工學碩士 學位論文

*Potassium ferrate(VI)*를 이용한 강물의 자연유기물질과 중금속 제거

Removal of Natural Organic Matter and Heavy Metals in River Water using Potassium Ferrate(VI)

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韓國海洋大學校 大學院

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Removal of Natural Organic Matter and Heavy Metals in River Water using Potassium Ferrate(VI)

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요 약

최근 산업성장에 따른 수질오염이 심각한 문제가 되고 있으며 그 처리를 위한 환경친화적인 방법이 요구되고 있다. 본 연구에서는 강력한 산화제/소독제 및 응집제로 작용하고 부산물로 무독성의 Fe(Ⅲ)를 생성하는 potassium ferrate(K_2FeO_4)를 합성하여 자연유기물질(humic acid, fulvic acid)과 중금속(Cu, Mn, Zn)으로 오염된 강물을 처리하는 실험을 수행하였다.

Ferrate 주입량(2~46mg/l as Fe)에 따른 humic acid(10mg/l)의 제거효율을 UV_{254}로 알아본 결과, 낙동강과 온천천시료에서 각각 21~74%, 26~73%의 제거효율을 얻었다. 하지만 humic acid 제거를 TOC로 분석한 결과는 0~20%로 낮은 효율을 보였다. pH와 반응온도에 따른 영향을 보면 염기성조건보다 산성조건에서 ferrate에 의한 humic acid 제거효율이 높게 나타났고(pH 3: 90%, pH 7.8: 70%, pH 11: 74%), 온도가 높을수록 humic acid 제거효율이 높아졌다 (10℃: 62%, 20℃: 70%, 30℃: 79%). 응집제로서 ferrate 효과를 기존 응집제들과 비교해 본 실험에서 ferrate(22~76%)는 $FeSO_4 \cdot 7H_2O$(13~55%)와 FeO(OH)(13~16%)보다 더 높은 효율을 보였다. 한편, alum의 경우 2~6mg/l(as Al)의 주입량에서는 ferrate에 비해 더 높은 효과를 보였지만 그 주입량을 초과(10~40mg/l as Al)하면 오히려 효율이 감소하는 결과를 보여 최적 주입량을 선정하는 것이 중요함을 알 수 있었다. 그리고 소량의 ferrate(2, 4mg/l as Fe)를 주입하여 humic acid를 전처리한 후 alum, Fe(II)와 같은 기존 응집제로 처리하였을 때가 ferrate로 전처리를 하지 않았을 때보다 효율이 향상되었다. Ferrate와 humic acid의 반응은 60초 이내에 완결되어 정상상태에 이르렀고 반응시간에 대해 1차 반응을 보였다.

Ferrate 주입량(2～46mg/l as Fe), pH(3, 7.8, 11)와 온도(10, 20, 30℃)의 영향에 따른 fulvic acid(10mg/l) 제거실험 결과는 humic acid의 결과와 모두 같은 경향을 보였고 그때의 제거효율(%)들은 humic acid와 비교해서 더 높았다.

0.1mM Cu, Mn, Zn의 세 가지 시료에 ferrate를 주입한 결과, ferrate의 농도가 0.3mM일 때, Cu는 99%, Mn은 73%, 그리고 Zn은 99%의 제거효율을 보였다. 이는 ferrate가 중금속을 효과적으로 응집·침전시킴을 의미한다. 또한, pH가 증가할수록 대상 중금속 모두 제거효율이 향상되는 경향을 보였고 온도는 ferrate와 중금속의 반응에 특별한 영향을 미치지 않았다.

그리고 낙동강원수에 humic acid(HA) 농도가 10mg/l, 각 중금속(Cu, Mn, Zn) 농도가 0.1mM이 되도록 제조하여 ferrate를 주입하는 실험에서, ferrate 주입 전에 HA의 음이온 작용기와 양이온 중금속은 착화합물을 형성하여 일부 침전 · 제거되었고, 이어서 제거되지 않고 남은 HA와 중금속을 ferrate로 처리한 결과 높은 제거효율을 얻을 수 있었다. HA(10mg/l)와 Cu(0.1mM)가 혼합된 시료에 ferrate(0.03～0.7mM)를 주입하면 HA는 70～82%, Cu는 93～100%의 제거효율을 보였다. 이는 HA만 따로 처리하였을 때의 21～72%와 Cu만 따로 처리하였을 때의 28～99% 보다 높은 효율이었다. HA와 대상 중금속(Cu, Mn, Zn)이 모두 혼합된 경우에도 HA와 중금속 제거에 ferrate는 효과적이었다 (HA: 33～83%, Cu: 68～100%, Mn: 16～96%, Zn: 9～90%). 또한, fulvic acid(FA)와 각 중금속이 혼합된 시료를 ferrate로 처리한 결과도 위에서 언급한 HA와 중금속 혼합시료를 ferrate로 처리한 결과와 비슷했다.

본 연구를 통해서 수중의 자연유기물질(humic acid, fulvic acid)과 중금속(Cu, Mn, Zn) 제거에 ferrate가 효과적임을 확인하였다. 이로써 실제 정수처리에서 분리되어 있는 산화 · 응집공정을 ferrate로 단일화할 수 있으며, 기존 응집제에 비해 아주 소량이 주입되는 ferrate를 사용함으로써 슬러지 발생량 또한 감소할 수 있을 것으로 보인다.

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CHAPTER Ⅰ*. INTRODUCTION*

The industralization and population growth have been accompanied with serious environmental pollution, and in particular, water pollution is most closely associated with public health issues. It is thus necessary to deal with contaminated water through water treatment processes.

Oxidation and coagulation are two important unit processes for removing organic and inorganic matters from waters. However, traditional oxidants and coagulants used for water treatment have several drawbacks. Ozone, a strong oxidant, cannot thoroughly decompose organic matters into carbonic dioxide and water by itself, and also forms carcinogenic disinfection by-products (DBPs) such as aldehydes, ketones, and bromate (Tomiyasu et al., 1985; Choi et al., 1998; Jiang et al., 2006 a). Chlorine, a cost-effective and widely used oxidant, produces harmful gas and DBPs such as trihalomethane (THM) and haloacetic acids (HAAs) (Rook, 1974; Alsheyab et al., 2006). Traditional coagulants such as alum, ferric sulfate, and ferric chloride also have drawbacks such as requiring high treatment cost due to abundant dose and sludge production (Jiang and Lloyd, 2002).

The increasing interests in the current drinking-water treatment processes are to minimize the formation of DBPs, suspected to be carcinogenic, mutagenic and teratogenic, and to improve the removal efficiencies of natural organic matter (NOM), a well known precursor of DBPs (Singer, 1999; Chiang et al., 2002; Wang et al., 2002; Villanuevaa et al., 2003; Rizzo et al., 2005; Bose et al., 2007). Meanwhile, it is necessary to remove heavy metals from drinking-water since heavy metals may cause fatal diseases by accumulating in human body (Malik, 2004; Ahluwalia et al., 2007).

In recent years, ferrate has emerged as an oxidant/disinfectant and coagulant for water treatment. Ferrate is an iron with 6+ oxidation state and acts as a powerful oxidant and coagulant throughout a whole range of pH. Also, it has a higher redox potential (2.2 V) than ozone (2.07 V) in acidic solutions. Furthermore, ferrate is an environmentally friendly chemical which produces non-toxic Fe(Ⅲ), a coagulant, as a by-product (Jiang and Lloyd, 2002; Sharma, 2002; Cho et al., 2006; Jiang et al., 2006 b). Using ferrate for water treatment has various favorable effects such as disinfecting viruses and bacteria, removing organic pollutants, oxidizing odor compounds and metals, reducing THM, as well as its coagulating effect (Cho et al., 2006; Yuan et al., 2002; Graham et al., 2004; Eng et al., 2006; Lee et al., 2003; Jiang et al., 2006 a; Ma and Lui, 2002). Moreover, it has been recently discovered that ferrate is also effective for NOM removal (Jiang et al., 2001; Qu et al., 2003; Jiang and Wang, 2003; Jiang et al., 2006 a).

In this study, various experiments on the removal of heavy metals as well as NOM using ferrate have been conducted. Specifically, humic and fulvic acids, major precursors of DBPs among NOM, were targeted. In this study, highly pure potassium ferrate was synthesized for water treatment first. And then, removal efficiencies of NOM depending on ferrate dose, pH, temperature, and reaction time were investigated. The effect of ferrate in removing humic acid was compared with that of the traditional coagulants, and the effect of ferrate preoxidation was also investigated. In addition, the removal of heavy metals (Cu, Mn, Zn) and the simultaneous removal of NOM (humic acid, fulvic acid) and heavy metals were performed.

CHAPTER Ⅱ. LITERATURE REVIEW

In order to carry out various experiments on treating contaminated waters with ferrate, the characteristics of Natural Organic Matter (NOM), heavy metals and ferrate were reviewed, and many recent studies on the remove of NOM and heavy metals using ferrate were also reviewed.

2.1 Characteristics of Natural Organic Matter (NOM)

2.1.1 Structural Components of Humic Substances

Humic substances are important because they serve as a major reservoir of organic carbon in soils and oceans for the global carbon cycle. The global cycling of organic carbon is presented schematically in Figure 2.1 (George et al., 1985). The composition of plant and animal remains in soil constitutes a basic biological process in that carbon is recirculated to the atmosphere as carbon dioxide and associated elements (nitrogen, phosphorus, sulfur, and micronutrient). In the process, some of the carbon is assimilated into microbial tissues (i.e., the soil biomass); part is converted into stable humic substances. Some of the native humic substances is mineralized concurrently; consequently, total organic matter content is maintained at some steady-state level characteristic of the soil and management system (Stevenson, 1994).

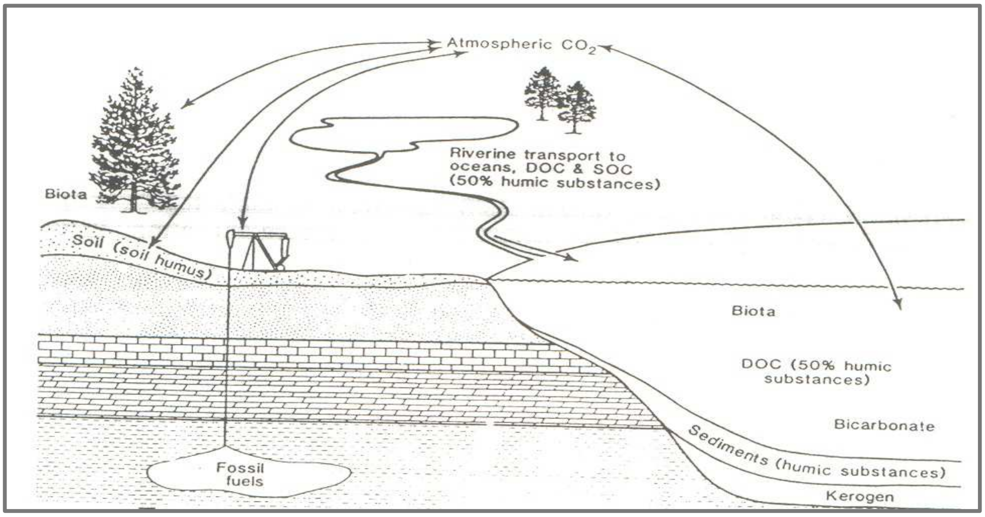


Figure 2.1. Diagram of the global carbon cycle, indicating the importance of humic substances (George et al., 1985)

Humic substances are classified into the three major fractions such as humin, humic acid, and fulvic acid depending on molecular weight and solubility (Figure 2.2).

Humin - The fraction of humic substances that is not soluble in water at any pH value. Its molecular weight is over 100,000 and its molecular structure is enormous.

Humic acid - The fraction precipitated by acid among fractions extracted with alkali. The fraction of humic substances that is not soluble in water under acid conditions (below pH 2), but becomes soluble at greater pH.

Fulvic acid - The fraction not precipitated by acid among fractions extracted with alkali. The fraction of humic substances that is soluble under all pH conditions.

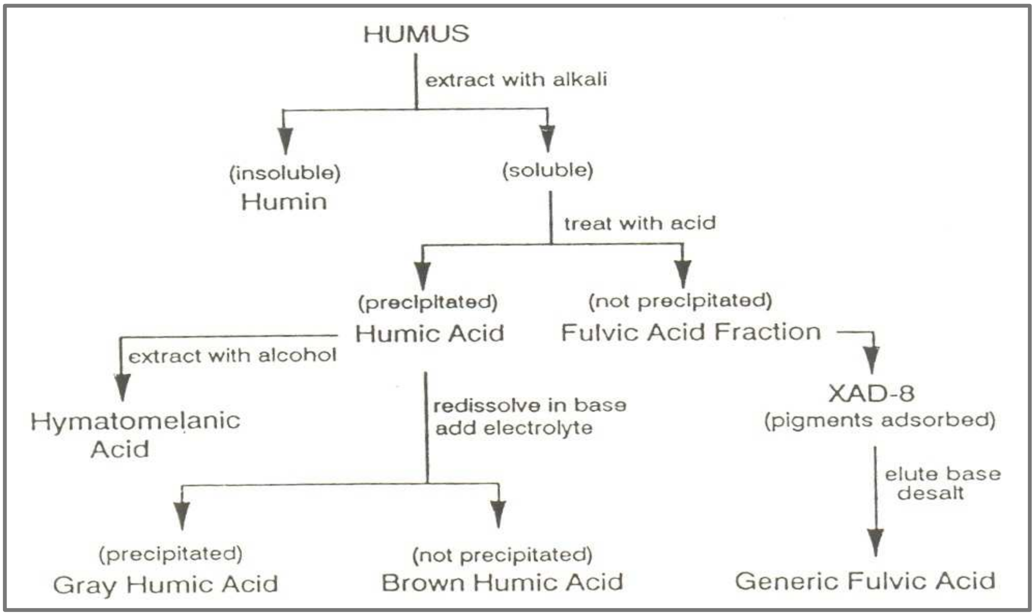


Figure 2.2. Scheme for the fractionation of soil organic matter (humus) (Stevenson, 1994)

The molecular weight and elemental composition of humic acid and fulvic acid are shown in Table 2.1. Humic acid has the molecular weights ranging from approximately 10,000 to 100,000 and the huge and complicated structure, and also the carbon content is higher than that of fulvic acid. The functional groups consisting of humic substances are shown in Table 2.2. The structure of humic acid contains free and bound phenolic OH groups, quinone structures, N and oxygen as bridge units, and COOH groups variously placed on aromatic rings, as shown in Figure 2.3. Whereas Figure 2.4 shows that fulvic acid has the lower carbon but higher oxygen content and somewhat higher content of COOH groups than humic acid.

