang et al., 2004; Zhao et al., 2008). Their content is closely related to the basicity or OH/Al molar ratio (*r* value) of the products. Previous investigations show that the content of Al_b increases with an increase in the *r* value, and reaches a maximum when r = 2.4 or 2.5 (Lu et al., 1999; Tang and Luan, 1996). As a result, to increase the Al_b content of the product, high *r* value is necessary.

2.1.5.2. Type and Concentration of Added base

The most common base reagent used to neutralize aluminum solution is NaOH. A number of previous investigations have proven that it is difficult to produce a stable high-concentration PACl using NaOH as the basification reagent because NaOH releases OH^- in water too rapidly (Tang and Luan, 1996; Tang et al., 2004). Some researchers found that using of Na_2CO_3 (rather than NaOH) was preferred as base so as to be able to control the pH gradient to achieve polyaluminum solution with high concentration of $Al_{T.}$ (Demirata et al., 2002; Huang et al., 2006; Koether, 2002; Zhao et al., 2009). It is clearly that basification reagent should have the following qualifications: its solid-state should provide OH^- in $AlCl_3$ solution for the polymerization of Al^{3+}; the rate of OH^- production should not be too slow or too fast; and the products should have no influence on the properties of PACl.

Small change in base concentration should not affect the titration results much, but a significant change in base concentration give an effect on Al species distribution. It should be expected that more polynuclear species to be formed when the base is more concentrated.

2.1.5.3. Total Al(III) Concentration

The total Al concentration (Al_T) of the product is also a factor affecting Al speciation and cannot be ignored in practical applications. High-concentration PACl can reduce the expense involved in the storage, transportation and dosing processes and therefore, PACl has commercial value only when it has a high Al_T. However, for example, high Al_b content more than 70% is found stable at total Al concentration (Al_T) below 0.5 mol/L; and in solution with Al_T above 2 mol/L, the content of Al_b would be less than 30% (Xu et al., 2003).

2.1.5.4. Base Injection

It is generally agreed upon that in the PACl preparation process, a low speed of base-feeding or base-injection is preferred for preparing a stable product with a high *r* value and Al_b content (Bottero et al., 1980; Tang et al., 2004; Thompson et al., 1987). In addition, the point of injection of base affects pre-hydrolysis process. The method of base-microinjection is usually used in the laboratory. Using this method, with NaOH as the basification reagent, PACl can be produced with a high *r* value ($r = 2.2 – 2.5$), Al_b content (> 70%), and low Al_T (< 0.6 mol.L^{-1}) (Shi et al., 2007b; Tang and Luan, 1996; Tang et al., 2004; Wang et al., 2002)

2.1.5.5. Mixing Conditions

Mixing affects the rate of micro-mixing and may control which of several competitive reactions may dominate at the interface between the mixed solutions. Inadequate mixing causes the persistence of local concentration heterogeneities. These local regions of high OH-concentration seem to favor the nucleation of $Al(OH)_s$. Shen and Dempsey (Shen and Dempsey, 1998a) also indicated that inadequate mixing also tends to produce polymeric species with smaller reaction rate constants (larger polymers) with ferron when compared to polymers formed using more rapid mixing.

It is possible to prevent rapid precipitation by promoting a full range of hydrolysis and polymerization reactions by minimizing pH gradients (e.g., by slow base injection below the solution surface, use of Na_2CO_3 instead of NaOH, etc...); thus the mode of mixing may be important in influencing the rate and extent of aluminium hydrolysis (Vermeulen et al., 1975).

2.2. Coagulation-Flocculation for the Treatment of Surface Water

Coagulation refers to all the reactions and mechanisms that result in particle aggregation in the water being treated. The first part of this review focuses on the properties of particles in water (colloidal particles and natural organic matter (NOM)). Knowing these properties is important to understand coagulation and flocculation mechanisms presented in the following part. Then, coagulation mechanisms will be underlined and finally the influence of specific parameters on the coagulation efficiency will be investigated.

2.2.1. Coagulation of Particulate Matter

2.2.1.1. Characteristics of Particulate Matter

Natural surface waters contain particulates of inorganic and organic origin. Inorganic particulate constituents, including clay, silt, and mineral oxides, typical enter surface water by natural erosion processes.

Suspended particles are generally larger than 1.0 μm and colloidal particles rangeg from 0.001 to 1.0 μm. Depending on pH of solution, the charge of hydroxyl groups on clay surface may be positive or negative, as shown in Fig. 2.15

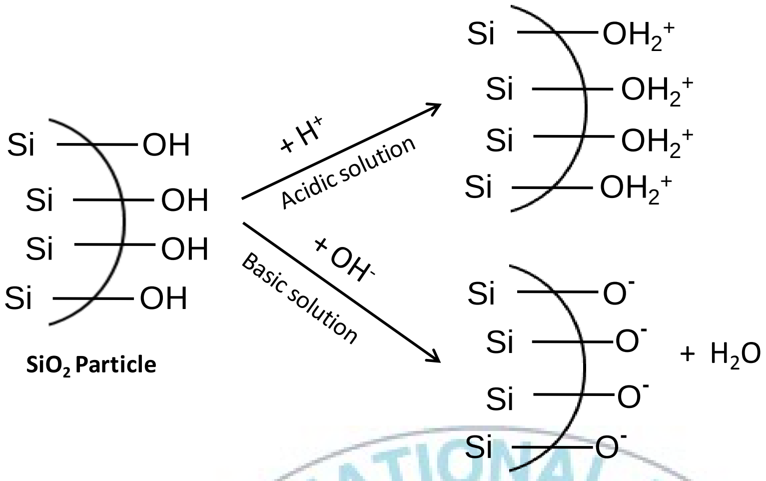


Fig. 2.15. Electrochemical behavior of hydroxyl groups on clay surface.

Direct measurement of the charge on the particle surface is currently not possible. One of the techniques used to measure this charge is zeta potential. Theoretically, it should correspond to the measure of the "electric potential at the inner boundary of the diffuse layer" (Gregory, 1993). It is the potential measured by electrophoresis. Schematic representation of zeta potential is shown in Fig. 2.16.

It has been demonstrated that there is a link between zeta potential and coagulation performance, with the production of strong agglomerates and low residual concentrations when the zeta potential is low.

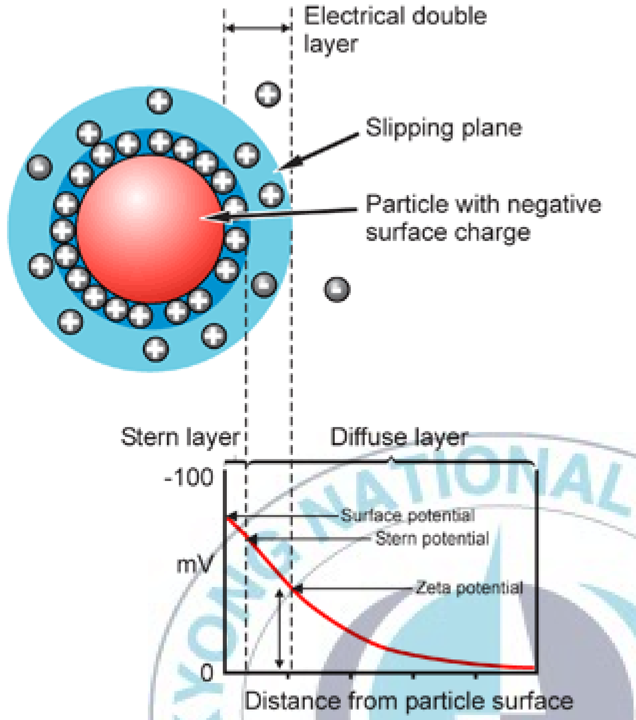


Fig. 2.16. Schematic representation of zeta potential.

2.2.1.2. Coagulation-Flocculation Mechanisms

Two removal mechanisms in coagulation of colloidal particles (or turbidity) have been identified: (a) charge neutralization of negatively charged particles by positively charged metal hydrolysis species followed by aggregation of the destabilized particles and (b) formation of flocs composed of metal hydroxide precipitates accompanied or followed by sweep flocculation of colloidal particles (Gregory and Duan, 2001b; Shin et al., 2008; Snodgrass et al., 1984). Charge neutralization of negatively charged particles by positively charged metal hydrolysis species followed by aggregation of the destabilized particles. This mechanism is predominant when high colloid concentrations present in water. At a certain colloid concentration, such as the order 50 to 100 mg/L, base on kaoline, contact opportunity is sufficient for hydrolysis species to become adsorbed and effect destabilization by charge effects or bridging, before precipitation takes place (Bratby, 2006; Kim et al., 1965; Packham, 1965). Colloidal particles in this case provide sufficient contact opportunities for aggregation of destabilized particles and hence require coagulant doses minimally sufficient to induce charge neutralization. Destabilized colloids can be aggregated by interparticle contacts if adequate mixing is provided.

When the dose of coagulants used are greater than those required for the precipitation of $Al(OH)_3$ (s), particles become enmeshed in these precipitates and settling. It is necessary to overwhelm the widely dispersed particles with a large quantity of coagulant in the “sweep floc” zone. This is typical of most natural surface waters that contain “low” turbidities, less than 50 JTU (Faust and Aly, 1998b). At low particle concentrations, the contact opportunities between particles are limited by low solid concentrations and thus removal must be achieved by sweep flocculation, which typically requires coagulant doses greater than those that would be required for charge neutralization. In this regime, the coagulant dose required for sweep flocculation of particles is not a “stoichiometric” function of particle concentration but is mostly determined by chemical conditions that influence metal hydroxide precipitation including the coagulant dose, pH, alkalinity, and temperature. Sweep flocs is the main mechanism in water treatment plants (pH 6~8 and oversaturation).

Alum coagulation diagram proposed by Amirtharajah and Mills, 1982 as illustrated in Fig. 2.17 and mechanisms for alum coagulation of colloidal particles is illustrated in Fig. 2.18.

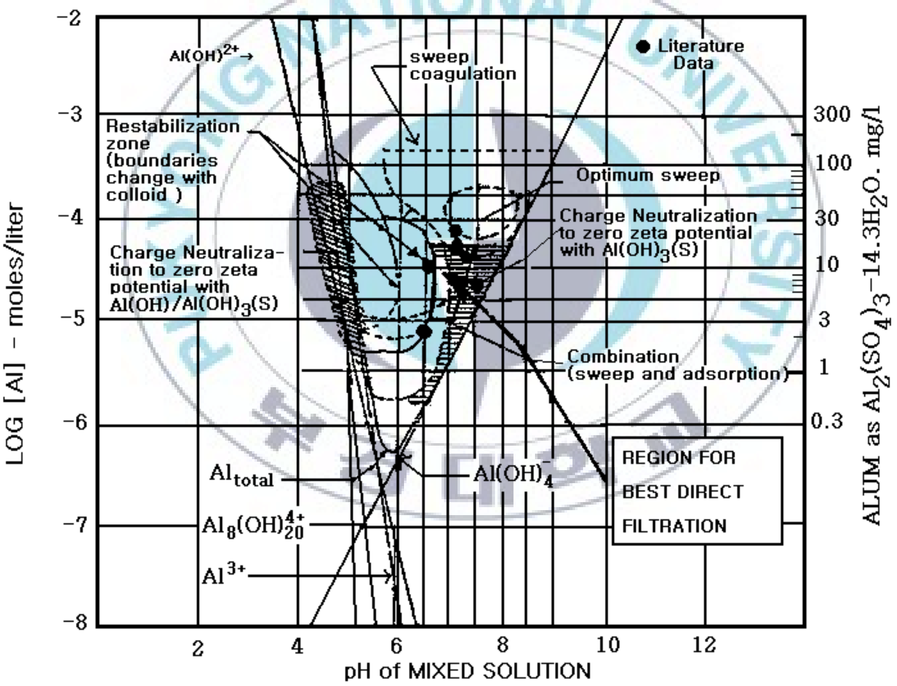


Fig. 2.17. Alum coagulation diagram (Amirtharajah and Mills, 1982).

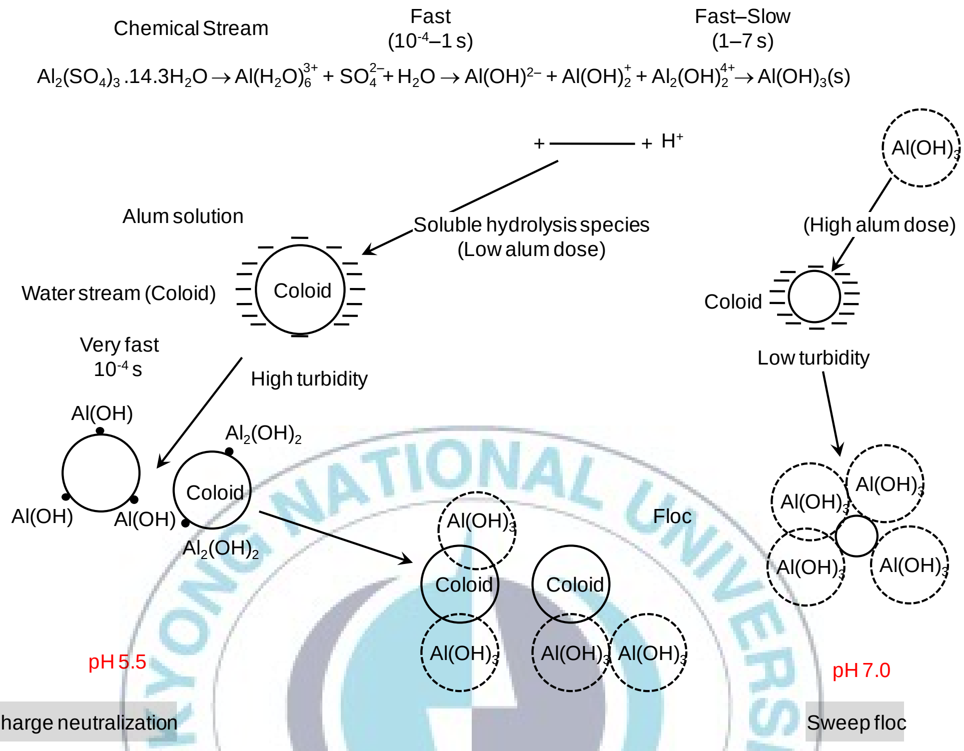


Fig. 2.18. Mechanisms for alum coagulation of colloidal particles.

2.2.2. Coagulation of Natural Organic Matter

2.2.2.1. Characteristics of NOM

Natural organic matter (NOM) is referred to as a heterogeneous mixture of organic chemicals, ubiquitous in all water bodies and originating from natural sources (Crittenden et al., 2005). Humic substances, which are typically the major component of NOM, include the more soluble fulvic acids (FAs) and the less soluble humic acids (HAs) with FAs predominating in most waters. Knowing characteristic of NOM is important to understand coagulation-flocculation behavior. The main characteristics of NOM are molecular weight, functional groups, hydrophobicity and charge.

Size and molecular weight of NOM are interrelated. As diffusion coefficients and removal efficiencies are directly dependent on the size of a solute, size is an important property need considering in water treatment. Size or molecular weight fractionation is often analysed using ultrafiltration process. A series of membrane with identical material and different MWCOs (Molecules Cut Off) is used. Generally, NOM with larger size is considered to be easier to remove than smaller size NOM.

Functional groups determine the characteristics of NOM such as chemical binding, UV absorbance, charge, hydrophobic interactions and solubility. Major functional groups of humic substances are carboxylic acids, phenolic hydroxyl, carbonyl and hydroxyl groups (Thurman, 1985b). FA is clearly more aliphatic and less aromatic than HA. Fig. 2.19 illustrates NOM molecules, which are large and contain many functional groups. HA is more soluble than FA at higher pH. HA has more phenolic groups than FA and is more hydrophobic.

Charge and acidity of NOM are directly related to their functional groups. The groups give the molecules their charge, which increases in negativity with increasing pH. An example is given in Fig. 2.20. Most of HA groups are dissociated at a pH > 4.0 and carry a negative charge (Nystrom et al., 1995. FA has a higher carboxylic acidity than HA (Küchler and Miekeley, 1994) and therefore a higher charge. The charge of natural organics determines their interaction with colloids, Al species in coagulation, and their solubility. Charge is therefore a very relevant characteristic for coagulation-flocculation and the distinction between the charges of functional groups is of particular interest in the interpretation of pH effects on coagulation-flocculation.

The solubility of NOM is also an important issue in coagulation. FA, by definition, is more soluble than HA at low pH. Metal complexes of FA are also more soluble than those of HA due to lower MW and the high charge of FA. The solubility of each compound depends on the saturation of the complex with metal ions (Stevenson, 1985). Precipitation of HS occurred when functional groups are neutralized or complexes, which is closely related to coagulation.

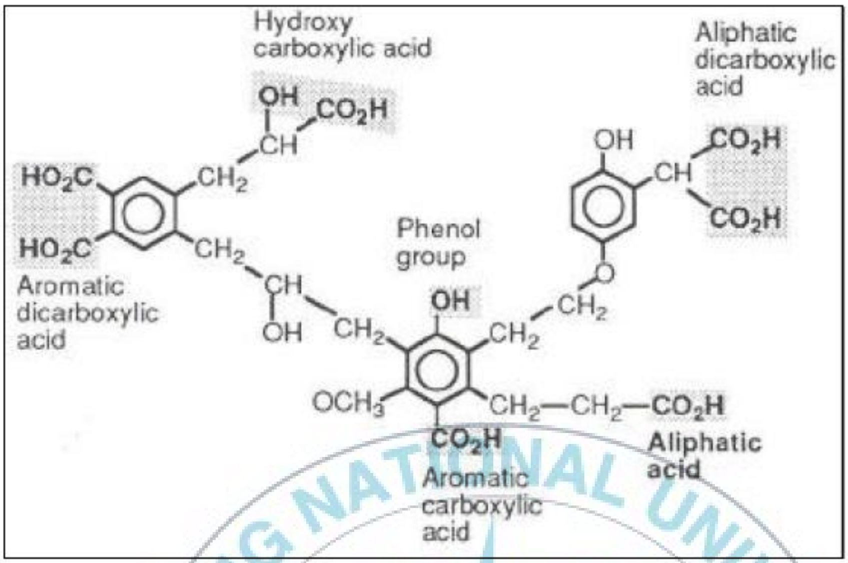


Fig. 2.19. Typical NOM molecule.

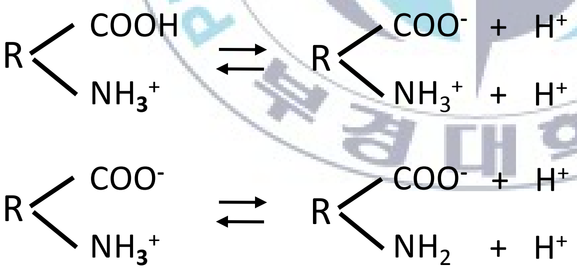


Fig. 2.20. Electrochemical behavior of carboxyl and amino groups on organic surface.

UV_{254} and specific UV absorbance (SUVA) are good surrogates for the hydrophobic content. SUVA is the ratio of UV absorbance at 254 nm to DOC (Dissolved Organic Carbon) concentration. Edzwald and Van Benschoten

(Edzwald and Van Benschoten, 1990) proposed the following guideline:

- SUVA values of 4 to 5: The DOC of water is composed largely of aquatic humics. The DOC is relatively hydrophobic, aromatic, and high molecular weight compared to waters with lower SUVA values. The DOC controls coagulant doses, but due to its nature, relatively high removals of DOC are expected by coagulation.
- SUVA values of less than 3: The DOC is composed largely of non-humic materials. The organic matter is relatively hydrophilic, less aromatic, and of lower molecular weight compared to waters with higher SUVA values. For these types of waters, the DOC will have a small, if any effect, on coagulant doses and relatively low removals of DOC are expected.

2.2.2.2. Coagulation-Flocculation Mechanisms

The presence of NOM would complicate the process of coagulation because of its complex structure such as high negative charge and wide molecular weight range. In treating waters that contain both NOM and colloidal particles, NOM predominantly determines the coagulant demand in most water (Shin et al., 2008). It has been suggested that Al hydrolysis products form insoluble aluminum-humates of fulvates with humic substances, producing a colloidal sol that settles very slowly. At higher coagulant doses, the aluminum-organic complexes may be removed by incorporation into $Al(OH)_3$ flocs.

Cationic aluminum interacts electrostatically with anionic NOM to form insoluble charge neutral products. Higher molecular weight NOM as well as colloidal particles (as mentioned above), which can act as nuclei for precipitate formation, may be removed by this mechanism. Charge neutralization is predominant in operation regions where aluminum hydroxide precipitation is minimal.

Adsorption onto aluminum hydroxide precipitates ($Al(OH)_3(s)$) is an important pathway for the removal of NOM under conditions favoring $Al(OH)_3(s)$ precipitation. Adsorption occurs by surface complexation or ligand exchange of NOM molecules with surface groups on $Al(OH)_3(s)$.

Complexation / precipitation is the chemical interaction of anionic functional groups on NOM with soluble coagulant metal ions to precipitate as an aluminum-NOM complex, particularly reactions with humic and fulvic acids that act as strong organic ligands for aluminum.

When the solution chemistry allows the presence of both soluble polymeric aluminum species and solid metal hydroxide precipitates simultaneously, the removal of NOM by this combined mechanism is considered more efficient than by adsorption or complexation-precipitation alone. Polynuclear aluminum species react with NOM and neutralize or substantially reduce the negative charge on the NOM, promoting its adsorption onto $Al(OH)_3(s)$ (Dempsey et al., 1984).

2.2.2.3. Alum Coagulation of Colloidal Particle and NOM

Colloidal particles as clay suspensions and NOM as humic substances are the two constituents which must be removed in surface water. The removal efficiency of them is different under various conditions of coagulation. Table 2.4 summarizes the difference in coagulation of dilute clay suspensions and humic substances.

Table 2.4. Comparison of alum coagulation of dilute clay suspensions and humic substances

	Dilute clay suspension	Humic substances
Optimum pH	6.5 – 7.5	5.0 – 6.0
Minimum residual	Minimum residual turbidity is independent on pH	Minimum residual color is dependent on pH
Coagulant dose	Slightly reduces when increasing clay concentration	Increases when increasing TOC concentration
Coagulant dose and optimum pH	Dependent on the presence of humic substances	Independent on the presence of clay

2.2.3. Factors Affecting Coagulation

Characteristics of particulate and NOM in raw waters affect their removal performance through coagulation-flocculation process. Besides, the following factors also contribute to coagulation-flocculation effectiveness.

The levels of pH, salts, and alkalinity in water are all ways of measuring the amounts of cations and anions in the water. As a result, all three factors also influence the amount of coagulant dose.

Alkalinity refers to the acid-neutralizing capacity of water, or water’s buffering capacity. Alkalinity is the capacity of the water to neutralize acids, based on the content of carbonate, bicarbonate, hydroxide, borate, silicate, and phosphate present in water. Adding metal coagulants, which are acidic, may consume the alkalinity of water and depress the pH of water. In case of using PACls, alkalinity consumption is related to basicity of PACl: high basicity PACls will consume less alkalinity than low or medium basicity ones (Pernitsky, 2003).

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

The temperature of the water can have a significant effect on coagulation and flocculation (Kang et al., 2001). Temperature affects the solubility of the metal hydroxide precipitate and the rate of formation of the metal hydrolysis products. In general, $Al(OH)_3$ decrease in solubility with decrease temperature. Low temperature of water hinders coagulation. First, low temperature makes water viscosity increase, alter coagulant solubility and retard almost all chemical reactions in the water. The cold water can also make it more difficult to evenly disperse the coagulants in the water. As a result, coagulation becomes less efficient. Second, cold water influences sedimentation processes or floc settling. At near freezing temperatures, water is very dense, which keeps the flocs suspended in the water.

Effect of coagulant dose in interaction with colloid concentration on destabilization of particles is illustrated in Fig. 2.21 .

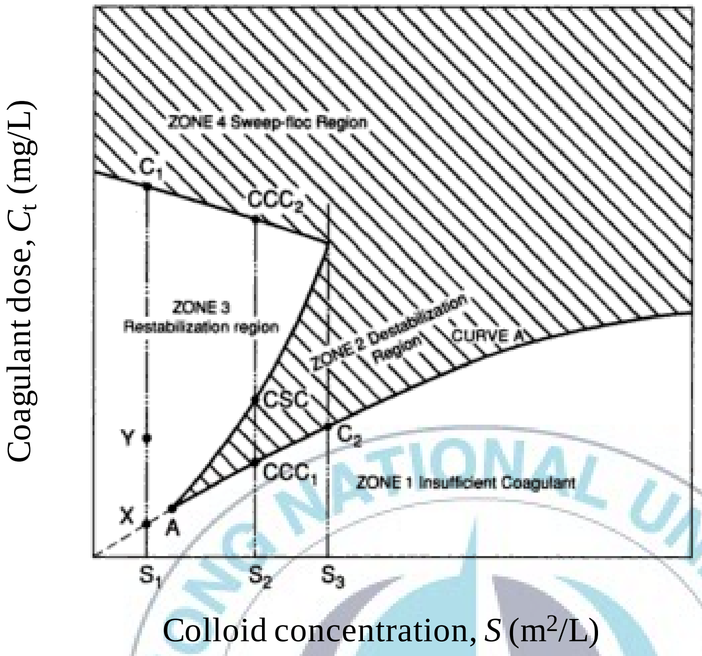


Fig. 2.21. Zone of destabilization and restabilization at a given pH value as relate to colloid concentration (S) and coagulant dose (Ct) (Stumm and O'Melia, 1968).

Bratby (Bratby, 2006) interpreted four zones as follows:

- Zone 1: indicates that insufficient coagulant has been applied to the colloidal suspension and that destabilization does not take place.
- Zone 2: refer to the region in which destabilization has taken place
- Zone 3: is that region where destabilization and then restabilization has taken place, due to excessive coagulant addition.
- Zone 4: is the region where the coagulant dose is high enough for

over saturation, and precipitation of metal hydroxide species to occur.

The pH at which coagulation occurs is the most important parameter for proper coagulation performance (Pernitsky, 2003), as it affects:

- Surface charge of colloids
- Charge of NOM functional groups
- Charge of the dissolved-phase coagulant species
- Surface charge of floc particles
- Coagulant solubility

As previously discussed, the predominance of a particular hydrolysis species during destabilization is very largely dependent on the pH value. The adjustment of pH to a range where the most effective hydrolysis species of the coagulant is formed is shown to be very essential in producing optimum coagulation.

Mixing is an important parameter to consider in the mechanism of coagulation/flocculation. The coagulants must be dispersed into the raw water stream as rapidly as possible (< 0.1 second) so that the hydrolysis products, which develop in 0.01 to 1 second will destabilize the particles. Therefore, at the first stage of coagulation, the requirements of rapid mixing are dispersing coagulant rapidly and uniformly throughout the total flow so that no concentration gradient and no local overdosing occur in solution. Secondly, in slow mixing stage, energy contributes to the rate of the flocculation reaction in promoting contacts between particles (Crittenden et al., 2005). Improving mixing is hence necessary to obtain good coagulation efficiency.

Mixing intensity is typically quantified with a number known as the velocity gradient or G value and this value is a function of the power input into the rapid mixing process and the volume of the reaction basin. Typical G values for rapid mixing coagulation were in range from 300 to 8000 sec^{-1} (Hudson, 1981). Time required to achieve efficient coagulation varies were depending on the coagulation mechanism involved. When the charge neutralization is involved, the detention time required may be one second or less but if the sweep-flocs or entrapment involved, a longer detention times (1 – 30 seconds) may be appropriate (Hudson, 1981; Kawamura, 1991).

2.3. Coagulation-flocculation in Treatment of Phosphorus in Wastewater Effluent

2.3.1. Phosphorus in Wastewater

Phosphorus is found in domestic wastewaters almost exclusively as phosphates (APHA, 1998) in concentrations ranging from 3 – 15 mg/L (Snoeyink and Jenkins, 1980). These phosphates are classified as orthophosphate ion, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates (APHA, 1998). Organic phosphates are contributed to sewage by body waste and food residues. Ortho phosphate and polyphosphates can be contributed by detergents. Various forms of phosphorus will convert to ortho phosphate during wastewater treatment and ortho phosphates are the most stable forms of phosphates and are used directly by plant cells (Bratby, 2006). In general, primary and secondary wastewater treatment is effective in removing/converting of condensed phosphates and organically bound phosphates into orthophosphate ions. Phosphorus in the secondary effluents is mostly dissolved and is present as orthophosphates (Duenas et al., 2003). Furthermore, only ortho-P is consumed for phytoplankton growth causing eutrophication in surface water bodies (Selig et al., 2002).

2.3.2. The needs of Phosphorus Removal from Wastewater

Eutrophication causes problems relating to water purification for portable use due to the excessive growth of algal and nuisance aquatic plants in surface water. Phosphorus (P) is considered as a limiting nutrient of the eutrophication and a significantly reducing of P load discharged into a receiving water body can control the eutrophication process (Chutter, 1990b; Dillon and Molot, 1996b). The most stable form of phosphorus, is known as ortho-phosphates (ortho-P), may cause the growth of algae at concentration as low as 0.05 mg/L, and an ortho-P concentration below 0.5 mg/L can inhibit algae's growth (Manahan, 2001). A significant source of phosphorus disposal into surface water comes from municipal wastewater and therefore, control of P discharge from wastewater treatment plants is necessary. The wastewater treatment plants must often meet effluent P discharge limitation. Table 2.5 summarizes the discharge criteria of phosphorus for some countries. In South Korea, a new stricter total phosphorus (TP) discharge limit range of 0.2 – 0.5 mg/L is imposed from 2012, instead of 0.5 – 1.0 mg/L as the current limit. This regulation forces the plants to find out more effective method to treat their secondary effluents before discharge.

Table 2.5. Phosphorus discharge limits set by some countries

	Country	P* (mg/L)	Note	Reference
1	South Korea	0.2 − 0.5	effective from January 2012	(NIER, 2010)
2	United States	0.5 − 1.0	–	(Özacar and Şengil, 2003)
3	Canada	0.4 − 1.0	depends on the Canadian province.	(Minnow Environmental Inc, 2005)
4	Europe	1.0 − 2.0	depends on works serving population.	(Council of the European Communities, 1999)

2.3.3. Phosphorus Treatment Using Al based Coagulants

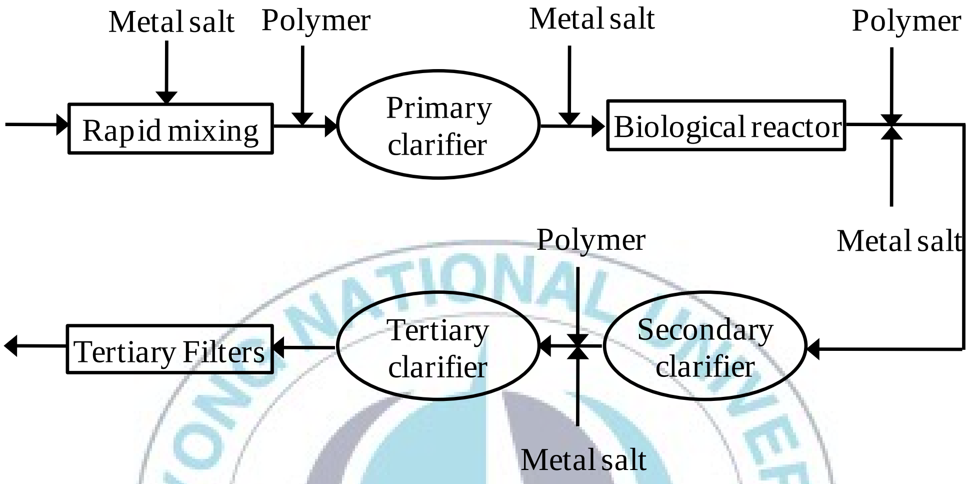


Fig. 2.22. Possible chemical dosage points for phosphorus removal (Bratby, 2006).

Fig. 2.22 shows the chemical addition at one or more of several locations within the wastewater treatment plants. Further treatment of the secondary effluent is required to meet the P standards. Chemical techniques using metal salts in coagulation process are reliable and well-established processes for achieving very low residual phosphorus concentration in wastewater treatment plant effluents (Ebeling et al., 2003; Jiang and Graham, 1998; Omoike and Van Loon, 1999; Yeoman et al., 1988). Phosphorus removal using PACl has been carried out by a number of researchers (Boisvert et al., 1997b; Gillberg et al., 1996; Ratnaweera et al., 1992).

Transformation of dissolved and fine colloidal P into particulate form	
Chemical precipitation	Formation of phosphate-Al-hydroxo complexes, e.g. $Al(OH)_x(PO_4^{3-})_{3-x}\,(H_2O)$
Adsorption	Selective adsorption of phosphates onto Al-hydroxo precipitates
Coagulation	Destabilization of P containing colloids by dissolved polynuclear Al hydroxo complexes and agglomeration to separate flocs by flocculation

↓

Solids separation of P-containing particles
e.g. sedimentation, flotation, filtration

Fig. 2.23. Overview of chemical precipitation and removal processes Bratby (Bratby, 2006), adapted from Maurer and Boiller (Maurer and Boller, 1999).

