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Flocculation Characteristics and Removal of Humic acid by Cationic Polymers

濟州大學校 大學院

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高　秉　徹

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指導敎授 甘 相 奎

高 秉 徹

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Flocculation Characteristics and Removal of Humic acid by Cationic Polymers

Byung-Churl Ko

(Supervised by professor Sang-Kyu Kam)

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국문요약

  본 연구에서는 휴민질의 많은 부분을 차지하고 있는 휴민산을 응집·제거함에 있어 전하밀도와 분자량이 다른 수종의 양이온성 고분자 응집제를 사용하여 각 응집제의 주입량, 점토 함유량, 이온강도 등에 따른 응집 특성 및 휴민산의 제거 정도를 검토하여 다음과 같은 결과를 얻었다.

1. 전하밀도가 큰 고분자 응집제를 사용할 경우 짧은 시간내에 응집이 시작되었고, 빠른 속도로 응집이 진행됨을 알 수 있었다.
2. 전하밀도가 낮은 고분자 응집제를 사용할 경우 넓은 응집제 주입량 범위에서 응집이 일어나고 전하밀도가 클 경우 짧은 응집제 주입량 범위에서 응집 현상이 관찰되었으며, 제거 효율은 고분자 응집제의 전하밀도가 클수록 증가하였다.
3. 용액 중 점토 함유량이 증가할수록 고분자 응집제의 종류에 관계없이 휴민산의 제거 정도가 증가하였는데, 이는 점토 함유시 큰 플럭이 형성되어 빠른 시간내에 침강이 이루어졌기 때문이라고 사료된다.
4. 고분자 응집제의 종류에 관계없이 응집이 일어나지 않는 응집제 주입량에서, NaCl을 첨가하여 이온강도를 증가시킬 경우 응집 현상은 관찰되어지지만 휴민산의 제거 효율은 고분자 응집제만으로 응집시켰을 때 보다 감소함을 알 수 있었고, 전하밀도가 높은 고분자 응집제는 전하밀도가 낮은 고분자 응집제에 비해 넓은 이온강도 범위내에서 응집 현상이 관찰되어졌다.

I. Introduction

The organic carbon component of upland surface waters is composed of an amorphous matrix of organic compounds ranging from simple dissolved molecules through colloidal to particulate matter. The dissolved organic carbon(DOC) fraction is the predominant phase in most upland streams and geochemically the more important, representing discrete, chemically reactive molecules(Malcolm, 1985; Thurman, 1985). The DOC content of originally colored waters is extremely variable, however, ranging from approximately 5 mgC/ℓ to greater than 50 mgC/ℓ. The composition of the DOC in organically colored waters also varies quite considerably from source to source. In general, about 20~25 % of the DOC component is comprised of simple compounds such as carbohydrates, carboxylic acids, amino acids and hydrocarbons. The remainder of the DOC component in most upland waters is a complex mixture of organic compounds that can only be defined operationally into two general groups: aquatic humic substances and hydrophilic acids(Thurman, 1985).

Aquatic humic substances occur in every natural water sample that has been analyzed for their presence(Malcolm, 1985). In most natural waters, they account for about 40~60 % of the DOC component(Rebhun and Lurie, 1993). Humic substances are a product of the microbiological, chemical and photochemical degradation of allochthonous and autochthonous organic matter(Langlais et al., 1991; Malcolm, 1985; Steelink, 1985). They are composed of a heterogeneous continuum of naturally-occurring organic compounds that can generally be considered to consist of a wide-range of molecular weight (polydisperse), non-volatile, hydrophilic, chemically-complex, polyelectrolytic organic acids that impart a yellow to almost black coloration in many natural waters(Aiken et al., 1985; Chiou, 1990; Thurman, 1985). Oden(1919) classified them in terms of four fractions based upon the solubility of the composite molecules: humic

acid(soluble in base but not in acid), fulvic acid(soluble in acid and base), humin(insoluble in water at any pH) and hymatomelanic acid(soluble in base and alcohol but not in acid). In natural waters, the predominant fractions present are fulvic and humic acids(Smith and Banks, 1986).