Table 2.1. Range for the elemental composition of humic substances

	Units	Humic acid	Fulvic acid
Molecular weight	g/mol	10,000-100,000	1,000-10,000
Carbon	%	53.8-58.7	40.7-50.6
Oxygen	%	32.8-38.3	39.7-49.8
Hydrogen	%	3.2-6.2	3.8-7.0
Nitrogen	%	0.8-4.3	0.9-3.3
Sulfur	%	0.1-1.5	0.1-3.6
Acid content	mol/kg	5	14

Table 2.2. Functional groups of humic substances

Carboxyl (COOH)	Hydroxyl (OH)
a. On aromatic rings b. On side chains	a. Aliphatic b. Phenolic
Amine	Carbonyl (C=O)
a. Primary ($-NH_2$) b. Secondary (—NH—) c. Tertiary (—N=)	a. Ketonic b. Quinone

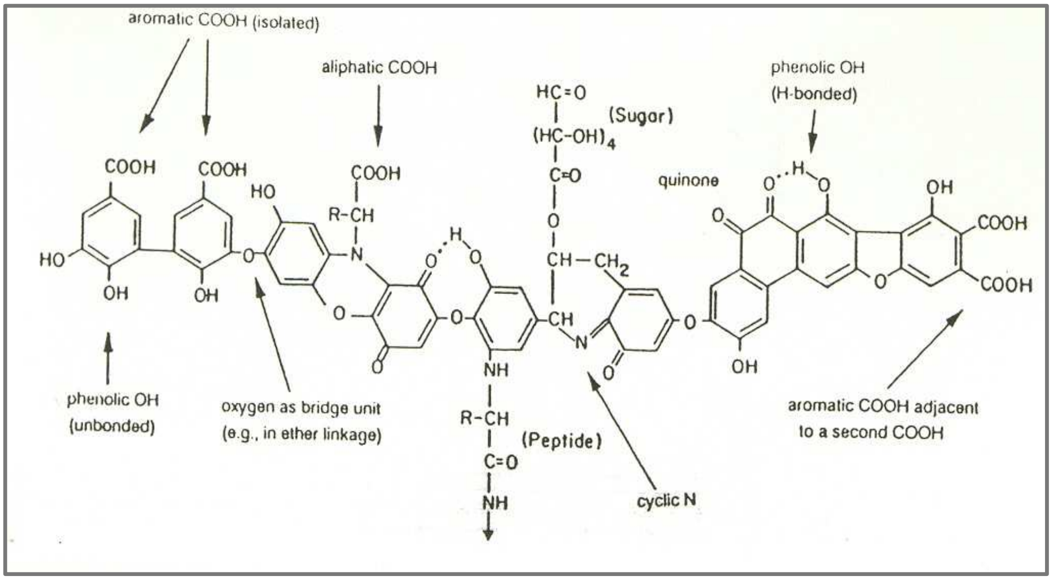


Figure 2.3. Hypothetical structure of humic acid (Stevenson, 1994)

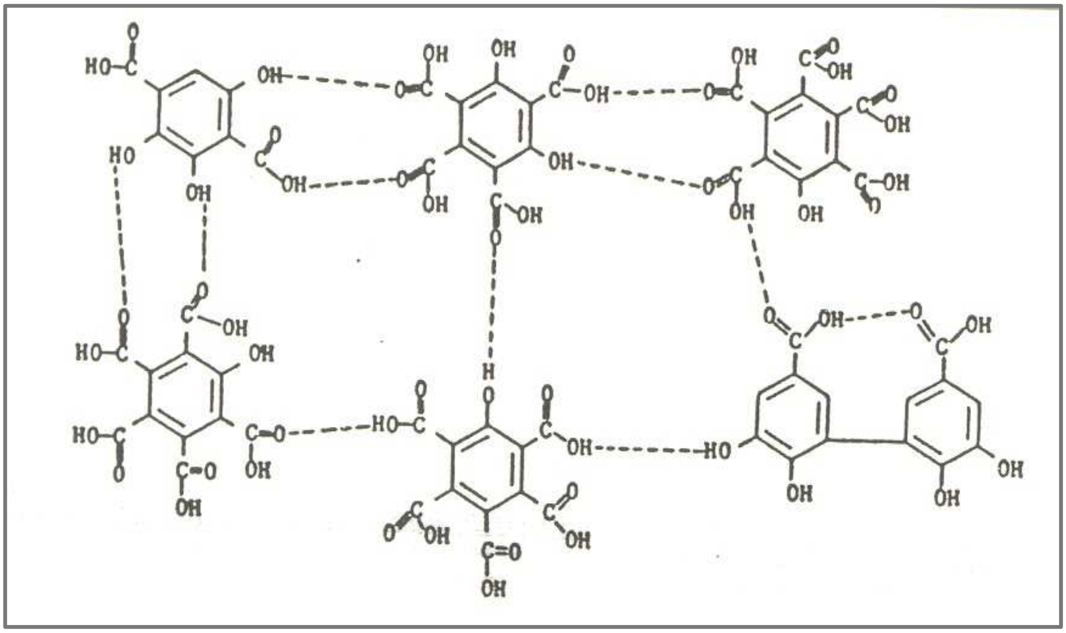


Figure 2.4. Structure of fulvic acid proposed by Schnitzer (Stevenson, 1994)

2.1.2 Acidic Characteristic of Humic Substances

The degree of acidity or acid strength of colloids depends on the characteristic of the reactive groups involved and of the associated structures on the molecule. In general, the OH group of carboxylic acids (R-COOH) dissociates more readily than aromatic or aliphatic alcohols. Phenolic compounds are stronger acids than water or alcohols but weaker than most carboxylic acids. The acidic characteristic of humic substances is usually attributed to the ionization of COOH and phenolic OH groups.

The acidic functional groups of humic substances show the different ionization reactions depending on pH (Figure 2.5). The carboxyl group (COOH) with pK_a values of 4.51-4.91 by Henderson-Hasselbach equation is ionized into COO^- at a weak acidic pH range, and the phenolic OH group with pK_a values of 8.0-8.7 is ionized into phenolate ion ($-O^-$) at a alkaline pH range.

$$pK = pK_a + \log\frac{[A^-]}{[HA]} \quad \text{(Henderson-Hasselbach equation)}$$

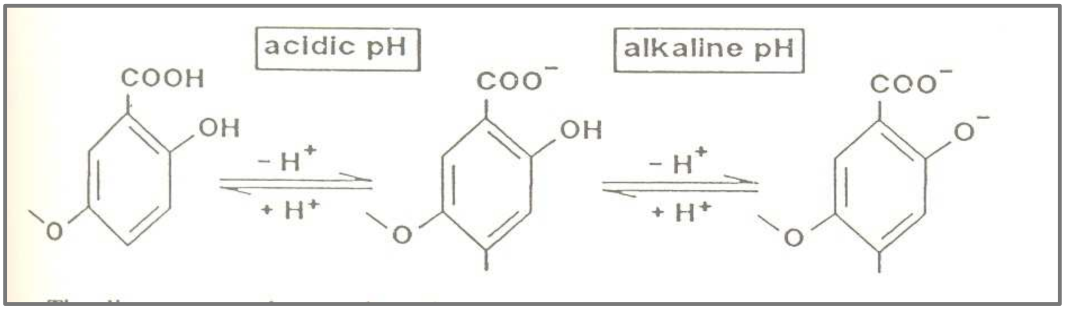


Figure 2.5. Ionization reaction of acidic functional groups in humic substances depending on pH (Stevenson, 1994)

Typical titration curves of humic acid are shown in Figure 2.6. The gradual rise in pH with added base attests to the high buffering capacity of humic substances and is consistent with the concept that they behave as weak-acid polyelectrolytes. The titration curves can be broken down into the three zones (Ⅰ,Ⅱ and Ⅲ). The zone marked Ⅰ is the lower acid region where COOH groups dissociate and the zone marked Ⅲ presents the dissociation of phenolic OH. The zone marked Ⅱ is the intermediate area where the ionization of weak (COOH) and very weak acid groups overlap.

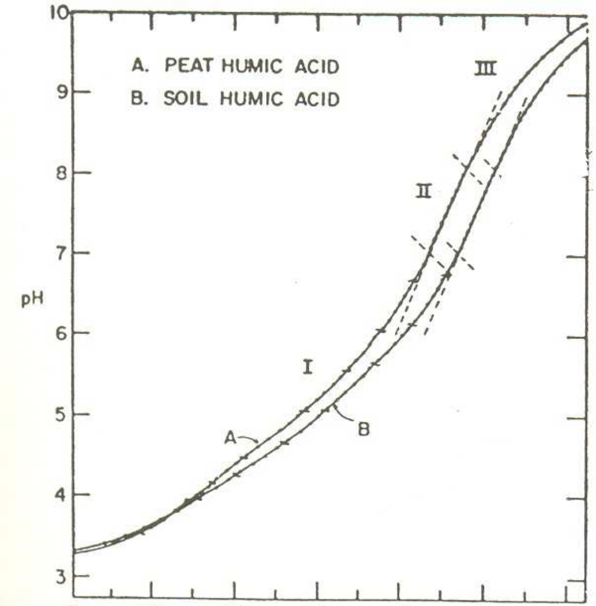


Figure 2.6. Titration curves of soil and peat humic acid (Stevenson, 1994)

2.1.3 Complexation of Humic Substances

Humic substances can form stable complexes with clay in soil and it can be accounted for in the two ways as shown in Figure 2.7; (a) the formation of the stable complex between metals (M) (polyvalent cation) adsorbing on clay and the functional groups of humic substances (clay-metal-organic complexes) and (b) the formation of the stable complex between clay and the functional groups (H-bonding) of humic substances (clay-organic complexes)

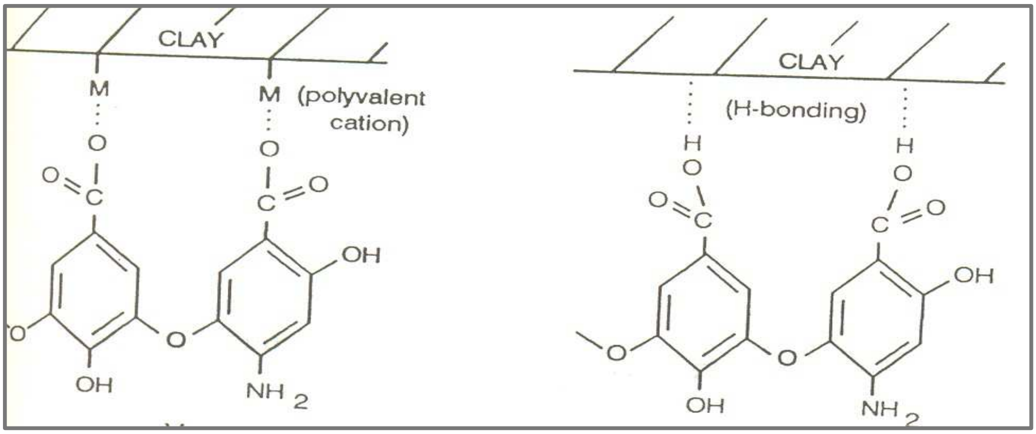


Figure 2.7. (a) clay-metal-organic complex (b) clay-organic complex (Stevenson, 1994)

Figure 2.8 presents the ability of humic substances to form stable complexes with trace elements and heavy metals. Chelation can occur when the oxygen-containing functional groups are in adjacent positions on the aromatic ring.

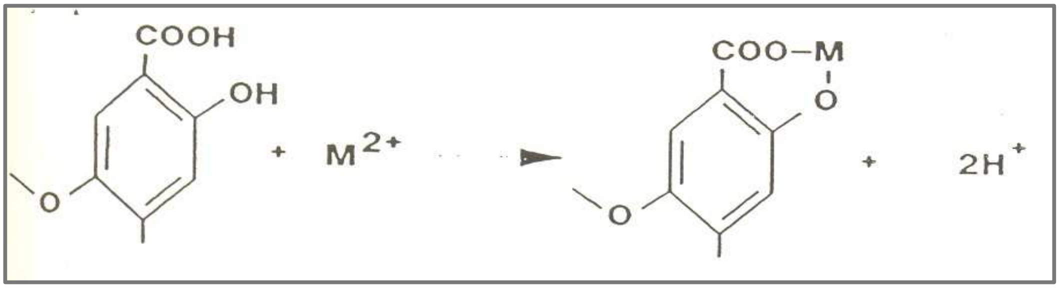


Figure 2.8. Formation of stable complexes with trace elements and heavy metals (M) (Stevenson, 1994)

Humic substances can also form stable complexes by bonding between soil organic matter and pesticides. A representative structure is shown in Figure 2.9.

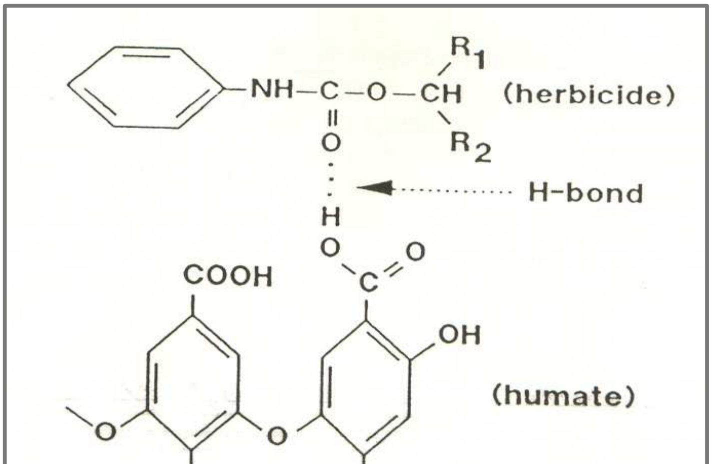


Figure 2.9. Representative structure between pesticides and functional groups of humic substance (Stevenson, 1994)

Figure 2.10 presents the way in which an individual monomers can be linked together to form chain-like matrixes that are relatively resistant to microbial degradation.

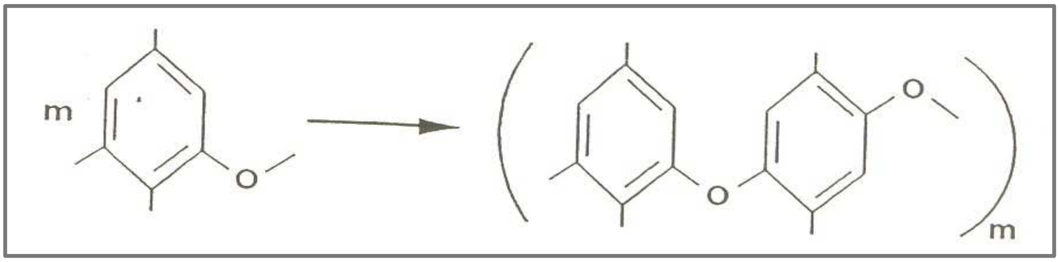


Figure 2.10. Formation of chain-like matrixes to resist decomposition (Stevenson, 1994)

2.2 Characteristics of Heavy Metals

2.2.1 Organic Matter Reactions Involving Metal Ions

Practically every aspect of trace element chemistry and reactions is related to the formation of stable complexes with organic substances. Whereas monovalent cations (Na^+, K^+, etc.) are held primarily by simple cation exchange through formulation of salts with carboxyl groups ($R\text{-}COO^-Na^+$, $R\text{-}COO^-K^+$), multivalent cations (Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+}, and others) have the potential for forming coordinate linkages with organic molecules.

The trace elements as soluble organic complexes (MCh_e) and as charge inorganic species serve as sources of water soluble ligands for complex formation. Some metals are held in insoluble organic and inorganic complexes.

With regard to complex formation and plant nutrition, the metals can be placed in the following groups:

1. Those which are essential to plants but that are not bound in coordinate compounds. Included are all of the monovalent cations, such as K^+, and the divalent cations Ca^{2+} and Mg^{2+}.
2. Those metals which are essential to plants and that form the coordinate linkage with organic ligands. They include nearly all of the metals in the first transitions series, including Cu^{2+}, Zn^{2+} and Mn^{2+}, as well as Mo of the second transiton series.
3. Those without a known function in plants but that are essential for animals, the most notable example being Co^{2+}.
4. Those without a known biochemical function in plants or animals but which accumulate in the environment. Included with this group are Cd^{2+}, Pb^{2+} and Hg^{2+}, which are introduced into soil as contaminations. Renewed interest in organic matter-metal complexes in soils, sediments, and natural waters has been generated by the nocuous introduction of toxic heavy metals into the environment.

A metal ion in aqueous solution contains attached water molecules oriented in such a way that the negative (oxygen) end of the water dipole is directed towards the positively charged metal ion. A complex arises when water molecules surrounding the metal ion are replaced by other molecules or ions, with the formation of a coordination compound. The organic molecule that combines with the metal ion is commonly referred as the ligand. The order of decreasing affinity of organic groupings for metal ions is as follows:

$$—O— \;>\; —NH_2— \;>\; —N{=}N— \;>\; N \;>\; —COO^- \;>\; —O— \;>\; C{=}O$$

enolate	amine	azo	ring N	carboxylate	ether	carbonyl

Most metal ions can accept more than one pair of electrons and a corresponding number of donor atoms can be coordinated simultaneously. The number of donor atoms held is called the coordinated number of the metal ion.

A chelate complex is formed when two or more coordinate positions about the metal ion are occupied by donor groups of a single ligand to form an internal ring structure. The formation of more than one bond between the metal and the organic molecule usually imparts high stability to the complex.

The reaction between an amino acid and Cu^{2+} to first form a 1:1 chelate complex and then a 2:1 chelate complex is illustrated in Figure 2.11.

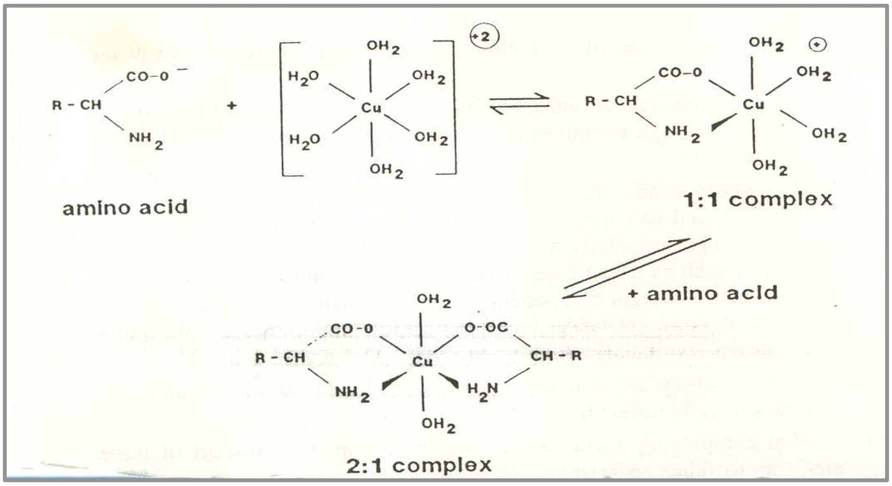


Figure 2.11. Formation of 1:1 and 2:1 Cu^{2+} complexes with an amino acid

The stability of a metal-chelate complex is determined by such factors as the number of atoms that form a bond with the metal ion, the number of rings that are formed, the nature and concentration of metal ions, and pH. The stability sequence for some select divalent cations is as follows:

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$$

Metal ions can be classified into two main classes based on their ability to form a coordinate linkage with specific atoms of the ligand. Class A metal ions are those that form complexes with ligands that contain oxygen as a donor atom, class B metal ions are those that coordinate preferentially with ligands containing N, P, and S donor atoms. The Cu^{2+} ion fits both categories and will thus coordinate with all active groups expected to be present in humic and fulvic acids. The Zn^{2+} ion is an example of a class B metal ion and therefore should from high-energy bonds with any N or S donor groups that might be present (Stevenson, 1994).