Al salts are conventionally considered as precipitants for P removal. However, it is over-simple to explain P removal mechanisms based only on the direct formation of insoluble $AlPO_4$. Because the pH of natural water in is the range from 5 to 9, Al^{3+} ion is unlikely exist in such water body when Al salts are added into water, as mentioned in previous “hydrolysis of aluminum” part. Al^{3+} ion is rapidly hydrolysed to form a range of Al hydrolysis products. Therefore, $AlPO_4$ precipitate might not present or only present with a limit extent due to the competition of OH^- and PO_4 for Al^{3+}

ion. Removal of P might relate to other mechanisms rather than only forming precipitation of $AlPO_4$. As shown in Fig. 2.23, the mechanisms involved with removal of phosphorus includes 1) Formation of Al-hydroxo-phosphate complexes: $Al(OH)_{3-x}(PO_4)_x$. These complexes either adsorb onto positively charged Al hydrolysis species or act as centres of precipitation for Al(III) hydrolysis products, 2) Adsorption of PO_4 ions on to the Al(III) hydrolysis species. In the case of using conventional coagulants such as $Al_2(SO_4)_3$, amorphous $Al(OH)_3$ are the predominant hydrolysis species in water treatment practice. If pre-polymerised inorganic coagulants are used, polymeric species are predominant, and PO_4 ions may also complex with the positive sites of such species, and 3) flocculation and co-precipitate of finely dispersed precipitate and other colloidal matter. The three mechanisms are likely occurred simultaneously when coagulants are added into water. The predominant mechanisms depend on Al species formed, which is strongly dependent on coagulation pH and original Al species in coagulants.

In addition to traditional coagulants, use of pre-polymerized coagulants for P removal has been studied previously. There has been the uncertainty in precise mechanisms and removal efficiencies of P removal by pre-polymerised Al coagulants. Works conducted by many researchers have shown that high basicity PACl was not favorable for P removal (Boisvert et al., 1997b; Fettig et al., 1990; Ratnaweera et al., 1992). However, Hatton and Simpson (Hatton and Simpson, 1985) reported an observation that PACl was superior to alum in removal of total P while the removal efficiency with respect to ortho-P was similar. Some workers explained the inferior performance of PACl based on charge density effects in which partially hydrolysed metal species have a reduced total cationic charge and therefore should be less efficient in the charge neutralization of P species (Fettig et al., 1990; Ratnaweera et al., 1992). However, adsorption of PO_4 onto $Al(OH)_3$ has strongly been suggested (Galarneau and Gehr, 1997).

Chapter 3

MATERIALS AND METHODS

This research involved lab-scale experiment. Surface water and sewage effluent were collected at water / waste water treatment plants in Busan city, Korea. Synthetic water prepared with various organic sources also was used. The water was coagulated using laboratory jar test equipment. Characteristics of coagulants and raw water were analyzed before conducting coagulation-flocculation. This chapter describes methods used to perform experiments, including water analysis, jar test performing, and specific chemical analysis. Preparation and characterization of PACl is presented in separate part in Chapter 4.

3.1. Raw Water

3.1.1. Water Source

Jar test was conducted using two types of water source as raw water to investigate coagulation-flocculation in surface water: The Nakdong River water which is the major water source of the city of Busan, Korea and synthetic water. Secondary sewage effluent collected from Nambu wastewater plant in Busan was used as raw water in coagulation-flocculation process to evaluate performance of coagulants in phosphorus removal. In order to be convenient in interpretation the relationship between the water nature and coagulation/flocculation effectiveness, characteristics of the waters were presented accompanied with their coagulation/flocculation performance in Chapter 5 and Chapter 6 for surface water and sewage effluent water, respectively.

3.1.2. Synthetic Water

3.1.2.1. NOM Isolating Procedures

In order to examine the coagulation behaviors of various dissolved organic matter (DOM) fraction, such as hydrophobic acids (humic acid and fulvic acid), hydrophilic organics, and transphilic organics, experiment using ion exchange resins was conducted to isolate these fraction from Nakdong river water.

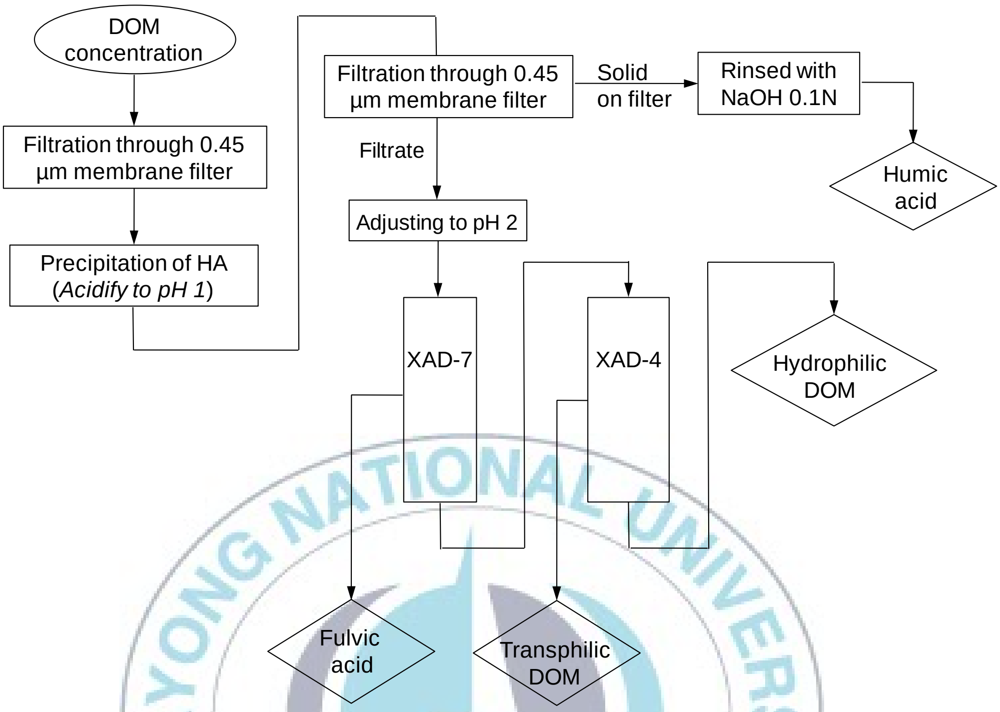


Fig. 3.1. DOC isolation procedure.

The procedure using ion exchange resin to isolate DOM is outlined in Fig. 3.1. Before use, the resin was Soxhlet-extracted sequentially for 24 hours with methanol, diethyl ether, acetone nitrile, and methanol and stored in methanol until used. After that, the resin was packed into a column (1.5 cm × 33 cm) and rinsed with about 50 bed volumes of distilled water. The packed column was then rinsed with 3 times, alternating from of 0.1N NaOH to 0.1N HCl before sample application.

The Nakdong River water was first concentrated using rotary evaporator and then filtered through 0.45μm membrane filter to remove suspended

NOM. The filtrate was acidified to pH 1.0 with concentrated HCl and the acidified sample was allowed to sit overnight at room temperature to precipitate humic acids. The next day the supernatant suspension was carefully filtered through the 0.45 µm membrane filter, followed by rinses with about 10 mL of 0.1 N HCl. The filter was then rinsed with 15 mL of 0.1 N NaOH and HA was re-dissolved and collected for later use.

The solution after removing HA precipitate was adjusted to pH 2 with 5N NaOH and then pumped through a column (1.5 cm × 33 cm) filled with 70 ml of XAD-7 resin slurry (Amberlite, Supelco, USA) at a rate of 2 bed volumes per hour (i.e. 140 mL/h). The portion that passed through the XAD-7 was pumped through a cleaned XAD-4 resin column. The resin column XAD-7 and XAD-4 were rinsed with an additional 200mL of 0.01 N HCl after all water was pumped. The water collected after passing through XAD-7 and XAD-4 was denoted as hydrophilic NOM (HiP). The portion that retained on the XAD-7 resin and XAD-4 resin was fulvic acids (FA) and transphilic organic (weakly hydrophobic organic, WhoA), respectively. These two fractions were eluted by backwashing with 1 L of 0.1N NaOH at a low rate of 2 bed volumes per hour (i.e. 140 mL/h) and collected separately. HiP, FA, and WhoA were stored for later use as DOM source of synthetic water in jar test.

3.1.2.2. Preparation of synthetic water

Three synthetic waters were prepared by mixing prescribed amounts of kaoline clay (Sigma Aldrich) and stock solution of four different DOM fractions, such as HiP, FA, HA, and WhoA, which was isolated from the Nakdong River water according to the procedure described above. An amount of 10^{-3} M NaCl was added as background electrolyte and $NaHCO_3$ was added as buffer (alkalinity was about 80 mg $CaCO_3$/L). After mixing kaoline and DOM, the water was equilibrated for 18 ± 2 h to allow DOM molecules to partition onto silica particle surface (Shin et al., 2008).

3.2. Coagulation-flocculation Procedures

3.2.1. pH Adjusting

To control the pH of coagulation process, it is necessary to predetermine the required amount of acid and base added to achieve a desired pH before dosing coagulants. This was done by taking 200 mL sample of raw water and adding the desired coagulant dose to be equivalent to the dose in the 2 L jar. Place the sample on a stirrer stand and titrate with 0.1 M HCl or 0.1 M NaOH, recording the amount of acid or base added to reach the desired pH level. Repeat the test for different coagulant doses.

3.2.2. Jar Test Procedures

Jar tests were performed to evaluate the coagulation performance. Coagulation experiments were carried out at room temperature, using 2 L square jars with six paddle stirrers. The time and speed for rapid and slow mixing were set with an automatic controller.

Doses of coagulants and acid (or base) were calculated and loaded into individual plastic syringes. After adding pH adjusting chemicals, coagulant was simultaneously injected to 6 jars and the coagulation-flocculation conditions were as follows:

- Rapid mixing: samples were mixed at 250 rpm (G = 550 sec^{-1}) for 1 min after coagulant addition to provide rapid dispersing of coagulant.
- Slow mixing: the impeller speed was reduced to 30 rpm (G = 22 sec^{-1}) for 30 min to provide flocculation.
- Sedimentation: after mixing was stopped, the settling was done for 30 min.

No effort was done to control temperature and the temperature of experiment was in the range from 20 to 25^{o}C.

3.3. Phosphorus Analyses

After performing jar test, to separate P containing particles, after 30 min of settling, the supernatant from each jar was withdrawn from the sampling port and analyzed for pH and residual phosphorus.

Total Phosphorus (TP) was oxidized using the Persulfate Digestion Method (Standard Method 4500-PB 5), and the released orthophosphate ion (PO_4^{3-}) from the oxidation was measured according to the Ascorbic Acid Method (Standard method 4500-PE) with a method detection limit (MDL) of 0.01 mgP/L (APHA, 1998). Ascorbic acid, ammonium molybdate, and potassium antimony potassium tartrate were used for color development. The ortho-P concentration was determined by a spectrophotometer based on a calibration curve between absorbance measured at 880 nm and a series of standard P concentration.

Total Reactive Phosphorus (TRP) as total amount of phosphorus that was directly measured by Ascorbic Acid Method without digestion/ oxidation and filtration.

Total Dissolved Phosphorus (TDP) as TP was filtered through 0.45 µm membrane (Millipore).

Dissolved Reactive Phosphorus (DRP, dissolved ortho-P) as DP was measured directly without digestion as determined by the Ascorbic Acid Method.

Suspended Phosphorus (SP) concentration was calculated as the difference between TP and DP.

Ortho-P, condensed-P, and organic-P in each form of SP and DP were also analyzed according to the Standard Methods (APHA, 1998).

- Ortho-P or “reactive P” is the phosphate that corresponds to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample.

- Condensed phosphate can be measured by converting dissolved and particulate condensed P to dissolved ortho-P using a judicious selection of acid strength and hydrolysis time and temperature, such as using a mixture of H_2SO_4 and HNO_3, heating 30 min in a autoclave. Determine reactive P of treated portions as a sum of poly-P and ortho-P in the sample. To calculate the content of condensed-P (acid hydrolysable P), determine reactive P in a sample portion that has not been hydrolysed using the same colorimetric method as for treated sample, and subtract.

- Organic-P was calculated as the difference between total P and reactive P and condensed P.

P analysis was completed immediately after sample collection. All glass containers for P analysis were acid-washed before use and the membrane filters were soaked in distilled water for 24 hours prior to use, according to Standard Methods (APHA, 1998).

3.4. Specific Chemical Analyses

All chemical reagents used were analytically pure chemicals. Deionised water with conductivity lower than 0.5 μS/cm was used in preparing all the solutions.

pH was recorded by a pH meter Horiba Model F-54W. The pH meter was calibrated using standard solution of pH 4, 7 and 10, according to a procedure recommended by the manufacturer.

Turbidity was measured immediately after 30 minutes of sedimentation by a HACH Turbidimeter Model 2100N. The turbidimeter was calibrated periodically against Formazin Standards and also standardized according to the manufacturer's recommendations using “Gelex” secondary standards before every test.

UV_{254}: Sample was filtered through a membrane of 0.45 μm pore diameter and measured at 254 nm in a 1 cm quartz cell using UV-Spectrophotometer (Shimadzu, UV-1201).

DOC is physically defined as an organic material which can penetrate a 0.45 μm filter. DOC is regarded as total organic carbon (TOC) after filtering the sample with a 0.45 μm filter. DOC was measured by a TOC Analyzer (TOC-VCPH, Shimadzu, Japan) using High Temperature Combustion Method.

Analysis methods and instruments were summarized in Table 3.1.

Table 3.1. Analysis methods and instruments

Item	Unit	Method*	Equipment
pH	–	SM 4500-H^+(Electrometric)	Horiba F-54BW
Alkalinity	$mgCaCO_3/L$	SM 2320B (Titration with H_2SO_4)	–
Turbidity	NTU	SM 2130 (Nephelometric)	HACH 2100N
UV_{254} absorbance	cm^{-1}	SM 5910 (Spectrophotometric)	Shimadzu UV-1201
TOC (DOC)	mg/L	SM 5310B (High Temperature Combustion)	Shimadzu TOC-VCPH

*: SM: Standard Methods for the Examination of Water and Wastewater (21th Edition) (APHA et al., 2005).

Chapter 4

PREPARATION AND CHARACTERIZATION OF Al-BASED COAGULANTS

The experimental results of this study are organized into three chapters. Chapter 4 presents the results of Al based coagulant preparation and characterization, focus on distribution of Al species using ferron assay. Chapter 5 presents analysis results of water quality (real surface water and synthetic water) and relationship between the characteristics of the coagulants and coagulation-flocculation performance. Similarly, chapter 6 presents the analysis results of wastewater quality, coagulants used, and their relationship with respect to the removal of phosphorus. Effects of coagulation pH and coagulants dosages were emphasized. Coagulation mechanisms in each case were discussed.

4.1. Preparation of PACl

PACl with different *r* value and total Al concentration (Al_T) were prepared using $AlCl_3.6H_2O$ (Sigma, USA) as aluminum coagulant source. A predetermined amount of base (NaOH or Na_2CO_3) was slowly added to a solution of $AlCl_3$ while stirring to obtain the desired *r* value of PACl. A 2-L double walled acrylic vessel was fitted with an acrylic lid on which 5 inlets were made, and 4 baffles were glued to the reactor wall. Through an inlet port in the lid, an acrylic capillary was lowered into the reactor to slowly inject a base solution. The aperture at the tip of the capillary was less than 0.15 mm in diameter to minimize diffusion of the metal solution into the capillary during mixing. A stainless shaft with propeller stirrer was inserted in another port for mixing solutions. The solution of temperature in the reactor was maintained by circulating a temperature controlled-water through the jacket of the reaction vessel. PACl preparation schematic diagram is shown in Fig. 4.1.

The $AlCl_3.6H_2O$ solution was prepared 1 day before using so that the $AlCl_3.6H_2O$ was completely dissolved and became transparent. Because NaOH releases OH^- in water too rapidly and it is difficult to control the pH gradient, Na_2CO_3 (instead of NaOH) was used as base in preparation of PACl with high Al_T .The Na_2CO_3 solution was filtered through 0.45 µm membrane filter before titration. Conditions for preparation of PACl are summarized in Table 4.1.

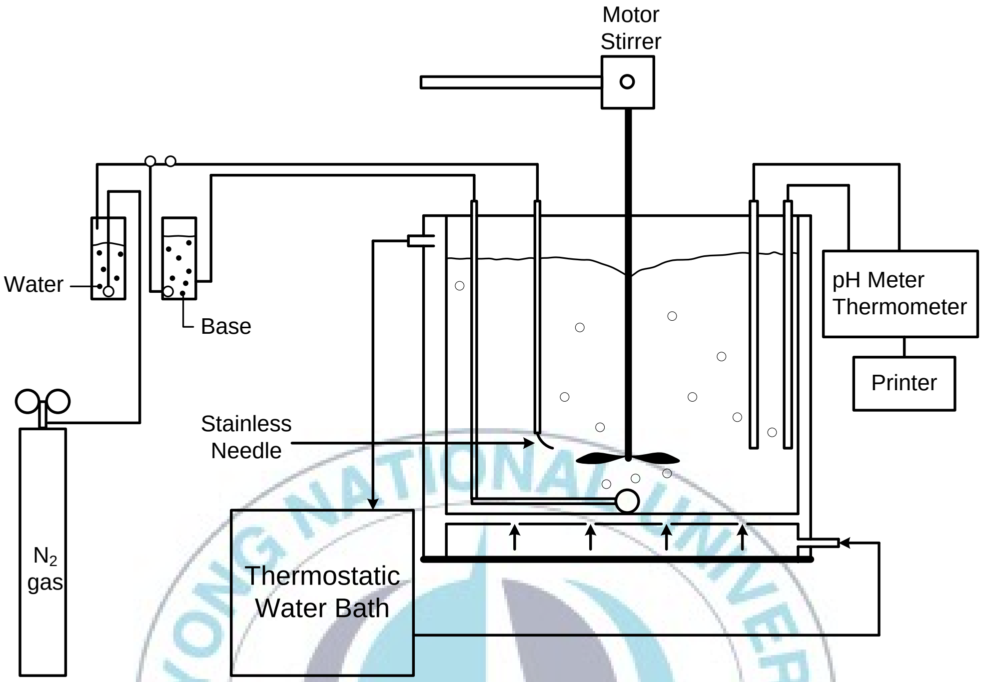


Fig. 4.1. Schematic diagram of PACl preparation.

Table 4.1. PACl preparation conditions

Al_T in PACl (M)	$AlCl_3.6H_2O$ (M)	Base reagent		Temp. (^oC)	Base injection rate (mL/min)	Mixing intensity (rpm)
		NaOH (M)	Na_2CO_3 (M)			
0.1	0.2	0.5	–	20	1	1800
0.5	1.67	–	1.25	70		
1.2	3.0	–	2.0	70		

It is generally agreed upon that in the PACl preparation process, a low speed of base-feeding or base-injection is preferred for preparing a stable product with a high *r* value and Al_b content (Bottero et al., 1980; Tang et al., 2004; Thompson et al., 1987). All PACl in this study were prepared with constant base injection rate of 1 mL/min and mixing intensity of 1800 rpm.

In order to evaluate the influences of *r* value to the changes of Al species, PACl with different *r* value was prepared at 2 levels of total aluminum concentration (Al_T): < 0.2 M Al and 0.5 M Al. The amount of reagent used in each case is shown in Table 4.2 and Table 4.3. Table 4.2 and Table 4.3 also present pH, density, basicity, and Al_2O_3 content of the Al solutions. Note that basicity of Al solution can be calculated from *r* value based on the formula basisity = $(r/3)\times100$. The density of PACl increased with the increase of Al_T.

Table 4.2. Calculated amount of reagents in preparation of low Al_T (< 0.2 M Al) concentration PACl with various *r* value

r ([OH]/[Al])	$AlCl_3$ 0.2 M (mL)	NaOH 0.5 M (mL)	Al_T (M)	Al_2O_3 (%)	Basicity (%)	pH	Density (g/L)
0.0	100	0	0.10	1.02	0.0	3.07	–
0.5	100	20	0.17	0.84	16.7	3.43	1008.98
1.0	150	60	0.14	0.72	33.3	3.56	1008.72
1.5	300	180	0.13	0.63	50.0	3.67	1006.17
2.0	200	160	0.11	0.56	66.7	3.86	1006.05
2.2	250	220	0.11	0.54	73.3	4.01	1006.48
2.5	175	175	0.10	0.50	83.3	4.55	1010.04

Table 4.3. Calculated amount of reagents in preparation of 0.5 M Al_T concentration PACl

r	$AlCl_3$ 1.67 M (mL)	Na_2CO_3 1.25 M (mL)	DI added (mL)	Al_T (M)	Al_2O_3 (%)	Basicity (%)	pH	Density (g/L)
0.0	50	0	117	0.5	2.38	0.0	2.64	–
0.5	50	17	100	0.5	2.38	17.0	2.72	1039.29
1.0	50	34	83	0.5	2.44	33.9	2.80	1040.15
1.5	50	50	67	0.5	2.13	49.9	3.05	1042.83
2.0	50	67	50	0.5	2.32	66.9	3.16	1040.62
2.2	50	74	43	0.5	2.34	73.9	3.17	1053.48
2.5	50	84	33	0.5	2.34	83.8	3.32	1065.62

To evaluate effects of Al_T on distribution of hydrolytic Al species, PACl (r = 2.0) with different Al_T concentration was made by firstly preparation of PACl 1.27 M Al and diluting or concentrating the mother solution to obtain the lower and higher Al_T concentration, respectively. The detail in making mother solution is given in Table 4.4. Deionized water was used to dilute the PACl. The concentrated PACls were made by using a vacuum rotary evaporator at temperature of 50°C and pressure of 72 mbar. PACl (r ≈ 2.0) with different Al_T concentration are shown in Table 4.5.

Table 4.4. Mother solution used for dilution or concentration.

$AlCl_3$ 3 M (mL)	Na_2CO_3 2 M (mL)	Al_T (M)	Al_2O_3 (%)	Basicity (%)	r	pH	Density (g/L)
100	150	1.27	2.62	72.1	2.16	3.03	1154.05

Table 4.5. PACl with different Al_T concentration PACl ($r \approx 2.0$)

PACl	Al (M)	pH	Density (g/L)	Al_2O_3 (%)	Note
r = 2.16	1.88	2.32	1248.91	7.68	Concentrating
	1.76	2.43	1223.42	7.36	Concentrating
	1.47	2.71	1248.91	5.98	Concentrating
	1.27	3.03	1154.05	5.62	Mother solution
	1.06	3.23	1058.58	5.11	Diluting
	0.79	3.40	1102.15	3.68	Diluting
	0.53	3.60	1075.48	2.51	Diluting
	0.26	3.81	1033.77	1.31	Diluting
	0.11	4.00	1011.11	0.53	Diluting

Theoretically, from the diluting and concentrating procedure, the Al concentration, and *r* values (or basicity) of PACl solution can be calculated. However, more exact values of Al_2O_3 content and basicity of PACl waere analyzed using Korean Standard Methods. The Al_2O_3 content was measured by titration using 0.02M Zn with 0.1% Xylynol orange indicator. Basicity was determined by titration method, using 0.5 N NaOH as tritant.

4.2. Aluminum Species Analysis by Ferron assay

Ferron assay was applied to characterize the coagulants in terms of Al_a, Al_b, and Al_c species in this study. The exact procedure was a modified method of Parker and Bertsch (Parker and Bertsch, 1992c), developed by Zhou et al. (Zhou et al., 2006a). The detail is given below:

– Reagent A: Under stirring, 1.05 g Ferron ($C_9H_6INO_4S$, Sigma Chemicals, USA) and 0.051 g 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$, Acros Organic Chemicals, USA) were dissolved in 500 mL deionized water which is boiled and cooled to room temperature to remove CO_2.

– Reagent B: 70 g sodium acetate ($C_2H_3O_2Na$, Junsei Chemicals, Japan) was dissolved in 200 mL of deionized water.

– Reagent C: 20 g hydroxylamine HCl ($NH_2OH.HCl$, Kanto Chemicals, Japan) and 10 mL concentrated hydrochloric acid (HCl 35%, Matsunoen Chemicals, Japan).

– Mixed Ferron solution: In 1 L-flask, mixing B, C and then adding A. Adding DW to 1L. Filter the mixture through 0.45 µm membrane filter. The mixed ferron reagent containing 3 mM Ferron ($C_9H_6INO_4S$), 0.26 mM 1,10-phenanthroline monohydrate ($C_{12}H_8N_2.H_2O$), 853 mM sodium acetate ($C_2H_3O_2Na$), 288 mM hydroxylamine HCl ($NH_2OH.HCl$), and 106 mM HCl.

The pH of mixture was 5.2 – 5.4. The mixed ferron can be used after 4 – 5 days and it should be discarded after 1 month.

Ferric/ferrous ions, which are introduced by the reagents during the preparation of hydroxy-Al solutions due to container, are the commonly encountered disturbing factors for Al speciation using ferron assay. Hydroxylamine reagent could reduce ferric ions to ferrous ions and then the ferrous ions were complexed by orthophenanthroline. Consequently, the formation of Fe-ferron complex could be minimized and the disturbance from ferric/ ferrous ions for Al speciation could also be avoided. Therefore, hydroxylamine and ortho-phenanthroline were often added to the ferron solution. However, adding of the two reagents could lead change of absorbance with ageing time, especially in the initial several days after preparation, results in higher instability of the colorimetric ferron solution Experiment was conducted to evaluate the stability of the ferron solution. Absorbance of ferron solution was recorded during 30 days and results are shown in Fig. 4.2. During the first 5 days after preparation, the spectra of ferron solution are significant changes vs. ageing time. After 5 days, the spectra did not show high stability at the wavelength of near 364 nm. Therefore, it is required to use the ferron colorimetric solution after 5 days of aging to obtain stable absorbance.

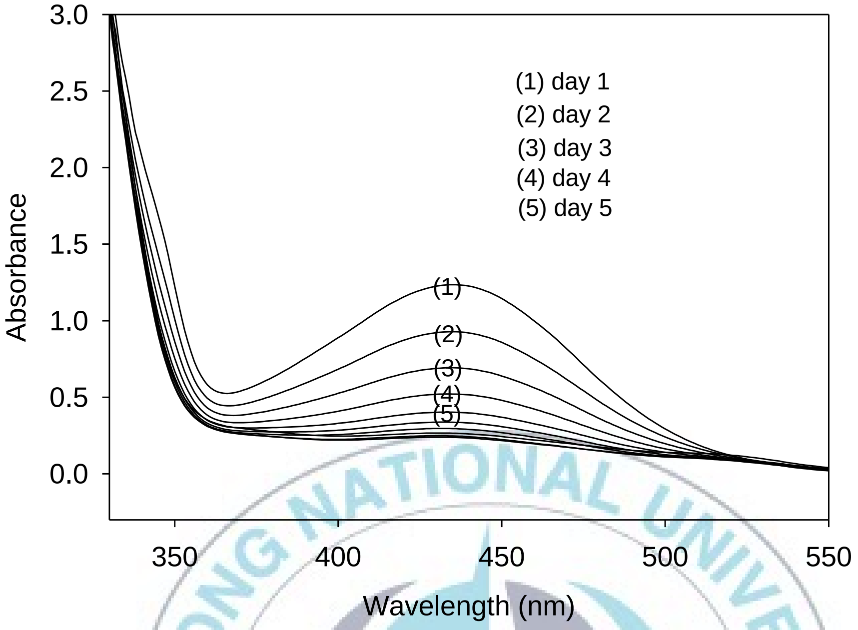


Fig. 4.2. Effects of ageing time on the absorbance spectra of ferron colorimetric solutions.

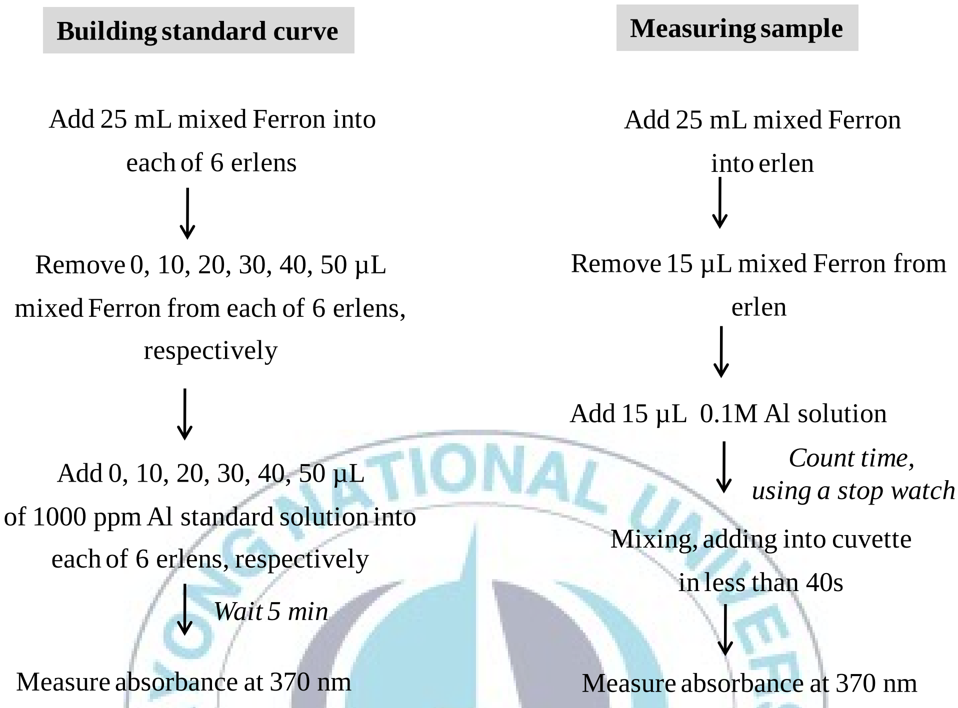


Fig. 4.3. Experiment procedure of speciation of Al solution using ferron.

The PACl was diluted to 0.1 M Al just before reacting with the ferron reagent. A volume of 15 µL of 0.1M Al coagulant was injected to a colorimetric solution containing (25 mL – 15 µL) mixed ferron reagent. The selected volumes of the PACl sample and the working solution assured the ferron/Al molar ratio kept at value ≥ 50. Reaction time was recorded immediately after adding the aluminum solution by a stop-watch. After homogeneous mixing, the reacting sample was quickly added to a 1-cm glass cell of a Shimadzu UV-1650 PC spectrophotometer and time absorbance measurements at 370 nm were automatically recorded for every 10 second during 2 hours. A standard Al concentration-absorbance equation was obtained by conducting experiments with a series of different Al concentrations diluted from Al monomer standard solution (1000 mg/L in 0.2 M HNO_3, Kanto Chemicals, Japan). It is noted that the blank for the spectrophotometric measure was solution of mixed ferron reagent. The procedure is summarized in Fig. 4.3. Absorbance-time data was fitted to a binary pseudo first order rate equation:

$$A=A_0+A_{b1}(1-e^{-k_1t})+A_{b2}(1-e^{-k_2t})$$

Where:

- A: absorbance at time t
- A_o: absorbance of Al_a-ferron
- $Al_b = Al_{b1}+Al_{b2}$
- A_{b1}: absorbance of Al_{b1}-ferron
- A_{b2}: absorbance of Al_{b2}-ferron
- $k_1=1/t_1$; $k_2=1/t_2$; t_1, t_2 are the reaction time of Al_{b1} and Al_{b2}

From model fitted parameters, the quantitative calculation of Al species can be made.

4.3. Characteristics of Coagulants

Fig. 4.4 to Fig. 4.6 show the reaction kinetics of ferron with hydroxy-Al solutions for PACl with different *r* values at low Al_T concentration of Al_T < 0.2 M, moderate Al concentration of Al_T = 0.5 M, and PACl (*r* value = 2.0) with different Al_T concentration. The common characteristics of the kinetic curves can be seen: an initial rapid absorbance increase followed by a gradual increase, and then ending in a plateau. However, the reaction behaviors of different types of hydoxy-Al solutions varied significantly. For *r* = 0 and *r* = 0.5, the absorbance started from a much high level, and then experienced a short period of gradual increase before reaching the plateau. But, in the cases of *r* = 1.5 and *r* = 2.0, the absorbance at the beginning was very low, and the gradual increase of absorbance lasted longer before reaching the plateau. At same *r* value, the different between the two trends is much more in PACl with higher Al_T (Fig. 4.4 vs. Fig. 4.5). The initial absorbance increase is believed to be associated with the reaction of ferron with mononuclear Al species, and the following gradually increasing phases are related to reactions of ferron with various hydroxy-Al polymers. When all of the Al species mentioned above react completely with ferron, the kinetic curve of Al ferron interaction would reach the plateau.

As can be seen in Fig. 4.6 for the same *r* value = 2.0 with different Al_T concentration, shape of reaction kinetics curves was much different, indicates that in addition to *r* value, Al_T also influences to the distribution of Al species in solution. It is noted that at same *r* value of 2.0, for Al_T = 0.5 M and 0.53 M as shown in Fig. 4.5 and Fig. 4.6, respectively, interaction of Al and ferron in the PACls was different. As shown in Table 4.7 and Table 4.8, the difference can be observed along with the decrease of Al_a and Al_{b1}, along with the increase of Al_{b2} and Al_c. This can be explained by the difference in preparation methods. Directly making PACl from $AlCl_3$ solution and Na_2CO_3 solution to achieve the desired Al_T (Table 4.7) and dilute from a high Al_T PACl (Table 4.8). Dilution for achieving lower Al_T PACl resulted in reducing of Al_a, significantly increasing of Al_{b1}, reducing Al_{b2} and also Al_c.