From a point of public health significance, the presence of humic substances in natural waters causes many problems, such as formation of potentially carcinogenic trihalomethanes(THMs) which form upon chlorination(Rook, 1974), undesirable color, taste and odor in drinking water. In addition, it is known that they are easily adsorbed on surfaces of many particles(Buffle, 1990). Adsorption on particles is very important process for regulating of their transport in natural waters as particles have a large surface area and high surface charge induced by the formation of coatings on their surface. Such humic coatings also contribute to the organic carbon content of clay particles, which has a far higher adsorption capacity and the much higher stability(Fairhurst and Warwick, 1998; Gibbs, 1983, Jekel, 1986; Tipping and Higgins, 1982). It has been speculated that a combination of electrostatic and steric stabilization is responsible for the increased colloidal stability of humic-clay complexes (Kretzschmar et al., 1998). For this reasons, it can make humic substances more difficult to remove by conventional water treatment processes.

Several methods, including flocculation, oxidation and adsorption processes, are used to remove aqueous organic materials or particles during water treatment and a very common method is coagulation/ flocculation, followed by either direct filtration, sedimentation or floatation. Since natural organics are nearly always anionic over the usual range of natural water pH(pH 6~8), they interact strongly with cationic additives, such as hydrolyzing metal salts and cationic polyelectrolytes.

Up to the present, a large number of studies have been conducted on the colloidal behavior or stability of particles, humic substances and particles coated with humic substances(Buffle and Leppard, 1995; Chandrakanth and Amy,

1996; Gregory, 1976; Kjellin et al., 1997; Malcolm, 1985; Tipping, 1993; Tsuruta et al., 1995), interaction of particles and humic substances(Zhou et al., 1994) and coagulation/flocculation of particles(Dentel, 1991; Gregory, 1988; Gregory and Nelson, 1986; Letterman et al., 1982) and humic substances(Babcock and Singer, 1979; Edzwald, 1977; Hall and Packham, 1965; Kam et al., 1997; Kavanaugh, 1978; Narkis and Rebhun, 1977). However, little reseach has been done on the flocculation of humic substances in the presence of particles for their removal. Also it is known that the ionic strength of the solution affects the flocculation(Dahlgren et al., 1995, Lee and Gregory, 1990).

In this study, the flocculation characteristics and the subsequent removal of humic acid were investigated, using several cationic polymers of different charge density and molecular mass, with several parameters such as the dosage of each polymer, the content of kaolin particles and the ionic strength of the solution.

Ⅱ. Literature Review

1. Characteristics and removal methods of humic substances

1) Characteristics of humic substances

Humic substances are present in practically all surface-near soil and aquatic environments. They are the organic compounds formed in soil, water and sediment by the decay of dead organisms(Vik and Eikebrokk, 1989) and are amorphous, acidic and predominately aromatic, hydrophillic, chemically complex polyelectrolytes that can have molecular weights ranging from several hundred to tens or hundreds of thousands(Tipping, 1993) and impart a yellow to almost black coloration in natural waters(Aiken et al., 1985; Chiou, 1990; Thurman, 1985). Because living organisms are made up of a very large number of different organic compounds, their degradation and the possible recombination of the resulting products may lead to an almost infinite number of different molecules(Buffle, 1990).

In the environment, the predominant fractions present are humic and fulvic acids(Vik and Eikebrokk, 1989). Humic and fulvic acids originating from soil include a large proportion of aromatic compounds(in particular benzenecarboxylic and phenolic compounds) (Zhou et al., 1994), whereas the humic and fulvic acids from sediments and the aquagenic type are much more aliphatic(Buffle, 1990).

Humic substances, humic and fulvic acids are enormously complex in structure and some proposed chemical structure are given in Fig. 1. The principal characteristics of humic and fulvic acids are summarized in Table 1.