2.3 Characteristics of Ferrate(Ⅵ)

2.3.1 Chemical Characteristic

2.3.1.1 Structural characteristic

Potassium ferrate (K_2FeO_4) is the best known member among the family of iron(Ⅵ) derivatives such as $Na_2FeO_4(s)$, $K_2FeO_4(s)$, $Ba_2FeO_4(s)$, and $Ag_2FeO_4(s)$, etc. It is made and purified more easily, and it can also keep its stability under a dry circumstance for a long term (Delaude et al., 1996). Ferrate has the molecular formula, FeO_4^{2-}, and the tetrahedron structure which has a covalent bond between an iron in the center and four oxygens such as Figure 2.12 (Yi, 2002).

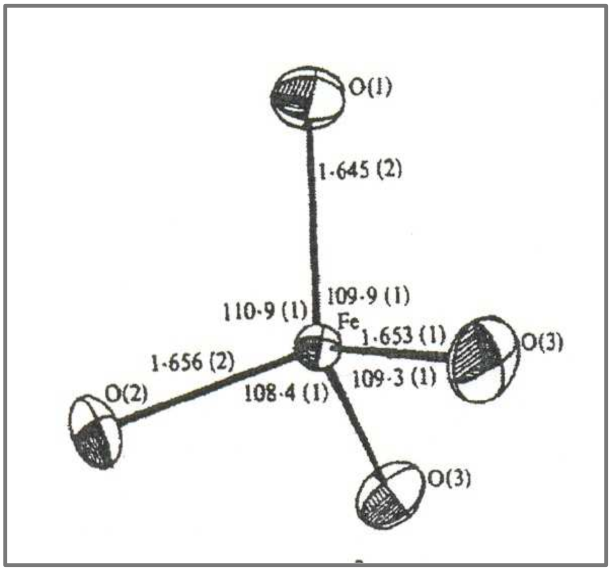


Figure 2.12. Structure of FeO_4^{2-}

2.3.1.2 Speciation of ferrate(Ⅵ) in solution

Ferrate presents the following four species: $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}, depending on pH value in solution as shown in Figure 2.13. And the four species have the pK_a values as follows:

$$H_3FeO_4^+ \rightleftarrows H^+ + H_2FeO_4 \qquad pK_1 = 1.6\pm0.2$$

$$H_2FeO_4 \rightleftarrows H^+ + HFeO_4^- \qquad pK_2 = 3.5$$

$$HFeO_4^- \rightleftarrows H^+ + FeO_4^{2-} \qquad pK_3 = 7.3\pm0.1$$

$HFeO_4^-$ and FeO_4^{2-} are the main species under neutral or alkaline conditions and the species can remain more steady under that conditions (Sharma, 2002).

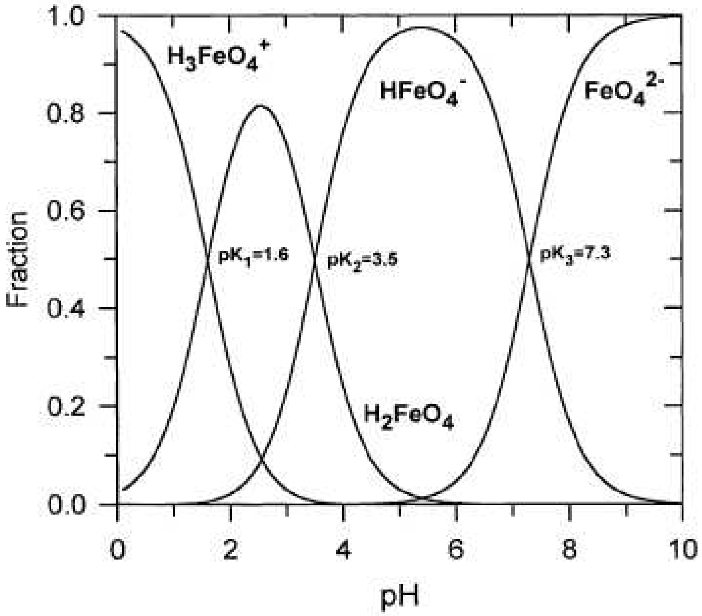


Figure 2.13. Speciation of Fe(Ⅵ) (Sharma, 2002)

2.3.1.3 Comparison of redox potential

Ferrate is a very strong oxidant and coagulant throughout a whole range of pH. In particular the redox potential of ferrate depends on pH: a high redox potential under acidic condition (2.20 V) and low redox potential under alkaline condition (0.7 V).

In acidic media: $FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad E^0 = 2.2\ V$

In basic media: $FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \qquad E^0 = 0.7\ V$

(Wood, 1958)

It means that ferrate acts as a very strong oxidant in acidic solutions and ferrate ion is simultaneously reduced to Fe(Ⅲ) ion or ferric hydroxide which can act as a coagulant (Sharma, 2002; Jiang et al., 2002; Eng et al., 2006).

Table 2.3. Redox potential for the oxidants/disinfectants used in aqueous solutions (Sharma, 2002)

Oxidant	*Acidic medium (E°, V)*	*Basic medium (E°, V)*
Fluorine	3.03	2.23
Hydroxyl Radical	2.80	2.06
Atomic Oxygen	2.42	1.78
Ferrate	***2.20***	***0.70***
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl Radical	1.70	1.25
Permanganate	1.68	1.24
Chlorine Dioxide	1.57	1.15
Chlorine	1.36	1.0
Oxygen	1.20	0.88

2.3.2 *Kinetics and Mechanisms of Ferrate*

Ferrate is decomposed by the reaction between itself (Self-decomposition reaction) as below Eq. (1) as well as the reactions with various compounds in solutions. The reactions show first or second-order kinetics (Carr et al., 1985)

$$\frac{-d[Fe(\mathrm{VI})]}{dt} = K_1[Fe(\mathrm{VI})] + K_2[Fe(\mathrm{VI})][P] \qquad (1)$$

$$\Downarrow \qquad\qquad \Downarrow$$

Self-Reaction   Reaction with Compounds

2.3.2.1 *Self-decomposition reaction*

Self-decomposition reaction consists of the two steps such as below Eq. (2)-(3). Diferrate is firstly formed by the reaction between two ferrate molecules as Eq. (2). And then, the formed diferrate is reduced to Fe^{3+} and produces oxygen through the reaction between the molecules as Eq. (3) (Sharma, 2002).

$$2H_3FeO_4^{+} \rightleftarrows [H_4Fe_2O_7]^{2+} + H_2O \qquad (2)$$

$$[H_4Fe_2O_7]^{2+} + 2H^{+} + 6H_2O \rightarrow Fe_2(OH)_2(H_2O)_8^{4+} + 1.5O_2 \qquad (3)$$

It has been reported that ferrate shows a second-order decomposition depending on its concentration and reaction time in phosphate buffer solution. And Figure 2.14 shows that the self-decomposition rate of ferrate decreases

by increasing alkalinity. It is consistent with the fact that the oxidation power of ferrate decreases under alkaline condition and ferrate remains more steady in alkaline condition (Jiang et al., 2002).

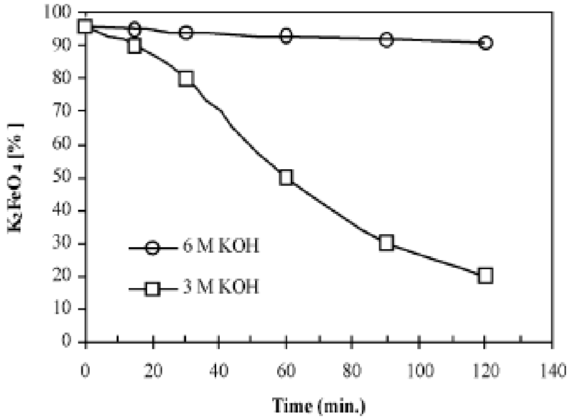


Figure 2.14. Effect of alkalinity on the stability of 0.01 M K_2FeO_4 solution (Jiang et al., 2002)

2.3.2.2 Reactions with contaminants in water

Ferrate reacts very actively with organic/inorganic contaminants containing S or N. As typical examples, the reaction expressions such as Eq. (4), (5), and (6) present the reactions between ferrate and cyanide, hydrogen sulfide, thiourea (Sharma et al., 1997; 1998 a; 1998 b; 1999).

$$2HFeO_4^- + 2HCN + 5/2O_2 + H_2O + 2OH^- \rightarrow 2Fe(OH)_3 + 2HCO_3^- + 2NO_2^- \qquad (4)$$

$$8HFeO_4^- + 3H_2S + 6H_2O \rightarrow 8Fe(OH)_3 + 3SO_4^{2-} + 2OH^- \qquad (5)$$

$$8HFeO_4^- + 3NH_2CSNH_2 + 9H_2O \rightarrow 8Fe(OH)_3 + 3NH_2CONH_2 + 3SO_4^{2-} + 2OH^- \qquad (6)$$

The mechanisms of the reactions between ferrate and organic/inorganic matters can be broken down into the three categories. In general, ferrate is known to allow organic/inorganic matters to be oxidized either by providing oxygen or by taking away electron or hydrogen atom from organic/inorganic matters. The reaction expressions such as Eq. (7), (8), and (9) show the examples of each mechanism. However, additional studies are necessary to prove those mechanisms (Sharma, 2002; Jiang et al., 2002; Carr et al., 1985).

Hydrogen abstraction: $HFeO_4^{2-} + H_2S \rightarrow H_2FeO_4^{-} + HS$ (7)

Direct election transfer: $HFeO_4^{-} + SCN^{-} \rightarrow HFeO_4^{2-} + SCN$ (8)

Oxygen transfer: $HFeO_4^{-} + SO_3^{2-} \rightarrow [HO_3FeO\text{-}SO_3]^{3-} \rightarrow Fe + SO_3^{2-}$ (9)

2.4 Review of Previous Water Treatments using Ferrate

In recent years, it has been actively carried out to apply ferrate for disinfecting microbes, decomposing organic matters, oxidizing inorganic matters, removing humic substances, treating wastewater and sewage sludge. In this section, previous studies on the removal of humic substances and heavy metals among those fields were reviewed.

2.4.1 Removal of Humic Substances

Many researchers have reported that ferrate is greatly effective in the removal of humic acid (HA) and fulvic acid (FA). Jiang and his co-workers have reported that ferrate eliminates UV_{254}-abs and DOC more effectively compared to ferric sulphate (FS) at the same doses. Figure 2.15.a shows that the removal efficiency of UV_{254}-abs by ferrate is 10~15% higher than that by FS at the doses of 8~14 mg/l (as Fe) and pH 6, and Figure 2.15.d shows that the removal efficiency of DOC by ferrate is 20% higher than that by FS at the doses of 4~18 mg/l (as Fe) and pH 8. Besides, ferrate is more effective than ferric sulphate on the removal of Specific UV_{254}-abs (SUVA) (Figure 2.16). These results indicate that ferrate oxidizes or decomposes FA first, and then the decomposed organic matters can be eliminated by coagulation (Jiang et al., 2006 a).

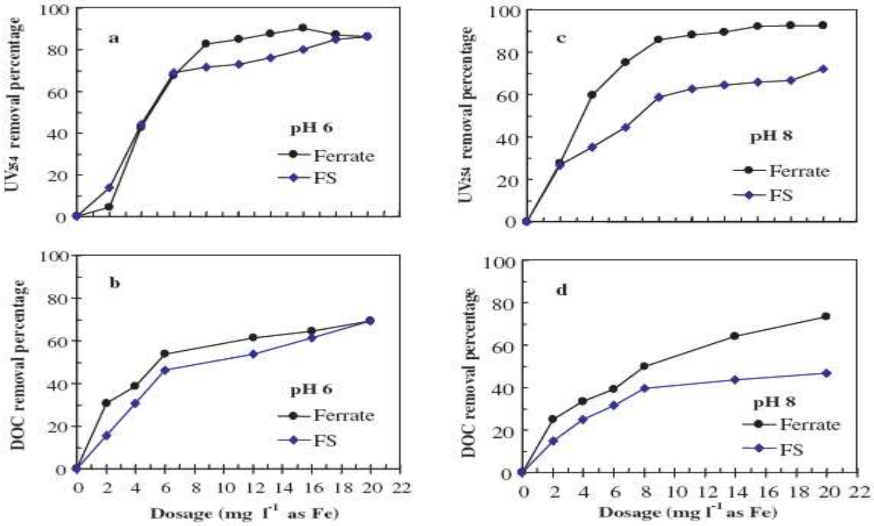


Figure 2.15. Comparative treatment performance for treating fulvic acid model water; (a) UV_{254}-abs removal at pH 6, (b) DOC removal at pH 6, (c) UV_{254}-abs removal at pH 8, and (d) DOC removal at pH 8.

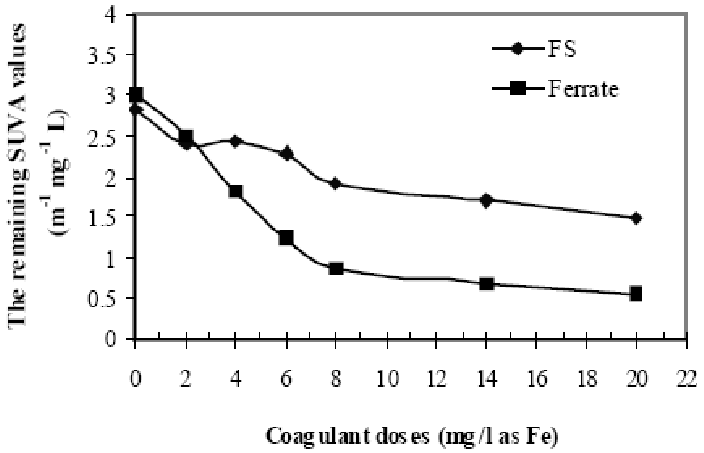


Figure 2.16. Comparative performance of ferrate(Ⅵ) and FS for the treatment of fulvic acid model water with pH 8 (SUVA)

And they also have studied about using ferrate for the treatment of organic matters in real lake water. The removal efficiency of UV_{254}-abs was approximately 60% by a ferrate dose of 4 mg/l at pH 3.5, but the removal efficiency decreased by increasing ferrate doses (more than 4 mg/l). On the other hand, the removal efficiency of UV_{254}-abs showed approximately 40% by the doses from 2 to 8 mg/l at pH 7.5. This result was 10~15% lower efficiency than that at pH 3.5. The maximum turbidity removal (approx. 100%) showed by all doses studied at pH 7.5, while only 40~45% of turbidity removal was achieved at pH 3.5. These results mean that pH has a great effect on turbidity removal by ferrate.

In addition, they reported that the removal efficiency of UV_{254}-abs depended on physicochemical characteristics of water samples. For instance, the removal efficiency of UV_{254}-abs was 83% for treating the upland colored water with a ferrate dose of 1.5 mg/l (as Fe) at pH 5 and 60% for treating the university lake water with a ferrate dose of 4 mg/l (as Fe) at pH 3.5, respectively. This result is consistent with that of the previous studies (Sinsabaugh et al., 1986; Jiang et al., 1994), where the characteristics of the organic matters (size, charge, and solubility) may directly have an affect on the removal efficiency. These researches indicated that the smaller molecular size fraction which the natural organic matter (NOM) consists of, the more difficult it is to remove the NOM by coagulation (Jiang et al., 2001).

2.4.2 Removal of Heavy Metals

The results on the removal of cyanide (Sharma et al., 1997), ammonia (Sharma et al., 1998), hydroxylamines (Johnson et al., 2003), and hydrogen sulphide (Sharma et al., 1997) using ferrate have been reported. It has been revealed that potassium ferrate can also remove heavy metals such as Mn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, and Hg^{2+} with low doses from 10 to 100 mg/l (as K_2FeO_4) by oxidation and coagulation at the same time (Bartzatt, 1992). Arsenic(Ⅲ) oxidation efficiency with ferrate was studied recently (Fan et al., 2002). Under given test conditions, the molar ratio of Fe(Ⅵ) to As(Ⅲ) and the reaction time were found to be important to achieve the high As(Ⅲ) removal efficiency. As(Ⅲ) was oxidized to As(Ⅴ) by ferrate with the molar ratio of 3:2 [As(Ⅲ):Fe(Ⅵ)] (Lee et al., 2003). Arsenic removal tests with river water showed that the arsenic concentration can be lowered from the initial 517 to below 50 ㎍/l with a ferrate dose of minimum 2.0 mg/l.