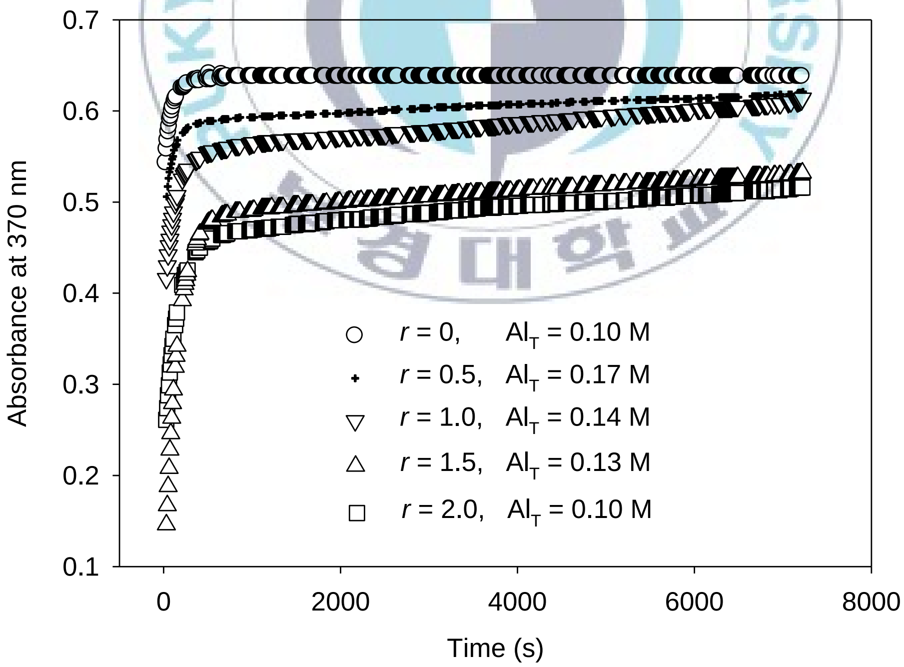


Fig. 4.4. Reaction kinetics of Ferron with reactive hydroxyl-Al polymers as comparison of different *r* values at $Al_T < 0.2$ M.

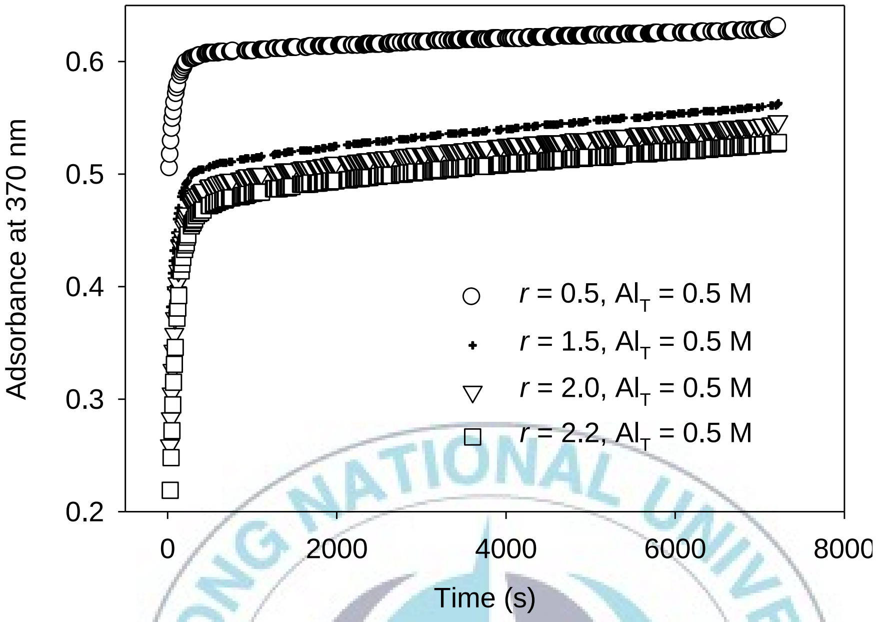


Fig. 4.5. Reaction kinetics of Ferron with reactive hydroxyl-Al polymers as comparison of different *r* values at Al_T = 0.5M.

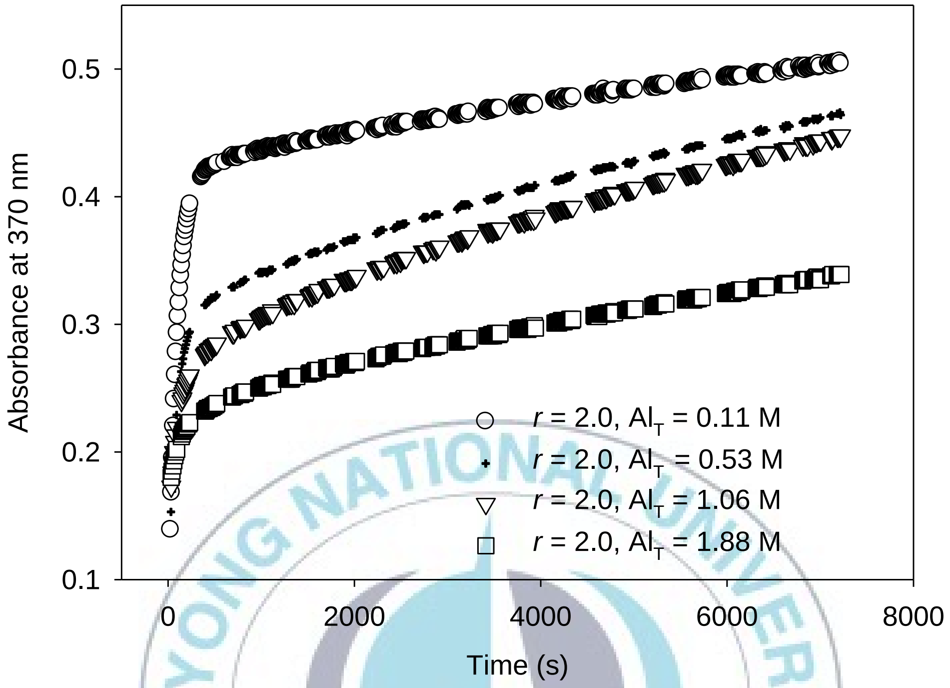


Fig. 4.6. Reaction kinetics of Ferron with reactive hydroxyl-Al polymers as comparison of different concentration of Al_T at *r* value = 2.0.

Distribution of Al species in PACl measuring by Ferron assay is shown in Tables from 4.6 to 4.8, for PACls with different *r* values at low concentration (Table 4.6), moderate concentration (Table 4.7), and PACl *r*= 2.0 at different Al_T (Table 4.8). Figures from 4.7 to 4.9 plot the respective data. The OH/Al ratio is an important parameter of the polymeric coagulant to indicate the polymeric extent of aluminum. As shown in Fig. 4.7 and Fig. 4.8, for both low Al concentration < 0.2 M Al and moderate Al concentration of 0.5 M Al, the higher the *r* value, the higher the Al_b present in PACl. $AlCl_3$ as PACl with *r* = 0 mainly contains monomeric Al species, ca. 97%. There was almost no Al_c present in $AlCl_3$.

Because of the difference in Al_T concentration, the density of PACl solution is different. The higher the Al concentration, the higher the density would be. Also, with same r value, the pH of more concentrated PACl solution was lower than pH of diluted PACl solutions. Actually, the pH of different concentration of the original $AlCl_3$ solution used to prepare PACl was also different. Value of pH of 0.1 M AlCl3 solution is 3.07 while this value for 0.5M $AlCl_3$ was 2.67. This explains the difference in density and pH of PACs with same r value.

Distribution of Al species in PACl was measured by Ferron assay and the effects of r value also total Al concentration is evaluated. The OH/Al ratio is an important parameter of the polymeric coagulant to indicate the polymeric extent of aluminum. As shown in Fig. 4.7 and Fig. 4.8, for both low Al concentration < 0.2 M Al and moderate Al concentration of 0.5 M Al, the higher the r value, the higher the Al_b exist in PACl. Alumnium Chloride $AlCl_3$ as PACl with $r = 0$ mainly contains monomeric Al species, ca. 97%. There was almost no Al_c present in $AlCl_3$.

Table 4.6. Ferron assay results for PACl with $Al_T < 0.2$ M

r value	pH	Al_a (%)	Al_{b1} (%)	Al_{b2} (%)	Al_c (%)
0.0	3.05	97.0	0.0	0.0	0.0
0.5	3.43	81.1	19.0	0.0	0.0
1.0	3.56	53.9	40.7	1.7	3.7
1.5	3.67	28.5	65.0	2.7	3.7
2.0	3.86	12.1	79.0	3.4	5.5
2.2	4.01	0.7	89.2	4.5	5.7
2.5	4.55	0.0	84.7	7.8	7.5

Table 4.7. Ferron assay results for PACl with $Al_T = 0.5$M

r value	pH	Al_a (%)	Al_{b1} (%)	Al_{b2} (%)	Al_c (%)
0.0	2.65	93.3	0.0	0.0	0.0
0.5	2.72	78.6	17.1	2.8	1.4
1.0	2.8	73.1	22.0	5.3	0.0
1.5	3.05	56.1	28.2	15.7	0.0
2.0	3.16	30.2	50.6	13.6	5.6
2.2	3.16	20.0	58.3	11.6	10.1
2.5	3.32	4.4	72.3	11.2	12.0

Table 4.8. Ferron assay results for PACl r = 2.0

Al (M)	pH	Al_a (%)	Al_{b1} (%)	Al_{b2} (%)	Al_c (%)	Note
0.11	4	11.6	56.8	17.7	13.9	Diluted
0.26	3.81	11.1	45.8	32.3	16.9	Diluted
0.53	3.6	13.4	29.3	39.5	17.7	Diluted
0.79	3.4	20.3	19.4	41.6	18.6	Diluted
1.06	3.23	21.3	15.9	43.7	19.1	Diluted
1.27	3.03	24.4	15.1	39.4	21.0	Original sol.
1.47	2.71	27.6	12.1	34.5	25.8	Concentrated
1.76	2.43	28.0	7.8	34.9	29.4	Concentrated
1.88	2.32	28.3	8.5	33.5	29.7	Concentrated

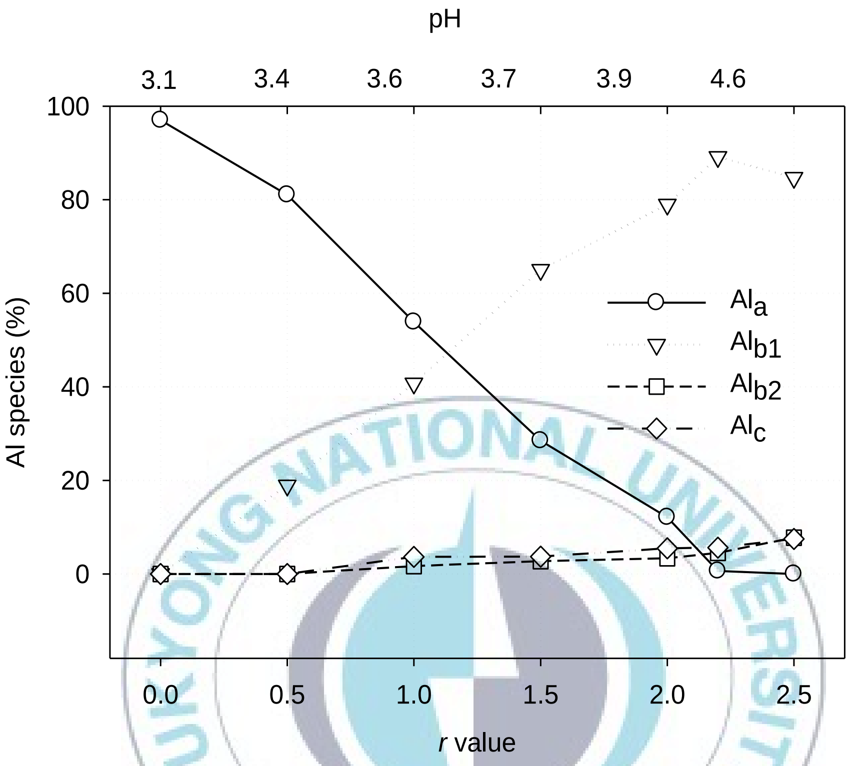


Fig. 4.7. Distribution of Al species as a function of the *r* value and pH at Al_T < 0.2 M.

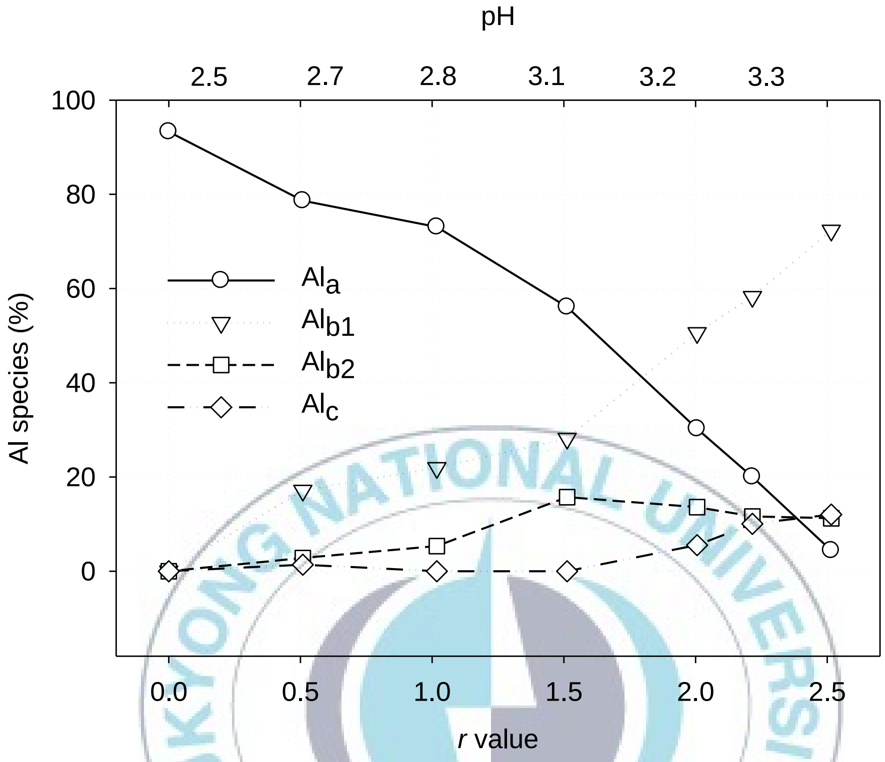


Fig. 4.8. Distribution of Al species as a function of the *r* value and pH at Al_T = 0.5M.

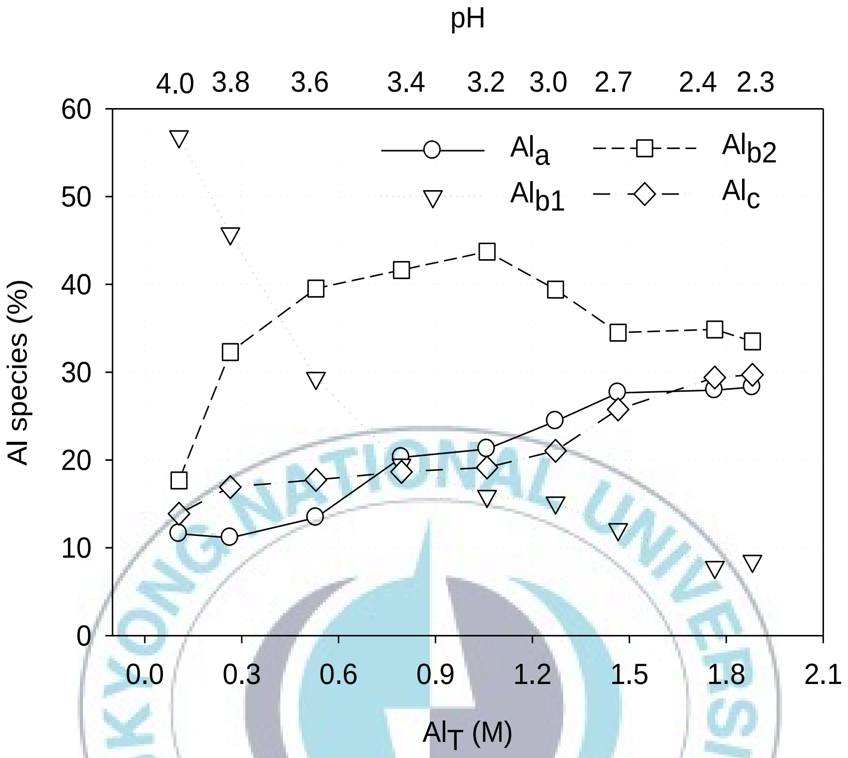
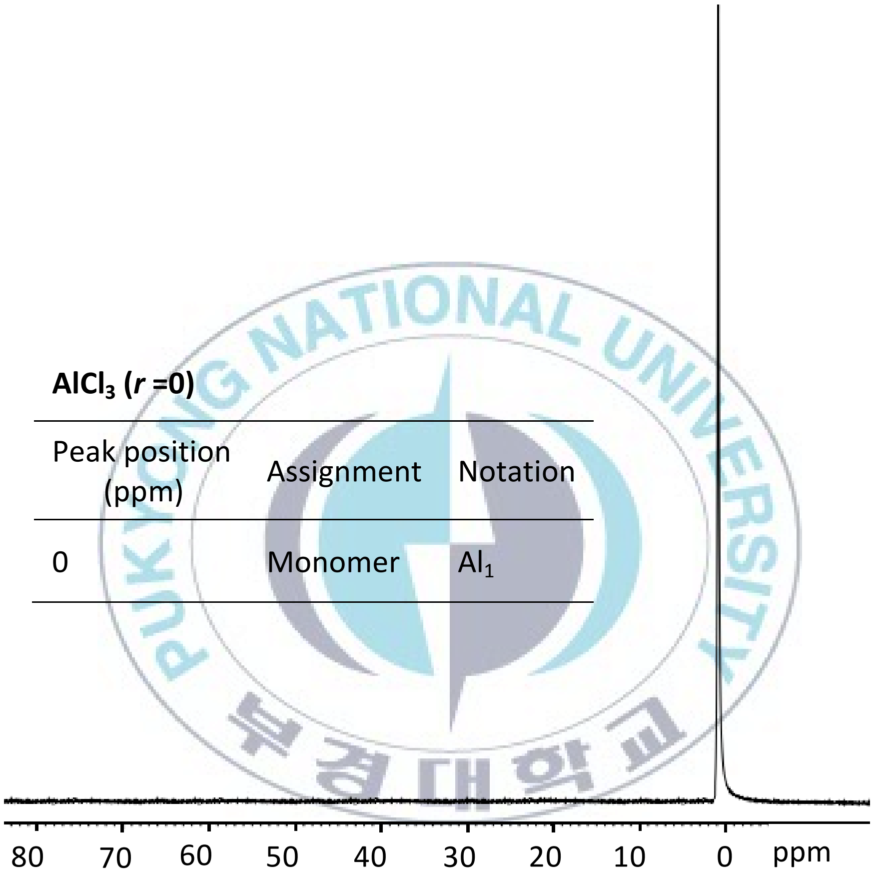


Fig. 4.9. Distribution of Al species as a function of the Al_T and pH at *r* value = 2.0.

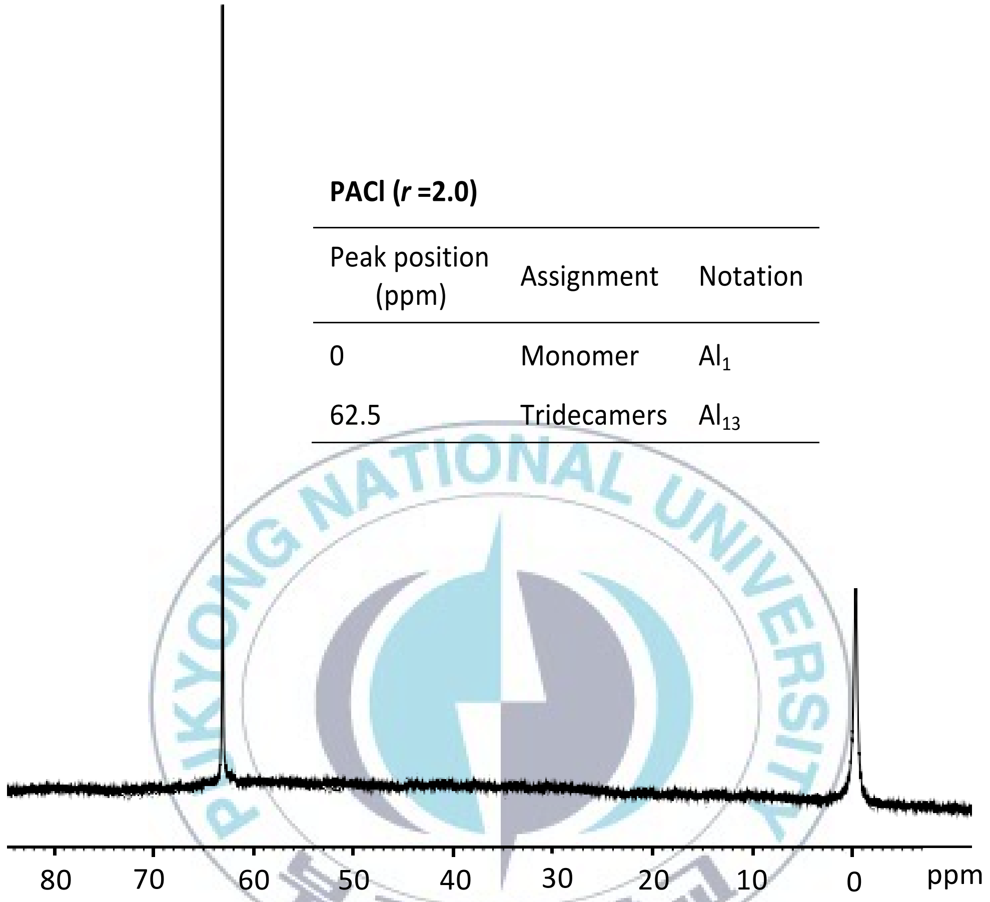
In order to verify the results of ferron method, ^{27}Al NMR analyses was performed for $AlCl_3$ and PACl (*r* = 2.0). Fig. 4.10 displays the ^{27}Al NMR spectra of $AlCl_3$ and PACl (*r* = 2.0). For $AlCl_3$, only one signal is appearing at chemical shift of 0 ppm, induced by the mainly presence of monomeric Al species. For PACl (*r* = 2.0), in addition to the signal at 0 ppm, one more signal are appearing at 62.5 ppm with bigger peak area, induced by the predominant presence of the central tetrahedral aluminum of Al_{13}. As previously mentioned in Chapter 2, Al_b is closely correlated to Al_{13} and this species is well known as the most effective Al species in coagulation-flocculation.



$AlCl_3$ (*r* =0)

Peak position (ppm)	Assignment	Notation
0	Monomer	Al_1

Fig. 4.10. ^{27}Al NMR spectra of $AlCl_3$.



PACl (*r* =2.0)

Peak position (ppm)	Assignment	Notation
0	Monomer	Al_1
62.5	Tridecamers	Al_{13}

Fig. 4.11. ^{27}Al NMR spectra of PACl (r = 2.0).

Chapter 5

COAGULATION OF TURBIDITY AND NATURAL ORGANIC MATTER

This Chapter describes the raw water quality (surface water and synthetic water), coagulants characterizations, and relationship between the characteristics of the coagulants and coagulation-flocculation performance. Effects of coagulation pH and coagulants dosages were emphasized. Coagulation mechanisms in each case were discussed.

5.1. Characteristics of Nakdong River Water

The characteristics of the Nakdong River water were given in Table 5.1. UV absorbance has been used for reasons of simplicity in many pilot plant studies. However, UV measures the aromatic compound preferentially and does not give correct results if the aromaticity is altered, as is the case of coagulation-flocculation. UV absorbance can therefore not be used to measure treatment efficiency.

NOM that occurs in natural brown water are polyphenolic molecules with MW ranging from 5,000 to 50,000 Dalton (Lin et al., 2000). In particular, NOM can be fractionated into three segments: hydrophobic (humic substances), hydrophilic and transphilic fractions. The hydrophobic fractions represent almost 40% of dissolved organic carbon (Fig. 5.1) with larger MW. The hydrophilic fraction is composed of 40% of dissolved organic carbon (DOC) with lower MW (polysaccharides, amino acids, protein, etc.) and is operationally defined as a non-humic fraction. The transphilic fraction is comprised of approximately 20% DOC in natural water but with MW in between hydrophobic and hydrophilic fractions. It is worthy to note that humic substances concentrations may vary with season and source. Therefore, the values reported above can change. However, the fractions illustrated in Fig. 5.1 can be considered as typical nature of DOM in the Nakdong River water. A major fraction of the NOM arises from humic substances which represent 40% of DOC the raw water and 49% as shown by Thurman in Fig. 5.2. Fan et al. (Fan et al., 2001) reported that the major fraction of NOM is composed of humic substances that are responsible for the colour of natural water

Hydrophobic was further divided into fulvic and humic acid. The result shows hydrophobic is mainly fulvic acids and humic acid present with a small amount < 10%. HA and FA are anionic polyelectrolyte with negatively charged carboxylic acid ($COOH^-$), methoxyl carbonyls (C=O) and phenolic (OH^-) functional groups. HA is soluble at higher pH normally, such as 10 while fulvic acid is soluble in water at any pH.

Table 5.1. Characteristics of Nakdong river water

Parameter	Range	Unit
Turbidity	8.5−11.5	(NTU)
UV_{254}	0.047−0.050	(cm^{-1})
DOC	2.50−3.80	(mg/L)
SUVA	1.27−1.33	($L.mg^{-1}.m^{-1}$)
pH	7.5−9.4	−
Alkalinity	60−85	(mg $CaCO_3$/L)

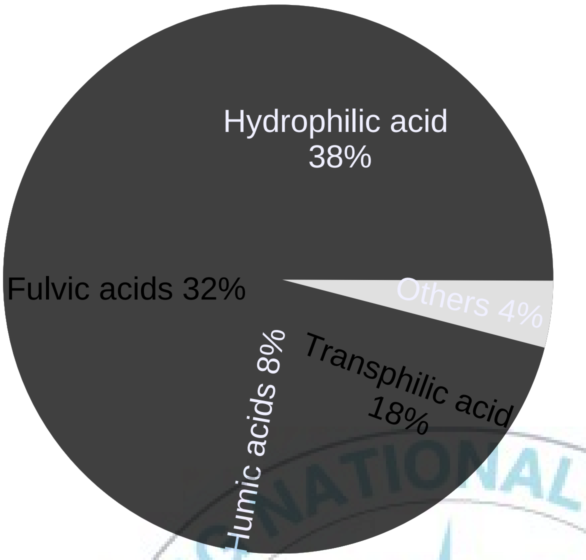


Fig. 5.1. Distribution of organics in the Nakdong River water .

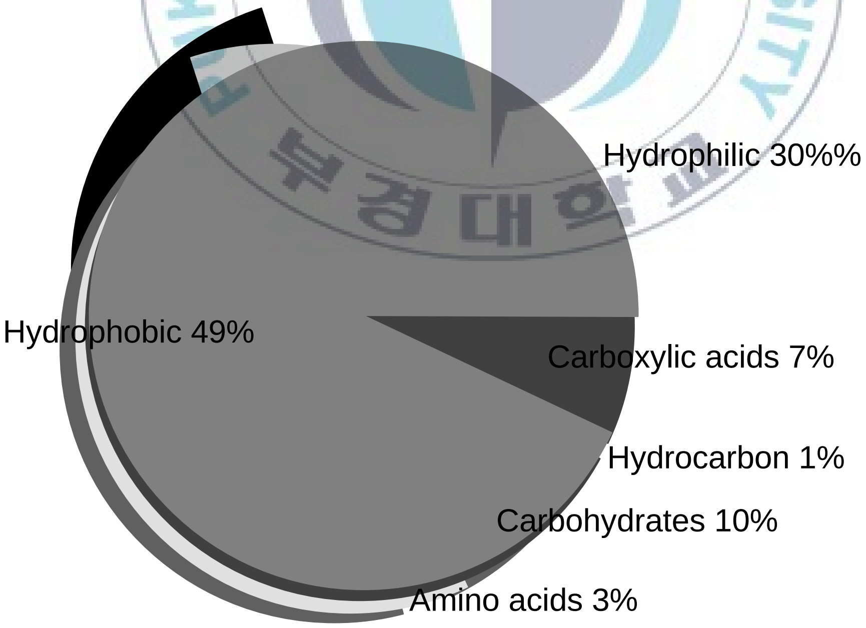


Fig. 5.2. Fraction of NOM in surface water based on DOC (Thurman, 1985a)

The chemical property of organic fractions was further characterized by ultra-filtration membranes and the distribution of apparent molecular weight (AMW) is illustrated in Fig. 5.3.

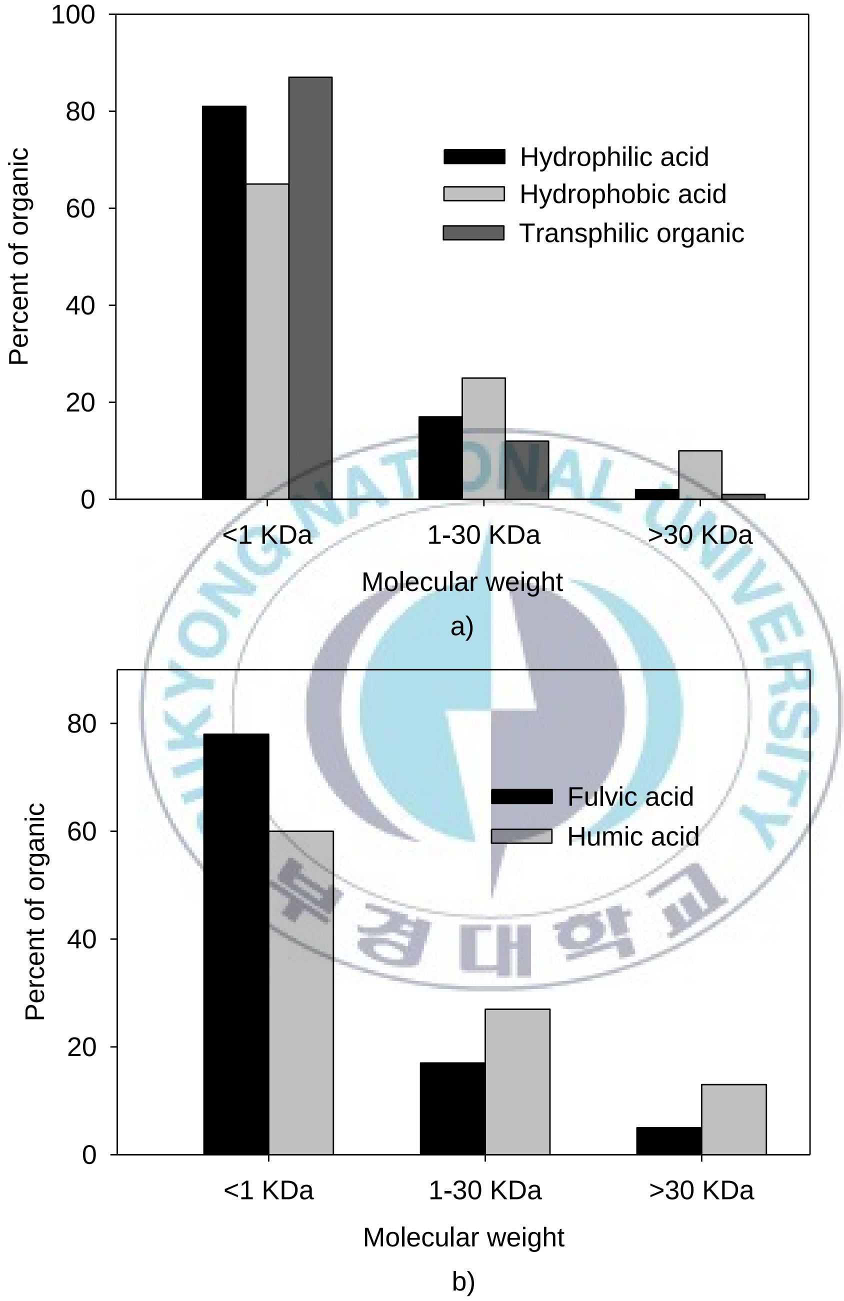


Fig. 5.3. AMW distribution of a) the Nakdong River raw water and b) hydrophobic acid fraction in the Nakdong River water.

The characteristics of synthetic water prepared from isolated organics and kaoline were given in Table 5.2.

Table 5.2. Characteristics of synthetic water with kaoline and isolated organic

Synthetic water	Turbidity (NTU)	UV_{254} (cm^{-1})	DOC (mg/L)	SUVA ($L.mg^{-1}.m^{-1}$)	pH	Alkalinity (mg $CaCO_3$/L)
Hydrophilic	10.50	0.050	3.64	1.37	7.0	88.90
Fulvic acid	9.97	0.102	3.12	3.27	6.8	90.56
Humic acid	10.03	0.075	2.57	2.91	7.2	83.56

5.1. Coagulant selection

Coagulant selection is mainly base on the distribution of their Al species. Alum and $AlCl_3$ ($r = 0$) as “zero basicity coagulants” and $PACl_{2.0}$ ($r = 2.0$) as high preformed Al_b (Al_{13}) coagulants were chosen among prepared coagulants to perform jar tests to reveal the role of various Al species of monomeric Al_a, polymeric Al_b, and colloidal/precipitate Al_c in coagulation-flocculation. With respect to highest Al_b species, PACl with r value = 2.2 (Al_b = 93.7%) should be selected. However, as consider the corresponding between laboratory prepared PACl and commercial PACl, with basicity in commercial PACl is < 70% for almost commercial PACls, the PACl with r = 2.0, corresponding to 67% basicity was selected. Total aluminum concentration Al_T of the selected coagulants is < 0.2 M Al and their characteristics is presented in detail in Table 5.3.