[a]

[b]

[c]
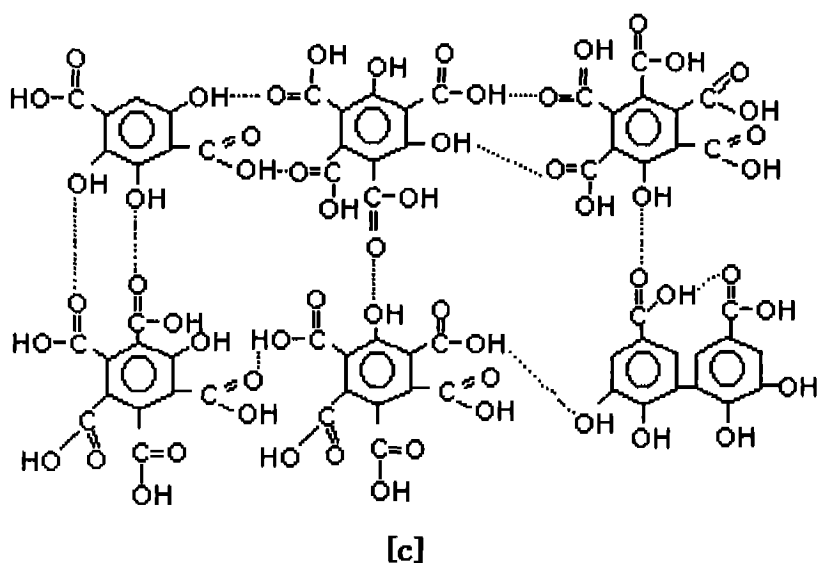
Fig. 1. Structure of humic substances([a]; Trussell and Umphres, 1978)
humic([b]; Rook, 1974) and fulvic acids([c]; Schnizer, 1971).

Table 1. Principal characteristics of humic and fulvic acids
(Smith and Banks, 1986)

Properties		Humic acids	Fulvic acids
Color		brown ~ black	yellow ~ clear
Molecular weight		$10^5 \sim 10^6$	500 ~ 5000
Aromatic carbon(%)		–	60
Elementary composition(%)	C	55 ~ 60	42 ~ 52
	O	32 ~ 36	45 ~ 47
	H	4 ~ 5	3 ~ 6
	N	2 ~ 5	1 ~ 2
Oxygen distribution	Carboxyle	25 ~ 45	55 ~ 65
	Phenolic	10 ~ 20	10 ~ 30
	Alcohol	10 ~ 15	10 ~ 15
	Carbonyle	10 ~ 25	5 ~ 10
	Methoxyle	1 ~ 2	1 ~ 2

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A common feature of humic substances is that they are fairly resistant to degradation, i.e., refractory ; their residence times are often in the range of centuries to millennia(Buffle, 1990).

Humic substances with predominantly carboxylic, hydroxyl, and phenolic functional groups are negatively charged at the pH of most natural waters, 6~8. These charged groups repulse one another and spread out the molecules (Kretzschmar et al., 1998; Tipping, 1993; Vik and Eikebrokk, 1989).

Humic substances possess ion-exchange and complex properties that are associated with most constituents of water, including toxic elements and organic micropollutants. They act as a vehicle for transport of toxic, water-insoluble elements and organic micropollutants, thus influencing processes such as dissolution, coagulation and crystal growth(Buffle, 1990; Collins et al., 1986; Edzwald, 1993; Fairhurst and Warwick, 1998; Vik and Eikebrokk, 1989).

When chlorine is added to drinking water supplies in the concentration required for disinfection, it has been found to react with humic substances of the water to produce a variety of chlorinated products. The most ubiquitous products, and the products found in the highest concentrations, are potentially carcinogenic chloform($CHCl_3$) and other trihalomethanes(THMs)(Jimenez et al., 1993). So the removal of humic substances and hence color from water is therefore important to reduce its THM formation potential(THMFP).

2) Removal methods of humic substances

A variety of methods have been used for the removal of aqueous organic compounds from potable water supplies, including coagulation, adsorption and oxidation processes.

(1) Coagulation

Conventional treatment for the removal of aqueous organic compounds usually

involves the use of a hydrolysing metal salt, such as aluminium sulphate, ferric sulfate, and polyelectrolytes followed by either direct filtration, sedimentation and filtration, or flotation and filtration. The removal of dissolved organic compounds from influent raw waters requires substantially more careful control of pH and coagulant dosing and the efficiency of conventional treatment is strongly related to the operational practice employed at a particular treatment plant, including the coagulant dose applied, the use of a coagulant aid, the order of chemical addition, the mixing intensity and the water pH maintained(Bragg et al., 1989; Logsdon and Fox, 1982). Removals also vary according to the nature and composition of the dissolved organic matter in the influent raw waters.