CHAPTER Ⅲ. MATERIALS AND METHODS

3.1 Experimental Materials

3.1.1 Background

Nakdong river is the longest river in South Korea, which rises from Taebak in Gangwon province and then joins Kumho river around Daegu and runs down to the sea around the west of Busan. However, the big industrial complex built around Nakdong river area in Daegu and Busan was accompanied with water pollution. The most serious water pollution was occurred by phenol drained from the factory in 1999, which had a very severe effect on its function as drinking-water. Since then, the water quality has improved for the third grade by strict policies of the government, and several policies are still being carried out to improve the water quality more highly than now. Nakdong river showed another problem that salty water from the sea entered into the river water due to its short water quantity during dry season near Busan. An artificial estuary dam has been built to solve this problem, whereas it produced new problem that the dam made the water quality bad by blocking the water flow (Figure 3.1) (www.Nakdong.bsbukgu.go.kr; www.nakdong.go.kr).

In the meantime, the ecosystem of Oncheon stream was considerably destroyed by the development thoughtless for the environment. Although the special policy has been carried out to recover its environment including water quality since 1995, most areas still need to be controlled except for some areas where the original natural condition were recovered (Figure 3.2) (www.oncheoncheon.or.kr).

Figure 3.1. Sampling site ①
Nakdong river in Busan

Figure 3.2. Sampling site ②
Oncheon stream in Busan

Figure 3.3. Sampling sites on a map

3.1.2 Sample collection, preservation and analysis

River water sample was collected from Nakdong river, Busan for the period of October and December 2006 for the study. Additionally water sample from Oncheon stream, a representative stream of Busan was also collected to investigate the effect of ferrate for NOM removal. Observationally, the sample collected for the month of December was a dry season and waster samples had much less water quantity and higher turbidity compared to sample collected for the period of October 2006. Samples were collected a plastic container for the capacity of 20 Litter and sealed the container immediately and transferred to the laboratory for preservation. And then, the suspended matters in the waters were eliminated by filtering (0.45 ㎛) and the water samples were being kept in a refrigerator (4 ℃) during carrying out the experiments. The physicochemical characteristics of the water samples were analyzed by UV-Vis spectrophotometer (Shimadzu, UV-1201), Turbidimeter (HACH 2100AN), pH meter (Orion, model 420), IC (Quatum Design, MPMS XL7), TOC Analyzer (Shimadzu, TOC-Vcph), and AAS (Perkin Elmer, AAnalyst 200), as shown in Table 3.1.

Table 3.1. Characteristics of the water samples taken from Nakdong river and Oncheon stream in Busan (ND: Not Detected)

Parameters	Units	Values	
		Nakdong river	Oncheon stream
UV_{254}	mg/l	3.34	2.86
Turbidity	NTU	7.08	4.38
pH		7.65	7.35
TOC	mg/l	5.01	4.76
Anion			
NO_3^-	mg/l	23.07	27.47
NO_2^-	mg/l	ND	ND
Cl^-	mg/l	4473	3026
SO_4^{2-}	mg/l	4845	813.9
Br^-	mg/l	ND	2.58
PO_4^{3-}	mg/l	ND	ND
F^-	mg/l	ND	ND
Metal			
As	mg/l	ND	ND
Cu	mg/l	ND	ND
Mn	mg/l	0.051	0.076
Zn	mg/l	0.040	0.038
Pb	mg/l	ND	ND

3.1.3 Synthesis and Characterization of Potassium Ferrate

Potassium ferrate (K_2FeO_4) was synthesized by the methods of Delaude and Laszlo (1996) and Licht et al. (2001). The solid powder was kept in a desiccator after the synthesis. The characteristic of potassium ferrate (K_2FeO_4) was analyzed by UV-Vis spectrophotometer (Shimadzu, UV-1201), FT-IR (Perkin Elmer, Spectrum GX), XRD (Philips, X'Pert-MPD system), SEM (Hitachi, S-2400) (Licht et al., 2001), and the purity was also determined by the chromite titration (Schreyer et al., 1950; Licht et al., 2001).

The detailed methods of the potassium ferrate (K_2FeO_4) synthesis and the chromite titration were explained below. All experimental instruments made of glass were washed with 5% HNO_3 solution and rinsed with ultra-pure water (Milli-Q) and then, dried in a UV disinfector for the experiments.

3.1.3.1 Synthesis of potassium ferrate (K_2FeO_4)

120 g of KOH ($\geq$ 90%, Aldrich) was dissolved into ultra-pure water (Milli-Q), chilled to below 10 ℃. The Cl_2 was slowly bubbled in an ice bath for more than 90 min at 0 ℃ (The KOH solution was vigorously stirred to saturate the gas). The Cl_2 was generated from the reaction between 53.4 g of $KMnO_4$ (99+%, Aldrich) in a Woulff flask (made by Schott of Duran glass, Germany) with 2 necks and 330 ml of HCl (35%, Merck) in a dropping flask. The five flasks were connected with a neck of the Woulff flask in a low (Figure 3.4). Droplets, HCl and water were removed from the evolved Cl_2

through the flasks connected in series. The first and third flasks were empty to prevent back flow and the second flask contained 200 ml of water to remove HCl in the generated Cl_2. The fourth flask contained 200 ml of H_2SO_4 (95%, Merck) to remove water and the fifth flask contained glass wool to remove droplets. The cleaned Cl_2 reacted with the chilled KOH solution in the sixth flask surrounded by an external ice bath (Figure 3.4). The reaction expressions are as follows:

$$KMnO_4 + 8HCl \rightarrow MnCl_2 \cdot 4H_2O + KCl + \frac{5}{2}Cl_2 \qquad (1)$$

$$2KOH + Cl_2 \rightarrow KClO + KCl + H_2O \qquad (2)$$

Figure 3.4. Experimental equipment for generating Cl_2 and KClO

Further, 180 g of KOH was added into the yellow KClO solution under less than 15 ℃, and the resulting suspension was cooled to 0 ℃. The precipitated KCl was removed by filtration with CF/C (Glass filter paper, Whatman). 75 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Iron nitrate nonahydrate, 98+%, Aldrich) was added into the filtrated KClO solution for an hour and stirred vigorously during the time. Then, the added Fe(Ⅲ) was oxidized into Fe(Ⅵ) in the strong alkaline solution and the color of the solution changed for dark purple. The solution was surrounded by an ice bath for less than 10 ℃ during the addition of Fe(Ⅲ). And the solution was stirred for one more hour additionally at 0 ℃ after all of 75 g of Fe(Ⅲ) had been added. The resulting dark purple slurry was cooled to 0 ℃ again after 120 g of KOH had been added as small portions into the solution, and the precipitate was quickly leached by a course-porosity fritted glass filter (G-1, pore size 100～150 ㎛, made in Germany) connected with a decompression pump. The related reaction expressions are as follows:

$$Fe(NO_3)_3 \cdot 9H_2O + 3OH^- \rightarrow Fe(NO_3) + 9H_2O + 3NO_3^- \qquad (3)$$

$$Fe(NO_3) + \frac{3}{2}ClO^- + 2OH^- \rightarrow FeO_4^{2-} + \frac{3}{2}Cl^- + 5/2H_2O \qquad (4)$$

$$\Downarrow$$

$$Fe(NO_3)_3 \cdot 9H_2O + \frac{3}{2}KClO + 5KOH \rightarrow K_2FeO_4 + \frac{3}{2}KCl + 3KNO_3 + \frac{23}{2}H_2O \qquad (5)$$

This precipitate was washed consecutive six times with 50 ml of the cold 1 M KOH. The precipitate should be washed as much as possible to improve the ferrate yield. The washed filtrate was quickly drawn for each time through the filter into a filtering flask containing 600 ml of the chilled, saturated KOH solution. The solution in the flask was stirred for 20 min at 0 ℃. The precipitate was filtered through a course-porosity fritted glass filter (G-4, pore size 10～16 ㎛, made in Germany) with a suction, and K_2FeO_4 of which the impurities had been removed was obtained.

K_2FeO_4 was washed with 50 ml of n-pentane (99+%, Aldrich) for consecutive four times to remove water in K_2FeO_4. This step is very critical because K_2FeO_4 might be decomposed from the reaction between water and methanol added in the next step if it is not dried thoroughly. Next, K_2FeO_4. was washed with 50 ml of methanol (99.8%, Aldrich) for consecutive four times to remove the remaining n-pentane, and washed with 50 ml of diethyl ether (99.9%, Aldrich) for two times to remove methanol. It was dried under vacuum. K_2FeO_4 dried thoroughly was obtained as a black powder state.

K_2FeO_4 was further purified as follows: The solid K_2FeO_4 was dissolved in 60 ml of the cold 3 M KOH and stirred for 10 min at less than 10 ℃. The precipitate was leached through a course-porosity fritted glass filter (G-4, pore size 10～16 ㎛, made in Germany), and the leached solution was dropped quickly into 125 ml of the chilled, saturated KOH solution. The resulting solution was stirred for 20 min at 0 ℃ and leached with GF/A (Whatman, Glass filter paper). The leached pure material was K_2FeO_4.

As mentioned above, K_2FeO_4. was rinsed again with 50 ml of n-pentane for four times, 50 ml of methanol for four times, 50 ml of diethyl ether for two times in sequence. The product was the stable and homogeneous black powder, which should be stored in a desiccator with P_2O_5.

3.1.3.2 Characterization of potassium ferrate (K_2FeO_4)

K_2FeO_4 was analyzed by UV-Vis spectrophotometer (Shimadzu, UV-1201), FT-IR (Perkin Elmer, Spectrum GX), XRD (Philips, X'Pert-MPD system) and SEM (Hitachi, S-2400), and the results were compared with the references.

For UV/Vis analysis, K_2FeO_4 was dissolved into the strong alkaline solution of over pH 9 (10 M KOH) because it is decomposed into Fe(Ⅲ) in a neutral or acidic solution of less than pH 9. The dissolved K_2FeO_4 was analyzed by UV-Vis spectrophotometer at the wavelengths from 200 to 1000 nm (Li et al., 2005; Licht et al., 2001).

3.1.3.3 Chromite titration

K_2FeO_4 purity can be analyzed by the chromite titration methodology. Fe(Ⅵ) in strong alkaline solution is reduced into Fe(Ⅲ) by the reaction that Cr(Ⅲ) is oxidized to Cr(Ⅵ). Next, Cr(Ⅵ) is reduced into Cr(Ⅲ) by the titration using Fe(Ⅱ), and the Fe(Ⅵ) content is measured by the volume of the decreased Fe(Ⅱ)

$$Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^- \qquad (6)$$

The solutions for the chromite titration were prepared as follows: First, 8.34g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Ammonium iron(Ⅱ) sulfate hexahydrate, 99.9%, Aldrich) was dissolved in 250 ml of ultra-pure water for Fe(Ⅱ) solution. This solution should be prepared just before the titration because Fe(Ⅱ) is oxidized into Fe(Ⅲ) as time goes on. Fe(Ⅱ) was titrated with 0.085 N Cr(Ⅵ) solution for its precise concentration. 1.042 g of $K_2Cr_2O_7$ (Potassium dichromate, 99+%, Aldrich) was dissolved in 250 ml of ultra-pure water for 0.085 N Cr(Ⅵ) solution. An acidic solution was prepared by mixing 25 ml of 0.085 N $K_2Cr_2O_7$ solution with 150 ml of ultra-pure water, 65 ml of 1/5 H_2SO_4, and 15 ml of H_2SO_4/H_3PO_4 solution (80 ml of water + 50 ml of H_3PO_4 + 20 ml of H_2SO_4) all together. Around 7~8 drops of an indicator were dropped into the acidic $K_2Cr_2O_7$ solution. The indicator was prepared by dissolving 0.5 g of sodium diphenylamine 4-sulfonate (Aldrich) in 100 ml of ultra-pure water, which shows dark purple in Cr(Ⅵ) solution and green in Cr(Ⅲ) solution. The precise concentration of Fe(Ⅱ) solution is calculated by the volume of Fe(Ⅱ) needed from the titration between Cr(Ⅵ) solution and Fe(Ⅱ) solution as Eq. (7)

$$N = 0.085 \times 25/V \tag{7}$$

(V = The volume of Fe(Ⅱ) needed for the titration with Cr(Ⅵ), ml)

The synthesized K_2FeO_4 was titrated as follows:

20 ml of concentrated NaOH solution was mixed with 5 ml of Cr(Ⅲ) solution and 5 ml of ultra-pure water, and then the mixed solution was cooled to room temperature in an ice bath (This solution should be prepared just before the titration). The Cr(Ⅲ) solution was prepared by dissolving 8.33 g of $CrCl_3 \cdot 6H_2O$ (Chromium(Ⅲ) chloride hexahydrate, Aldrich) in 100 ml of ultra-pure

water. 150 mg of K_2FeO_4 was added in the solution mixed with the concentrated NaOH solution and the Cr(Ⅲ) solution, and then the solution was stirred until K_2FeO_4 can be dissolved thoroughly (K_2FeO_4 should not remain on the wall of the flask). Next, 100 ml of ultra-pure water, 65 ml of 1/5 H_2SO_4 solution, 15 ml of H_2SO_4/H_3PO_4 solution, and 7~8 drops of the indicator were added in the K_2FeO_4 solution. This solution was titrated by the prepared standard Fe(Ⅱ) solution ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), and K_2FeO_4 purity was calculated by Eq. (8).

$$\%\ \mathrm{K_2FeO_4} = \frac{V\times N\times FW\times 100}{3\times M\times 1000} \tag{8}$$

FW = 198.04 g/mol, 3 = Fe(Ⅱ) equivalent (eq/mol),
M = K_2FeO_4 weight (g), N = Fe(Ⅱ) normality (eq/l),
V = Fe(Ⅱ) volume needed in the titration (ml)

3.2 Experimental Methods

Removal of NOM (Humic acid (HA) and fulvic acid (FA)) and heavy metals (Cu, Mn, and Zn) from the water samples (Nakdong river and Oncheon stream) using ferrate have been investigated.

Water treatment experiments can be greatly classified into the three sections as follows:

1) Removal of NOM using ferrate

2) Removal of heavy metals using ferrate

3) Simultaneous removal of NOM and heavy metals

Every experiment was conducted with various physicochemical factors in detail and also repeated two times for its reproducibility. Potassium ferrate was added in the water samples as a solid powder state for all experiments. The detailed methods of each experiment are explained below.

3.2.1 Removal of NOM using Ferrate

The experiments on the removal of NOM in the real waters taken from Nakdong river and Oncheon stream were performed. NOM is classified into humin, humic acid (HA), and fulvic acid (FA) depending on molecular weight. In this study, HA, a major precursor of THM formation, was a main target and the five experiments were performed depending on various factors between ferrate and HA as follows:

1) Removal efficiency of HA depending on ferrate dose

2) Effect of pH and temperature on the reaction between ferrate and HA

3) Removal efficiency of HA depending on reaction time

4)Comparative removal efficiency of HA by ferrate with traditional coagulants

5) Effect of ferrate preoxidation on HA removal by traditional coagulants

Meanwhile, the following experiments on the removal of FA by ferrate were performed. This results were compared to those of HA removal.

1) Removal efficiency of FA depending on ferrate dose

2) Effect of pH and temperature on the reaction between ferrate and FA

3.2.1.1 Humic acid (HA) removal

Two HA samples were prepared by adding a commercial HA (Fluka) in both Nakdong river water and Oncheon stream water for approximately 10 mg/l of natural organic matter. This concentration of natural organic matter generally shows in most drinking-water treatment plants.

0.5 g of the HA was added in every 1 ℓ of each water sample and the solutions were mixed for approximately 24 hr at 250 rpm and 20 ℃ because HA dose not saturate readily in natural water. Next, the solutions were diluted with each water sample for a concentration of approximately 10 mg/l. The mixed solutions were equally divided into each 100 ml in 250 ml flasks.

HA concentrations in the solutions were measured by UV_{254}. Stock solutions were prepared as follows: The solid HA was dissolved in 1 M NaOH solution for a precise 500 mg/l because HA has high solubility in alkaline solution. Next, the solution was diluted with ultra-pure water for the standard solutions of 5, 10, and 15 mg/l, and an absorbance of each standard solution was measured with UV_{254} (Nam et al., 2003).

1) Removal efficiency of HA depending on ferrate dose

Ferrate was added in each 100 ml of the water samples mixed with HA, and the solutions were rapidly mixed for 1 min at 300 rpm and 20 ℃, and then allowed to flocculate for 20 min at 35 rpm. The ferrate doses ranged from 2 to 46 mg/l (as Fe). Next, $Na_2SO_3 \cdot 7H_2O$ (sodium sulfite) was added with a rapid mixing for 2 min at 300 rpm to reduce the residual ferrate and stop the reaction. Then, $Na_2SO_3 \cdot 7H_2O$ (Sodium sulfite) dose was determined by the molar ratio between Na_2SO_3 and K_2FeO_4 as shown in Eq. (9).

$$3SO_3^{2-} + 2FeO_4^{2-} + 5H^{+} \rightarrow 3SO_4^{2-} + 2Fe^{3+} + 5OH^{-} \qquad (9)$$

The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were tested with UV_{254} and TOC analyzer.