Table 5.3. Coagulants used in jar test of surface water

No.	Name	Al_2O_3 (%)	Al_T	Basicity (%)	Density (g/cm^3)	pH	Al_a	Al_b	Al_c
1	Alum	1.2	0.12	0	0	1.085	88.1	11.9	0
2	$AlCl_3$	1..0	0.10	0	0	1.024	97.0	–	3.0
3	$PACl_{2.0}$	0.6	0.11	67	2.0	1.021	12.1	82.4	5.5

5.3. Effect of pH on Coagulation-flocculation

In order to get more insight into the removal mechanism of contaminants from water, jar test was carried out at different pH value ranged from 4 to 9. Effects of coagulation pH on turbidity, UV absorbance, and DOC removal from Nakdong river water was investigated at three coagulant doses: low dose of 0.03 mM Al, moderate dose of 0.1 mM Al, and high dose of 0.18 mM Al.

5.3.1. Turbidity Removal

Removal efficiency obtained as a function of coagulation pH using alum and $PACl_{2.0}$ at Al doses of 0.03 mM, 0.1 mM, and 0.18 mM are plotted in Fig. 5.4, Fig. 5.5, and Fig. 5.6, respectively. At optimum pH values, higher 95%

turbidity was removed from bulk water using alum and $PACl_{2.0}$. Turbidity is reduced most efficiently at neutral and basic pH values, especially for $PACl_{2.0}$. The PACl showed more efficient turbidity removal at high pH values and as pH decreases, i.e. below 6, turbidity removal efficiency decreases obviously. This phenomenon was observed for all Al doses of 0.03, 0.1, and 0.18 mM Al. The alum show a broad optimum pH range and towards acidic pH at low dose and as dose is increased, the optimum pH range extend to neutral and basic regions.

As comparison between turbidity removal of alum and PACl in considering the influence of coagulation pH, a trend was observed: at acidic pH values, alum show superior performance while at basic pH values, the performance was reversed. This is much related to the relationship between removal mechanisms and behavior of Al species formed in situ during coagulation-flocculation process rather than those in the coagulant itself. It was found that the concentration of OH^- in water should determine the degree of hydrolysis products of aluminum based coagulants. It is well-known that monomeric Al (Al_a) in the primary coagulants is the most unstable species and when added into water, this species would quickly hydrolyzed to form other Al species, i.e. polymeric Al (Al_b), and finally colloidal/ precipitated Al (Al_c), depending on coagulation pH. On the contrary, the polymeric and colloidal species, once preformed, are relatively stable (Zouboulis and Traskas, 2005.) The higher the r value of the PACls, the less the Al_a species, and the more stable the Al speciation after dosing. At the acidic pH region, the mechanism of turbidity removal is mainly through charge neutralization of particles by positively charged Al species. Alum which mainly composed of monomer Al (Al_a), produced Al polymer (Al_b) in situ with an amount more than the amount of stable preformed Al_b in PACl. Because Al_b (Al_{13}) is considered as the most effective Al species in neutralization due to its highly positively charge, the superior of alum to PACl at low pH range can be explained. As pH is increased, Al_b formed in situ of alum transform into Al_c while Al_b in PACl is stable during change of pH, and therefore the superior of alum disappeared. However, it is worth to note that, at high Al dose, forming Al_c (highly polymeric Al and precipitate $Al(OH)_{3)}$ with increase in pH is also benefit for removal of turbidity due to the “sweep flocs” mechanism. A proof that at high Al doses enough for enmeshment of particles in precipitates the superior of PACl at high pH gradually disappeared (Fig. 5.5), and alum shows better performance (Fig. 5.6).

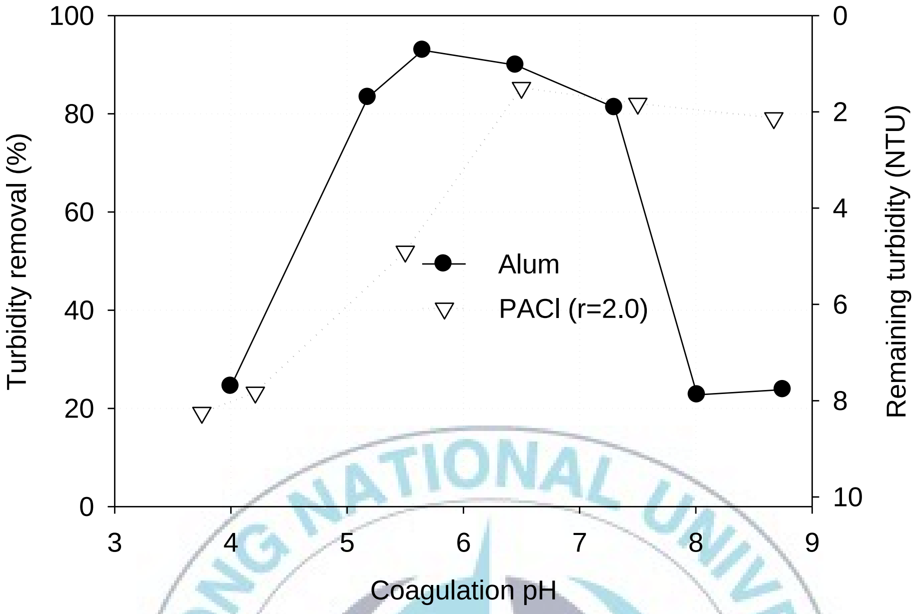


Fig. 5.4. Turbidity removal as a function of coagulation pH (0.03 mM Al)

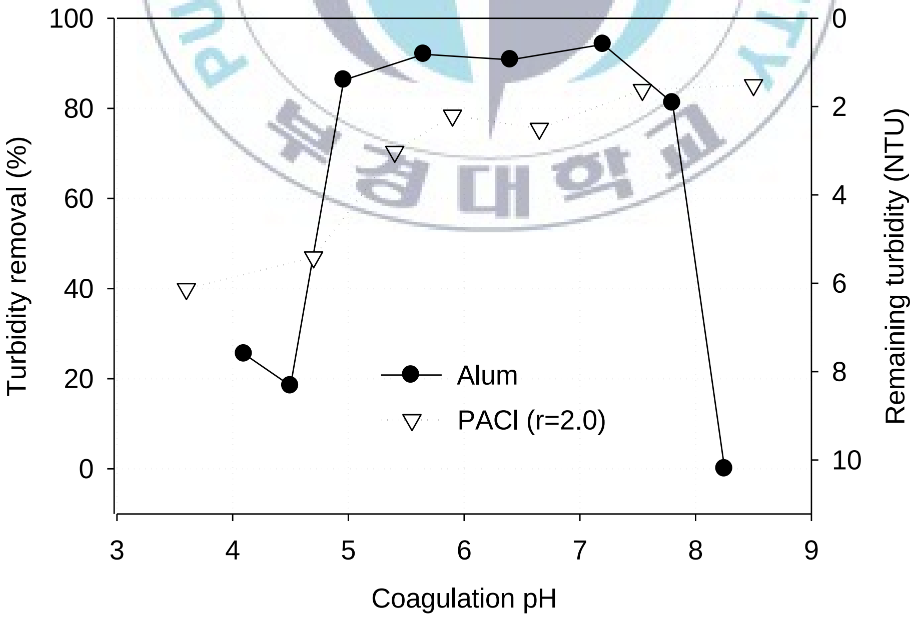


Fig. 5.5. Turbidity removal as a function of coagulation pH (0.10 mM Al).

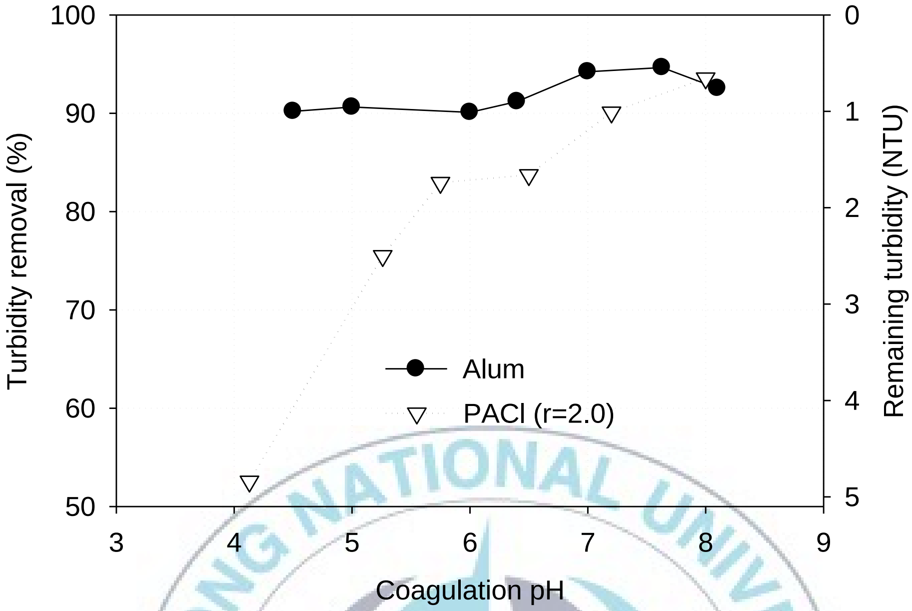


Fig. 5.6. Turbidity removal as a function of coagulation pH (0.18 mM Al).

5.3.2. NOM removal

Although the removal rate of UV_{254} was higher than DOC removal, effect of pH on UV_{254} and DOC removal shows a similar trend, as can be seen in Fig. 5.7 to Fig. 5.12. The removal of UV_{254} quickly increases with increase of pH from 4 to 6 and maximum efficiency was observed in the range of pH from 5.0 – 6.5, depending on the coagulants used. The optimum pH range extended towards acidic pH when using alum and towards neutral / alkaline pH in case where PACl used. Turbidity removal by alum is largely pH dependent illustrated by the sharp curves showing the rapid increase in acidic pH and rapid decrease as increasing pH to neutral / alkaline regions.

The PACl, however, is more stable through the pH range investigated, showing wider optimum pH range towards higher pH.

Similarly to the removal of turbidity, PACl showed superior effectiveness to alum in the neutral/alkaline pH while at acidic pH, the trend was reversed. Again, coagulation performance is strongly influenced by coagulant species formed in situ, and these species is largely dependent on coagulation pH. At acidic pH, the removal of NOM is mainly through formation of insoluble complexes of aluminum humates or fulvates in a manner similar to charge neutralization. This mechanism could result from specific chemical reactions between positively charges Al species and the negatively charged NOM molecules, or it could arise from shielding of negatively charged NOM sites, causing a contraction and collapse of molecule, thus leading to precipitation (Edwards and Amirtharajah, 1985). A large amount Al_b formed in situ at acidic pH by transformation of Al_a in high monomer Al coagulants contribute to the superior performance of alum in neutralization of negatively charged NOM. Al_a consumes a limit amount of OH^- at acidic pH to hydrolyze and forming Al_b, and then Al_b neutralizes organic ligands without or with a less competition of OH^-. However, as pH is increased to value above 6, Al_c is the predominant species formed in situ of alum and the possible mechanism in this situation is adsorption of DOM onto metal hydroxide $Al(OH)_3$ floc. But unfortunately, the surface charge of DOM is more negative as increasing pH. Therefore, it is difficult to obtain effective adsorption. With PACl, this pH allows the simultaneously presence of both soluble polymeric aluminium species, Al_b and solid metal hydroxide precipitates, Al_c. That is Al_b react with DOM and neutralize or substantially reduce the negative charge on the DOM, promoting its adsorption onto $Al(OH)_3$ (s).

It is worth to note that the influence of pH in PACl and alum with respect to UV_{254}/DOC removal is similar to turbidity removalexcept a fact that at high dose of 0.18 mM Al, PACl still maintained the superior performance versus alum (the superior of PACl to alum in removal of turbidity disappeared at high dose of Al). This can be explained by the difference in removal mechanisms of turbidity and UV/DOC. At high pH, the predominant mechanism to remove turbidity is “sweep flocs” of particles while neutralization/adsorption of NOM onto $Al(OH)_3$ is primary mechanism governing the UV/DOC removal. For “sweep flocs”, alum with more Al_c formed in situ is favorable while PACl with predominant Al_b is better for neutralization and then adsorption.

For summarizing, coagulation pH influences the organic matter removal (UV_{254} and DOC removal) due to the two reasons: dependence on pH of Al species formation in situ and change of NOM surface charge with the change of pH. Considering the first aspects, preformed Al species in PACl is stable and less sensitive to the change of pH in coagulation-flocculation process while Al species in alum is unstable and quickly transformed to other Al species. The second is the change of NOM surface charge with the change of pH. It is known that the higher pH, the higher negatively charge of NOM would be and generally, NOM with high negative charge is not favorable for neutralization by positively charged Al species. At lower pH, Al species products could react more effectively with organic ligands without the competition of OH^-.

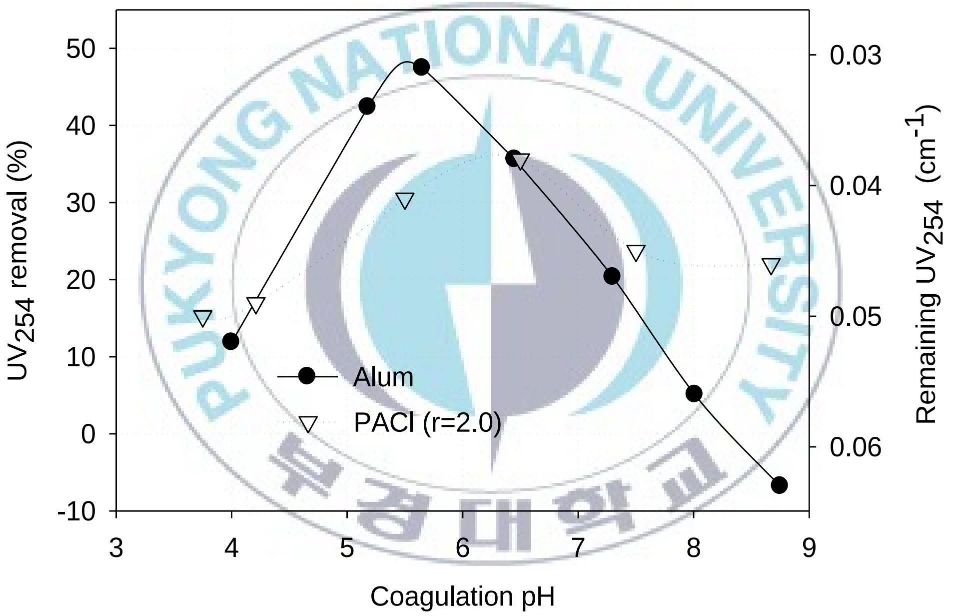


Fig. 5.7. UV_{254} removal as a function of coagulation pH (0.03 mM Al).

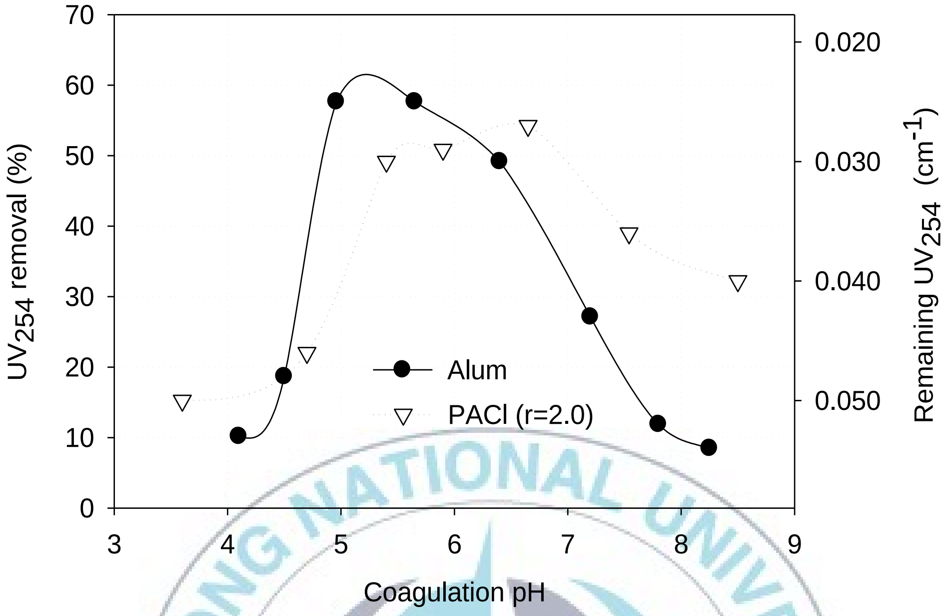


Fig. 5.8. UV_{254} removal as a function of coagulation pH (0.10 mM Al).

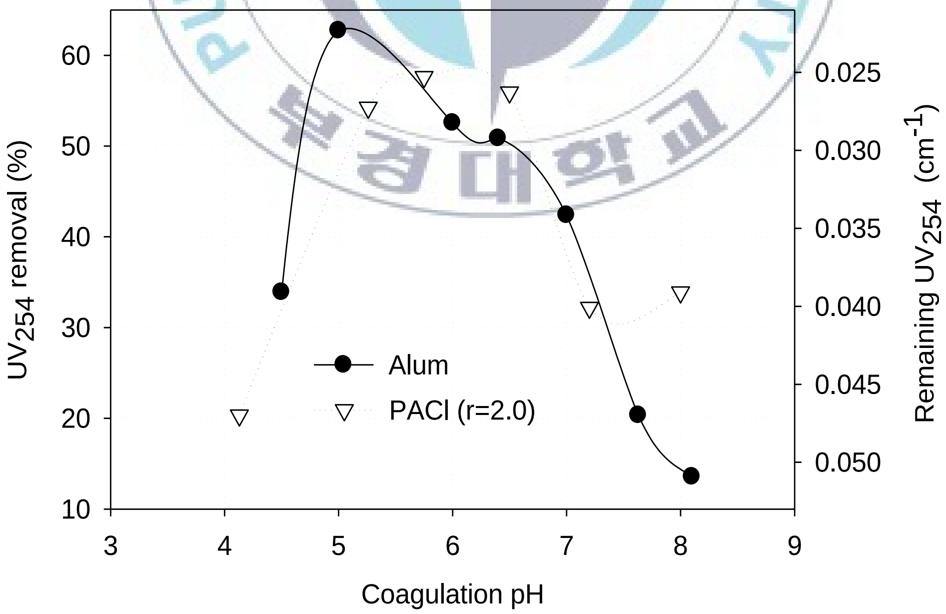


Fig. 5.9. UV_{254} removal as a function of coagulation pH (0.18 mM Al).

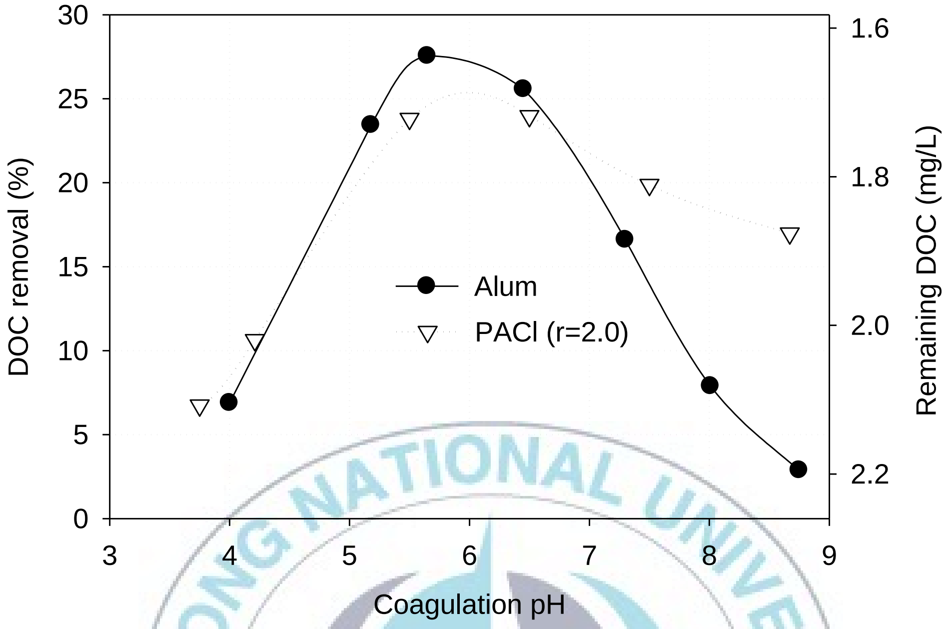


Fig. 5.10. DOC removal as a function of coagulation pH (0.03 mM Al).

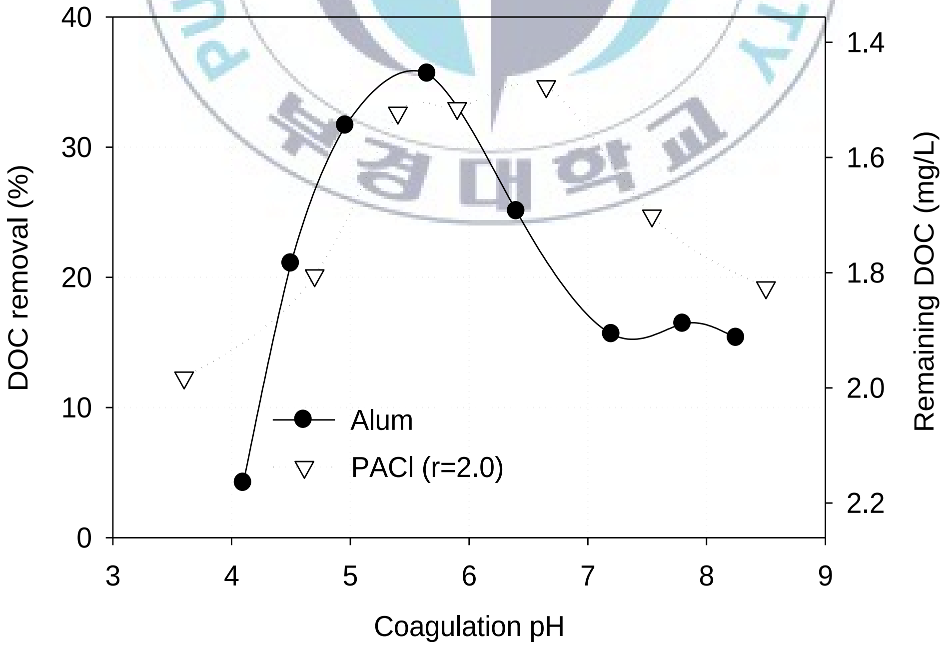


Fig. 5.11. DOC removal as a function of coagulation pH (0.10 mM Al).

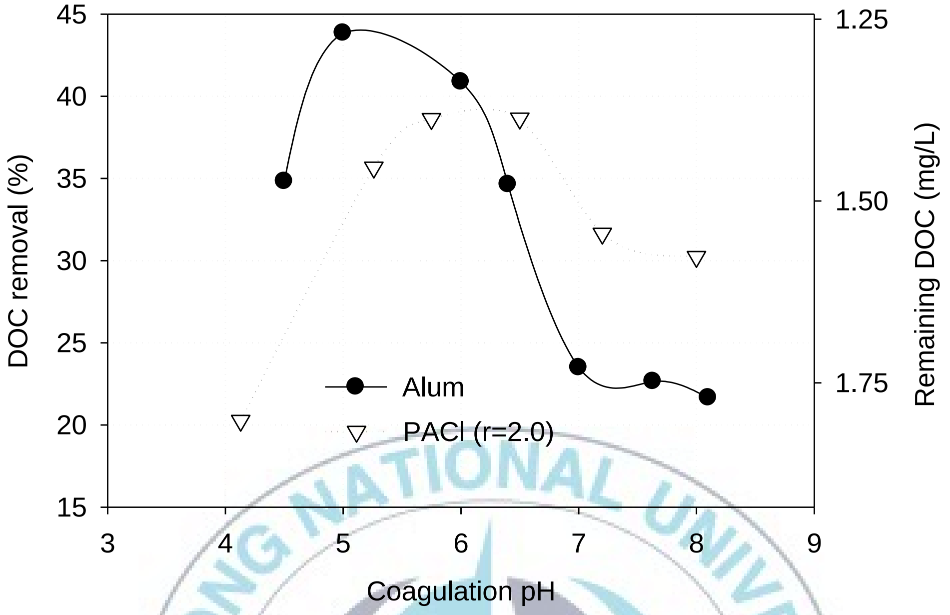


Fig. 5.12. DOC removal as a function of coagulation pH (0.18 mM Al).

5.4. Effect of Coagulant Dose on Coagulation-flocculation

Coagulation-flocculation to removal contaminants from bulk water is much dependent on coagulation pH as shown in previous section. To evaluate effects of coagulant dose, the pH was kept at 7. This pH is most common in water treatment. Applying a small amount of Al salts gave a dramatically removal of about 90% turbidity. Further increasing of dosage in the range from 0.03 to 0.1 mM Al, removal efficiency increased slowly and reached a plateau, except with PACl. At Al dose higher than 0.1 mM, there was a slight decrease of the removal which might be due to restabilization of particles, which is ascribed to the charge reverse of particles. Although it is known that at high pH such as 7 in the experiment, restabilization does not occur because the predominant removal mechanism is bridging by negative hydrolysis species with a continuous transition to precipitate enmeshments as the dose is incrementally increased. However, predominantly stable $Al_{b,}$ in PACl with positive charge is still exist at pH 7, lead charge reversal of particles as an excess dose supplied.

Although DOC concentration is the accepted measure of DOM content in natural waters, UV_{254} absorbance is often used as a surrogate for DOC concentration. UV_{254} absorbance is attributed to the presence of aromatic compounds, show increasing of removal efficiency with coagulant dose. These compounds were more easily removed than DOC illustrated by a higher percent of removal than those of UV_{254}. As shown in Fig. 5.14 and

Fig. 5.15, higher than 50% UV_{254} could be removed while DOC removal at highest dose of the experimental range was about 40%.

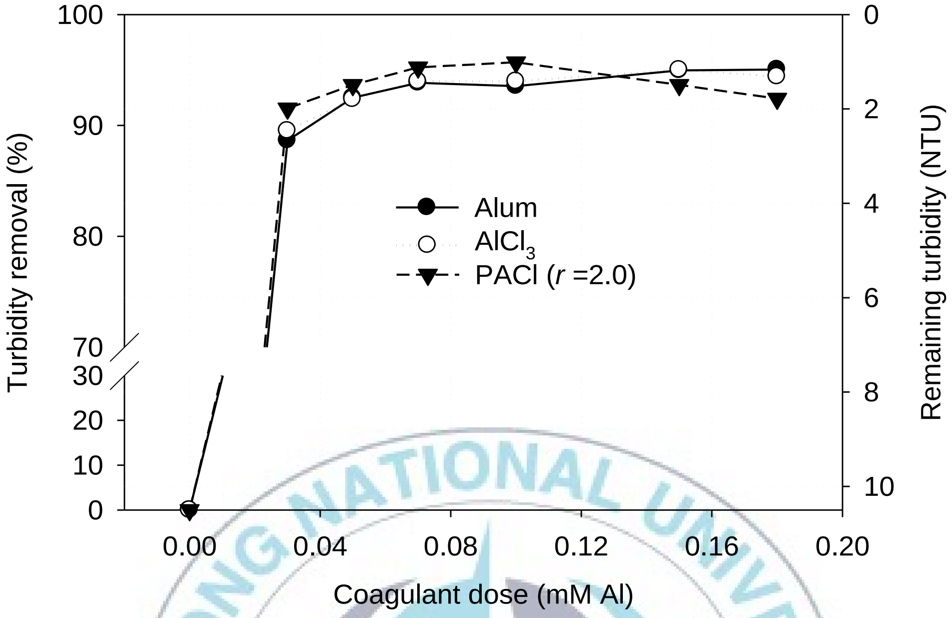


Fig. 5.13. Nakdong river water - Turbidity removal as a function of Al dose (pH 7.0).

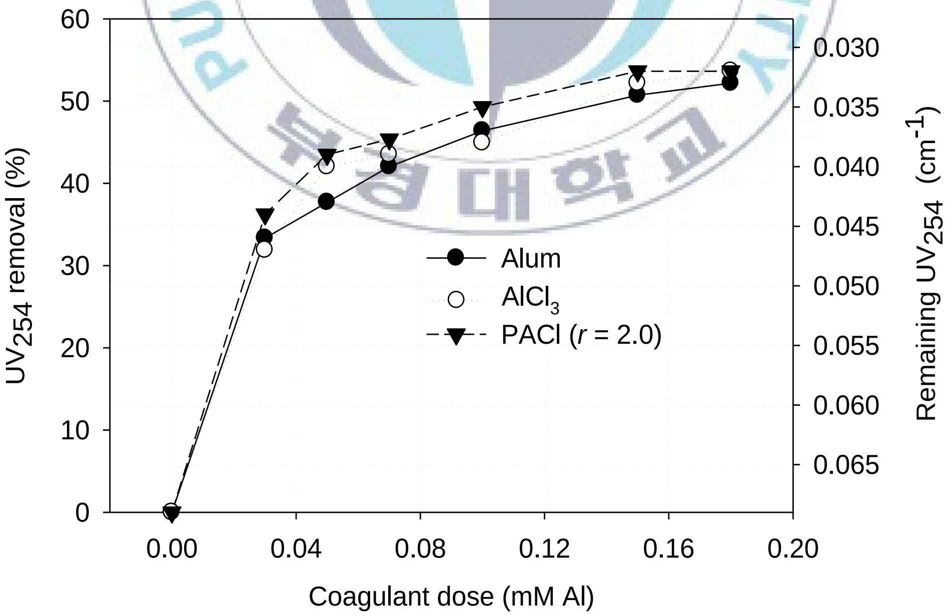


Fig. 5.14. Nakdong river water - UV_{254} removal as a function of Al dose (pH 7.0).

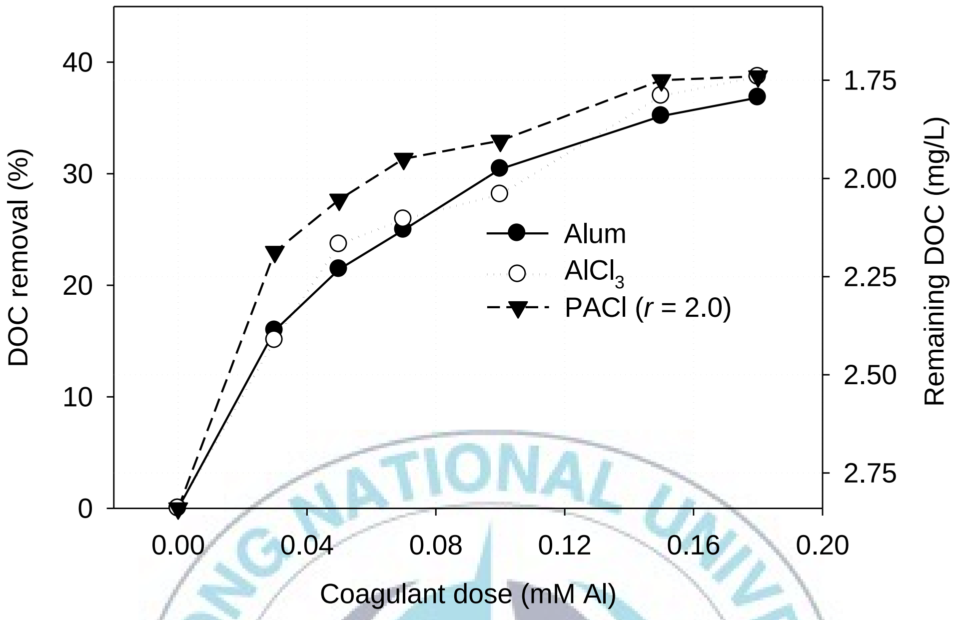


Fig. 5.15. Nakdong river water - DOC removal as a function of Al dose (pH 7.0).

5.5. Coagulation-flocculation of Different Organic Fractions

Experiments were conducted with synthetic waters prepared with kaoline and various organic fractions which previously isolated from the Nakdong River water. Coagulation-flocculation was carried out at pH 7. The coagulation results obtained from hydrophilic, fulvic acid, and humic acid synthetic water were shown in figures from Fig. 5.16 to Fig. 5.24.

UV absorbance has been used for reasons of simplicity in many pilot plant studies. However, UV measures the aromatic compounds preferentially and does not give precise results if the aromaticity is altered, as is in the case of coagulation-flocculation. UV absorbance can therefore not be used to measure treatment efficiency. DOC value is used to measure organic in treatment. For isolated organic synthetic water, DOC is surrogate for content of each organic fraction.

For each organic fraction, UV_{254} absorbance removal increases rapidly at low Al doses and little reduction in UV_{254} absorbance occurs at high doses. The same trend is observed for DOC removal.

Table 5.4 summarizes removal efficiency of UV254 absorbance and DOC at highest dosage of 0.18 mM Al. The removal of UV254 was higher than of DOC for the all of investigated organic fractions, and the difference was observed most significant in humic acids (80% UV254 removal vs. 50% DOC removal). Both humic acids and fulvic acids are known as hydrophobic fraction of NOM. However, as previously shown in Fig. 5.3, organic molecules in humic acid are bigger than that of fulvic acids. The UV absorbance removal and molecular weight analysis for organics further supports the idea that aromatic structures and high molecular weight organic are preferentially removed by coagulation-flocculation.