A review of the literature reveals that the typical organic color removals from upland raw waters by coagulation processes is approximately 80%(Lambert and Graham, 1992).

(2) Adsorption

Adsorption has become one of the most significant processes for the treatment of potable waters over recent years and is increasingly being considered for the removal of natural organic compounds from upland sources. It is associated with the removal of dissolved contaminants from solution by their accumulation at the surface of a solid, applied either directly in to the process stream in a powdered form, or more frequently in a granular form as a filter media. The solid-phase material is termed the adsorbent, while the contaminant accumulated at the adsorbents surface is termed the adsorbate.

Adsorption occurs when the relative affinity of an adsorbate molecule for an adsorbent surface is thermodynamically greater than the affinity of either the adsorbate or adsorbent for molecules of the water. This is therefore dependent upon the interacting properties of the adsorbate, adsorbent and components of the aqueous environment in which they are placed. Properties of the adsorbates important to their adsorption from solution are primarily molecular weight, steric

structure and functional group content. As a surface phenomenon, the properties of an adsorbent important to the adsorption of organics are primarily the physico-chemical nature of the adsorbent's surface and the extent of the surface area available to potential adsorbates(Bernadin, 1985; Faust and Aly, 1987; Weber, 1985).

(3) oxidation

Oxidation processes have been an integral part of potable water treatment operations since the 18th century, when the employment of aeration, to aid in the removal of aqueous organic compounds, became common practice. The aeration of raw waters has only a limited effect, however, and more powerful oxidising agents, such as permanganate, chlorine dioxide, chlorine and ozone, became increasingly employed by treatment utilities throughout the 19th century.

In this country, the most commonly used chemical oxidant has been chlorine. Applied extensively for the disinfection of finished water supplies prior to distribution, chlorine used for the preoxidation of raw waters has the additional advantages over other oxidants of low cost and ease of application. Chlorine is also very effective not only as a pretreatment for the removal of aqueous organic compounds, but also for the removal of some organic taste and odor compounds. However, it has recently become evident that the chlorination of potable waters containing a dissolved organic component results in the formation of large quantities of potentially harmful halogenated organic compounds. As a consequence, the application of chlorine as a raw water pretreatment process has become particularly undesirable and interest in the use of alternative oxidants has increased(Reynolds et al., 1989).

Of the alternative oxidants, ozone is currently receiving the most significant interest. Due largely to the stringent requirements for water quality of current legislation however, and increased consumer water quality expectations, ozone has recently found a more extensive role as a raw water oxidant for a wide

variety of quality problems. These have been reviewed by Hyde and Zabel(1984) and others(Langlais et al., 1991).

2. Flocculation by polymers

1) Polymeric flocculants

Chemical additives are used to improve the separation of particles or organic materials by processes such as sedimentation, filtration and flotation. The use of synthetic organic polymers in water treatment began in the late 1950's.

There are a few characteristics of polymers that make them more suitable for a certain specific water treatment application. The most important characteristics of polymers are the nature of the monomer unit that make up the polymer, the type of charged group, the varying charge density, the molecular weight and the structure(linear or branched)of the polymer(Lee, 1991).

The organic polymers used in water treatment are chains of individual monomer units, linked together in a linear or branched configuration. Functional groups are located periodically along the chain and they may possess a negative charge(anionic polymers), positive charge(cationic polymers), or an overall neutral charge(nonionic polymers). These polymers are also referred to as "polyelectrolytes", although the term strictly applies only to the cationic and anionic types. The length of the polymer chain is indicated by the molecular weight of the polymer, but this is actually an overall average for the many individual molecules.

Polymer charge density refers to the concentration of positive or negative charge on a polymer, either per unit weight or as a percent of potentially ionized monomer content. Charge density depends on the number of ionisable

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groups and the degree of ionization and it is a function of polymer type, polymer content in the product, product concentration when added to water, and solution pH for some polymer types. The number of ionisable groups is determined during polymer synthesis e.g., the degree of hydrolysis of polyacrylamide or the proportion of cationic monomer incorporate(Lee, 1991)

The charge density and the molecular mass of the polymer can affect the rate of flocculation. Charge density has been shown to be the more important characteristic for coagulant polymers when used in dilute particle systems(Lee and Gregory, 1990; Ghosh et al., 1985; Gregory, 1993), but molecular weight has also been indicated as an important factor in some cases(Treweek and Morgan, 1979).