2) Effect of pH and temperature on the reaction between ferrate and HA

Only Nakdong river sample mixed with HA was used for all following experiments including this experiment. For the experiment on pH effect, the water pHs were adjusted to both 3 using HCl and 11 using NaOH, and the other was the same as natural water (7.8±0.2). The temperature of every reaction was 20℃ then. On the other hand, the temperatures studied in the experiment on temperature effect were 10, 20, and 30 ℃, and the water pH was the same as the natural condition without special adjustment (7.8±0.2).

Ferrate 30 mg/l (as Fe) was added in each water sample whose pH and temperature were adjusted, including both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm and 20 ℃ (Then, the ferrate dose was determined by the previous experiment on the removal efficiency of HA depending on ferrate dose). Next, $Na_2SO_3 \cdot 7H_2O$ (sodium sulfite) was added with a rapid mixing for 2 min at 300 rpm and 20 ℃ to stop the reaction. The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with UV_{254}.

3) Removal efficiency of HA depending on reaction time

Ferrate was added in Nakdong river water mixed with HA, including mixing for the periods varied from 10 to 180 sec at the three doses of ferrate such as 10, 20, and 30 mg/l (as Fe). After reacting during each period, $Na_2SO_3 \cdot 7H_2O$ (sodium sulfite) was added with mixing for 2 min at 300 rpm to stop the reaction. The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with UV_{254}.

4) Comparative removal efficiency of HA by ferrate with traditional coagulants

The removal efficiency of HA by ferrate was compared with that by traditional coagulants. $Al_2(SO_4)_3 \cdot 18H_2O$ (aluminum sulfate), $FeSO_4 \cdot 7H_2O$ (Ferrous sulfate) and FeO(OH) (Iron(Ⅲ) hydroxide) generally used in drinking-water and sewage treatments, were selected among traditional coagulants. Especially, FeO(OH) was selected to investigate a coagulating effect of Fe(Ⅲ), a by-product of ferrate. Each coagulant was added in 100 ml of the water sample with both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm. Then, the coagulant doses ranged from 2 to 40 mg/l (as Fe(VI), Al, Fe(II), and Fe(III)). The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with UV_{254}.

5) Effect of ferrate preoxidation on HA removal by traditional coagulants

First, the water sample was pretreated by 0, 2, and 4 mg/l (as Fe) of ferrate, respectively. Next, the solutions were treated by $Al_2(SO_4)_3 \cdot 18H_2O$ (alum) from 1 to 6 mg/l (as Al) and $FeSO_4 \cdot 7H_2O$ from 2 to 18 mg/l (as Fe(Ⅱ)), including both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm and 20 ℃. The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with UV_{254}. The dose ranges were determined by the previous experiment.

3.2.1.2 Fulvic acid (FA) removal

Two FA samples were prepared by adding a commercial FA (IHSS) in both Nakdong river water and Oncheon stream water for approximately 10 mg/l of natural organic matter. This concentration of natural organic matter generally shows in most drinking-water treatment plants. 10 mg of the solid FA was added in every 1ℓ of each water sample and then the solutions were used immediately because FA was dissolved readily in natural water.

FA concentrations in the solutions were measured by UV_{254}. The stock solutions were prepared as follows: The solid FA was dissolved in ultra-pure water for a concentration of 500 mg/l. Next, the solution was diluted with ultra-pure water for the standard solutions of 5, 10, and 15 mg/l, and an absorbance of each standard solution was measured with UV_{254}.

The two detailed experiments on FA removal were carried out. The experimental methods are same as those on HA removal explained above.

1) Removal efficiency of FA depending on ferrate dose

2) Effect of pH and temperature on the reaction between ferrate and FA

3.2.2 Removal of Heavy Metals using Ferrate

3.2.2.1 Removal efficiency of heavy metals depending on ferrate dose

Each 0.1 mM solution of Cu, Mn, and Zn was prepared by adding the heavy metal compounds such as $Cu(NO_3)_2$ (Copper(Ⅱ) nitrate), $Mn(NO_3)_2$ (Manganese nitrate), and $Zn(NO_3)_2$ (Zinc nitrate) separately into ultra-pure water. Ferrate was added in every 100 ml of each water sample with both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm and 20 ℃. Then, the ferrate doses ranged from 0.03 to 0.7 mM. The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with AAS (Perkin Elmer, AAnalyst 200).

On the other hand, removal efficiencies of heavy metals in a water sample mixed with various heavy metals were evaluated by ferrate. The three heavy metal compounds were mixed in 1ℓ of ultra-pure water all together. Then, the heavy metals had a concentration of 0.1 mM for 1ℓ solution. The reaction conditions including a range of ferrate doses are same as mentioned in the experiment on HA removal.

3.2.2.2 Effect of pH and temperature on the reaction between ferrate and Heavy metal

Each 0.1 mM solution of Cu, Mn, and Zn was prepared. pH of each sample was adjusted to both 3 using HCl and 11 using NaOH, and the other was pH of the ultra-pure water without special adjustment (approx. 6). Then, the temperature of the reactions was 20 ℃. On the other hand, the temperatures studied in the experiment on temperature effect were 10, 20, and 30 ℃, and the sample pH was not adjusted.

Ferrate 0.1 mM (as Fe) was added in each sample whose pH and temperature were adjusted, including both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm and 20 ℃ (Then, the ferrate dose was determined from the previous experiment on the removal efficiency of heavy metals depending on ferrate dose).

3.2.3 Simultaneous Removal of NOM and Heavy Metals

This experiments are classified into the two sections such as simultaneous removal HA and heavy metals, simultaneous removal FA and heavy metals. Cu, Mn, and Zn were selected among heavy metals same as the previous experiment. The detailed experiments in this section are explained below.

3.2.4.1 Simultaneous removal of HA and heavy metals

Prepared water samples are greatly classified into the two types. In the frist one, Nakdong river sample is mixed with both HA (Fluka) and one among Cu, Mn, and Zn. In the second one, Nakdong river sample is mixed with both HA and all of the three heavy metals. Then, each heavy metal compound of a solid state was added in 1ℓ of Nakdong river water mixed with HA 10 mg/l for a concentration of 0.1 mM. The prepared mixtures are namely: 1) HA+Cu, 2) HA+Mn, 3) HA+Zn, and 4) HA+Cu+Mn+Zn

Ferrate was added in every 100 ml of each mixture at different doses from 0.03 to 0.7 mM with both a rapid mixing for 1 min at 300 rpm and 20 ℃, and a slow mixing for 20 min at 35 rpm and 20 ℃. The resulting solutions were filtrated with 0.45 ㎛ pore size nylon membrane filter and the filtrates were analyzed with UV_{254}. and AAS.

3.2.4.2 Simultaneous removal of FA and heavy metals

The experiments were conducted by adding various doses of ferrate in a mixture of FA (IHSS) and one among Cu, Mn, and Zn, and also in a mixture of FA and all of the heavy metals. The detailed methods are same as those mentioned in 3.2.4.1. The prepared mixtures are namely:
1) FA+Cu, 2) FA+Mn, 3) FA+Zn, and 4) FA+Cu+Mn+Zn

CHAPTER Ⅳ. RESULTS AND DISCUSSIONS

4.1 Synthesis and Characterization of Potassium Ferrate(Ⅵ)

Potassium ferrate, a black-purple powder, was synthesized by the methods of Delaude and Laszlo (1996) and Licht et al. (2001) as shown in Figure 4.1. It was very essential to maintain the appointed temperature and time in every reaction, and they had great effects on the yield of ferrate. The black-purple ferrate readily changed into some brown material if its wet state was exposed to air for a long time during its synthesis. It is thus important to minimize the period of every filtration. The yield and purity of potassium ferrate were determined immediately after its synthesis, and the particular peaks of ferrate were verified by several experimental instruments.

The yield, ranging from 48 to 53%, was calculated by the molar ratio of the synthesized K_2FeO_4 to the added $Fe(NO_3)_3 \cdot 9H_2O$. The purity, ranging from 93 to 96%, was also obtained by the chromite method in which the color change from purple to green indicated an end point.

Potassium ferrate was analyzed by UV/Vis, FT-IR, and XRD, and the results were compared with those shown in the references (Licht et al., 2001; Li et al., 2005). Figure 4.2 shows a particular peak of ferrate at 505 nm by UV/Vis spectrum and Figure 4.3 shows a peak at 800 cm^{-1} by FT-IR spectrum, and also Figure 4.4 shows XRD spectrum of potassium ferrate.

These results are consistent with those reported in the references. The results demonstrate that the synthesized black-purple material is potassium ferrate. Figure 4.5 shows a result analyzed by SEM.

Figure 4.1. The synthesized potassium ferrate; black-purple powder

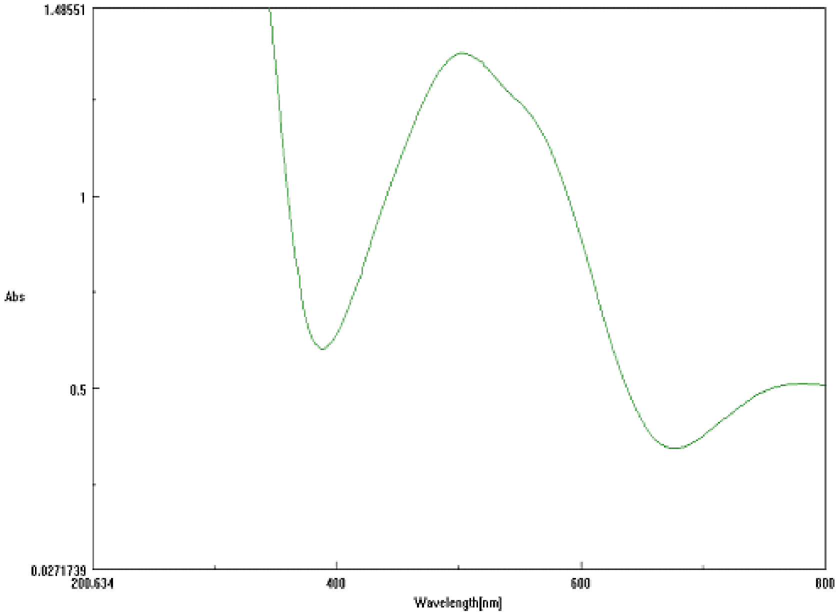


Figure 4.2. UV/Vis spectrum of potassium ferrate in 10M KOH solution (200~800nm ; a peak at 505nm)

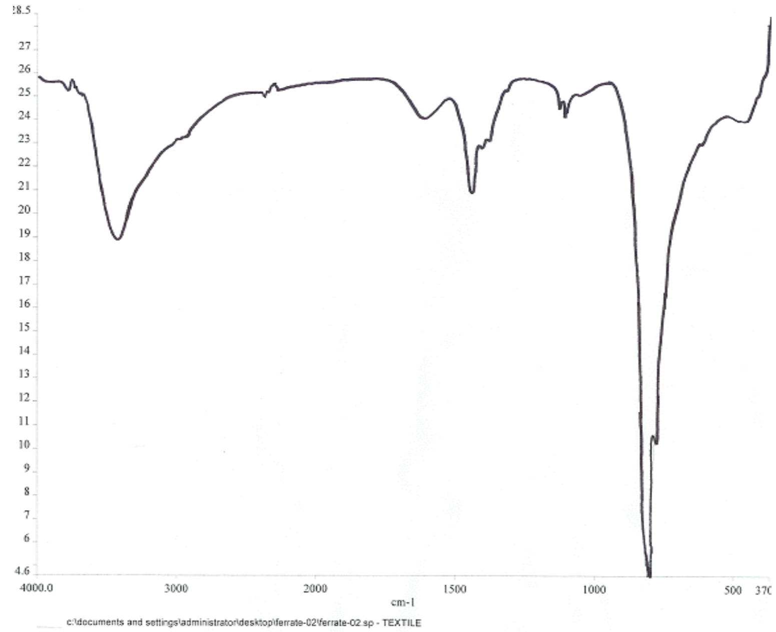


Figure 4.3. FT-IR spectrum of potassium ferrate (300~4000 cm^{-1}; a peak at 800 cm^{-1})

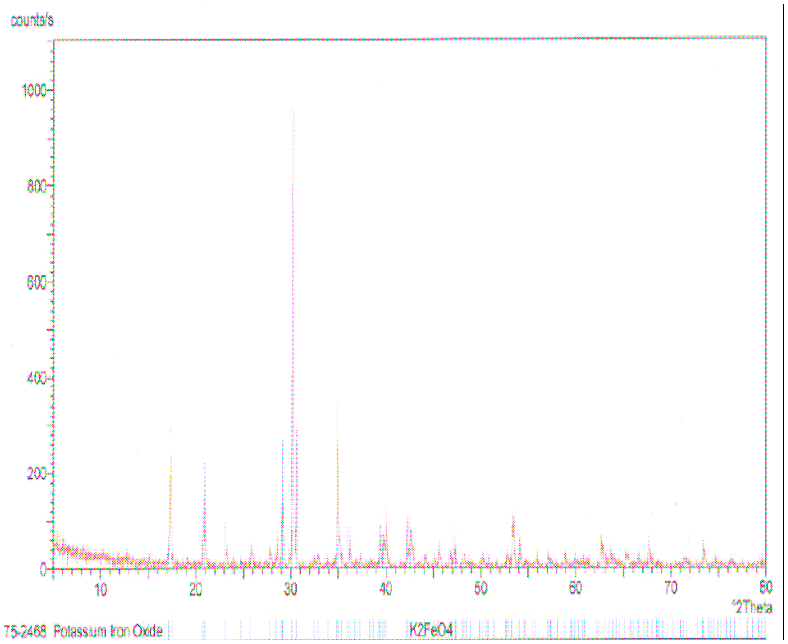


Figure 4.4. XRD spectrum of potassium ferrate

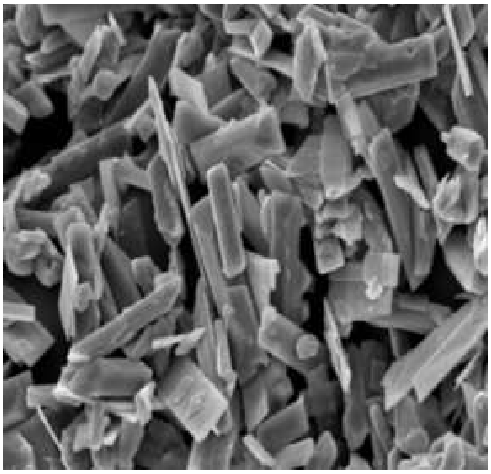


Figure 4.5. SEM image of potassium ferrate

4.2 Removal of NOM using Ferrate

4.2.1 HA Removal

4.2.1.1 Removal efficiency of HA depending on ferrate dose

The purple ferrate was changed into brown materials by reacting with HA in the water samples. This phenomenon indicates that ferrate(Ⅵ) is reduced into Fe(Ⅲ). The water samples containing HA became colorless and transparent from yellow color as most HA had been removed by ferrate. pHs of the water samples treated by ferrate increased in proportion to ferrate dose (2~46 mg/l as Fe) as shown in Table 4.1. pH of the water sample was increased because of OH^- ion, which was produced by the reduction of ferrate in water as shown in Eq. (1).

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe^{3+} + \frac{3}{2}O_2 + 10OH^- \qquad (1)$$

(Eng et al., 2006)

The removal efficiencies of HA analyzed by UV_{254} ranged from 20.7 to 73.6% for the Nakdong river sample and from 25.6 to 72.7% for the Oncheon stream sample. This result shows that ferrate is effective on HA removal (Figure 4.6).

It has been reported that ferrate(Ⅵ) reduces to Fe(Ⅲ) and produces oxygen with the reaction between one ferrate molecule and another ferrate molecule in water (Self-decomposition reaction) as shown in below Eq. (2), (3) and (4). This also allows contaminants to be oxidized in the reactions between ferrate and contaminants (Carr et al., 1985; Sharma, 2000).

$$FeO_4^{2-} + H_2O \rightarrow HFeO_4^{-} + OH^{-} \quad (2)$$

$$HFeO_4^{-} + FeO_4^{2-} \rightarrow Fe_2O_7^{2-} + OH^{-} \quad (3)$$

$$Fe_2O_7^{2-} + 2H_2O \rightarrow O_2 + H_2FeO_4^{-} + H_2FeO_3^{-} \quad (4)$$

(Sharma, 2000)

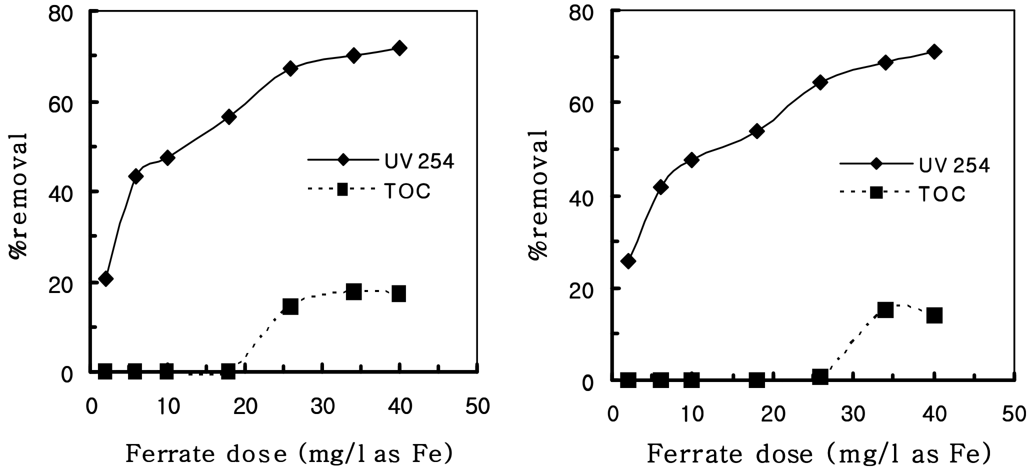
While the mechanism between ferrate and HA is not completely understood, the characteristic of ferrate described above suggests that HA can be oxidized or decomposed by oxygen produced by the self-decomposition reaction between ferrate molecules or by the direct reaction between HA and ferrate.