DOC and UV_{254} removals indicate that humic acids were more amenable to removal than the corresponding fulvic and hydrophilic acids. As can be seen in Table 5.4, at 0.18 mM al, 55.6 % DOC of humic acid was removed while this value for fulvic acids and hydrophilic acids was 43.8% and 21.7%, respectively. However, it is important to note that humic acids are present generally a relatively small fraction of the DOC of surface water, less than 10%. Therefore, although humic acid show most amenable to removal, the contribution of humic acids to the total DOC removal in surface waters is not significant when compared with fulvic and hydrophilics acids.

This study shows hydrophobic organics (fulvic and humic acids) were much easier to remove than hydrophilic organics. The percent removal of hydrophobic DOC was typically more than twice that of hydrophilic DOC. A study conducted by (Croué et al., 1993) showed that hydrophilic acids were removed in similar proportion to hydrophobic substances, our result, however, showed different removal. Coagulation-flocculation preferentially removed hydrophobic NOM over hydrophilic NOM as measured by DOC. This trend is consistent with other results observed by many researchers (Howe and Clark, 2002; Owen et al., 1993; Yeh and Huang, 1993), and further supported by the decrease in SUVA (an index of hydrophobic acids) after coagulation as show in Table 5.4.

Table 5.4. Summary of UV_{254} absorbance and DOC removal efficiency

Organic fraction	Initial UV_{254} (mg/L)	% UV_{254} absorbance removal at 0.18 mM Al		
		Alum	$AlCl_3$	PACl (*r*=2.0)
Hydrophilic	0.050	34.0	38.0	38.0
Fulvic acid	0.102	49.0	51.0	58.0
Humic acid	0.075	–	83.0	84.0
Organic fraction	**Initial DOC (mg/L)**	**% DOC removal at 0.18 mM Al**		
		Alum	$AlCl_3$	PACl (*r*=2.0)
Hydrophilic	3.64	21.6	21.7	23.2
Fulvic acid	3.04	43.4	43.8	45.5
Humic acid	2.25	–	55.6	46.8
Organic fraction	**Initial SUVA (mg/L)**	**SUVA of treated water at 0.18 mM Al**		
		Alum	$AlCl_3$	PACl (*r*=2.0)
Hydrophilic	1.37	1.16	1.09	1.11
Fulvic acid	3.36	3.03	2.93	2.6
Humic acid	3.33	–	1.3	1.0

As a comparison between investigated coagulants, PACl with high preformed polymer Al shows the most superior performance to the other coagulants in coagulation of hydrophilic acids which have smallest AMW among the 3 fractions of hydrophilic, fulvic, and humic acids. This can be explained by the main mechanism to remove NOM at experimental pH of 7. At this pH, DOM removal mechanism is adsorption onto $Al(OH)_3$ precipitate rather than neutralization. For the PACl with simultaneous presence of Al polymer and $Al(OH)_3$, negatively charged organic molecules of NOM is neutralized by polymeric Al, promoting the adsorption of neutralized DOM onto $Al(OH)_3$. This mechanism is considered more effective than adsorption onto $Al(OH)_3$ alone as in the case of alum or $AlCl_3$.

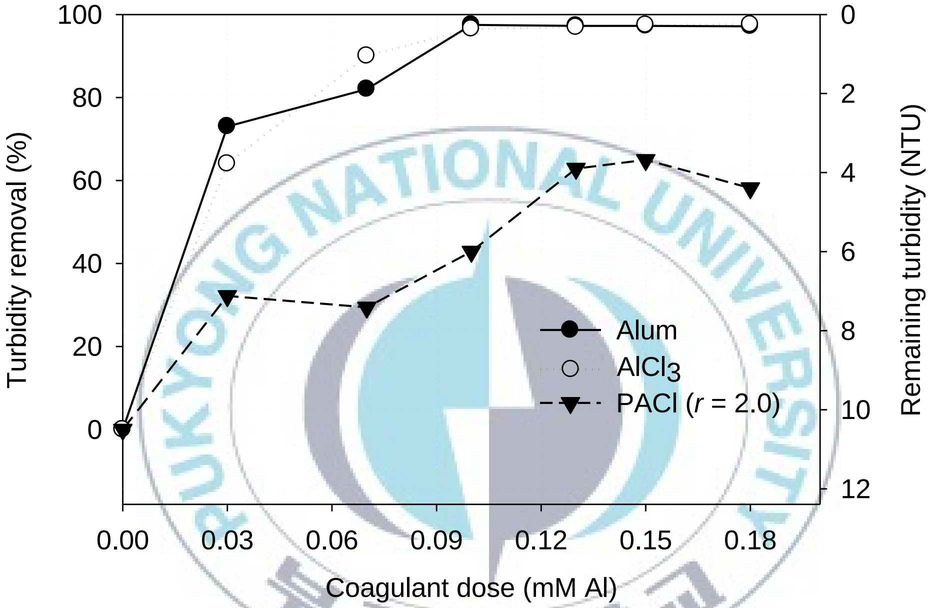


Fig. 5.16. Hydrophilic synthetic water - turbidity removal as a function of Al dose (pH 7.0).

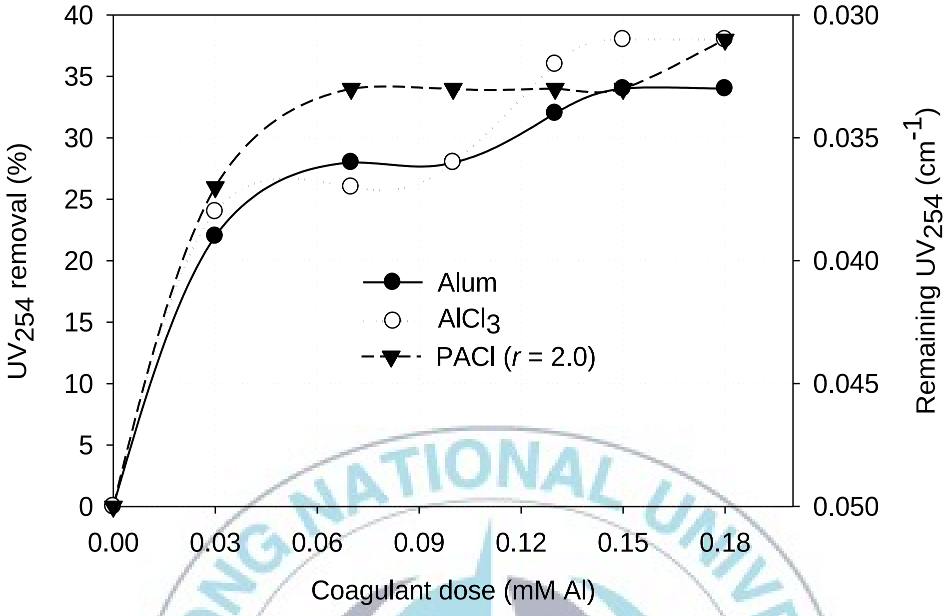


Fig. 5.17. Hydrophilic synthetic water - UV_{254} removal as a function of Al dose (pH 7.0).

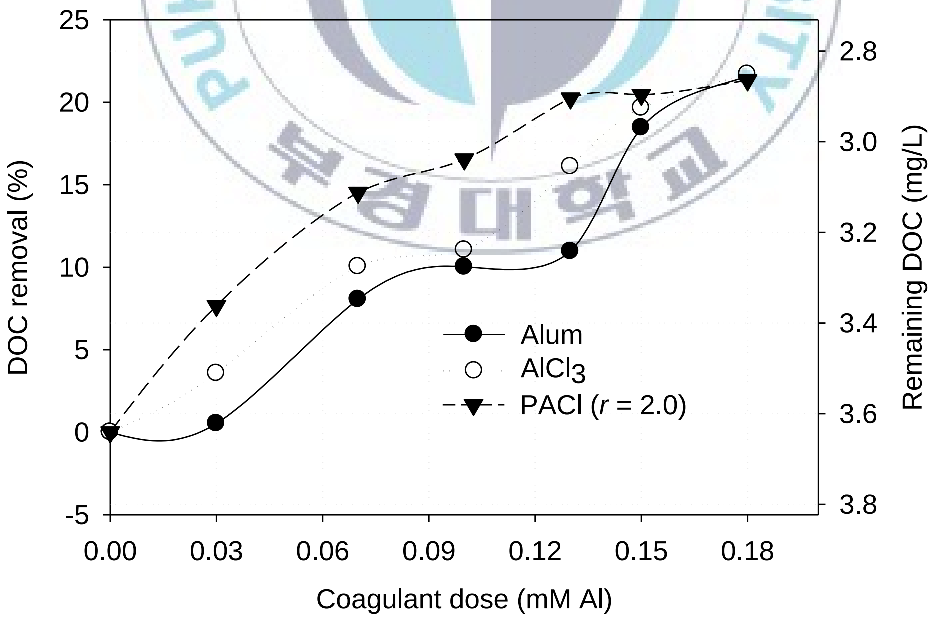


Fig. 5.18. Hydrophilic synthetic water - DOC removal as a function of Al dose (pH 7.0).

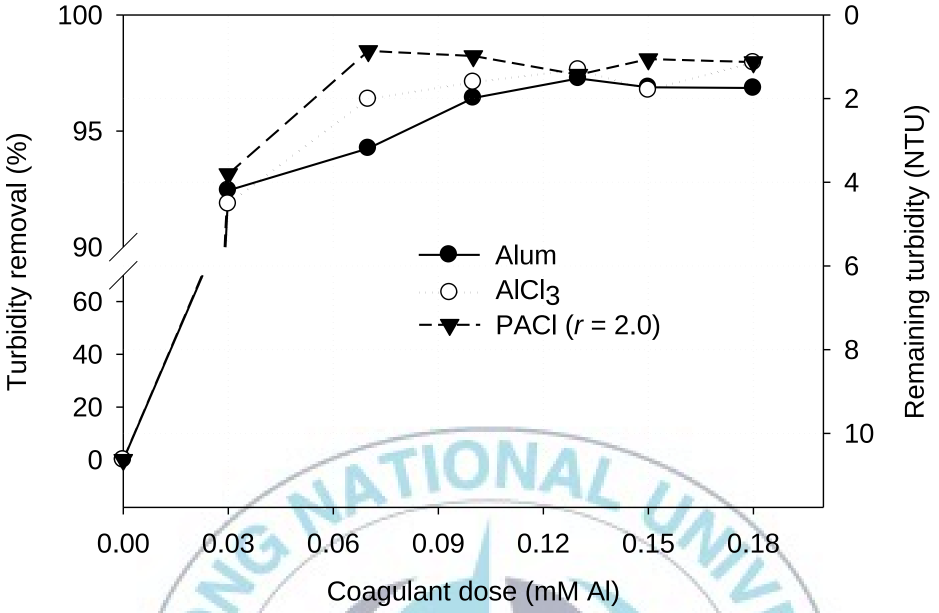


Fig. 5.19. Fulvic acid synthetic water - Turbidity removal as a function of Al dose (pH 7.0).

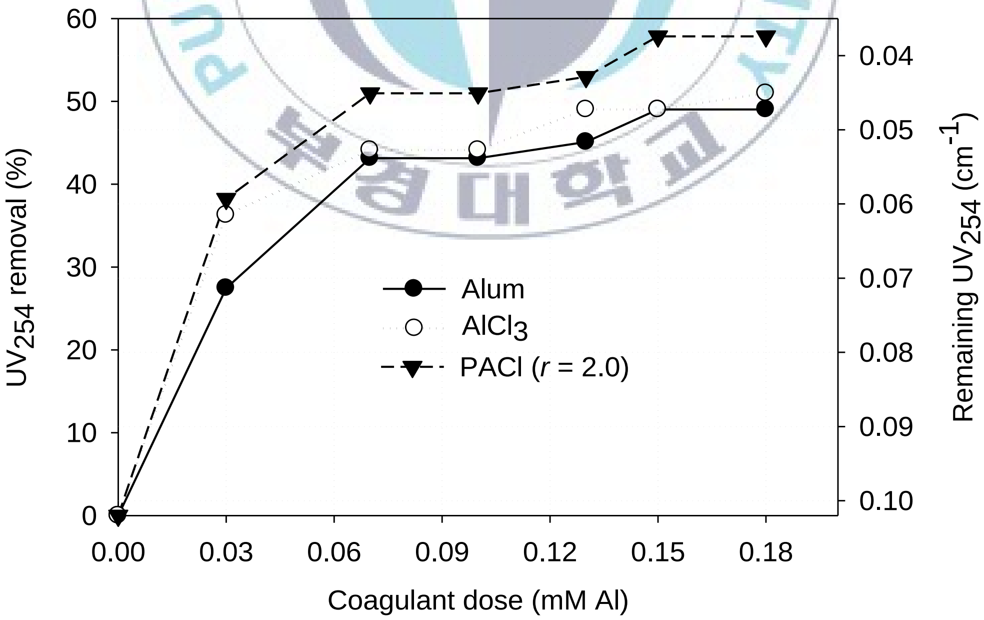


Fig. 5.20. Fulvic acid synthetic water - UV_{254} removal as a function of Al dose (pH 7.0).

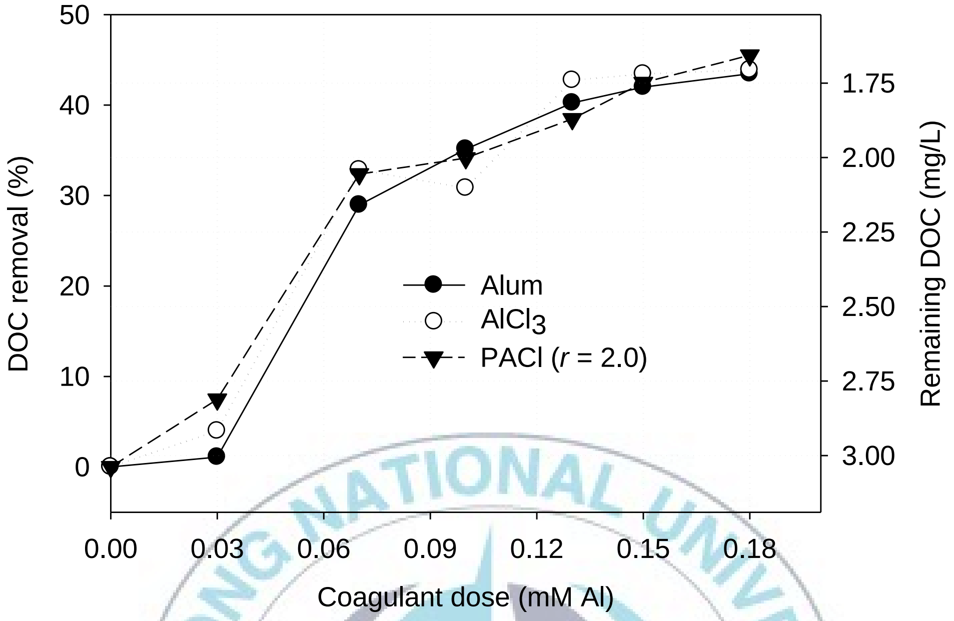


Fig. 5.21. Fulvic acid synthetic water - DOC removal as a function of Al dose (pH 7.0).

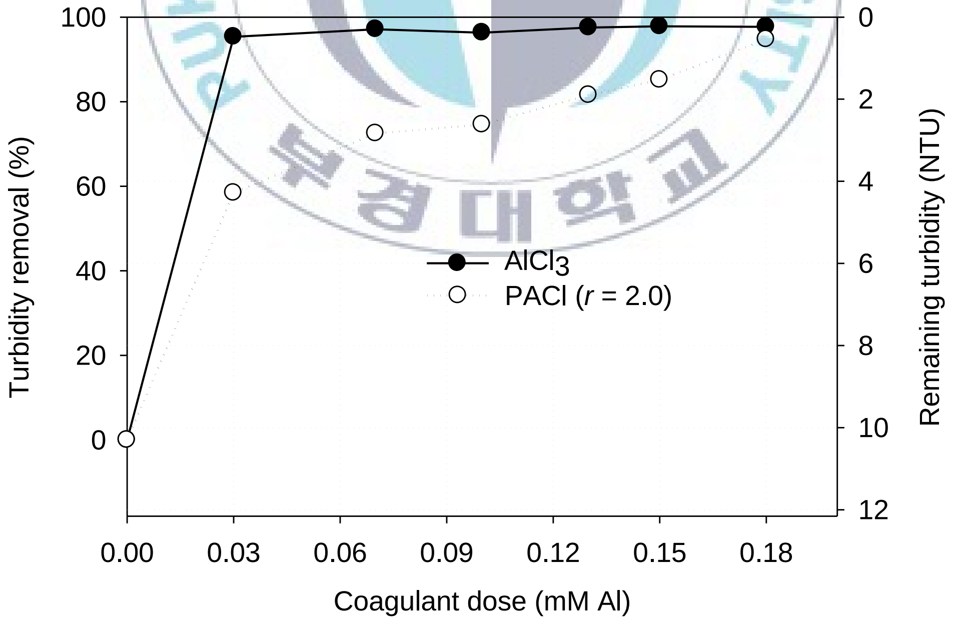


Fig. 5.22. Humic acid synthetic water - Turbidity removal as a function of Al dose (pH 7.0).

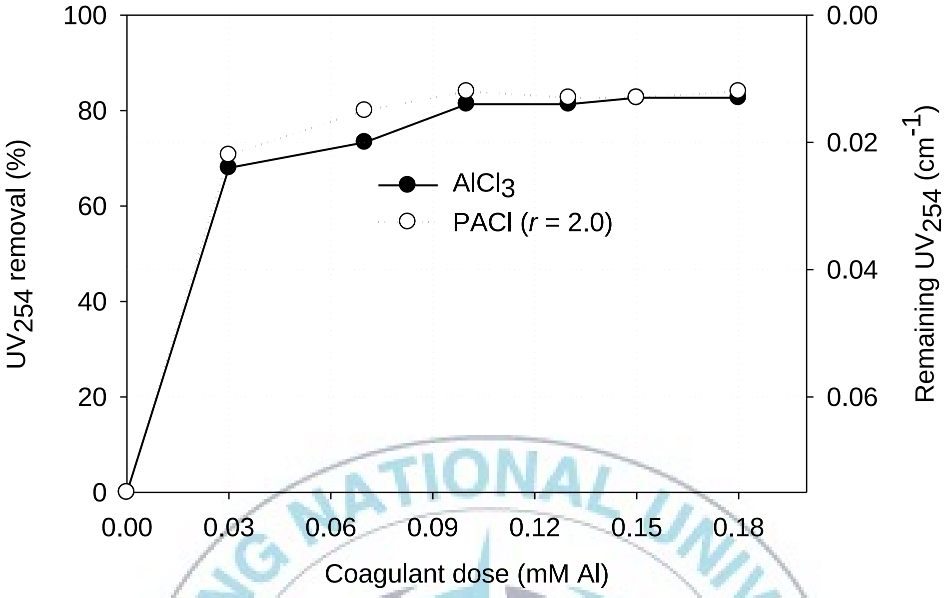


Fig. 5.23. Humic acid synthetic water - UV_{254} removal as a function of Al dose (pH 7.0).

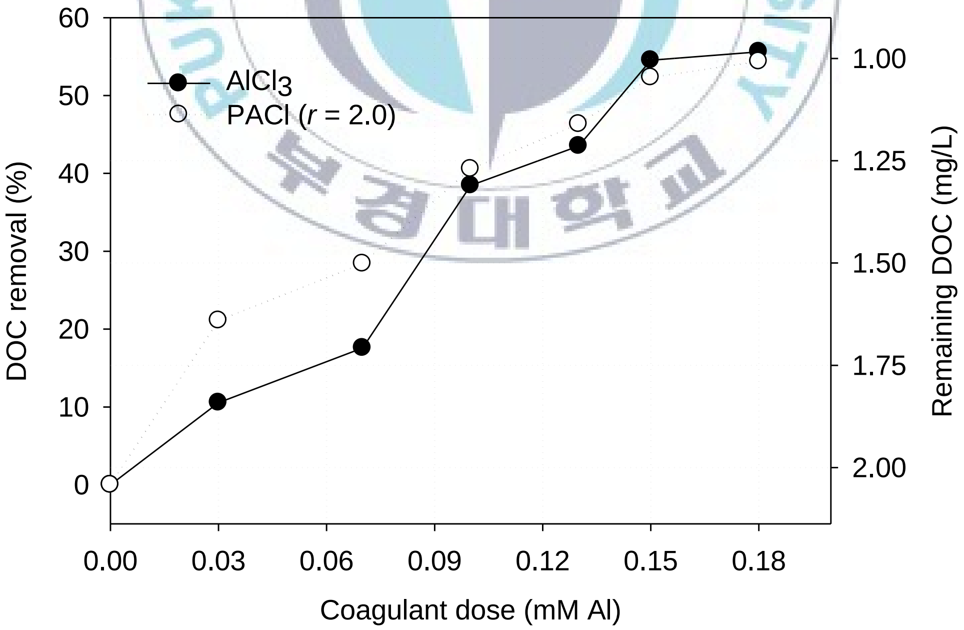


Fig. 5.24. Humic acid synthetic water - DOC removal as a function of Al dose (pH 7.0).

Chapter 6

COAGULATION OF PHOSPHORUS

This Chapter describes the characteristics of Phosphorus in sewage effluents taken from Nambu Sewage Treatment Plant in Busan city, South Korea. Laboratory prepared PACl and commercial PACl were used to coagulate phosphorus in the raw water. Relationship between the characteristics of the coagulants and coagulation-flocculation performance was discussed. Effects of coagulation pH and coagulants dosages were emphasized. Coagulation mechanisms in each case were discussed.

6.1. Characteristics of Sewage Effluents

Secondary wastewater effluent was used as raw water in coagulation process. The water was collected from the Nambu Sewage Treatment Plant in Busan city, South Korea. The characteristics of wastewater effluent are listed in Table 6.1. Also, phosphorus in the primary effluent taken before the activated sludge treatment was analyzed to reveal the distribution of phosphorus species for comparison.

Table 6.1. The physicochemical characteristics of secondary sewage effluent

Parameter	Unit	Range
Turbidity	NTU	1.50 – 2.10
COD	mg/L	8.50 – 10.20
BOD	mg/L	5.60 – 6.50
SS	mg/L	3.50 – 4.20
TN	mg/L	16.50 – 17.30
TP	mg/L	2.06 – 3.43
pH	–	6.09 – 7.30
Alkalinity	mg /L as $CaCO_3$	103.90 – 125.40

Distribution of P species in the wastewater is shown in Fig. 6.1 and Fig. 6.2. Ortho-P was found to be predominant in the wastewater, except for suspended form of the primary effluent. The suspended form of phosphorus, however, contributed a small amount to TP in secondary effluent (Fig. 6.1).

Organically bound phosphates (organic-P), which contribute to sewage by body wastes and food residues, were mainly found in suspended form of the wastewater. Activated sludge process converted the condensed-P (pyro-, meta-, and other polyphosphates) and organic-P in the primary effluent to ortho-P resulted in a considerable increasing of ortho-P in the secondary effluent. The secondary effluent as raw water of jar test experiment in this study contained more than 90% ortho-P, and the ortho-P was found mainly in dissolved form. The suspended form of the secondary effluent also contained condensed-P and organic-P, in addition to the ortho-P. The results are full agreement with the findings of the previous studies that total phosphorus concentration in the secondary effluent is mostly soluble (dissolved) and this is mainly phosphate (Duenas et al., 2003).

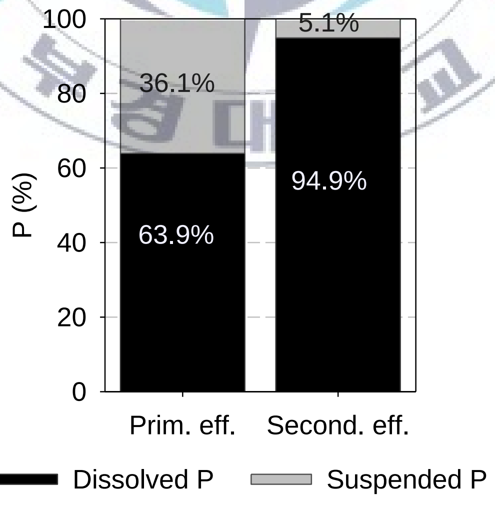


Fig. 6.1. Fraction of suspended phosphorus and dissolved phosphorus in wastewater.

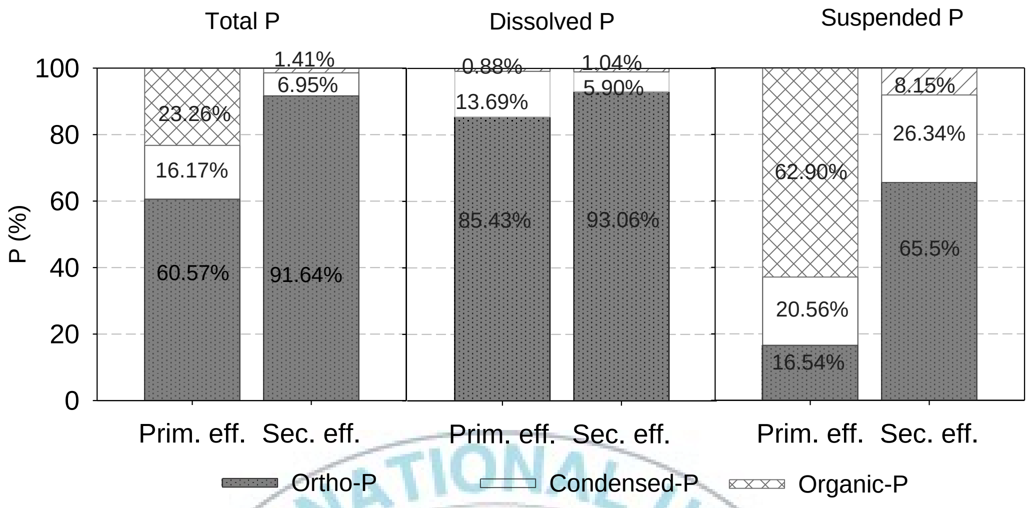


Fig. 6.2. Distribution of phosphorus species in primary effluent wastewater and secondary effluent wastewater.

6.2. Phosphorus Removal Using Laboratory Prepared PACl

6.2.1. Characteristics of Laboratory Prepared Coagulants

Laboratory prepared PACl coagulants with different degree of neutralization *r* = [OH]/[Al], or basicity, were prepared in the laboratory by adding 0.5 M NaOH into 0.2 M $AlCl_3$ solution according to a procedure described in Chapter 4. In addition, alum ($Al_2(SO_4)_3 \cdot 16H_2O$) was purchased from Sigma, USA and used as “zero basicity” coagulant. The properties of laboratory prepared PACl are shown in Table 6.2.

Table 6.2. Properties of laboratory prepared PACl used for phosphorus removal

No.	Name	Al_2O_3 (%)	Basicity (%)	*r*	pH	Density (g/L)
1	Alum	0.15	0.0	0.0	3.07	1.0855
2	PACl (*r*=0.0)	1.02	0.0	0.0	3.05	1.0238
3	PACl (*r*=0.5)	0.85	16.7	0.5	3.52	1.0170
4	PACl (*r*=1.0)	0.73	33.3	1.0	3.64	1.0202
5	PACl (*r*=1.5)	0.64	50.0	1.5	3.83	1.0241
6	PACl (*r*=2.0)	0.57	66.7	2.0	4.04	1.0205
7	PACl (*r*=2.5)	0.51	83.3	2.5	4.55	1.0255

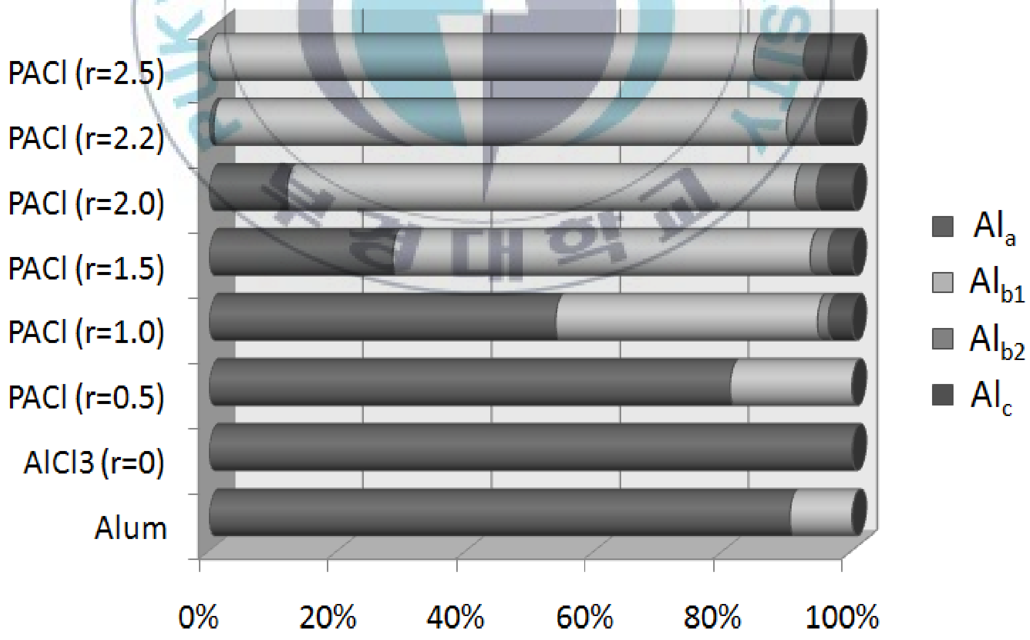


Fig. 6.3. Laboratory prepared coagulants: distribution of Al species.

Ferron assay analyzed the distribution of Al species and the results are shown in Fig. 6.3. The higher the basicity of PACl, the lower the Al_a, higher the Al_b, and higher the Al_c. Alum and $AlCl_3$ (as PACl with r=0) contained highest Al_a. The Al_b content in laboratory prepared PACl can be obtained the value of 90% at r value of 2.2

6.2.2. Phosphorus Removal Performance

6.2.2.1. Effect of pH on Phosphorus Removal

Jar tests were performed using alum (0% basicity, 90% Al_a and 10% Al_b) and laboratory prepared $PACl_{2.0}$ to investigate the effect of coagulation pH on P removal. The PACl used, named $PACl_{2.0}$, was synthesized at basicity of 66.7% and Al species analyses for it showed 12.1% Al_a, 82.4% Al_b, and 5.5% Al_c. The experiment was carried out at two dosages of the coagulants: the ratio of mole Al to mole TP in raw water [Al]:[P] = 1.0:1.0 and [Al]:[P] = 1.8:1.0, as shown in Fig. 6.4. The experimental results demonstrate that the patterns of TP and DRP removal were similar. In other words, pH affected the removal of TP and DRP in the similar way. The alum showed a narrower pH range of 5.0 to 6.0 for optimal P removal at [Al]:[P] = 1.0:1.0. As higher alum dosage, of [Al]:[P] = 1.8:1.0, the optimum pH range widened to the direction of higher pH. The coagulation of P by PACl, however, behaved in a different manner to alum. The optimum pH range using PACl at [Al]:[P] = 1.0:1.0 was rather wider while this range at [Al]:[P] = 1.8:1.0 was narrower.

It seems that at the low [Al]:[P] of 1.0:1.0, the fraction of Al ion in PACl which is used to form complexes with P was not sufficient, evidenced by a rather low TP and DRP removal efficiency. A maximum of 40% DRP removal was obtained in comparison with higher than 90% DRP removal in case of using alum. With increasing the Al:P mole ratio to 1.0:1.8, the P removal efficiency also increased and at optimum pH of 4.7, removal efficiency for PACl was similar to alum.

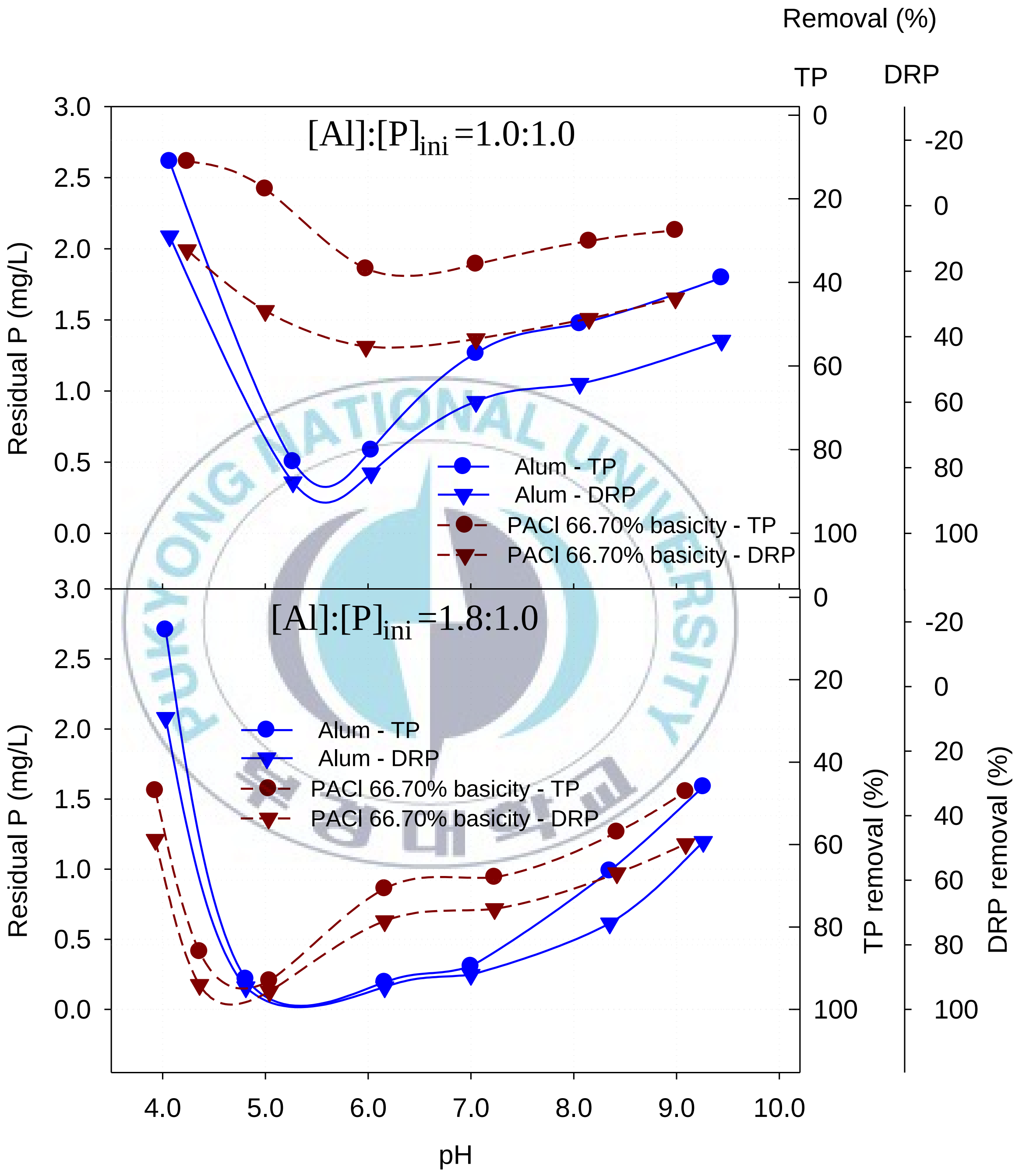


Fig. 6.4. Effects of pH on P removal efficiency.