Stumm and O'Melia(1968) reported on a linear stoichiometric relationship between the optimum dosage of positively charged flocculants necessary for adsorption coagulation with charge neutralization and the concentration of negatively charged particles.

2) Flocculation mechanisms by polymers

The flocculation of suspended particles by polymers is a complex process involving an initial period of polymer adsorption followed by particle aggregation. The following sequence of steps was envisaged by Akers(1972).

(a) Transport of polymer molecules to the suspended particles.

(b) Adsorption of polymer chains on the particles.

(c) Re-arrangement of the adsorbed polymer chains to give an equilibrium configuration.

(d) Collisions of particles to form stable flocs either by bridging or by electrostatic patch effects.

(e) Break-up of flocs.

Glaser and Edzwald(1979) thought that coagulation of humic substances by

polymers was two-step process in which the humic acid and polymer behave as flexible macromolecules with opposite charge. The first step is a polymer-humic interaction induced by electrostatic attraction and leading to a neutral net charge as these two chains intermingle. Floc formation ensues due to collision with further macromolecules and interweaving to form an extensive cross-linked network. However, these processes are not easy to separate and may occur simultaneously, making analysis of the overall process rather difficult.

The charge neutralization effect of the adsorbed polymer is the main mechanism for flocculation. The amount of positive charge adsorbed at optimum dosage is about the same for all of the polymers used and then they serve to produce an overall charge in the adsorption region that approaches electrical neutrality

Table 2. Summary of characteristic of flocculation parameters for polymers(Lee, 1991)

| Parameter	Charge neutralization	Bridging
Molecular mass	· little effect · very high molecular mass can give bridging effect	· high molecular mass more effective
Charge density	· more effective with high charge density because of greater neutralization effect	· more effective with high charge density because of expansion of polymer chains
Optimum dose	· near zero charge · dose proportional to the total surface charge of particles	· usually not zero charge · dose proportional to particle concentration
Overdose	· restabilization due to charge reversal	· restabilization due to no vacant bridging sites available

Many studies of coagulation using polymers have showed that optimum polymer dosages lead to near zero electrophoretic mobility or electrical charge(Lee and Gregory, 1990). The reversal of particles charge is also found to occur at a dosage very close to the optimum flocculation dosage(Lee, 1991). The characteristics of flocculation parameters for polymers are shown in Table 2.

The stability of a colloidal particles can be reduced by the addition of a small quantity of polymer and two models have been suggested to explain the flocculation of colloidal particles on addition of polymer. In the polymer bridging model, as shown in Fig. 3[a], segments of polymer molecules attached to particles at many points and adsorb on more than one particle, especially when the molecular dimensions of the polymer are comparable with the size of colloidal particles. The particles are said to be "bridged" and this flocculation mechanism is defined bridging flocculation. In order to bring about bridging flocculation, adsorbed polymers must extend far enough from the particle surface to attach to other particles and there must be sufficient unoccupied surface available for adsorption of segments from these extended polymer chains(Ruehrwein and Ward, 1952). The bridging may be too weak to withstand the shearing forces induced by the shear condition, if too few bridging contacts are made(Black et al., 1965). Conversely the bridging will be hindered if too many adsorption sites are occupied by adsorbed polymer segments. According to Pelssers et al.(1990), polymers may lose their ability to "bridge" colliding particles if the thickness of the adsorbed layer becomes shorter than the range of electrostatic repulsive forces, due to the flattening of adsorbed polymer molecules with time. In dilute suspension and for low polymer dosages, the effect of the flattening of polymer molecules on the flocculation of the suspension can be significant. Generally, the most effective bridging flocculation is found with linear polymers of very high molecular weight(several million), so that extended loops and tails can form, increasing the probability of attachment to other particles(Fig. 2). Also, it is found that there is an optimum dosage

range for effective flocculation. At lower dosages, there is insufficient polymer to form adequate bridging links between particles. With excess polymer, there is no longer enough bare particle surface for attachment of segments and the particles become restabilized, which may involve some steric repulsion. Bridging flocculation can give flocs which are much stronger than those produced just by the addition of salts(i.e. by reducing electrical repulsion).