HA consists of carboxyl groups with a pK_a value of 4.5 and phenolic hydroxyl groups with a pK_a value of 8.0 on aromatic rings. Only some phenolic hydroxyl groups are ionized at the pH value of natural water (approx. 7.8), whereas most carboxyl groups are ionized at that pH value and exist as anions (George, 1985; Stevenson, 1994). Therefore, the ionized functional groups of HA can combine with Fe(Ⅲ) cations produced by the reduction of ferrate or adsorb on the surface of $Fe(OH)_3$.

On the other hand, any removal efficiency of HA by TOC analyzer was not observed at a range of ferrate doses between 2 and 18 mg/l (as Fe) in both the Nakdong river and the Oncheon stream samples. However, the removal efficiencies were from 14.3 to 17.5% for the Nakdong river sample and from 0.9 to 14.2% for the Oncheon stream sample at greater ferrate doses ranging from 18 to 40 mg/l (as Fe) (Figure 4.6). This suggests that ferrate can break carbon bonds which absorb UV at 254 nm but cannot thoroughly decompose organic carbons into inorganic carbons and waters.

Table 4.1. pH change of the solutions by the addition of various ferrate doses

Ferrate dose (mg/l as Fe)		0	2	6	10	18	26	34	40	46
Nakdong river sample	pH	7.87	7.91	8.36	8.63	9.27	9.44	9.66	9.83	9.98
Oncheon stream sample	pH	7.61	7.83	8.15	8.53	8.95	9.29	9.52	9.76	9.87



(a) Nakdong river sample

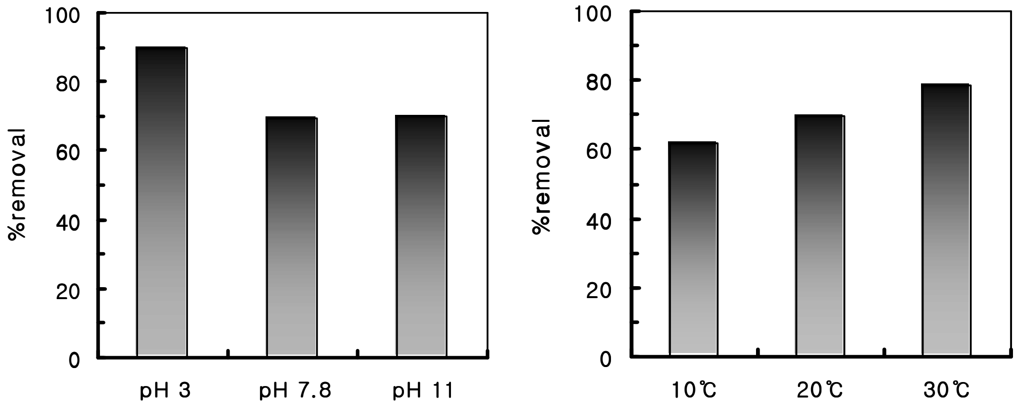
(b) Oncheon stream sample

Figure 4.6. Removal efficiencies of HA depending on ferrate dose at UV_{254} and TOC analysis

4.2.1.2 Effect of pH and temperature on the reaction between ferrate and HA

The removal efficiency of HA at pH 3 was higher than that both at pH 7.8 (natural water) and pH 11 (Figure 4.7). This is consistent with the observation that ferrate(Ⅵ) is reduced into Fe(Ⅲ) and produces oxygen with a stronger oxidation power in acidic conditions, and this has also been reported in other studies (Sharma and Bielski, 1991; Sharma et al., 2000; Sharma, 2002; Cho et al., 2006).

On the other hand, the removal efficiency of HA increased with the greater reaction temperature (Figure 4.7). This result indicates that the reaction between HA and ferrate is endothermic and accelerated by external heat, which is consistent with the results of Sharma et al. (1997, 1999, 2000) in which they reported that temperature has an effect on the reactions between ferrate and hydrogen sulfide, thiourea, thioacetamide.



(a) pH effect (b) Temperature effect

Figure 4.7. Effect of pH and temperature on HA removal by 30 mg/l (as Fe) ferrate at UV_{254}

4.2.1.3 Removal efficiency of HA depending on reaction time

When HA solutions of 10 mg/l were mixed for various periods from 10 to 180 sec with three such ferrate doses of 10, 20, and 30 mg/l (as Fe), HA concentration in the solution decreased gradually from an initial time to 60 sec and then reached a steady state after 60 sec, indicating a high reaction rate (Figure 4.8.a). This high reaction rate can be an important factor for decreasing water treatment period in practical process.

The reaction rate of HA removal with ferrate can be expressed as Eq. (5):

$$-\frac{d[ferrate]}{dt} = -\frac{d[HA]}{dt} = k[\mathrm{ferrate}]^{m}[\mathrm{HA}]^{n} \qquad (5)$$

where [ferrate] = concentration of ferrate (mg/l as Fe)
[HA] = concentration of HA (mg/l)
t = reaction time (s) *m, n* = orders of the reaction
k = reaction rate constant (s^{-1})

Equation (5) above can be re-written as Eq. (6) and (7) with respect to the concentration changes of HA and reaction time.

$$-\frac{d[HA]}{dt} = k_1[\mathrm{HA}]^{n} \qquad (6)$$

$$\ln\frac{[HA]_t}{[HA]_0} = -k_1 \cdot \mathrm{t} \qquad (7)$$

where $[HA]_0$ = initial concentration of humic acid (mg/l)
$[HA]_t$ = concentration of humic acid on a time, t (s)
k_1 = $k[\mathrm{ferrate}]^{m}$ = reaction rate constant (s^{-1})

The decrease rate of HA by ferrate was linear on a semi-log graph with the high correlation coefficients (r^2 = 0.9976, 0.9950, 0.9837, respectively), which was studied at the three ferrate doses depending on reaction time (Figure 4.8.b). This indicates that the reaction is first-order with respect to reaction time. The removal efficiency of HA also increased with greater ferrate dose since the higher molecular concentration accelerates the motion between their molecules. The direct proportionality of k_1 to ferrate dose suggests that the reaction is first-order with respect to ferrate dose (r^2 = 0.9993) (Figure 4.8.c)

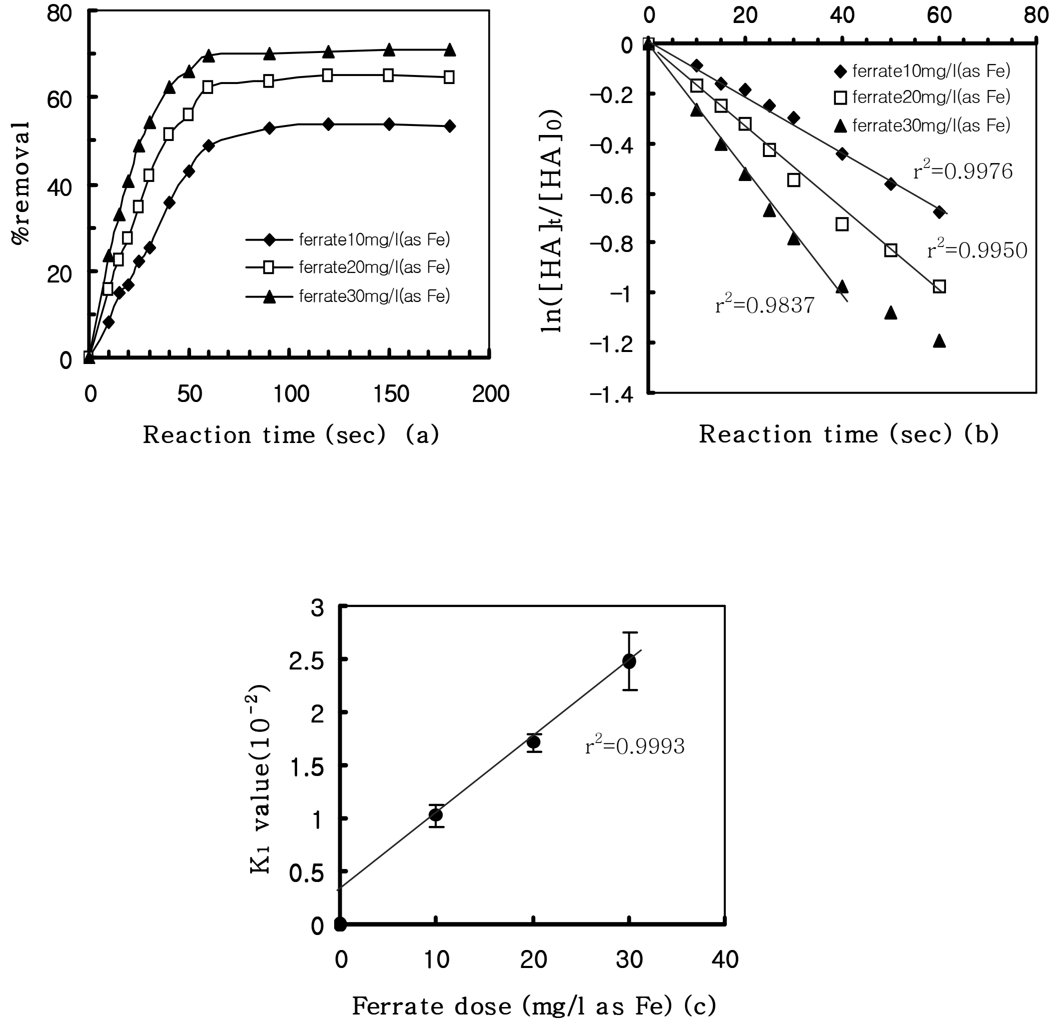


Figure 4.8. Kinetics of the reaction between ferrate and HA

(a) Removal efficiencies of HA depending on reaction time at UV_{254}

(b) Linear relationship between decrease of [HA] and time

(c) Linear relationship between K_1 and ferrate dose

4.2.1.4 Comparative removal efficiency of HA by ferrate with traditional coagulants

Figure 4.9 shows the removal efficiency of HA by ferrate with respect to using traditional coagulants. The removal efficiencies ranged from 21.7 to 76.0% by using ferrate, from 13.4 to 55.3% by using $FeSO_4 \cdot 7H_2O$, and from 13.2 to 15.9% by using FeO(OH), respectively.

It is remarkable that ferrate shows a much greater efficiency than FeO(OH), a coagulant of trivalent iron. This suggests that either ferrate improves the coagulating effect of HA by oxidizing HA and reducing itself, or the coagulating effect of Fe(Ⅲ) produced by the reduction of ferrate (as discussed in Section 4.2.1.1) may be superior to that of FeO(OH).

And the result with $FeSO_4 \cdot 7H_2O$ was consistent with the previous study of Jiang et al. (2006). In their study, ferrate showed a higher efficiency than $FeSO_4 \cdot 7H_2O$ in the removal of fulvic acid because of its dual function (oxidation/coagulation).

On the other hand, alum showed a particular efficient phase depending on its dose. It showed a higher efficiency (55.7～70.4%) than ferrate (21.7～46.5%) at a range of low doses from 2 to 6 mg/l (as Al), but its efficiency gradually decreased with doses more than 6 mg/l (as Al). Alum is considered as an economical coagulant since it has higher removal efficiencies with the lower dose compared to ferrate. It, however, shows demerits as its efficiency decreases at higher doses and as it produces more sludge than ferrate. Also, alum acts only as a coagulant, while ferrate acts as an oxidant and disinfectant as well as a coagulant. It is therefore suggested that ferrate can be an alternative chemical to traditional coagulants.

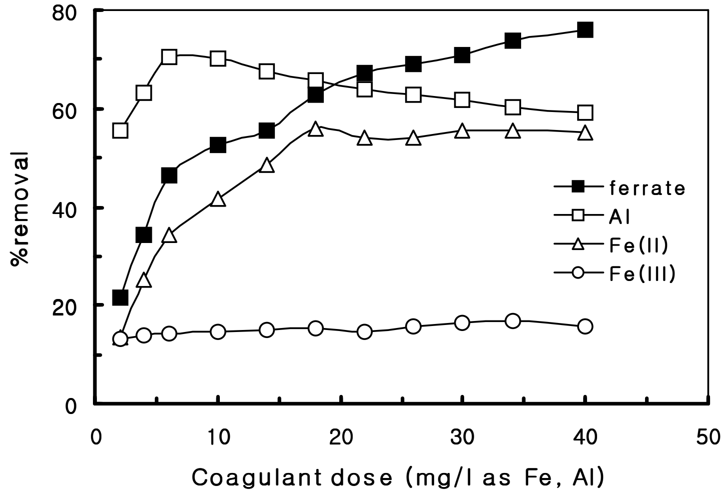


Figure 4.9. Removal efficiencies of HA by various coagulants at UV_{254}

4.2.1.5 Effect of ferrate preoxidation in HA removal by traditional coagulants

In this study, the HA water sample was treated by the traditional coagulants such as alum and Fe(Ⅱ) after preoxidizing HA with two small doses of ferrate.

The removal efficiency of HA ranged from 49.6 to 72.1% at alum doses from 1 to 6 mg/l (as Al) without preoxidizing HA with ferrate, while it ranged from 58.6 to 78.7% after preoxidizing HA with 2 mg/l (as Fe) ferrate and from 66.2 to 80.0% after preoxidizing HA with 4 mg/l (as Fe) ferrate.

The removal efficiency of HA was also improved by adding Fe(Ⅱ) after preoxidizing HA with ferrate. Without preoxidizing HA with ferrate, the removal efficiency of HA ranged from 13.8 to 59.3% at Fe(Ⅱ) doses from 2 to 18 mg/l (as Fe), and from 33.3 to 65.1% in case of preoxidizing HA with 2 mg/l (as Fe) ferrate, and from 45.1 to 76.0% in case of preoxidizing HA with 4 mg/l (as Fe) ferrate at the same Fe(Ⅱ) doses (Figure 4.10).

Preoxidizing HA with small ferrate doses allows the coagulating effect of HA to improve and reduces the necessary doses of traditional coagulants. Also, using lower doses of chemicals would reduce accompanying sludge production and treatment costs.

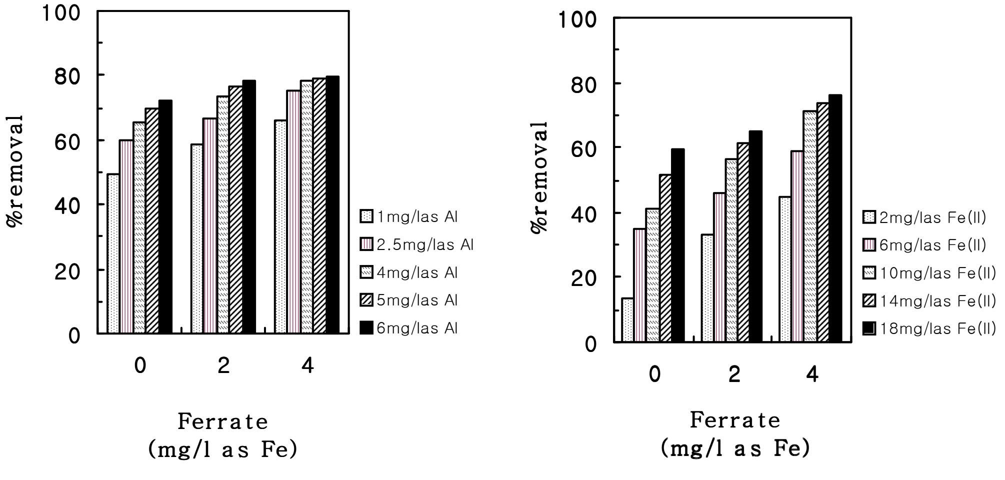


Figure 4.10. Removal efficiencies of HA by traditional coagulants after HA preoxidation by ferrate at UV_{254}

4.2.2 FA Removal

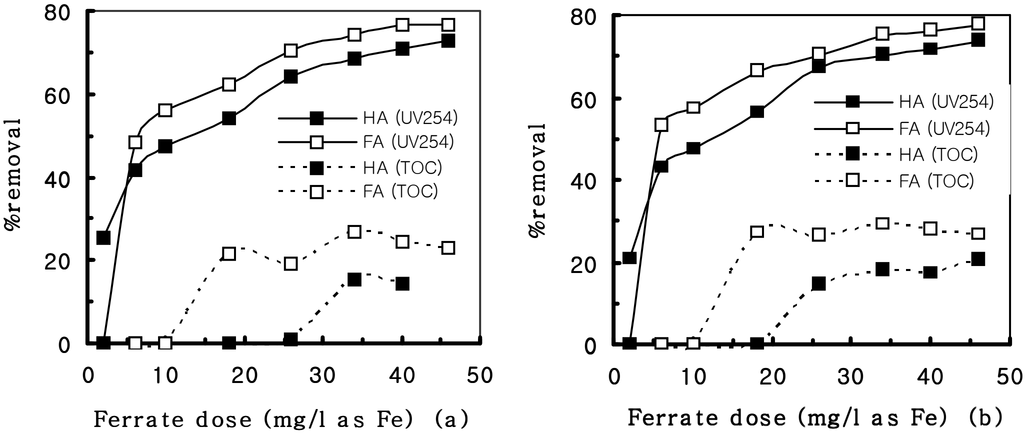
4.2.2.1 Removal efficiency of FA depending on ferrate dose

Figure 4.11 shows the results of treating the Nakdong river and the Oncheon river samples mixed with FA using ferrate doses from 2 to 46 mg/l (as Fe), which are analyzed by UV_{254} and TOC, and compared with the results of HA shown above.