The phosphorus precipitation can be seen as a result of the competitive action of phosphates, hydroxyls and other ions to react with metal ion. The optimum pH is the pH where the phosphorus fraction in the complexes is largest. The increase of aluminum dose may provide more opportunities for PO_4^{3-} to complex with Al ion, and then increased the formation of metal-hydroxide-phosphate complexes. In addition, at high metal dose, the optimum pH range tended to widen towards higher pH values. This phenomenon was also reported by (Bratby, 2006). The acceptability of higher pH values (at high Al doses, where $Al(OH)_3$ was predominantly formed) for optimal phosphorus removal suggests a shift in the predominant removal mechanisms, with an increasing influence of adsorption to the hydroxide complexes, in addition to complexation.

The lower P removal of PACl at [Al]:[P] = 1.0:1.0 suggests that Al in the PACl, although used at the same amount with alum, did not form $Al(PO_4)_x(OH)_{3-3x}.(H_2O)_y$ complexes effectively as alum. As PACl dosage increased to [Al]:[P] = 1.8:1.0, existed an very tight pH range of 4.3 − 5.0, at which the DRP removal efficiency was comparable to alum as shown in Fig. 6.4. However, obtaining the optimal P removal efficiency at this pH range should be infeasible in practice. Lower or higher pH values beyond this range quickly worsened the P removal. Al_b predominated in PACl showed less effective in complexation at lower pH values. At high pHs where adsorption mechanism might be promoted due to the forming of $Al(OH)_3$, it is unlikely that Al_b species was favorable for adsorption of P onto hydroxide complexes.

Fig. 6.5 and Fig. 6.6 illustrate phosphates speciation diagram produced at Al]:[P] ratio of 10:1.0 and 1.8:1.0, respectively. As can be seen in these figures, phosphates can be removed completely by formation of the $AlPO_4$ precipitate in a wide pH range of 3 to 8. However, in practical treatment, phosphorus precipitation is a result of the competitive action of phosphates, hydroxyls and other ions to react with aluminum hydrolysis products. Therefore, the P removal efficiency never gains 100% at [Al]:[P] = 1.0:1.0 and the true optimum pH range is not the range of 3 to 8. The findings in this study demonstrated an optimum pH range from 4.5 to 6.5, depends on the coagulant dosages and the coagulant type used. The optimum pH for P removal using aluminum coagulants is normally within the range 5.5 to 6.5, although some removal occurs above pH 6 (Ferguson and King, 1977; Fytianos et al., 1996; USEPA, 1987). The differences in P removal at different pH range are probably due to difference in wastewater quality.

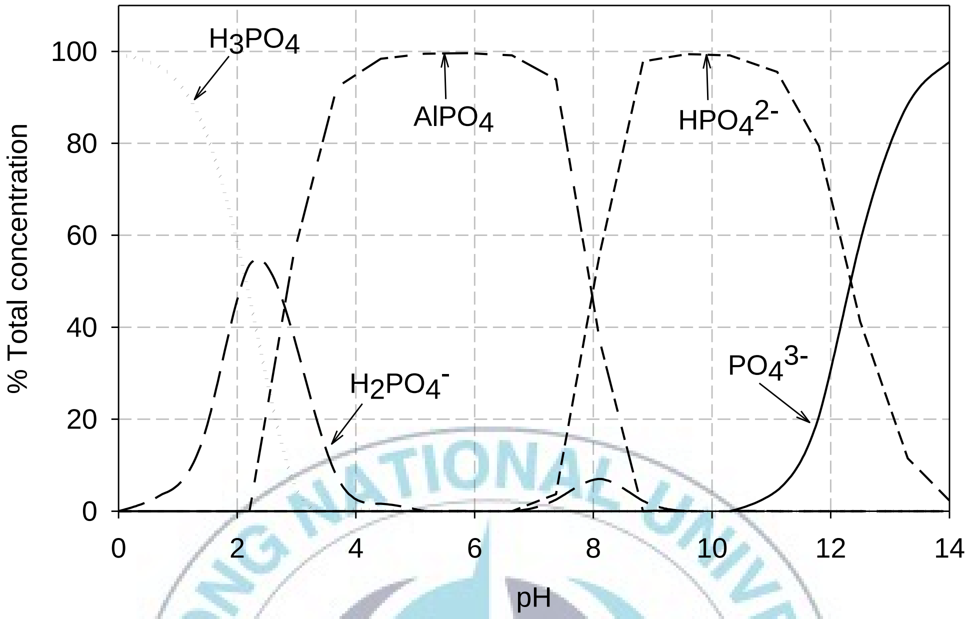


Fig. 6.5. Phosphates speciation diagram (using thermochemical data at 25°C, 1 atm; without crystalline solids and ionic strength corrections; 9 mgPO_4/L or 2.9 mgP/L) in the presence of aluminium species at [Al]:[P] ratio of 10:1.0.

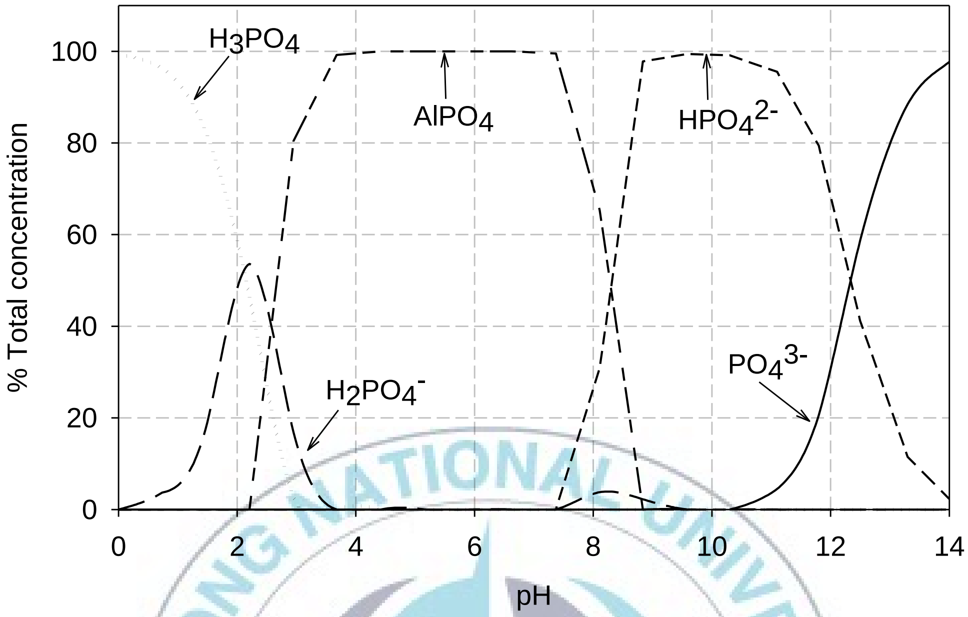


Fig. 6.6. Phosphates speciation diagram (using thermochemical data at 25°C, 1 atm; without crystalline solids and ionic strength corrections; 9 mg PO_4/L or 2.9 mgP/L) in the presence of aluminium species at [Al]:[P] ratio of 1.8:1.0.

6.2.2.2. Effect of *r* value of PACl on Phosphorus Removal

For all jar test experiment used in the study, although coagulation pH changed with changes of basicity of PACls, pH values were measured in the range of 6.0 – 6.7 (data not shown).

Jar tests were performed and the residual of TP, DRP, TDP, and DRP were analyzed as shown in Fig. 6.7 to Fig. 6.10. The results indicate that the P removal was strongly affected by *r* values, or basisity of PACl. For all fractions of phosphorus, the higher the basicity the lower the P removal efficiency would be. With increasing of coagulant dosage, phosphorus removal efficiency also increased, under the [Al]:[P] ranged from 0.8 to 1.8 (0.09 to 0.2 mM Al), as showing the removal efficiency increased from 60% to 95%.

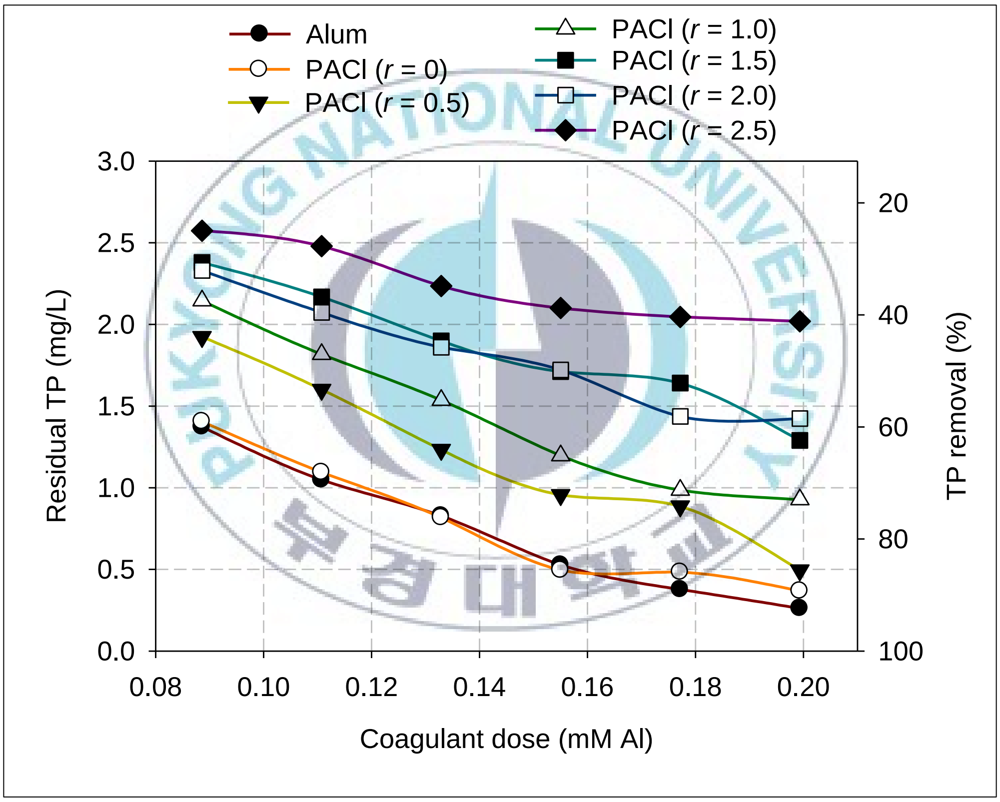


Fig. 6.7. TP removal using various coagulants.

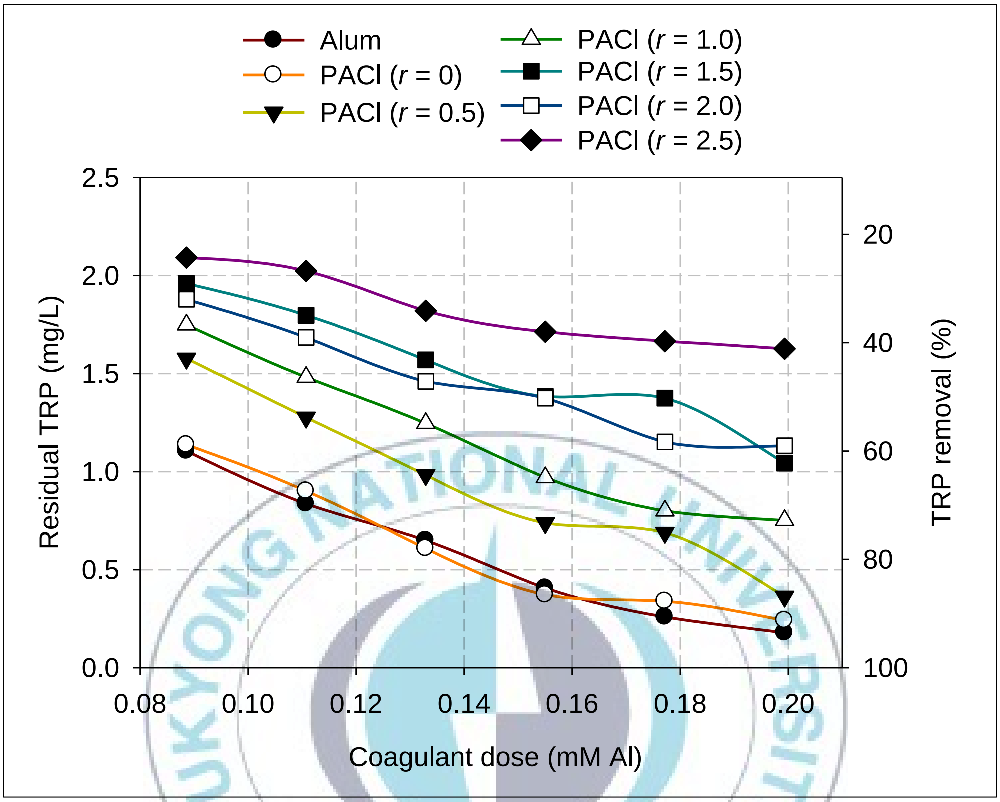


Fig. 6.8. TRP removal using various coagulants.

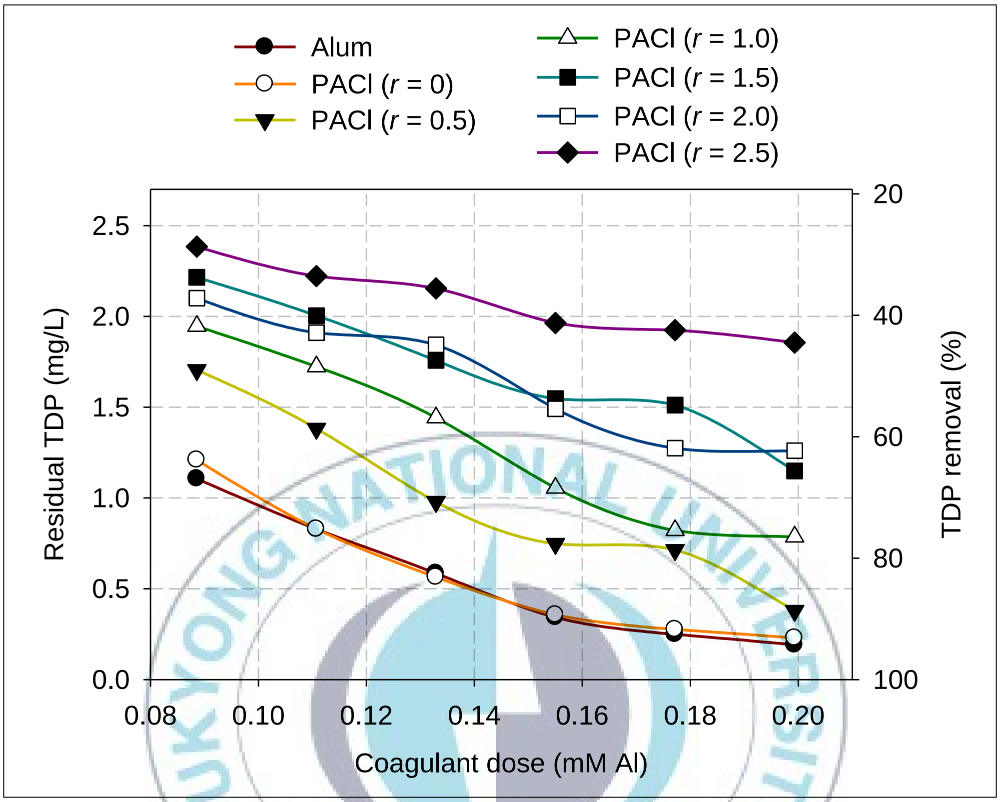


Fig. 6.9. TDP removal using various coagulants.

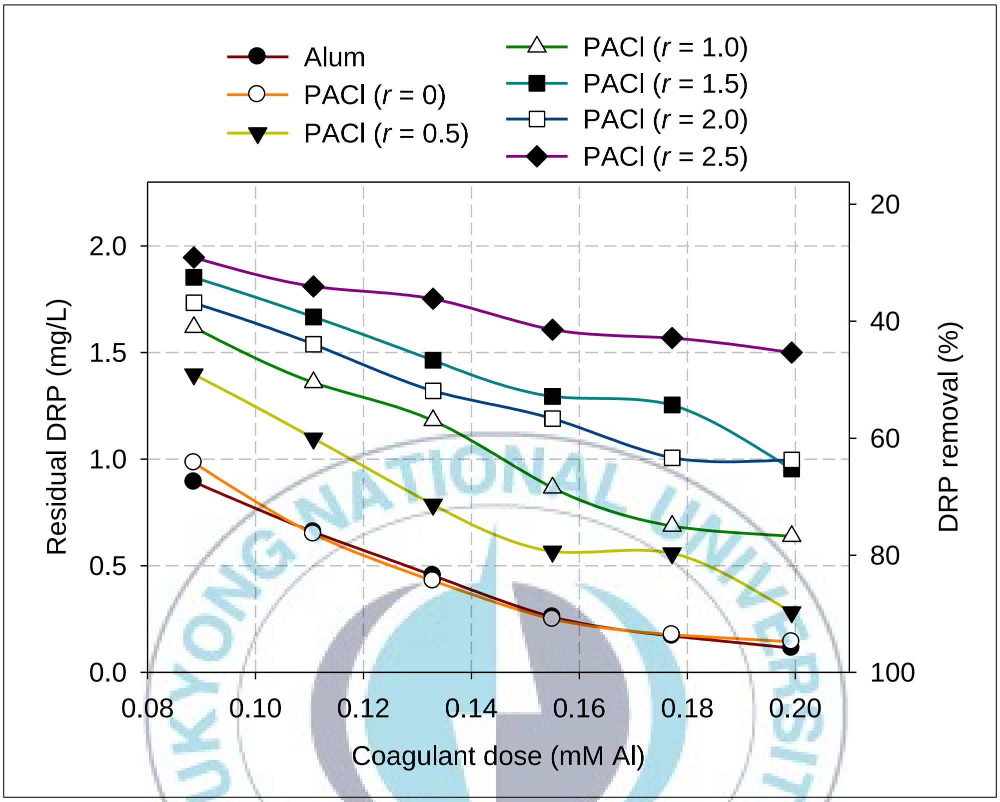


Fig. 6.10. DRP removal using various coagulants.

As an effort to find out the relationship between P fractions and their removal efficiency, such as which fraction of P in wastewater is most difficult to remove and what kind of coagulant is favored for a particular P fraction, the residual P concentration were analyzed as the two main fractions: condensed and organic P (C and O-P) and ortho P (o-P). Fig. 6.11 plots P removal efficiency of all of coagulants investigated under various [Al]:[P] ratios ranged from 0.8 to 1.8. For all coagulants, used alum and low basicity PACl gave a higher P removal efficiency than high basicity PACl, not only for C and O-P, but also for o-P. However, it is interesting to note that, at low coagulant dosages, removal efficiency of C and O-P was higher than it was for o-P, especially at high *r* values. It can be explained due to the superior of high *r* value PACl in removal the suspended form of phosphorus (i.e. “particles”) which mainly contains C and O-P, by charge neutralization. As the Al dosage increase, $Al(OH)_3(s)$ is formed, “sweep flocs” occur, low *r* value coagulants are favor for $Al(OH)_3(s)$ formation, and the superior of high *r* value PACl disappears. Therefore, the o-P, which mainly exist in dissolved form, was removed better than C and O-P as the [P]:[Al] ratio increased (e.g. 1:1.2), and this phenomenon is clearer at low *r* values.

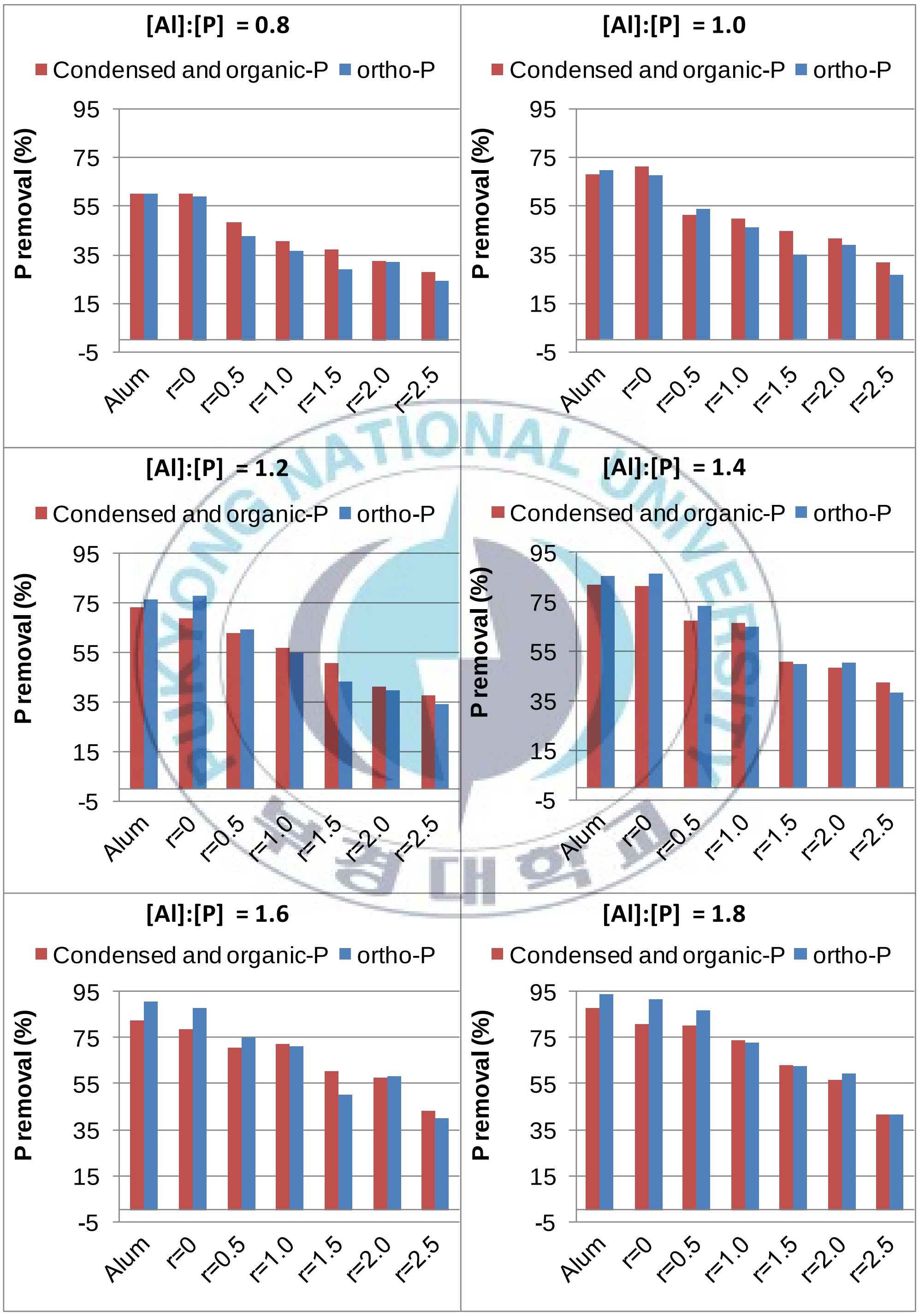


Fig. 6.11. Condensed and organic P removal vs. ortho-P removal.

6.2.2.3. Simultaneously Effect of coagulant dose and coagulation pH on Phosphorus Removal

Traditional coagulants with predominant monomeric Al_a are favorable for P removal. As a most common traditional coagulant, alum was used to conducted experiment using Response Surface Method (RSM) to investigate co-effects of Alum dose and coagulation pH on phosphorus removal, and to find out the best combination of the two factors to produce the optimum P removal. The theory and application of RSM methods are described in many papers and an application to find out the optimum conditions for treatment of drinking water is performed in our previous research (Trinh and Kang, 2011). Central Composite Design (CCD) was used to design the experiment. The detail of CCD and obtained result is shown in Table 6.3.

Table 6.3. CCD and results obtained

Run no.	CCD				Results
	Alum dose (X_1, mg/L)		Coagulation pH (X_2)		Residual TP (Y) (mg/L)
	Coded	Actual	Coded	Actual	
1	–1	96.7	–1	4.0	1.16
2	+1	139.7	–1	4.0	1.19
3	–1	96.7	+1	7.0	0.2
4	+1	139.7	+1	7.0	0.1
5	–1.414	87.8	0	5.5	0.42
6	+1.414	148.6	0	5.5	0.12
7	0	118.2	–1.414	3.4	1.28
8	0	118.2	+1.414	7.6	0.56
9	0	118.2	0	5.5	0.24
10	0	118.2	0	5.5	0.230
11	0	118.2	0	5.5	0.22
12	0	118.2	0	5.5	0.02
13	0	118.2	0	5.5	0.03

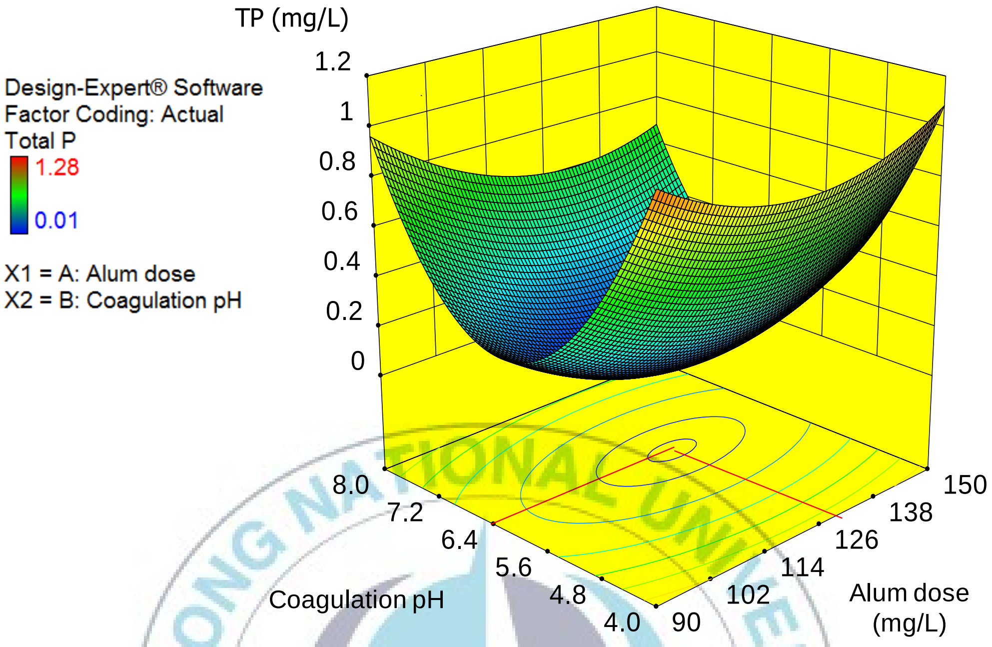


Fig. 6.12. Co-effects of coagulation pH and Alum dose on P removal.

Fig. 6.12 illustrates the 3D response surface plots with respect to Residual TP. To obtain a minimum value of 0.1 mg/L residual TP, the optimum pH ranges from 5.5 to 6.6 and optimum alum dose is 110 to 140 mg/L alum (based on solid reagent of $Al_2(SO_4)_3 \cdot 16H_2O$).

6.3. Phosphorus Removal Using Commercial PACl

6.3.1. Characteristics of Commercial Coagulants

The pre-hydrolyzed PACl solutions with different basicity and aluminum concentration (shown as % Al_2O_3) were supplied by M Chemical (Seoul, Korea). Al_2O_3 content (% w/w) and basicity (%) of PACl were determined according to the Korean Standards (Korea MOE, 2007). Although commercial PACl is often supplied with high Al_2O_3 content, a set of 1% Al_2O_3 PACl also were prepared by the company as a comparison with other set of the same basicity and difference in Al content. Physicochemical characteristics of the coagulants are shown in Table 6.4.

Table 6.4. Physicochemical characteristics of commercial PACl

No.	Name in text	Al_2O_3 (%)	Al_T (M)	Basicity (%)	r	Density (g/cm^3)	pH
1	PACl 10-10	10.0	2.50	10	0.3	1.286	0.69
2	PACl 10-50	10.0	2.50	50	1.5	1.250	2.12
3	PACl 10-70	10.0	2.50	70	2.1	1.270	2.35
4	PACl 01-10	1.0	0.20	10	0.3	1.032	3.65
5	PACl 01-50	1.0	0.20	50	1.5	1.026	3.76
6	PACl 01-70	1.0	0.20	70	2.1	1.029	3.80
7	PACl 17-40	16.9	4.83	40	1.2	1457.2	0.39

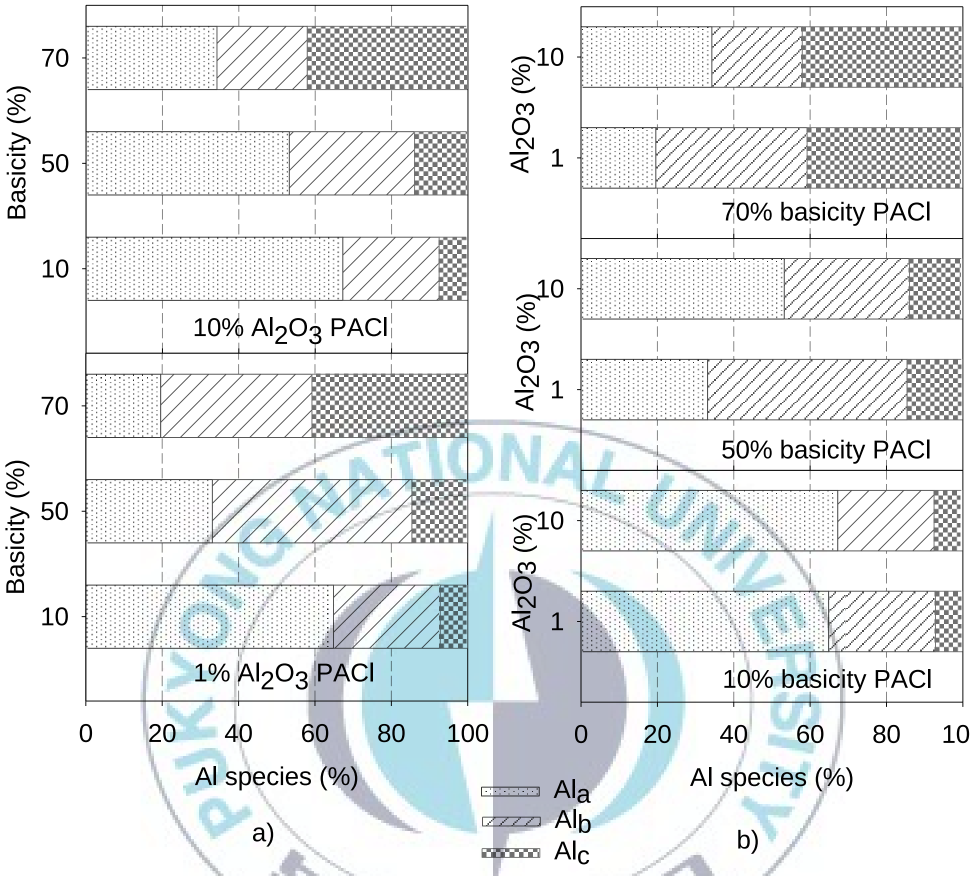


Fig. 6.13. Commercial coagulants: distribution of Al species, a) comparison of different basicity and b) comparison of different Al_2O_3 content in PACl.

Fig. 6.13 a) shows the effects of basicity on distribution of aluminum species in the coagulants. Basicity, a commonly used term in PACl manufacturing to indicate the degree of polymerization (or hydrolyzed), increases with the addition of base. The basicity dictates that certain types of species of monomers, dimers, trimers, polymers, and precipitates are present. With the increase of basicity, Al_a content in the commercial PACl decreased, whereas Al_b content increased. The highest (52%) Al_b could be observed in 50% basicity PACl containing 1% Al_2O_3. However, increase of the basicity up to 70% resulted in a decrease of Al_b. Al_c increased slowly at the basicity values from 0−50%, and then increased rapidly as further increase in basicity to 70%. This trend was found for both cases of 10% and 1% Al_2O_3 content in PACl, although there was difference in the quantity of the Al species.