The electrostatic patch effect can be regarded as another form of bridging interaction, the difference being the thickness of the adsorbed layer. In the electrostatic patch model, the polymer adsorb on oppositely charged particles so that there are areas of either excess positive or excess negative charges on the surface(Gregory, 1973). Attraction of particles occurs when positive areas of one particle come into contact with the negative areas of another particle, as shown in Fig. 3[b]. This model of flocculation can be significant in using high charge density polymers. At low ionic strengths, this extra attraction can give measurable increase in flocculation rate due to the long range of the attractive double layer forces(Gregory, 1976).

Flocculation of a suspension does not begin immediately after an addition of polymer. For both the bridging mechanism and the electrostatic patch effect, colliding particles need to acquire enough adsorbed polymer to be sufficiently destabilized for flocculation to occur.
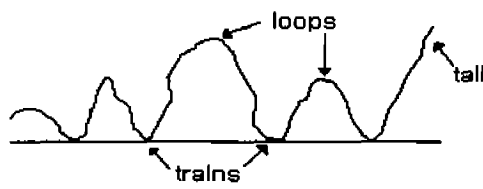
Fig. 2. A schematic diagram showing the conformation of an adsorbed polymer molecule in train, loops and tails.
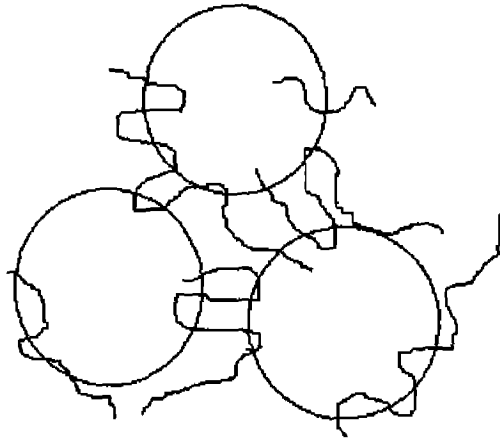
[a]
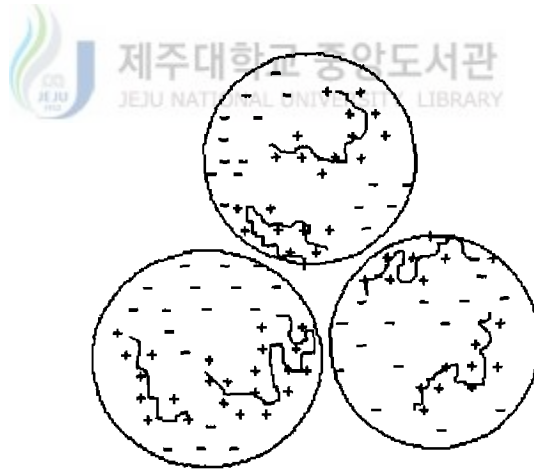
[b]

Fig. 3. Schematic illustration of bridging flocculation[a] and electrostatic patch model[b].

In the flocculation of charged particles by oppositely charged polymers, the adsorbed polymer changes a three dimensional coil into a nearly two dimensional flattened coil on the particle surface(Lee, 1991). But there is no information on the time taken for polymers to re-arrange on the particles.

The lag time between the addition of polymer and the onset of flocculation can be more pronounced in dilute suspensions(Lee, 1991).

3. Flocculation monitoring methods

Measurement of the light scattered by suspended particles and of often made to monitor the flocculation of suspension. In general, there are two types of light-scattering experiments that may be performed: angular light scattering, where the intensity of the scattered light is measured as a function of scattering angle, and turbidity(or optical density) determination, where the intensity of the transmitted beam is measured. A third flocculation monitoring technique, based on fluctuations in the intensity of transmitted light, was developed by Gregory and Nelson(1986). This technique is described below.