The water samples containing FA became colorless and transparent from yellow color as most FA had been removed by ferrate, same as that shown in the experiment of HA removal. pHs of the water samples treated by ferrate increased in proportion to ferrate doses (2~46 mg/l as Fe). The removal efficiencies of FA were measured to be ranging from 52.6 to 77.5% for the Nakdong river sample and from 48.2 to 76.8% for the Oncheon stream sample by UV_{254} analysis. This result is higher than that of HA (20.7~73.6% for the Nakdong river sample, 25.6~72.7% for the Oncheon stream sample). On the other hand, the removal efficiencies of FA were 0~26.6% for the Nakdong river sample and 0~23.0% for the Oncheon stream sample by TOC analysis. This result is also higher than that of HA.

As mentioned in the section of literature review, FA has a smaller molecular weight (FA: 1000~5000, HA: 10,000~100,000) and carbon content than HA (FA: 40.7~50.6%, HA: 53.8~58.7%), but the larger oxygen content than HA (FA: 39.7~49.8%, HA: 32.8~38.3%) (Stevenson, 1994). These structural characteristics of FA molecule suggest the following two reasons explaining the higher removal efficiency of FA than that of HA at UV_{254} analysis. The frist reason is the carbon bonds in FA can be more easily broken than those in HA. As for the second reason, FA has more COOH groups and OH groups compared to HA, and the ionized COO^- and O^- can be removed by combining them with Fe^{3+} produced from ferrate.

On the other hand, the reason why the removal efficiency of FA by TOC analysis is relatively lower than that by UV_{254} is the same as that explained in 4.2.1.1.



(a) Nakdong river sample (b) Oncheon stream sample

Figure 4.11. Removal efficiencies of NOM depending on ferrate dose at UV_{254} and TOC analysis

4.2.2.2 Effect of pH and temperature on the reaction between ferrate and FA

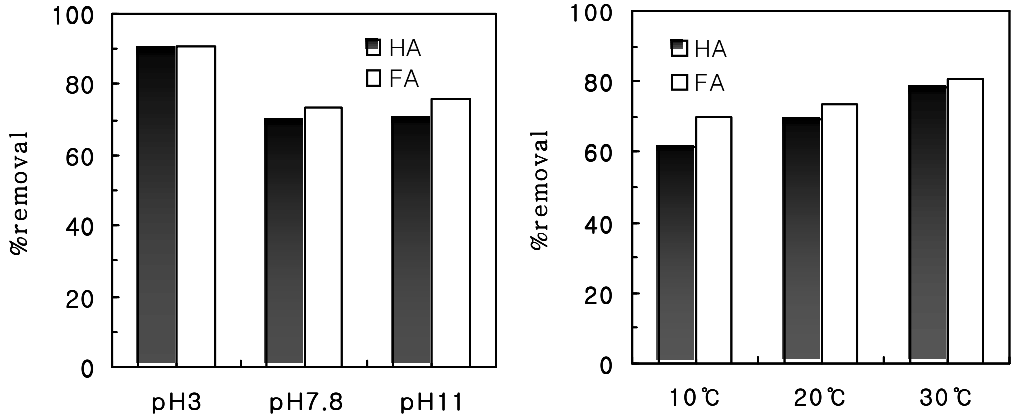
Figure 4.12 presents the removal efficiencies of FA depending on pH and temperature as compared with those of HA. The removal efficiencies of both HA and FA in acidic conditions were much higher than those in alkaline conditions, and the reason of this result is the same as that mentioned in 4.2.1.2. However, the removal efficiencies of HA and FA did not show any remarkable difference between pH 7.8 and pH 11. Table 4.3 shows the pH changes of the solutions in which ferrate reacted with HA or FA. pH increased in all of the solutions after adding ferrate, and especially, the solution with an initial pH value of 3 showed the greatest pH change compared to others. The reason of this is ferrate, which has a higher redox potential in acidic conditions as shown in Eq. (8)-(9), can produce Fe(Ⅲ) and H_2O more rapidly at pH 3 than at other pH values (Sharma et al., 2006).

In acidic media: $FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3} + 4H_2O \quad E^0 = 2.2V \quad (8)$

In basic media: $FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \quad E^0 = 0.7V \quad (9)$

(Wood, 1958)

Meanwhile, the removal efficiencies of both HA and FA increased with greater reaction temperature. The reactions between FA and ferrate as well as between HA and ferrate were endothermic, and external heat can make the reaction between ferrate and NOM molecule more active.



(a) pH effect

(b) Temperature effect

Figure 4.12. Effect of pH and temperature on NOM removal by 30 mg/l (as Fe) ferrate at UV_{254}

Table 4.3. pH change of the solutions by the addition of ferrate

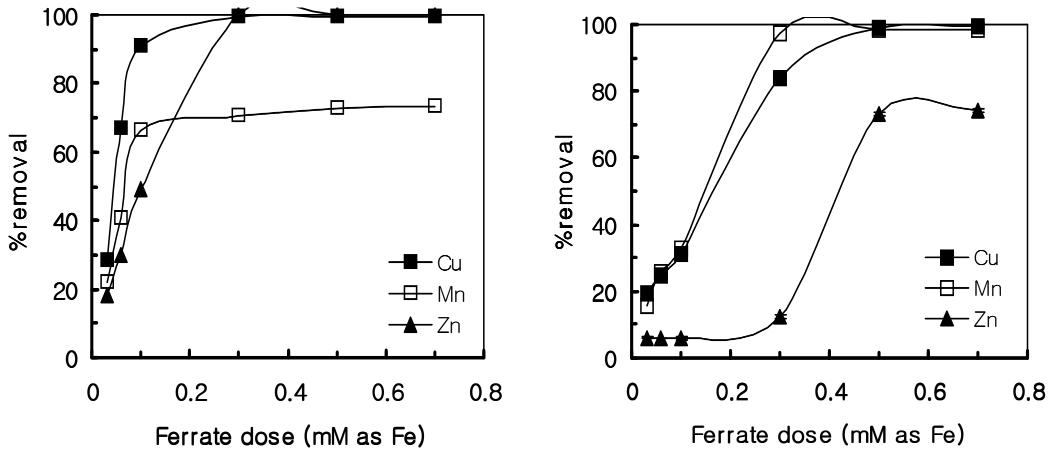
HA	Initial pH values	3.05	7.78	11.32
	Increased pH values by 30 mg/l ferrate	6.08	8.76	11.79
FA	Initial pH values	3.11	7.72	10.96
	Increased pH values by 30 mg/l ferrate	6.73	8.38	11.62

4.3 Removal of Heavy Metals using Ferrate

4.3.1 Removal Efficiency of Heavy Metals depending on Ferrate Dose

Ferrate shows a great efficiency on the removal of heavy metals. Specifically, the removal efficiencies of heavy metals ranged from 28.3 to 99.3% for 0.1 mM Cu, from 21.8 to 73.2% for 0.1 mM Mn, and from 18.3 to 99.8% for 0.1 mM Zn at a range of ferrate doses between 0.03 and 0.7 mM (Figure 4.13.a). The removal efficiencies of each heavy metal were low in treating a mixture of all of the three heavy metals with small ferrate doses from 0.03 to 0.1 mM, compared with the treatment of single heavy metal. However, the removal efficiencies improved with ferrate doses more than 0.3 mM (Fig. 4.13.b; Cu: 19.4~99.6%, Mn: 15.4~98.3%, Zn: 6.0~74.1%).

The removal of heavy metals by ferrate can be described with the following two mechanisms. Ferrate presents the following four species; $H_3FeO_4^+$, H_2FeO_4 (pK_a=1.6), $HFeO_4^-$ (pK_a=3.5), and FeO_4^{2-} (pK_a=7.3) depending on the pH value of the solutions. In particular, ferrate exists as $HFeO_4^-$ in water with a neutral pH value (approx. 6), which is the condition of this experiment (Lee et al., 2003; Graham et al., 2004). Therefore, heavy metal cations can be precipitated by combining them with $HFeO_4^-$. Also, ferrate is rapidly reduced because it is very unstable at other pH values except at pH 9-10, and $Fe(OH)_3$ produced from the reduction of ferrate can remove heavy metal ions by adsorbing them on its surface.



(a) single Cu, Mn, and Zn solution (b) mixture of Cu, Mn, and Zn

Figure 4.13. Removal efficiencies of Cu, Mn and Zn in single heavy metal solution and a mixture of heavy metals depending on ferrate dose

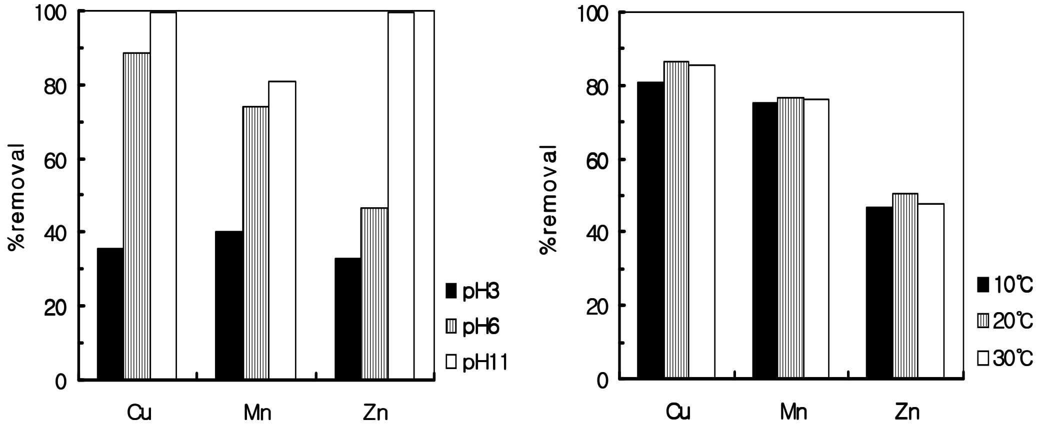
4.3.2 Effect of pH and Temperature on the Reaction between Ferrate and Heavy Metals

The reaction between ferrate and heavy metals depended on pH. Specifically, the removal efficiencies of heavy metals increased with greater pH values as shown in Figure 4.14.a.

As mentioned in 4.3.1, this result can be explained with the speciation of ferrate depending on pH. In alkaline solutions, the most stably existing species of ferrate is FeO_4^{2-} (Lee et al., 2003; Graham et al., 2004). This suggests that divalent heavy metal cations such as Cu^{2+}, Mn^{2+}, and Zn^{2+} can be precipitated as $M(FeO_4)$ by combining them with the divalent negative ion,

FeO_4^{2-}. Also, the divalent heavy metal cations can form an insoluble complex, $M(OH)_2$ by combining with OH^-, which exists relatively more in alkaline solutions.

On the other hand, the removal efficiencies of heavy metals at 20 ℃ were slightly higher than at the other temperatures studied in the experiment (10, 30 ℃), but in generally speaking, temperature did not show any special effect on the reaction between ferrate and heavy metals (Figure 4.14.b).



(a) pH effect

(b) Temperature effect

Figure 4.14. Removal efficiencies of heavy metals by 0.1 mM ferrate depending on pH and temperature (Fe(Ⅵ):heavy metal=1:1 as mol)

4.4 Simultaneous Removal of NOM and Heavy Metals

4.4.1 Simultaneous Removal of HA and Heavy Metals

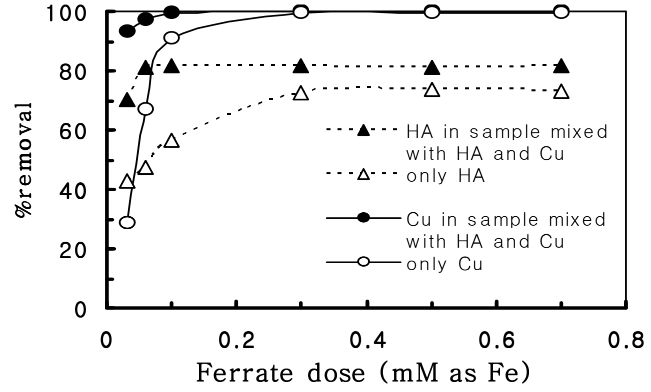
Ferrate was greatly effective on the simultaneous removal of HA and heavy metals as shown in Figure 4.15. The light yellow complexes were formed in every mixture of HA and each heavy metal. Then, the formation rates of complexes were found to be as; 1) 59.6% for HA and 46.1% for Cu in a mixture of HA and Cu, 2) 7.3% for HA and 1.6% for Mn in a mixture of HA and Mn, 3) 26.0% for HA and 11.8% for Zn in a mixture of HA and Zn

The removal efficiencies ranged from 70.3 to 81.5% for HA and from 93.2 to 100% for Cu in a mixture of HA and Cu in which complexes were removed at a range of ferrate doses from 0.03 to 0.7 mM, which are higher than 20.7 to 71.6% for HA and 28.3 to 99.3% for Cu in single HA and Cu solution at the same ferrate doses (Figure 4.15.a). And the removal efficiencies in a mixture of HA and Mn or mixture of HA and Zn showed the same trend as those of HA and Cu in a mixture mentioned above (Figure 4.15.b-c). In addition, ferrate was greatly effective in a mixture of HA and all of the three heavy metals, as shown in Figure 4.15.d. The removal efficiencies of HA and every heavy metal in the mixture were higher than those in single HA, Cu, Mn, and Zn solution (Figure 4.15.e). Some of HA and heavy metals were removed by complexation between them before adding ferrate, and then the remaining HA and heavy metals in the mixtures were removed by ferrate.

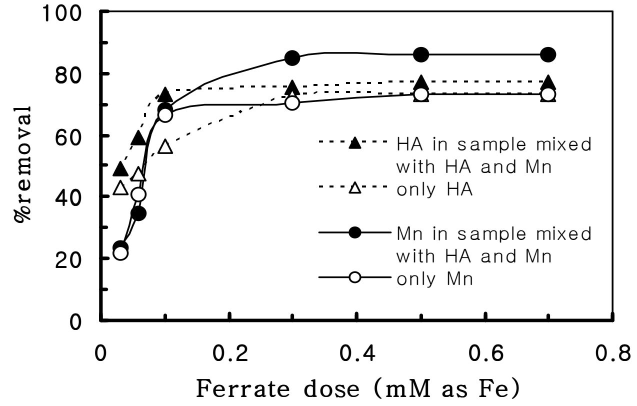
The mechanism of the reaction between HA and heavy metal can be described as complexation, that is, binding heavy metal cations with functional groups of HA (e.g. COO^-, O^-) (Stevenson, 1994; Seki and Suzuki, 1995). The stability of a metal-chelate complex is determined by various factors such as the number of atoms that form a bond with the metal ion, the number of rings that are formed, the nature and concentration of the metal ion, and pH. The stability sequence for divalent cations is as follows:

$$Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$$

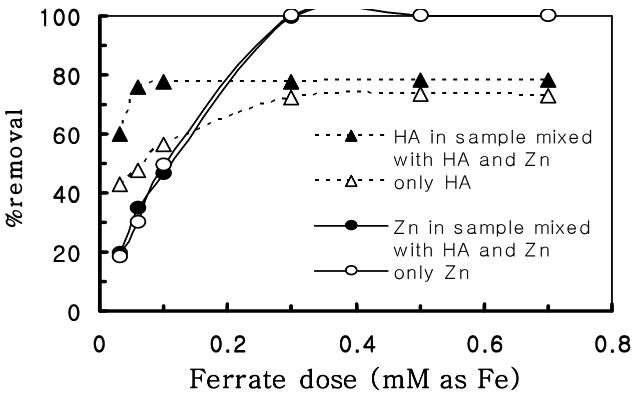
Heavy metal ions can be classified into the two main classes based on their ability to form a coordinate linkage with specific atoms of the ligand. Class A metal ions are those that form complexes with ligands that contain oxygen as a donor atom. Class B metal ions are those that coordinate preferentially with ligands containing N, P, and S donor atoms. The Cu^{2+} ion fits both categories and will thus coordinate with all active groups expected to be present in humic and fulvic acids. The Zn^{2+} ion is an example of a class B metal ion and therefore should form high-energy bonds with any N or S donor groups (Stevenson, 1994). These characteristics of heavy metal cations were consistent with the formation rates of complexes in the mixtures of HA and heavy metals, and was related to the removal efficiencies as shown in 4.3.1.