Effects of Al_T on the distribution of Al species is shown in Fig. 6.13 b). Decrease of Al_T (as Al_2O_3) from 10% of 1%, Al_c species did not change but Al_a decreased and Al_b increased. Al_b species increased with the same amount as the decrease of Al_a. The increase of Al_b species corresponding to the decrease of Al_a happened mostly in 50% basicity PACls, as showing 20% difference. The difference was 15% in 70% basicity PACls, and was very small in 10% basicity PACls. The 10% basicity PACls contained about 65% Al_a, 25% Al_b, and less than 10% Al_c for both high and low Al_T.

Al_b quickly decreases as increase of Al_T. This phenomenon was also verified by conducting experiment with laboratory prepared PACl. Total aluminium concentration, in addition to basicity, perhaps governed the formation of Al_b. Therefore, if considering Al_b as the most effective species for charge neutralization and particle bridging actions in coagulation processes (Bottero et al., 1987b; Shen and Dempsey, 1998b; Tang and Luan, 1996), and this species need optimizing in preparing PACl, low concentration of Al_T is recommended. However, due to economic reasons, commercial

PACl is often manufactured at high Al_2O_3 content of 10 − 12%. or 2.5 M Al). Hence, at the same basicity, Al_b was often found lower in commercial PACl than in laboratory PACl which is prepared with lower concentrations of Al_T.

6.3.2. Phosphorus Removal Performance

Effects of coagulant dosages on TP and DRP removal are shown in Fig. 6.14 and Fig. 6.15, respectively. In these figures, the dotted-line, solid-line, and dashed-line represent for alum/$AlCl_3$, 10% Al_2O_3 PACl, and 1% Al_2O_3 PACl, respectively. Residual P tends to decrease quickly with increase of coagulant dosage up to 0.22 mM. With further increase of the coagulant dosage, the residual P decreased slowly. To meet the discharge limit of 0.2 mg/L as TP (corresponding to 94% TP removal), the required coagulant depended much on the coagulant type used. A dosage of 0.23 mM Al ([Al]:[P] = 2.1:1.0) was enough for alum, $AlCl_3$, and 10% basicity PACl to meet the P standard. However, the discharge limit required a dosage at least 0.295 mM Al for 50% basicity PACl and much more dosage for 70% basicty PACl (higher than 0.33 mM Al). At highest dosage investigated, i.e. 0.33 mM Al ($[Al]:[P]_{ini}$ = 2.9:1.0, $[Al]:[P]_{removed}$ = 4.16:1.0), alum showed the best performance of 97.5% and 99.5% for TP and DRP removal, respectively. The residual TP and DRP at this dosage were 0.086 mg/L and 0.01 mg/L, respectively. The theoretical molar ratio for the phosphorus removal using aluminium is 1.0:1.0 and this ratio is never achieved in practice. De Hass (De

Hass et al., 2000) reported that the actual ratio of aluminum dosed to P removed is always higher than 2.0. According to Wang (Wang et al., 2005), a [Al]:[P]$_{removed}$ ratio of 4.13:1.0 was required to reach a residual P of 0.12 mg/L for secondary wastewater effluent. To achieve a low (<0.1 mg-P/L) residual PO_4-P concentration, treatment requires metal dosages far in excess of the stoichiometric 1.0 mole metal/mole P ratio (Szabó et al., 2008).

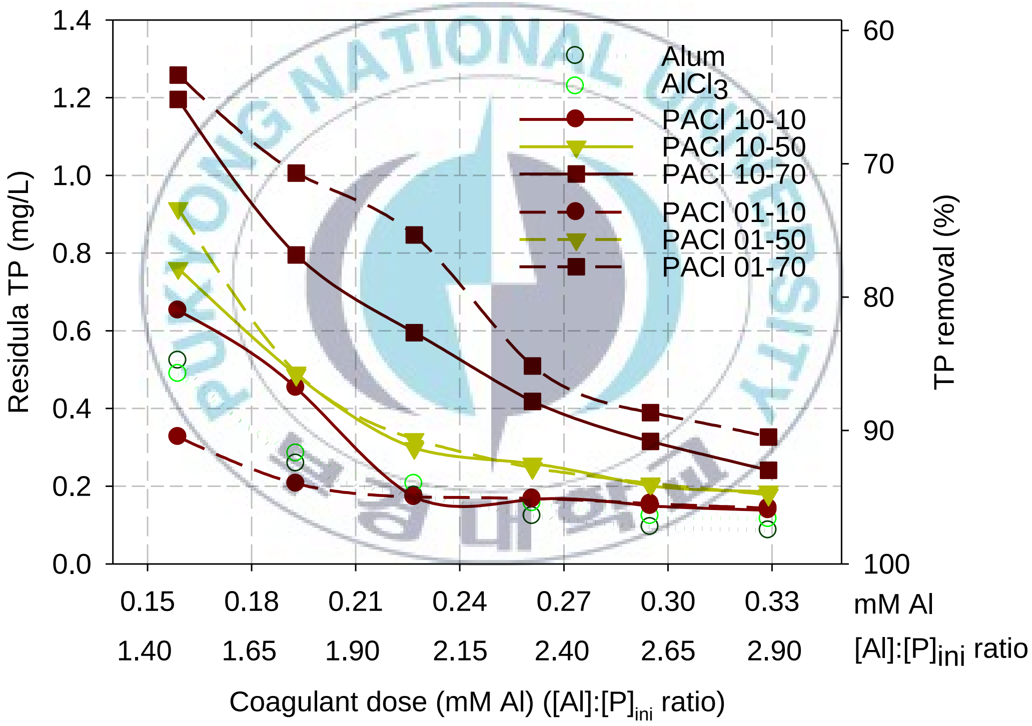


Fig. 6.14. Effects of coagulant dose on TP removal.

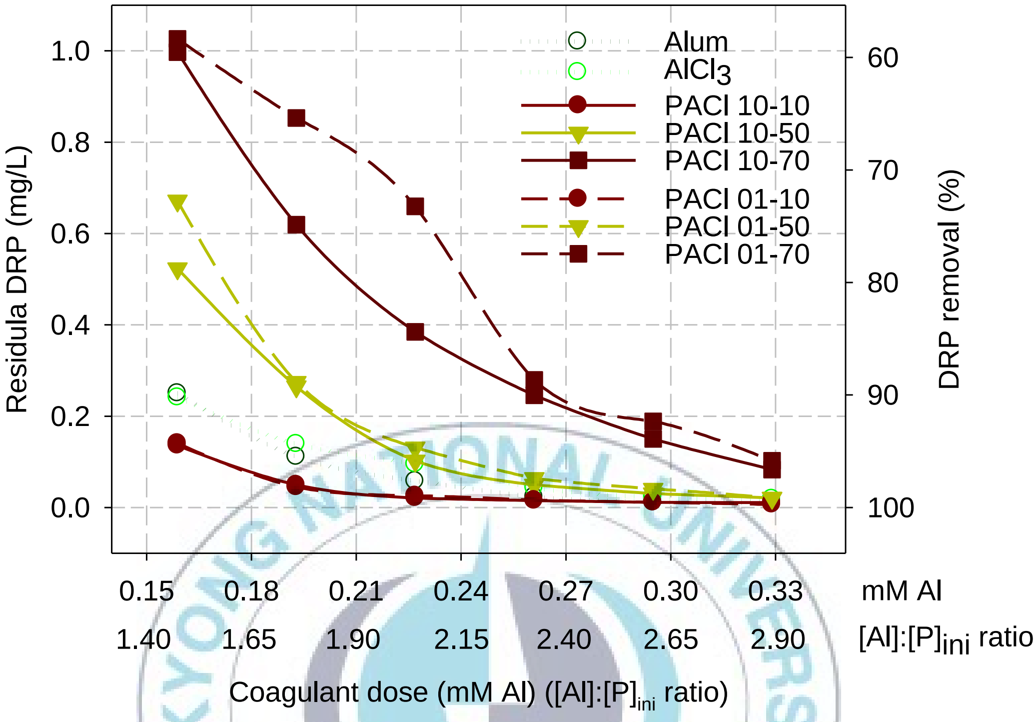


Fig. 6.15. Effects of coagulant dose on DRP removal.

Fig. 6.16 shows a comparison between TP and DRP removal. Alum, $AlCl_3$ and 10% basicity PACl showed a DRP removal efficiency better than TP removal at all dosages investigated. However, it is interesting to note that the higher basicity PACls, when used at low dosages, resulted in TP removal efficiencies close to or even better than DRP removal efficiencies. At low dosage, higher basicity coagulant removed TP better than DRP. This did not occur to alum, $AlCl_3$, and 10% basicity PACls. This trend was observed along with the increase of Al_c species due to increase of basicity. The Al_c, as mentioned earlier, is the inert large polymer or colloidal species. The higher amount of TP was removed might be due to an extra P in suspended form which was removed by entrapment of P containing colloids with Al_c, although this form of P contributed to TP with a small amount of about 5.2%. At high dosages, this trend disappeared. This can be explained by more $Al(OH)_{3(s)}$ formed in low basicity coagulants, and this precipitate accelerated “sweep flocs” and aggregated the P containing colloids. The results in this experiment revealed that better removal of TP than DRP occurred at low dosage, but the removal efficiencies of high basicity PACls were still lower in comparison with lower basicity coagulants. It can be suggested that high basicity PACl with predominant Al_c would be better for water containing higher fraction of suspended P (high turbidity and SS content). A result observed by (Hatton and Simpson, 1985) showed PACl was superior to alum for TP removal while DRP removal efficiency was similar. In their study, they used four different sewage waters with the SS contents of 274, 151, 218, and 363 mg/L, respectively.

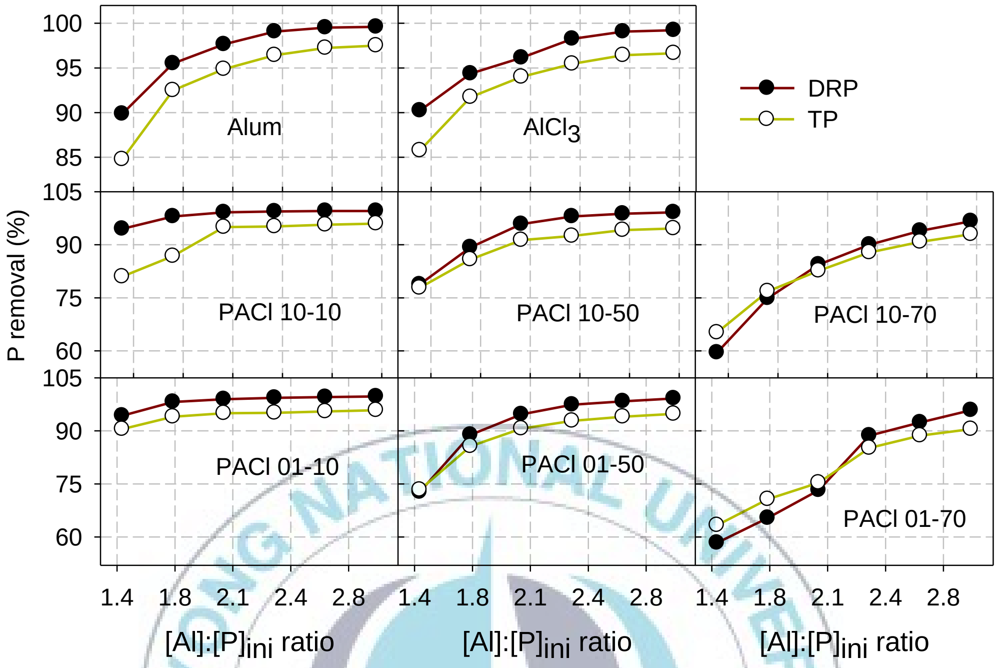


Fig. 6.16. Comparison of TP and DRP removal.

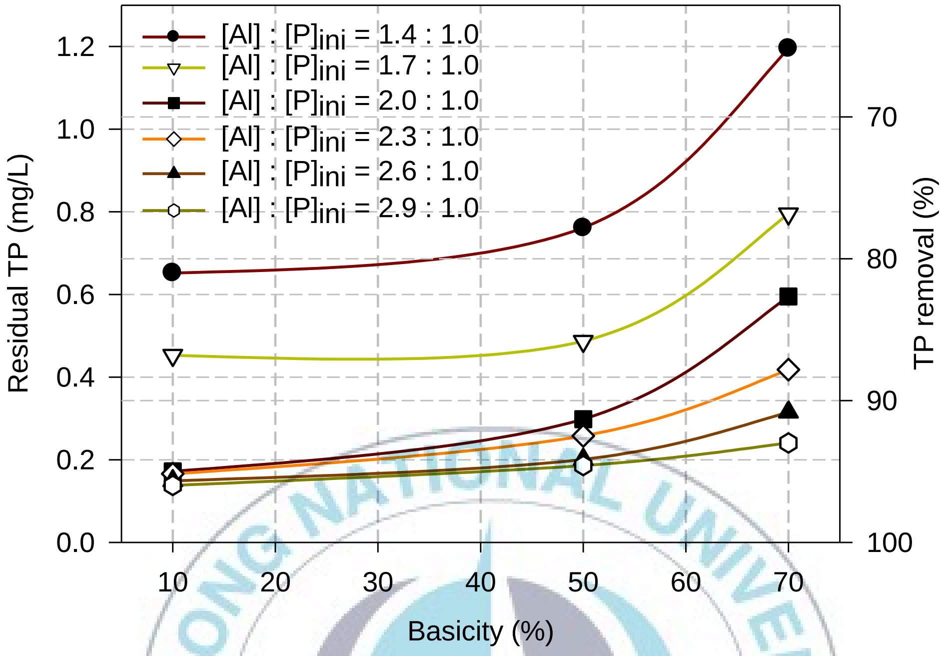


Fig. 6.17. Effects of basity on TP removal using 10% Al_2O_3 PACls.

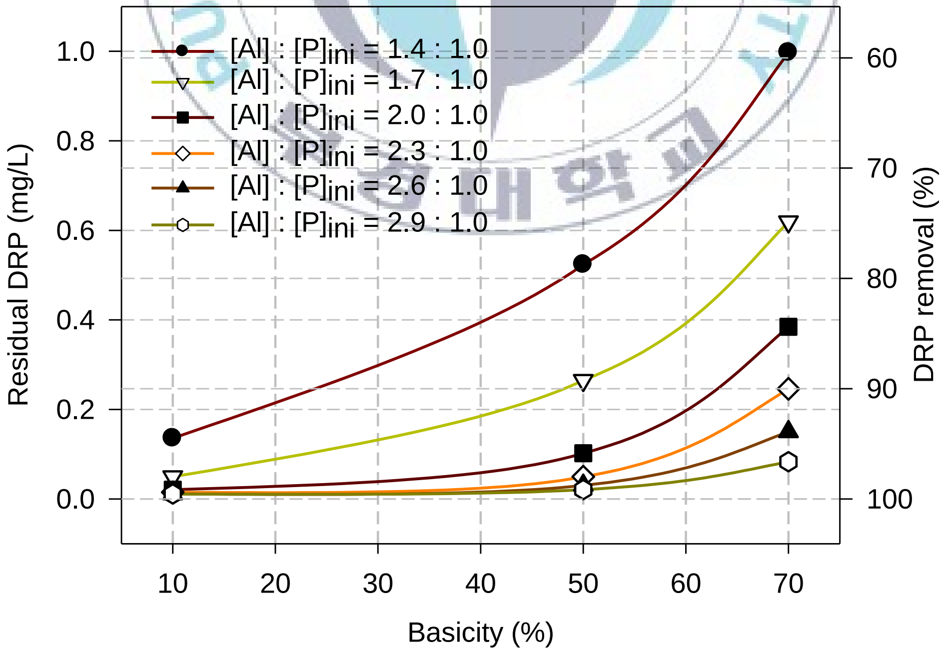


Fig. 6.18. Effects of basity on DRP removal using 10% Al_2O_3 PACls.

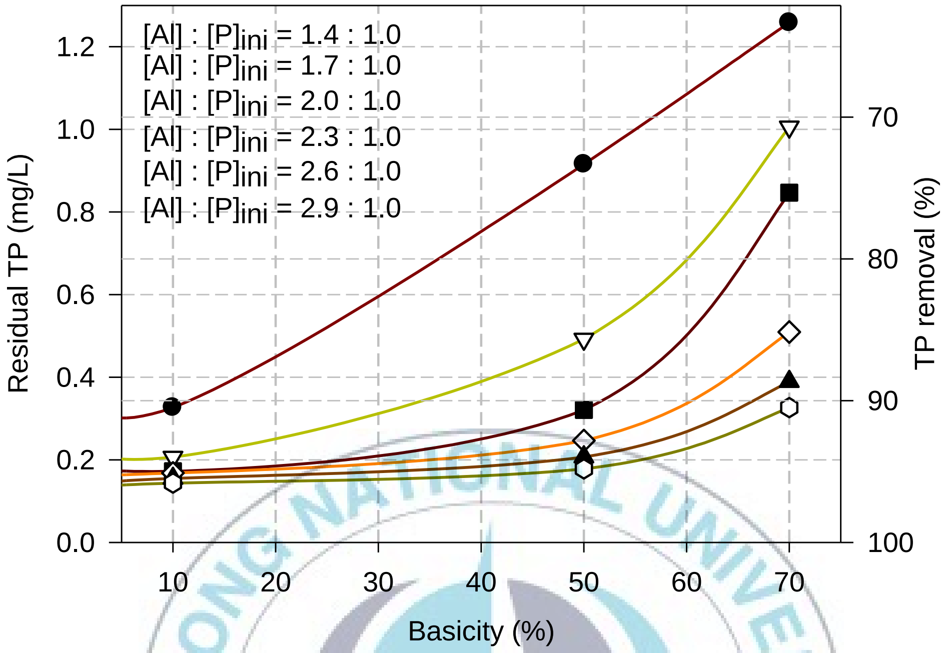


Fig. 6.19. Effects of basity on TP removal using 1% Al_2O_3 PACls.

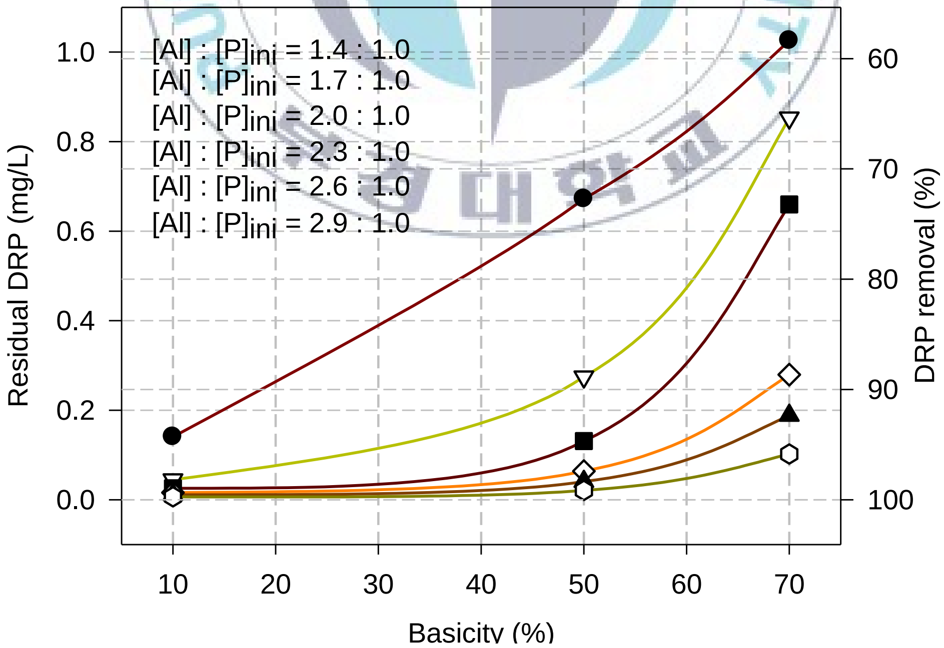


Fig. 6.20. Effects of basity on DRP removal using 1% Al_2O_3 PACls.

Pre-hydrolysed metal salts with high basicity were found to give many advantages over the conventional metal salts in water and wastewater treatment (Dempsey et al., 1984; Gregory and Duan, 2001a; Zouboulis and Traskas, 2005.). These results, however, did not show any superiority of PACls over alum and $AlCl_3$ in P removal. As shown in Fig. 6.17 to Fig. 6.20, the higher the basicity of PACl, the higher the residual P concentration, and consequently, the lower the P removal efficiency would be. When considering the distribution of Al species as previous shown in Fig. 6.13, that is higher basicity PACls contained higher Al_c and lower Al_a. Increase of Al_c or decrease of Al_a was probably not favorable for P removal. Increasing Al_b by increasing basicity in coagulants from 0 to 50% decreased P removal efficiency. When decreasing Al_b (in case of 70% basicity PACl), the P removal still decreased. The P removal was not affected by increase or decrease of Al_b, although this species is considered as the most efficient Al species for colloidal removal because of their high stable and positively charged species (Zouboulis and Traskas, 2005.). The most effective species in P removal should be Al_a, and the higher the Al_a in the lower basicity PACls, the higher the P removal.

Correlation between Al species and P removal was also found as considering the effect of Al_2O_3 content in PACl. As Al_2O_3 content in PACl decreases, Al_c was little changed while Al_b increases but Al_a decreases. This trend was observed for all PACls with 10%, 50%, and 70% basicity (Fig.

6.13 b). At the same Al_c content, increase in Al_b along with decrease in Al_a resulted in decrease of P removal efficiency Fig. 6.14 and Fig. 6.15, in comparison of the two groups of 10% Al_2O_3 PACl and 1% Al_2O_3 PACl, corresponding to the dash-lines and the solid-lines, respectively). As shown in these figure, except for 10% basicity PACl at some dosages, (i.e. PACl 10-10 and PACl 01-10), the residual P curves of 1% Al_2O_3 PACl coagulants (the dashed lines) are located above the ones of 10% Al_2O_3 PACl coagulants (the solid lines) and they gradually come close to each other with decrease of basicity.

A high correlation was observed between Al_a and P removal efficiency both in the same basicity PACls with different Al_2O_3 contents and in the same Al_2O_3 content PACls with different basicity. The higher the Al monomer (Al_a) and the lower the Al polymer (Al_b) present and the higher the P removal efficiency of PACl achieved. It appears that P removal decreased along with increase of Al_c when increasing basicity. However, this effect did not seem to be due to the influence of Al_c. Probably, the decrease of Al_a when increasing basicity were the predominant effects.

As can be seen in phosphates speciation diagram predicted by MineQL$^+$ program as previous shown in Fig. 6.5 and Fig. 6.6, phosphates can be removed completely by formation of the $AlPO_4$ precipitate in a wide pH range of 3 to 8. However, as previous mentioned, the phosphorus precipitation is a result of the competitive action of phosphates, hydroxyls and other ions to react with aluminum hydrolysis products. Because hydroxyl ions are the strongest competitors, the addition of these to the coagulant reduces the phosphorus removal efficiency (Özacar and Şengil, 2003). Therefore, with respect to the chemical precipitation mechanism, high OH/Al ratio coagulants are less effective than lower OH/Al ratio coagulants. In other words, polymeric Al_b and Al_c in the pre-hydrolyzed Al species containing more OH^- in their formulae, e.g $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and $(AlO_4)_2Al_{28}(OH)_{56}(H_2O)_{26}^{18+}$, are not effective in precipitating of P with Al_a.

Adsorption mechanism that involves the PO_4 sorption onto $Al(OH)_3(s)$, has also been strongly suggested as primary mechanism for P removal (Galarneau and Gehr, 1997). A range of studies showed that at low phosphate concentrations (1 – 5 mg/L), phosphate is removed largely by the adsorption of phosphate ions onto formed $Al(OH)_3$ flocs (Boisvert et al., 1997b; Goldshmid and Rubin, 1988; Özacar and Şengil, 2003). The phosphate concentration in the secondary effluent used in this study was relatively low (average 3.43 mg/L), and the coagulation pH range of 6.0 to 6.7 was considered to be favorable for the formation of $Al(OH)_3(s)$. This suggests that adsorption of phosphates onto $Al(OH)_3(s)$ also contributed to P removal, especially at high dosages of coagulants used in this experiment. Since monomeric Al coagulant is the most unstable species after dosing, it would quickly hydrolyzed to form hydrolysed species (in competition between PO_4 and OH^-) and finally $Al(OH)_3(s)$ (if a large enough amount of Al dosage is applied). With respect to the adsorption of phosphates onto $Al(OH)_3(s)$, Al_b in PACl is also not superior to Al_a because polymeric Al_b species are relatively stable and resistant to hydrolysis, thus they remain for a greater duration in solution and hydroxide precipitates is formed slowly.

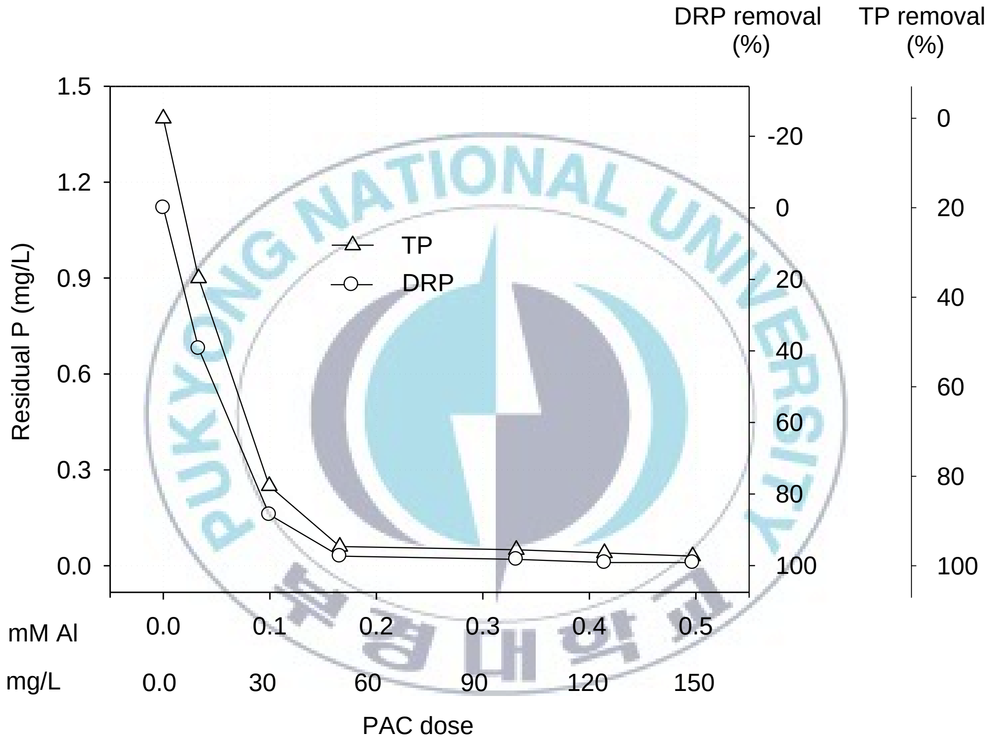


Fig. 6.21. P removal using 17% Al_2O_3 content commercial PACl.

An additional experiment conducted using commercial PAC with high Al_2O_3 content of 16.9% and 40% basicity, which is one of common commercial PACl used in water treatment. Content of Al_a, Al_b, and Al_c was 60.5, 23.1 and 16.4, respectively. Treated samples were filtered through a GFC filter before measuring residual P and results are shown in Fig. 6.21.

The results show that with combination of filter, residual P can reduce to a very low concentration, i.e. 0.1 mg/L P at low PACl dose of 0.16 mM Al (50 mg/L PAC).

Chapter 7

SUMMARY

This research investigates the effects of Al species on coagulation/ flocculation process in treatment of surface water and sewage effluent. Al based coagulants was characterized using Ferron assay. Organic in river water was fractionated and isolated using resin adsorption. Coagulation at different conditions of pH and coagulant doses was performed to investigate the coagulation mechanisms and behavior of Al species in coagulants. Information obtained from characterizing organic matter and coagulation/flocculation was combined to evaluate behavior of each organic fraction in coagulation/ flocculation. Similarly, phosphorus in sewage effluent was also characterized before conducting coagulation/flocculation. The relationship between Al species of coagulants and coagulation performance was discussed. This chapter summarizes the results of this research and identifies further research.

SUMMARY

Characteristics of the coagulants as an important factor affecting coagulation/flocculation were firstly investigated. Al based coagulants prepared in laboratory at different *r* values and different total Al concentration was characterized using ferron assay. Difference in reaction kinetics of hydrolytic Al species and ferron allowed classify the Al species into monomeric Al_a, polymeric Al_b, and colloid / precipitate Al_c. The higher *r* value of PACl, the lower Al_a and the higher Al_b and Al_b content would be. A range of *r* value from 2.0 to 2.2, corresponding to 67 to 73% basicity was proved to be optimal for generating optimum Al_b content. Total Al concentration of PACl also affected the distribution of hydrolytic Al species. With same *r* value, as Al_T increased, Al_b decreased significantly while both Al_a and Al_c increased. The results give an explanation for the low polymeric Al_b content in commercial PACl. Commercial PACl, which is manufactured with high content of Al_T for economic reason (commonly 10% Al_2O_3 or 2.5 M Al) showed a average amount of 40% Al_b at basicity of 50% while Al_b content in laboratory prepared at Al_T of 0.1M can obtain a value of 90%.

To aid in the interpretation results of coagulation/flocculation performance with respect to a specific substance, surface water source collected from the Nakdong River, Busan, Korea, was characterized. Ion exchange resin analysis shows DOC in the water contains a similar percent of about 40% of hydrophobic and hydrophilic fraction, and a lower percent of 20% arises from hydrophilic organics. Between the two hydrophobic fractions, such as fulvic acids and humic acids, fulvic acids were predominant and humic acids exist with a small amount of less than 10%. Ultra-filtration analysis illustrated the large molecular weight of humic acids, follows by fulvic acids and hydrophilic acid.

Coagulation performance of two kinds of coagulants, one is predominant monomeric Al_a such alum and $AlCl_3$ and another one is predominant polymeric Al_b PACl, was performed using the Nakdong River water. In an effort to find out the relationship between hydrolytic Al species and coagulation performance with respect to removal of a specific fraction of organics, experiments was conducted with isolated organic synthetic water. It has been long known that hydrophobic organics are easier to remove by coagulation than hydrophilic organics. This study further indicated humic acids were more amenable to removal than the corresponding fulvic acids and hydrophilic acids. PACl with high preformed polymer Al_b shows the most superior performance to the other coagulants in coagulation-flocculation of hydrophilic acids, the fraction with smallest molecular weight among the 3 fractions of hydrophilic, fulvic, and humic acids.

It was observed that performance of the coagulants is controlled not only by preformed species but also by those forming in situ during coagulation. At neutral and basic pHs, PACls containing more stable preformed Al_b are more efficient for turbidity and organic matter removal. At slightly acidic pH, low basicity coagulants are more efficient since more Al_b is formed in situ. The optimum pH for the removal of turbidity was in the range of 6–8 for alum and > 6.5 for PACl. Overall, alum was superior to PACl in removal turbidity at common pH of treatment (6 – 7). With respect to DOC removal, PACl showed widen optimum pH range and towards high pH (of 5.5 – 7.0 versus 5.0 – 6.0). Overdosing of PACl caused restabilization of particles due to charge reverse while this phenomenon did not happen with alum. The role of Al species can be summarized as following:

(1) Al_b (preformed and in situ formed) is the most efficient species for DOC removal, especially for the removal of hydrophilic fraction of NOM. Al_b could destabilize particles efficiently by charge neutralization, but the flocs formed by Al_b are not large to settle well and an overdosing of Al_b cause charge reversal. Therefore, Al_b might not show high superior to other Al species in coagulation of low turbidity water. It might be favorable for the treatment of high turbidity water.

(2) Al_a transforms to Al_b at slightly low pH and finally to Al_c at high pH. At high dose, forming Al_c resulted in effectively removal of turbidity due to bulk structure of this species in sweep flocs of particles. Al_c can absorb particle and organic matter to form larger flocs.

The laboratory prepared coagulants and commercial PACls were also used for coagulation of phosphorus in sewage effluent. Characterizing P species in wastewater showed that condensed-P and organic-P were mainly found in the suspended form of phosphorus. Ortho phosphates were predominant species among various P species in wastewater, and this form is easier to be removed by coagulation-flocculation than the other forms of phosphorus. The optimum pH for P removal was in the range of 5.5 – 6.6 for alum and a narrow optimum range was observed for PACl. At high metal dose, the optimum pH range tended to widen towards higher pH values. Al hydrolytic species showed the following different behaviors in coagulation of phosphorus:

(1) Preformed Al_a was responsible for the removal of phosphorus due to high ability of Al monomer in forming the $Al(OH)_x(PO_4^{3-})_{3-x}$ precipitates and in adsorption of phosphates into $Al(OH)_3$ precipitates that are formed predominantly in hydrolysis process of Al_a coagulants. Al_a can complex with phosphorus in the competition with OH^- in water. Preformed Al_a is hydrolyzed to form Al_c and this Al_c is effective for adsorption of P.

(2) Although Al_b has been known as the most effective species in coagulation, it did not show any superior performance in P removal

(3) Al_c (preformed and in situ formed) might be favorable for adsorption of P and this species also showed a positive effect on removal of suspended P due to its superior performance in removal of turbidity from the water.