The PDA 2000 manufactured by Rank Brothers Ltd., was used as an on-line monitoring system to detect changes in the state of aggregation of a suspension(Ching et al., 1994; Gregory, 1984; Gregory, 1987; Gregory, 1988; Gregory, 1990; Gregory and Guibai, 1991; Guibai and Gregory, 1991; Kayode and Gregory, 1988; Lee, 1991; Lee and Gregory, 1990). When a flowing suspension is illuminated by a narrow light beam, the transmitted light intensity varies randomly about a mean value(see Fig. 4). These variations are caused by random changes in the number and type of particles in the beam, since the sample is continuously renewed by flow. Number fluctuations follow the Poisson distribution, so that the standard deviation about the mean is just the

square-root of the mean value. Thus, if there were 100 particles in the beam, on average, then the standard deviation would be 10 and the actual number would mostly be in the range 100 ± 20, i.e. within 2 standard deviations of the mean. As the mean value decreases, so the fluctuations, relative to the mean, become larger.
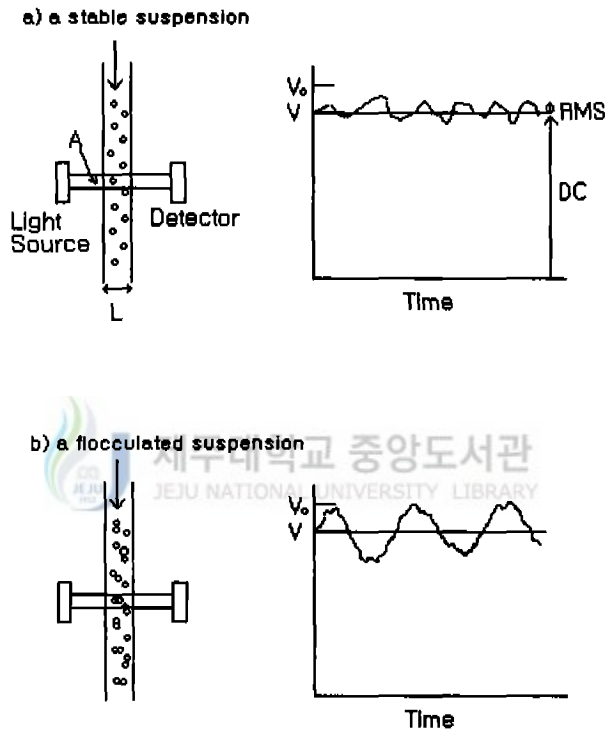
Fig. 4. Schematic diagram of the turbidity fluctuation technique (a] a stable suspension and b] a flocculated suspension).

It has been shown that fluctuations in transmitted light intensity (or turbidity fluctuation) increase greatly as particles aggregate, and this principle has been exploited in monitoring flocculation processes(Gregory and Nelson, 1986). In practice, the root mean square(RMS) value of the fluctuating(AC) component of

the transmitted light signal is derived. This can be divided by the steady(DC) component(related to the turbidity of the suspension) to give a Ratio value. The theoretical basis has been given by Gregory(1984), who showed that the Ratio value R for a suspension of similar particles is given by :

$$R(=RMS/DC)=\sqrt{\frac{NL}{A}}\,C \qquad (1)$$

where L is the optical path length, A is the effective cross-sectional area of the light beam, N is the number concentration and C is the light scattering cross-section of the particles. This value, R, remains essentially unaffected by contamination of optical surfaces or electronic drift(Guibai and Gregory, 1991).

For a suspension of different types of particles, the appropriate expression is:

$$R=\sqrt{\frac{L}{A}\sum N_i C_i^2} \qquad (2)$$

The fact that the sum in equation(2) contains the square of the light scattering cross-section, means that larger particles have a very important influence. It is also important to note that the Ratio value depends on the square-root of the particle concentration.

More recently, it has been recognised that essentially the same method can give a very sensitive measure of particulate impurities in liquids(Gregory 1990). By measuring the AC component of transmitted light, rather than the steady(DC) value, problems due to fouling of optical surfaces or electronic drift are greatly reduced. The turbidity fluctuation technique is very much more sensitive than conventional turbidity measurements for particles greater than about $1\sim2\mu m$ in size. It is also more convenient to restrict attention to the case of uniform particles. The conclusions apply equally well to the case of non-uniform particles.