(a) mixture of HA and Cu

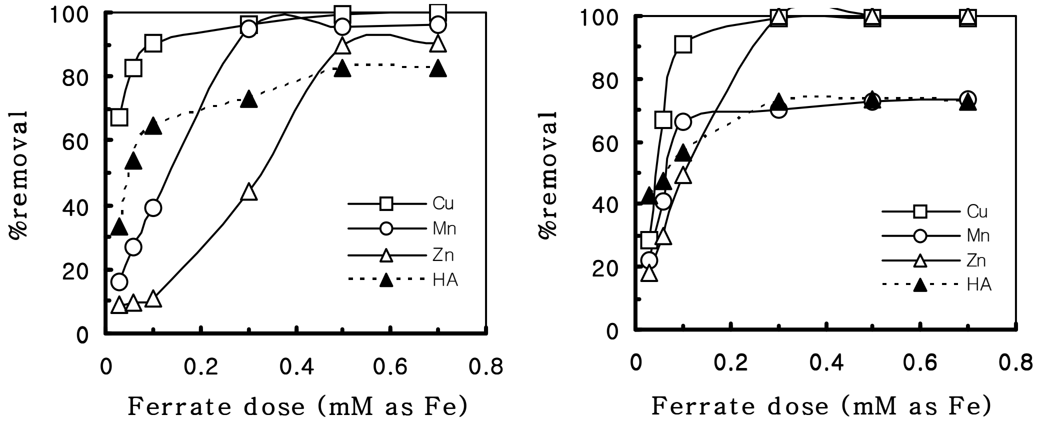


(b) mixture of HA and Mn



(c) mixture of HA and Zn

Figure 4.15. Removal efficiencies of HA and heavy metals depending on ferrate dose in mixtures



(d) mixture of HA, Cu, Mn, and Zn (e) single HA, Cu, Mn, and Zn solution

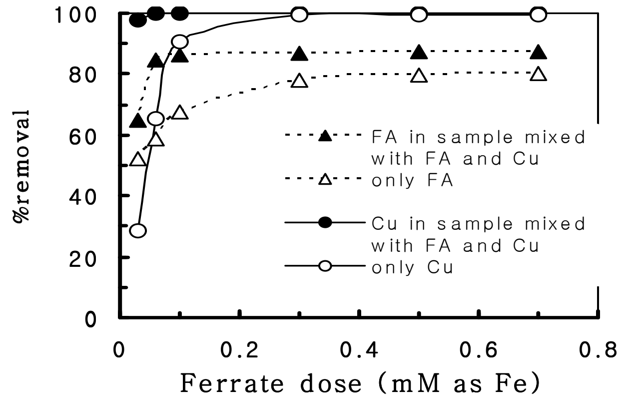
Figure 4.15. (continued)

4.4.2 Simultaneous Removal of FA and Heavy metals

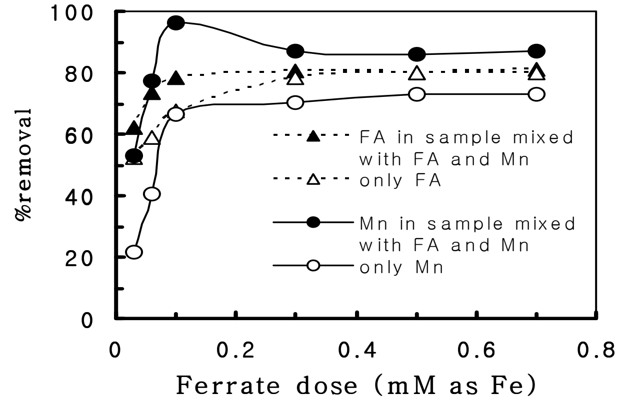
Figure 4.16 shows the result on the simultaneous removal of FA and heavy metals. The light yellow complexes between FA and heavy metals were formed, same as between HA and heavy metals. Then, the formation rates of complexes were found to be as: 1) 40.15% for FA and 44.86% for Cu in a mixture of FA and Cu, 2) 5.47% for FA and 6.51% for Mn in a mixture of FA and Mn, 3) 28.76% for FA and 12.69% for Zn in a mixture of FA and Zn

The removal efficiencies ranged from 65.0 to 87.39% for FA and from 97.6 to 100% for Cu in a mixture of HA and Cu in which complexes were removed at a range of ferrate doses from 0.03 to 0.7 mM, which are higher than 52.6 to 77.5% for FA and 28.3 to 99.3% for Cu in single FA and Cu solution at the same ferrate doses (Figure 4.16.a). And the removal efficiencies in a mixture of FA and Mn or mixture of FA and Zn showed the same trend as those of FA and Cu in a mixture mentioned above (Figure 4.16.b-c). In addition, ferrate was greatly effective in a mixture of FA and all of the three heavy metals, as shown in Figure 4.16.d. Then, the removal efficiencies of FA and every heavy metal in the mixture were higher than those in single FA, Cu, Mn, and Zn solution (Figure 4.16.e).

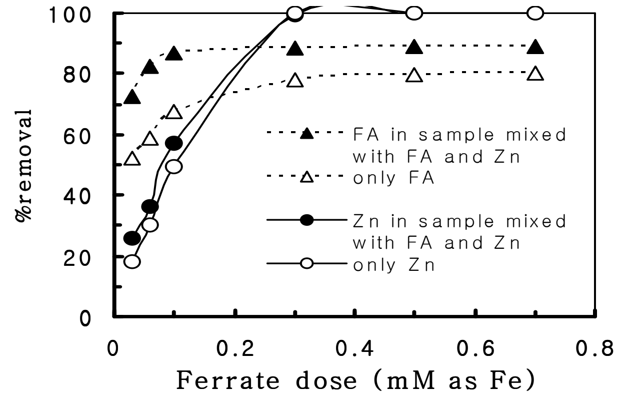
Some of FA and heavy metals were removed by complexation between them before adding ferrate, and then the remaining FA and heavy metals in the mixtures were removed by ferrate. This result demonstrates that ferrate is also effective for the simultaneous removal of FA and heavy metals.



(a) mixture of FA and Cu

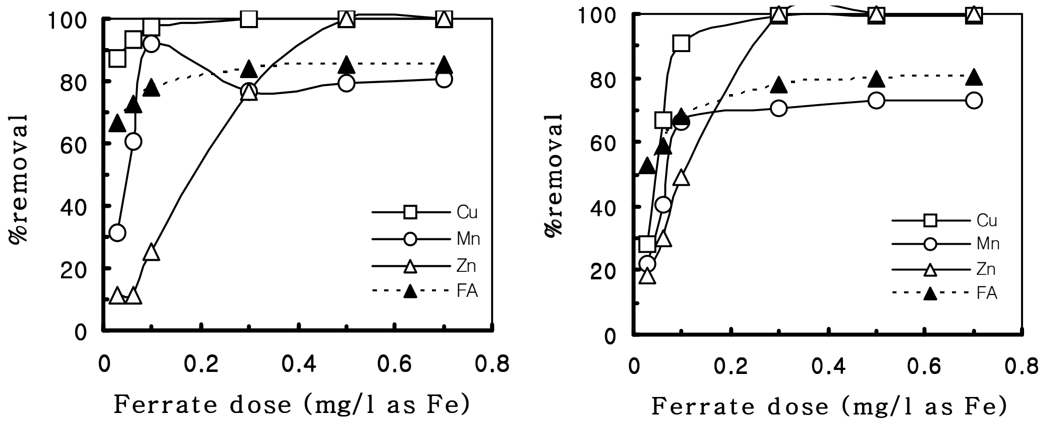


(b) mixture of FA and Mn



(c) mixture of FA and Zn

Figure 4.16. Removal efficiencies of FA and heavy metals depending on ferrate dose in mixtures

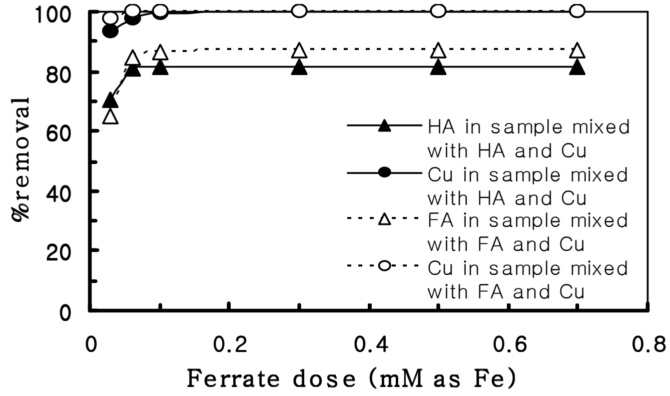


(d) mixture of FA, Cu, Mn, and Zn (e) single FA, Cu, Mn, and Zn solution

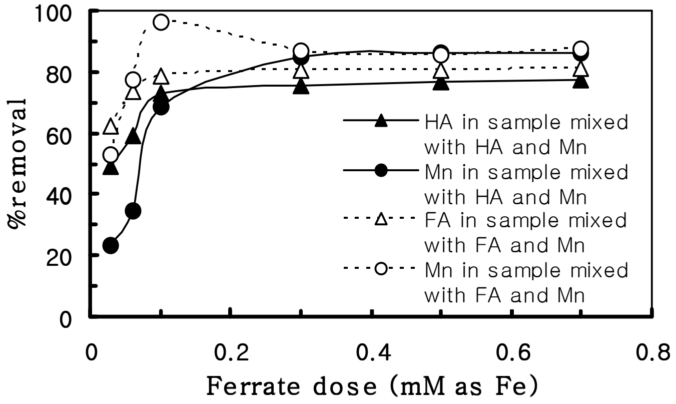
Figure 4.16. (continued)

Figure 4.17 shows three different results of the simultaneous removal of HA and a heavy metal, compared with the simultaneous removal of FA and a heavy metal. Specifically, Figure 4.17.a shows the removal efficiencies of HA and Cu in a mixture of HA and Cu by various ferrate doses, compared with those of FA and Cu in a mixture of FA and Cu. The removal efficiency of Cu in both mixtures was 100% with a ferrate dose of 0.1 mM, and the removal efficiencies of HA and FA were respectively 81% and 87% with the same ferrate dose. Figure 4.17.b shows the removal efficiencies of HA and Mn in a mixture of HA and Mn by various ferrate doses, compared with those of FA and Mn in a mixture of FA and Mn. The removal efficiency of Mn in both mixtures was 85% at a ferrate dose of 0.3 mM, and the removal efficiencies of HA and FA were respectively 75% and 80% with the same ferrate dose. Finally, Figure 4.17.c shows the removal efficiencies of HA and Zn in a mixture of HA and Zn by various ferrate doses, compared with those of FA and Zn in a mixture of FA and Zn. The removal efficiency of Zn in both mixtures was 100% at a ferrate dose of 0.3 mM, and the removal efficiencies of HA and FA were respectively 75% and 88.5% with the same ferrate dose.

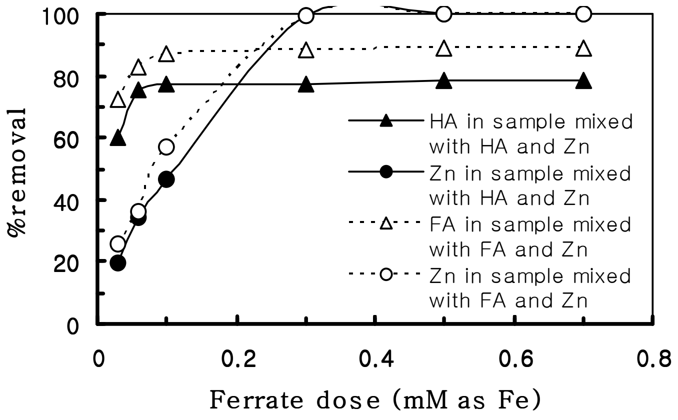
In all the cases, the removal efficiency of FA was higher than that of HA. This result agrees with the previous result of 4.2.2.1, which suggested the removal efficiency of FA in single FA solution is higher than that of HA in single HA solution. As mentioned in 4.2.2.1, this result is associated with the molecular structures of HA and FA.



(a) HA-Cu, FA-Cu



(b) HA-Mn, FA-Mn



(c) HA-Zn, FA-Zn

Figure 4.17. Removal efficiencies of HA, FA and heavy metals depending on ferrate dose in mixtures

CHAPTER Ⅴ. CONCLUSIONS

The results of removing natural organic matter and heavy metals from river water using highly pure potassium ferrate are summarized below. And conclusion and further study to be carried out are also suggested.

1. Removal of NOM using Ferrate

1) Ferrate was greatly effective for the removal of both HA and FA, showing its dual function such as oxidation and coagulation. Then, the removal efficiencies of HA (10 mg/l) ranged from 20.7 to 73.6% for the Nakdong river sample and from 25.6 to 72.7% for the Oncheon stream sample using ferrate doses from 2 to 46 mg/l (as Fe). The removal efficiency of FA was also high in both the water samples, and particularly higher than that of HA because of its molecular structure.

2) Ferrate showed higher removal efficiencies for HA and FA in acidic solutions than in alkaline solutions because it has a stronger redox potential in acidic solutions. Also, the removal efficiencies of HA and FA increased with greater reaction temperature. This result means that the reaction between NOM and ferrate is endothermic and accelerated by external heat.

3) The reaction between ferrate and HA was completed within 60 seconds and then reached a steady state, indicating a high reaction rate. HA showed a first-order reaction with ferrate depending on reaction time. This high reaction rate between ferrate and HA can be an important factor for decreasing water treatment period in practical process.

4) The removal efficiency of HA by ferrate was higher than that by $FeSO_4 \cdot 7H_2O$ and FeO(OH). This suggests that either ferrate improves the coagulating effect of HA by oxidizing HA and reducing itself, or the coagulating effect of Fe(Ⅲ) produced by the reduction of ferrate may be superior to that of FeO(OH). Meanwhile, the removal efficiency of HA by alum was higher than that by ferrate at a range of low doses from 2 to 6 mg/l (as Al), but it gradually decreased with doses from 10 to 40 mg/l (as Al), which indicates an importance of its optimum dose. Also, alum produced a lot of sludge compared to ferrate.

5) The effectiveness of traditional coagulants was improved by preoxidizing HA with very small doses of ferrate. This is the useful way to reduce the dose of traditional coagulants in HA removal and reduce the by-product of sludge further, this way is economically feasible.

2. Removal of Heavy Metals using Ferrate

1) Ferrate was greatly efficient in removing heavy metals such as Cu, Mn, and Zn. The removal efficiencies ranged from 28.3 to 99.3% for Cu, from 21.8 to 73.2% for Mn, and from 18.3 to 99.8% for Zn at ferrate doses from 0.03 to 0.7 mM and every 0.1 mM of each heavy metal. Heavy metal cations can be precipitated by combining them with $HFeO_4^-$, one of ferrate species, in neutral pH water. Also, ferrate is rapidly reduced because it is very unstable at the other pHs except at pH 9-10, and $Fe(OH)_3$ produced from the reduction of ferrate can remove heavy metal ions by adsorbing them on its surface.

2) The removal efficiencies of heavy metals increased with greater pH. This suggests that divalent heavy metal cations can form; ⅰ) $M(FeO_4)$ by combining with the most stable species, FeO_4^{2-} in an alkaline solution or ⅱ) an insoluble complex, $M(OH)_2$ by combining with OH^- which exists more in an alkaline solution. Meanwhile, the removal efficiencies of heavy metals at 20 ℃ were slightly higher than those at other temperatures studied in the experiment (10, 30 ℃), whereas the overall temperature did not show any special effect on the reaction between ferrate and heavy metals.

3) Complexes were formed by the reaction between functional groups of NOM and heavy metal cations in the mixtures, before adding ferrate. After removing complexes from the mixtures, high removal efficiencies of NOM and heavy metals were achieved by ferrate (HA: 49～81%, FA: 62～89%, Cu: 93～100%, Mn: 23～87%, Zn: 20～100%).

3. Further study

The author suggests following conclusion and further work to be carried out. The optimum ferrate dose was determined as 30 mg/l (as Fe) for removing 10 mg/l of NOM and 20 mg/l (as Fe) for removing 20 mg/l of heavy metal. The results of this research indicate that the separated oxidation and coagulation units in current water treatment process may be unified by using ferrate. In addition, sludge production can be reduced and lower treatment costs can be achieved by using small doses of ferrate.

In a further study, it is necessary to investigate the toxicity of potential by-products and mechanisms of the reactions between ferrate and other contaminants. Also, it is essential to improve a skill of ferrate synthesis and to carry out a full scale trial.

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