FURTHER RESEARCH NEEDS

Finding out the correlation between various Al species in coagulants and their coagulation performance for the treatment of a specific raw water suggests a further research in making a special coagulant for a preferential aim of removal. As shown in this study, Al_b species in high Al content coagulant, especially in commercial PACl is relative low, generally lower than 50% while this value of low Al content. A further research in making high Al concentration coagulants with high Al_b is needed.

Furthermore, future research should investigate in detail the Al species formed during coagulation of a real water source. It should be noted that this work might be difficult due to the chemical distribution of aluminum in water is very sensitive to its environments. In addition, the compositions of real water are very complex. This requires systematic experimental studies with considering at least pH, formation times, Al concentration, temperature and mixing conditions.

From the work of investigation the Al species formed during coagulation of a real water source, more detail in interaction mechanisms between Al_a, Al_b, and Al_c and each NOM fraction (ex. Hydrophobic, hydrophilic, humic, fulvic acid) and phosphate should be made

REFERENCES

Akitt, J.W., 1990. Structural determination of inorganic compounds, in: Brown, P. (Ed.), Modern NMR techniques and their application in chemistry. Headington Hill Hall, Marcel Dekker Inc., NY, pp. 427–483.

Akitt, J.W., Elders, J.M., 1985. Aluminium-27 nuclear magnetic resonance studies of the hydrolysis of aluminium (III). Part 7-Spectroscopic evidence for the cation $[AlOH]^{2+}$ from line-broadening studies at high dilution. Journal of the Chemical Society, Faraday Transactions 81, 1923-1930.

Akitt, J.W., Elders, J.M., Fontaine, X.L.R., Kundu, A.K., 1989. Multinuclear magnetic resonance studies of the hydrolysis of aluminium(III). Part 9. Prolonged hydrolysis with aluminium metal monitored at very high magnetic field. Journal of the Chemical Society, Dalton Transactions, 1889-1895.

Akitt, J.W., Farthing, A., 1978. New 27Al NM studies of the hydrolysis of the aluminum(III) cation. Journal of Magnetic Resonance Series A 32, 345-352.

Akitt, J.W., Farthing, A., 1981. Aluminium-27 nuclear magnetic resonance studies of the hydrolysis of aluminium(III). Part 2. Gel-permeation chromatography. Journal of the Chemical Society, Dalton Transactions, 1606-1608.

Akitt, J.W., Greenwood, N.N., Khandelwal, B.L., Lester, G.D., 1972. 27Al nuclear magnetic resonance studies of the hydrolysis and polymerisation of the hexa-aquo-aluminium(III) cation. Journal of the Chemical Society, Dalton Transactions, 604-610.

Akitt, J.W., Greenwood, N.N., Lester, G.D., 1969a. Aqueous aluminum salt solutions. Journal of Chemical Society D 17.

Akitt, J.W., Greenwood, N.N., Lester, G.D., 1969b. Resonance studies of acidic solutions of aluminum salts. Journal of the Chemical Society A: Inorganic, Physical, Theoretical 5, 803–807.

Allouche, L., Taulelle, F., 2003. Conversion of Al13 Keggin ε into Al30: a reaction controlled by aluminum monomers. Inorganic Chemistry Communications 6, 1167-1170.

Amirtharajah, A., Mills, P., 1982. Rapid mix design for mechanism of alum coagulation. J. Am. Water Works Assoc., 210–216.

Anderson, H.A., Berrow, M.L., Farmer, V.C., Hepburn, A., Russell, J.D., Walker, A.D., 1982. A reassessment of podzol formation processes. Journal of Soil Science 33, 125-136.

APHA, 1998. Standard methods for the examination of water and wastewater, 20 ed. American Public Health Association, Washington, DC.

Åström, M., Corin, N., 2000. Abundance, Sources and Speciation of Trace Elements in Humus-Rich Streams Affected by Acid Sulphate Soils. Aquatic Geochemistry 6, 367-383.

Baes, C.F., Mesmer, R.E., 1976. The Hydrolysis of Cations. John Wiley & Sons, New York.

Bersillon, J.L., Brown, D.W., Fiessinger, F., Hem, J.D., 1978. Studies of hydroxyaluminum complexes in aqueous solution.

Bersillon, J.L., Hsu, P.H., Fiessinger, F., 1980. Characterization of Hydroxy-Aluminum Solutions1. Soil Science Society of America Journal 44, 630-634.

Bertsch, P.M., 1987. Condition for Al_{13} polymer formation in partially neutralized aluminum solutions. Soil Science Society of America Journal 51, 825–828.

Bertsch, P.M., Anderson, M.A., Layton, W.J., 1989. Aluminum-27 nuclear magnetic resonance studies of ferron—hydroxo—polynuclear Al interactions. Magnetic Resonance in Chemistry 27, 283-287.

Bertsch, P.M., Barnhisel, R.I., Thomas, G.W., Layton, W.J., Smith, S.L., 1986a. Quantitative determination of aluminum-27 by high-resolution nuclear magnetic resonance spectrometry. Analytical Chemistry 58, 2583-2585.

Bertsch, P.M., Layton, W.J., Barnhisel, R.I., 1986b. Speciation of hydroxy-aluminum solutions by wet chemical and aluminum-27 NMR methods. Soil Science Society of America Journal 50, 1449-1454.

Bertsch, P.M., Parker, D.R., 1996. Aqueous polynuclear aluminum species, in: Sposito, G. (Ed.), The environmental chemistry of aluminum, 2 ed. CRC Press, Boca Raton, Florida, pp. 117–168.

Bertsch, P.M., Thomas, G.W., Barnhisel, R.I., 1986c. Characterization of hydroxy-aluminum solutions by aluminum-27 nuclear magnetic resonance spectroscopy. Soil Science Society of America Journal 50, 825–828.

Bi, S., Wang, C., Cao, Q., Zhang, C., 2004. Studies on the mechanism of hydrolysis and polymerization of aluminum salts in aqueous solution: correlations between the "Core-links" model and "Cage-like" Keggin-Al13 model. Coordination Chemistry Reviews 248, 441-455.

Boisvert, J.-P., To, T.C., Berrak, A., Jolicoeur, C., 1997a. Phosphate adsorption in flocculation processes of aluminium sulphate and poly-aluminium-silicate-sulphate. Water Research 31, 1939-1946.

Boisvert, J.P., To, T.C., Berrak, A., Jolicoeur, C., 1997b. Phosphate adsorption in flocculation processes of aluminium sulphate and poly-aluminium-silicate-sulphate. Water Res. 31, 1939–1946.

Bottero, J.Y., Axelos, M., Tchoubar, D., Cases, J.M., Fripiat, J.J., Fiessinger, F., 1987a. Mechanism of formation of aluminum trihydroxide from keggin Al13 polymers. Journal of Colloid and Interface Science 117, 47-57.

Bottero, J.Y., Axelos, M., Tchoubar, D., Cases, J.M., Fripiat, J.J., Fiessinger, F., 1987b. Mechanism of formation of aluminum trihydroxide from Keggin Al13 polymers. J. Coll. Interface Sci. 117, 47–57.

Bottero, J.Y., Bersillon, J.L., 1989. Aluminum and iron(III) chemistry: some implications for organic substance removal, in: Suffet, I.H., MacCarthy, P. (Eds.), Aquatic humic substances: influence on fate and treatment of pollutants. American Chemical Society, Washington, DC, pp. 425–442.

Bottero, J.Y., Cases, J.M., Fiessinger, F., Poirier, J.E., 1980. Studies of hydrolyzed aluminum chloride solutions. 1. Nature of aluminum species and composition of aqueous solutions. The Journal of Physical Chemistry 84, 2933-2939.

Bottero, J.Y., Tchoubar, D., Cases, J.M., 1988. New developments in knowledge of aluminum colloids, in: Attia, Y.A., Moudgil, B.M., Chander, S. (Eds.), Interfacial phenomena in biotechnology and materials processing: proceedings of the International Symposium on Interfacial Phenomena in Biotechnology and Materials Processing, August 3-7, 1987, Boston, Massachusetts, U.S.A, Process technology proceedings. Elsevier, Amsterdam ; New York, pp. xii, 554 p.

Bottero, J.Y., Tchoubar, D., Cases, J.M., Fiessinger, E., 1982. Investigation of file hydrolysis of aqueous solutions of aluminum chloride. 2. Nature and structure by smallangle X-ray scattering. Journal of Physical Chemistry 86, 3667-3673.

Bratby, J., 2006. Coagulation and flocculation in water and wastewater treatment, 2 ed. IWA Publishing, London.

Brosset, C., 1952. On the reactions of the aluminum ion with water. Acta Chemica Scandinavica 6, 910–940.

Brosset, C., Biedermann, G., Sillén, L.G., 1954. Studies on the Hydrolysis of Metal Ions. Acta Chemica Scandinavica 8, 1917-1926.

Cambier, P., Sposito, G., 1991. Interactions of citric acid and synthetic hydroxyl-aluminum montmorillonite. Clays and Clay Minerals 39.

Casey, W.H., Olmstead, M.M., Phillips, B.L., 2005. A New Aluminum Hydroxide Octamer, [Al8(OH)14(H2O)18](SO4)5·16H2O. Inorganic Chemistry 44, 4888-4890.

Casey, W.H., Phillips, B.L., Furrer, G., 2001. Aqueous Aluminum Polynuclear Complexes and Nanoclusters: A Review. Reviews in Mineralogy and Geochemistry 44, 167-190.

Chutter, F.M., 1990a. Evaluation of the impact of the 1 mgP/l phosphate P standard on the water quality and trophic status of Hartebeespoort Dam. Water Sewage and Effl. 10, 29–33.

Chutter, F.M., 1990b. Evaluation of the impact of the 1 mgP/l phosphate P standard on the water quality and trophic status of Hartebeespoort Dam. Water Sewage and Effl. 10, 29–33.

Council of the European Communities, 1999. Directive concerning the collection, treatment and discharge of urban wastewater and the discharge of wastewater from certain industrial sectors (91/271/EEC). Official Journal L 135.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., 2005. Water Treatment - Principles and Design (2nd Edition). John Wiley & Sons.

Croué, J.P., Lefebvre, E., Martin, B., Legube, B., 1993. Removal of Dissolved Hydrophobic and Hydrophilic Organic Substances during Coagulation/Flocculation of Surface Waters. Water Science and Technology 27, 143–152.

De Hass, D.W., Wentzel, M.C., Ekama, G.A., 2000. The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal. Part 1: Literature review. Water SA 26, 439–452.

De Hek, H., Stol, R.J., De Bruyn, P.L., 1978. Hydrolysis-precipitation studies of aluminum(III) solutions. 3. The role of the sulfate ion. Journal of Colloid and Interface Science 64, 72-89.

Demirata, B., Apak, R., Gümüs, G., Afsar, H., 2002. The Effect of the Order of Reagent Addition on the Settling Rate of Aluminium Hydroxide in the Al(III)-Na2CO3 System. Water, Air, & Soil Pollution 133, 265-282.

Dempsey, B.A., Ganho, R.M., O' Melia, C.R., 1984. The coagulation of humic substances by means of aluminum salts. J. Am. Water Works Assoc. 76, 141–150.

Dillon, P.J., Molot, L.A., 1996a. Long-term phosphorus budgets and an examination of a steady-state mass balance model for central Ontario lakes. Water Research 30, 2273-2280.

Dillon, P.J., Molot, L.A., 1996b. Long-term phosphorus budgets and an examination of the steady-state mass balance model for central Ontario lakes. Water Res. 20, 2273–2280.

Driscoll, C.T., Schecher, W.D., 1990. The chemistry of aluminum in the environment. Environmental Geochemistry and Health 12, 28-49.

Duan, J.M., Gregory, J., 2003. Coagulation by hydrolysing metal salts. Adv. Colloid Interface Sci., 100–102, 475–502.

Duenas, J.F., J.R., A., Rey, A.F., Ferrer, A.S., 2003. Characterisation of phosphorus forms in wastewater treatment plants. Journal of Hazardous materials 97, 193–205.

Ebeling, J.M., Sibrell, P.L., Ogden, S., Summerfelt, S.T., 2003. Evaluation of chemical coagulation-flocculation aids for the removal of phosphorus from recirculating aquaculture effluent. Aquacult. Eng. 29, 23–42.

Edwards, G.A., Amirtharajah, A., 1985. Removing color caused by humic acids. J. Am. Water Works Assoc. 77, 50-57.

Edzwald, J.K., 1993. Coagulation in drinkingwater treatment—particles, organics and coagulants. Water Sci. Technol 27, 21–35.

Edzwald, J.K., Van Benschoten, J.B., 1990. Aluminum coagulation of natural organic matter, in: Hahn, H., Klute, R. (Eds.), Chemical Water and Wastewater Treatment Springer Verlag, New York.

Fan, L., Harris, J.L., Roddick, F.A., Booker, N.A., 2001. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. Water Research 35, 4455-4463.

Faust, S.D., Aly, O.M., 1998a. Chemistry of water treatment. CRC Press, Boca Raton.

Faust, S.D., Aly, O.M., 1998b. Removal of particulate matter by coagulation, in: Faust, Aly (Eds.), Chemistry of water treatment, 2nd ed. CRC Press, Florida, USA, pp. 217–270.

Ferguson, J.F., King, T., 1977. A model for aluminum phosphate precipitation. J.WPCF 49, 646–658.

Fettig, J., Ratnaweera, H.C., Ødegaard, H., 1990. Simultaneous phosphate precipitation and particle destabilization using aluminium coagulants of different basicity. Springer-Verlag, Berlin.

Fratiello, A., Lee, R.E., Nishida, V.M., Schuster, R.E., 1968. Proton magnetic resonance coordination number study of aluminium(III), beryllium(II), gallium(III), indium(III), and magnesium(II), in water and aqueous solvent mixtures. Journal of Chemical Physics 48, 3705–3711.

Fu, G., Nazar, L.F., Bain, A.D., 1991. Aging processes of alumina sol-gels: characterization of new aluminum polyoxycations by aluminum-27 NMR spectroscopy. Chemistry of Materials 3, 602-610.

Fytianos, K., Voudrias, E., Raikos, N., 1996. Removal of phosphate from aqueous and wastewater samples using aluminum salts. J. Environ. Sci. Health A 31, 2621–2634.

Galarneau, E., Gehr, R., 1997. Phosphorus removal from wastewaters: Experimental and theoretical support for alternative mechanisms. Water Res. 31, 328–338.

Gillberg, L., Nilsson., D., Akesson, M., 1996. The Influence of pH when precipitating orthophosphate with aluminum and iron salts, in: Hahn, H.H., Hoffmann, E., Ødegaard, H. (Ed.), Chemical Water and Wastewater treatment IV - Proceedings of the 7th Gothenburg Symposium Edinburgh. Springer-Verlag: New York p. 95.

Gillberg, L., Nilsson., D., Akesson, M., 1996. The Influence of pH when precipitating orthophosphate with aluminum and iron salts, in: Hahn, H.H., Hoffmann, E., Ødegaard, H. (Ed.), Chemical Water and Wastewater Treatment. Springer, Edinburgh, Scotland, p. 95.

Goldshmid, T., Rubin, A.J., 1988. Determination of soluble species and precipitates of aluminum phosphate. Separ. Sci. Tech. 23, 2269–2291.

Gregory, J., 1993. The role of colloid interactions in solid-liquid separation. Water Science and Technology 27, 1–17.

Gregory, J., Duan, J., 2001a. Hydrolyzing metal salts as coagulants. Pure Appl. Chem. 73, 2017–2026.

Gregory, J., Duan, J., 2001b. Hydrolyzing metal salts as coagulants. Pure and Applied Chemistry 73, 2017-2026.

Hargrove, W.L., 1986. Solubility of aluminum-organic matter and its implication in plant uptake of aluminum. Soil Science 142, 179-181.

Hatton, W., Simpson, A.M., 1985. Use of alternative aluminium based chemicals in coagulation with particular reference to phosphorus removal. Environ. Technol. Letters 6, 225–230.

Hem, J.D., Roberson, C.E., 1967. Form and stability of aluminum hydroxide complexes in dilute solution. U.S. G.P.O.

Hem, J.D., Roberson, C.E., 1990. Aluminum hydrolysis reactions and products in mildly acidic aqueous systems, in: Melchior, D.C., Bassett, R.L. (Eds.), Chemical Modeling of Aqueous Systems II, ACS Symp. Ser. ACS, pp. 429–446.

Howe, K.J., Clark, M.M., 2002. Coagulation pretreatment for membrane filtration. WWA Research Foundation and AWWA, Denver.

Hsu, P.H., 1989a. Aluminium hydroxides and oxihydroxides, 2 ed. Soil Sci. Soc. Am, Madison, Wisconsin.

Hsu, P.H., 1989b. Minerals in soil environments. Soil Science Society of America.

Hsu, P.H., Bates, T.F., 1964. Formation of X-ray amorphous and crystalline aluminum hydroxides. Mineral Mag. 33 33, 749–768.

Hu, C.Z., Liu, H.J., Qu, J.H., Wang, D.S., Ru, J., 2006. Coagulation behavior of aluminum salts in eutrophic water: significance of Al-13 species and pH control. Environmental Science and Technology 40, 325–331.

Huang, L., Wang, D., Tang, H., Wang, S., 2006. Separation and purification of nano-Al13 by UF method. Colloids and Surfaces A: Physicochemical and Engineering Aspects 275, 200-208.

Hudson, H.E., 1981. Water clarification processes : practical design and evaluation. Van Nostrand Reinhold Co., New York.

Jardine, P.M., Zelazny, L.W., 1986. Mononuclear and Polynuclear Aluminum Speciation through Differential Kinetic Reactions with Ferron. Soil Science Society of America Journal 50, 895-900.

Jiang, J.Q., 2001. Development of coagulation theory and pre-polymerized coagulants for water treatment. Sep. Purif. Methods 30, 127–141.

Jiang, J.Q., Graham, N.J.D., 1998. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation—a review. Water SA 24, 237–244.

Jiang, J.Q., Graham, N.J.D. , 1998. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation–a review. Water SA 24, 237–244.

Jolivet, J.P., Henry, M., Livage, J., 2000. Metal oxide chemistry and synthesis: from solution to solid state. Wiley & Sons, Chichester, UK.

Kang, L.-S., Han, S.-W., Jung, C.-W., 2001. Synthesis and characterization of polymeric inorganic coagulants for water treatment. Korean Journal of Chemical Engineering 18, 965-970.

Kawamura, S., 1991. Integrated design of water treatment facilities. Wiley, New York.

Kim, W., Ludwig, H.F., Bishop, W.D., 1965. Cation exchange capacity and pH in the coagulation process. J. Am. Water Works Assoc. 57, 327–348.

Koether, M.C., 2002. The role of size exclusion chromatography-flame atomic absorption spectrometry in the treatment chemistry of potable water. Journal of Environmental Monitoring 4, 16-19.

Korea MOE, 2007. Standards and specifications for water treatment. Notification No. 92. Korea Ministry of Environment, Seoul.

Küchler, I.L., Miekeley, N., 1994. Ultrafiltration of humic compounds through low molecular mass cut-off level membranes. Science of the Total Environment 154, 23-28.

Letterman, R.D., 1981. Theorical principles of flocculation, Seminar Proceedings, AWWA Sunday Seminar Series, AWWA Annual Conference, st. Louis, June.

Letterman, R.D., 1991. Filtration strategies to meet the surface water treatment rule, Filtration strategies to meet the surface water treatment rule. AWWA, Denver CO.

Letterman, R.D., Iyer, D.R., 1985. Modeling the effects of hydrolyzed aluminum and solution chemistry on flocculation kinetics. Environmental Science and Technology 19, 673-681.

Lin, C.-F., Lin, T.-Y., Hao, O.J., 2000. Effects of humic substance characteristics on UF performance. Water Research 34, 1097-1106.

Lu, G., Qu, J., Tang, H., 1999. The electrochemical production of highly effective polyaluminum chloride. Water Research 33, 807-813.

Manahan, S.E., 2001. Fundamentals of environmental chemistry. Lewis Publishers, Boca Raton, FL.

Matsui, Y., Yuasa, A., Furaya, Y., Kamei, T., 1998. Dynamic analysis of coagulation with alum and PACl. J. Am. Water Works Assoc. 90, 96–106.

Maurer, M., Boller, M., 1999. Modeling of phosphorus precipitation in wastewater treatment plants with enhanced biological phosphorus removal. Water Science and Technology 39 147–163.

Minnow Environmental Inc, 2005. Environmental risk-based approaches for managing municipal wastewater effluent (MWWE). Report prepared for Canadian council of Ministers of the Environment Winnipeg.

NIER, 2010. A manual for phosphorus control, in: Research, K.N.I.o.E. (Ed.).

Nordstrom, D.K., May, H.M., 1996. Aqueous Equilibrium Data for Mononuclear Aluminum Species, in: Sposito, G. (Ed.), The environmental chemistry of aluminum. CRC Press, Boca Raton, Florida, pp. 39-80.

Okura, T., Goto, K., Yotuyanagi, T., 1962. Forms of Aluminum Determined by 8-Hydroxyquinolate Extraction Method. Analytical Chemistry 34, 581-582.

Omoike, A.I., Van Loon, G.W., 1999. Removal of phosphorus and organic matter by alum during wastewater treatment. Water Res. 33, 3617–3627.

Owen, D.M., Amy, G.L., Chowdhury, Z.K., 1993. Characterization of natural organic matter and its relationship to treatability. The Foundation and American Water Works Association, Denver, CO.

Özacar, M., Şengil, İ.A., 2003. Effect of tannins on phosphate removal using alum. Turk. J. Eng. Environ. Sci. 27, 227–236.

Packham, R.F., 1965. Some studies of the coagulation of dispersed clays with hydrolyzing salts. Journal of Colloid and Interface Science 20, 81–92.

Parker, D.R., Bertsch, P.M., 1992a. Formation of the "Al13" tridecameric aluminum polycation under diverse synthesis conditions. Environmental Science and Technology 26, 914-921.

Parker, D.R., Bertsch, P.M., 1992b. Identification and quantification of the "Al13" tridecameric aluminum polycation using ferron. Environmental Science and Technology 26, 908-914.

Parker, D.R., Bertsch, P.M., 1992c. Identification and quantification of the 'Al13' tridecameric polycation using ferron. Environ. Sci. Technol. 26, 908–914.

Pernitsky, D.J., 2003. Coagulation 101, Asscociated Engineering, Calvary, Alberta.

Ratnaweera, H.C., Ødegaard, H., Fettig, J., 1992. Coagulation with prepolymerised aluminium salts and their influence on particle and phosphate removal. Water Sci. Technol. 26, 1229-1237.

Ratnaweera, H.C., Ødegaard, H., Fettig, J., 1992. Coagulation with prepolymerised aluminium salts and their influence on particle and phosphate removal. Water Sci. Technol. 26, 1229-1237.

Schutz, A., Stone, W.E.E., Poncelet, G., Fripiat, J.J., 1987. Preparation and characterization of bidimensional zeolitic structures obtained from synthetic beidellite and hydroxy-aluminum solutions. Clays and Clay Minerals 35, 251–261.

Seichter, W., Mögel, H.-J., Brand, P., Salah, D., 1998. Crystal Structure and Formation of the Aluminium Hydroxide Chloride [Al13(OH)24(H2O)24]Cl15 · 13 H2O. European Journal of Inorganic Chemistry 1998, 795-797.

Selig, U., Hubener, T., Michalik, M., 2002. Dissolved and particulate phosphorus forms in a eutrophic shallow lake. Aquat. Sci. 64, 97–105.

Shen, Y.-H., Dempsey, B.A., 1998a. Synthesis and speciation of polyaluminum chloride for water treatment. Environment International 24, 899-910.

Shen, Y.H., Dempsey, B.A., 1998b. Synthesis and speciation of polyaluminum chloride for water treatment. Environ. Int. 24, 899–910.

Shi, B.Y., Li, G.H., Wang, D.S., Tang, H.X., 2007b. Separation of Al13 from polyaluminum chloride by sulfate precipitation and nitrate metathesis. Separation and Purification Technology 54, 88–95.

Shi, B.Y., Wei, Q.S., Wang, D.S., Zhu, Z., Tang, H.X., 2007. Coagulation of humic acid: the performance of preformed and non-preformed Al species. Colloids Surf. A: Physicochem. Eng. Asp. 296, 141–148.

Shin, J.Y., Spinette, R.F., O'Melia, C.R., 2008. Stoichiometry of Coagulation Revisited. Environmental Science & Technology 42, 2582-2589.

Sinha, S., Yoon, Y., Amy, G., Yoon, J., 2004. Determining the effectiveness of conventional and alternative coagulants through effective characterization schemes. Chemosphere 57, 1115-1122.

Smith, R.W., 1971. Relations Among Equilibrium and Nonequilibrium Aqueous Species of Aluminum Hydroxy Complexes, Nonequilibrium Systems in Natural Water Chemistry. Am. Chem. Soc., pp. 250-279.

Smith, R.W., Hem, J.D., 1972. Effect of aging on aluminum hydroxide complexes in dilute aqueous solutions.

Snodgrass, W.J., Clark, M.M., O'Melia, C.R., 1984. Particle formation and growth in dilute aluminum(III) solutions: Characterization of particle size distributions at pH 5.5. Water Research 18, 479-488.

Snoeyink, V.L., Jenkins, D., 1980. Water Chemistry. Wiley, New York.

Stevenson, F.J., 1985. Geochemistry of soil humic substances. Wiley, New York (USA).

Stumm, W., O'Melia, C.R., 1968. Stoichiometry of coagulation. J. Am. Water Works Assoc. 60, 514–539.

Swaddle, T.W., Rosenqvist, J., Yu, P., Bylaska, E., Phillips, B.L., Casey, W.H., 2005. Kinetic Evidence for Five-Coordination in AlOH(aq)2+ Ion. Science 308, 1450-1453.

Szabó, A., Takács, I., Murthy, S., Daigger, G., Licskó, I., Smith, S., 2008. Significance of design variables in chemical phosphorus removal. Water Environ. Res. 80, 407–416.

Tang, H.X., Luan, Z.K., 1996. The differences of behavior and mechanism between pre-polymeric inorganic flocculants and traditional coagulants, in: Hahn, H.H., Hoffmann, E., Ødegaard, H. (Ed.), Chemical Water and Wastewater treatment IV - Proceedings of the 7th Gothenburg Symposium Edinburgh. Springer-Verlag: New York pp. 83–93.

Tang, H.X., Wang, D.S., Xu, Y., 2004. Optimization of the concepts for polyaluminum species

in: Hahn, H.H., Hoffmann, E., Ødegaard, H. (Eds.), Chemical Water and Waste Water Treatment VIII. IWA Publishing, UK.

Thompson, A.R., Kunwar, A.C., Gutowsky, H.S., Oldfield, E., 1987. Oxygen-17 and aluminium-27 nuclear magnetic resonance spectroscopic investigations of aluminium(III) hydrolysis products. Journal of the Chemical Society, Dalton Transactions, 2317-2322.

Thurman, E.M., 1985a. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr W. Junjk, Dordrecht.

Thurman, J.E., 1985b. Organic geochemistry of natural waters. Dordrecht, Neitherlands, Martinus Nijhoff/ Dr. W. Junk Publishers.

Trinh, T.K., Kang, L.S., 2011. Response surface methodological approach to optimize the coagulation–flocculation process in drinking water treatment. Chemical Engineering Research and Design 89, 1126-1135.

USEPA, 1987. Design manual: phosphorus removal EPA/625/1-87/001, Cincinnati, Ohio.

Van Benschoten, J.E., Edzwald, J.K., 1990. Chemical aspect of coagulation using aluminum salts-I: hydrolytic reactions of alum and polyaluminum chloride. Water Research 24, 1519–1526.

Vermeulen, A.C., Geus, J.W., Stol, R.J., De Bruyn, P.L., 1975. Hydrolysis-precipitation studies of aluminum (III) solutions. I. Titration of acidified aluminum nitrate solutions. Journal of Colloid and Interface Science 51, 449-458.

Wang, D.S., Tang, H.X., Gregory, J., 2002. Relative importance of charge neutralization and precipitation on coagulation of kaolin with PACI: effect of sulfate ion. Environmental Science and Technology, 1815–1820.

Wang, Y., Han, T., Xu Bao, G., Tan, Z., 2005. Optimization of phosphorus removal from secondary effluent using simplex method in Tianjin, China. J. Hazard. Mater. 21, 183–186.

Xu, Y., Wang, D.S., Liu, H., 2003. Optimization on the separation and purification of Al13. Colloids Surf. A: Physicochem. Eng. Asp. 231, 1–9.

Yan, M., Wang, D., Yu, J., Ni, J., Edwards, M., Qu, J., 2008. Enhanced coagulation with polyaluminum chlorides: Role of pH/Alkalinity and speciation. Chemosphere 71, 1665-1673.

Yeh, H.H., Huang, W.J., 1993. The Fate of Dissolved Organics in Water Purification Processes Treating Polluted Raw Water. Water Science and Technology 27, 71–80.

Yeoman, S., Stephenson, T., Lester, J.N., Perry, R., 1988. The removal of phosphorus during wastewater treatment: A review. Environmental Pollution 49, 183-233.

Zhao, H., Hu, C.Z., Liu, H.J., Zhao, X., Qu, J.H., 2008. Role of aluminum speciation in the removal of disinfection byproduct precursors by a coagulation process. Environmental Science and Technology 42, 5752–5758.

Zhao, H.Z., Liu, C., Xu, Y., Ni, J.R., 2009. High-concentration polyaluminum chloride: preparation and effects of the Al concentration on the distribution and transformation of Al species. Chemical Engineering Journal 155, 528–533.

Zhou, W., Gao, B., Yue, Q., Liu, L., Wang, Y., 2006a. Al-Ferron kinetics and quantitative calculation of Al(III) species in polyaluminium chloride coagulants. Colloids Surf. A: Physicochem. Eng. Asp. 278, 235–240.

Zhou, W., Gao, B., Yue, Q., Liu, L., Wang, Y., 2006b. Al-Ferron kinetics and quantitative calculation of Al(III) species in polyaluminum chloride coagulants. Colloids and Surfaces A 278, 235-240.

Zouboulis, A.I., Traskas, G., 2005. Comparable evaluation of various commercially available aluminum-based coagulants for the treatment of surface water and for the post-treatment of urban wastewater. Journal of Chemical Technology and Biotechnology 80, 1136–1147.

ACKNOWLEDGEMENTS

The help and continuous support from professors, colleagues, friends, and family to whom I am most grateful, will never be forgotten. Without you, all of you, I would not be what I am today. I would like to thank each of you individually by word, but I do so in my heart.

Being a graduate student under the supervision of Professor Lim Seok Kang has been a great honor. He is recognized as a famous researcher in the field of water treatment science and technology, and has shared his tremendous knowledge about water treatment, science, and research in general with me on a daily basis. Through his mentorship I have come to appreciate how the combination of strong fundamentals and an eye for beautiful science leads to the most interesting and challenging work. Without his guidance, I would not have had anything to show for in the scientific community, and I feel with this that I at least have something. Also, financial supports from the Professor during my Ph.D. studying period are also gratefully acknowledged.

Special thanks are also extended to Professor Byung Hun Lee, Professor Seok Jun Yeo, Professor Sang Dan Kim and Dr. Seung Woo Han, committees of this dissertation, for their helpful suggestions and recommendations as well as their valuable comments.

Sincere gratitude is extended to Professors from the Department of Environmental Engineering in Pukyong National University and from the Faculty of Chemical Engineering in Ho Chi Minh City University of Technology, who have provided many engineering tools and background that I have gained from their classes.

I am really grateful to members of Clean Water Lab. for giving me a comfortable environment as well as enthusiastic and invaluable help during the periods of time I worked with them: Jung Sun Kim, Dong Min Son, Kwang Hun Choi, Ju Hee Park, Dong Jin Kim, Byung Seok Kim, and Young Wook Jeong. They all, in this way or another, have helped me a lot from the time of my first step here to the time of my graduation. Also, thanks are sent to Vietnamese students who have studied in Pukyong National University for their abroad friendly atmosphere and their encouragement.

Finally, and perhaps most importantly, I would also like to express deepest gratitude from the bottom of my heart to my parents and my parents-in-law for their continuous encouragement. And thanks to my husband, Manh Vu Tran, who always supports, loves, sacrifices, and encourages me in every day and forever. Without all of you, this study would not have been possible.

Pukyong National University, Busan, Korea

February, 2012

Thuy Khanh Trinh

PUBLICATIONS

Domestic Conferences

Thuy Khanh Trinh, Lim Seok Kang, 2009. Optimization of Coagulation Process for a Drinking Water Treatment using Response Surface Methodology. Clean Water, Green Growth Conference, Korea Society on Water Quality and Korea Society of Water and Wastewater, Suwon, Korea, April 17th – 18th.

Thuy Khanh Trinh, In Sung Lee, Sang Ju Park, Lim Seok Kang, 2009. Application Response Surface Method and Experimental Design to Optimize Coagulation Tests. Korean Society of Environmental Engineering Conference, Changwon, Korea, April 30th – May 1st.

International Conferences

Thuy Khanh Trinh, Lim Seok Kang, 2011. Removal of Phosphorus using Aluminum Based coagulants: Importance of Al hydrolytic species (Al_a Al_b, and Al_c). 1st Green Environmental Technology Conference, Busan, Korea, August 21th –24th.

International Journals

Thuy Khanh Trinh, Lim Seok Kang, 2010. Application Response Surface Method as an Experimental Design to Optimize Coagulation Tests. Environmental Engineering Research, 15(2), 63–70.

Thuy Khanh Trinh, Lim Seok Kang, 2011. Response surface methodological approach to optimize the coagulation–flocculation process in drinking water treatment. Chemical Engineering Research and Design, 89(7), 1126–1135.