Although the value of Ratio are measured in an arbitrary unit and it does not give a quantitative correlation of the particle concentration, an overall measure of the state of flocculation can be adequately monitored by measuring fluctuations in the intensity of a light beam transmitted through a flowing suspension.

III. Experimental Materials and Methods

1. Materials

1) Humic acids

Humic acid was obtained from Aldrich Chem. Co., UK. The stock solution(5 g/ℓ) was prepared by dissolving 2.5 g of humic acid in a 500 ㎖ of 0.1 N sodium hydroxide and the solution was filtered through a glass microfibre filters(Whatmann). Working standard solution(1g/ℓ) was diluted five times.

2) Kaolin suspensions

Suspensions of kaolin were prepared as follows ; 50 g dry clay were added to about 400 ㎖ deionized water. After adding NaOH solution to bring pH up to 7 5 giving complete dispersion, mixed for 1 hour. The suspensions were made up to 1ℓ with deionized water and allowed to stand for 24 hr in 500 ㎖ cylinders The top 300 ㎖ from each cylinder was carefully taken and the rest part of the solution was rejected. The particle sizes measured with a particle analyzer, MALVERN Instrument SR 20, were mainly in the range of 5.33 ~ 6.18 ㎛.

3) Cationic polymers

These samples were kindly donated by Allied Colloids Ltd., UK. The properties of the polymers used, designated P-A ~ P-D, are listed in Table 3 and the molecular structures are shown in Figure 5. All of the polymers were

essentially linear except the P-C. P-A and P-B were the copolymers of acrylamide and dimethylaminoethyl acrylate(DMAEA). DMAEA is fully quaternized with methyl chloride and so these polymers are positively charged over a wide pH range. The molar portion of DMAEA determines the charge density and is given as "% Cationic(mol % of cationic monomer)". The charge density of the polymers listed were given by the manufacturer.

P-A and P-B were supplied as solids and were prepared as 0.1 %(W/V) aqueous solution by wetting 0.1 g of the solid with 3 ㎖ of methanol, adding 97 ㎖ of deionized water and agitating for approximately 60 min. P-C(a 50 % active solution of a polyamine) and P-D(a 40 % active solution of a polydiallyldimethyl ammonium chloride(polyDADMAC)) were diluted with deionized water to make 0.1 % solution. All of the 0.1 % aqueous solution were used within a week.

Table 3. Properties of polymers used

Polymer	% Cationic	Molecular mass	Diameter (nm)[1]
P - A	20	$2 \sim 3 \times 10^6$	110
P - B	40	$2 \sim 3 \times 10^6$	140
P - C	100	$3 \sim 4 \times 10^4$	70
P - D	100	$3 \sim 4 \times 10^4$	70

[1] The dimensions of the polymers in 0.5M NaCl were quoted from Lee(1991).
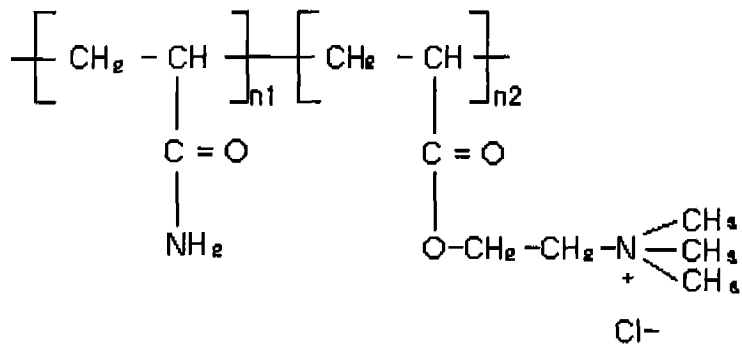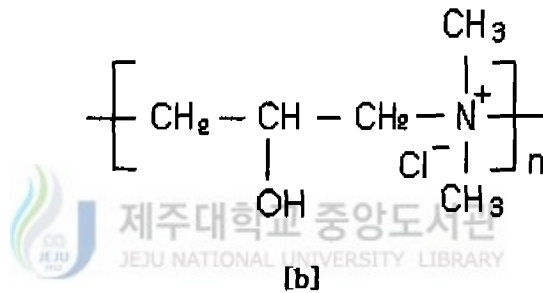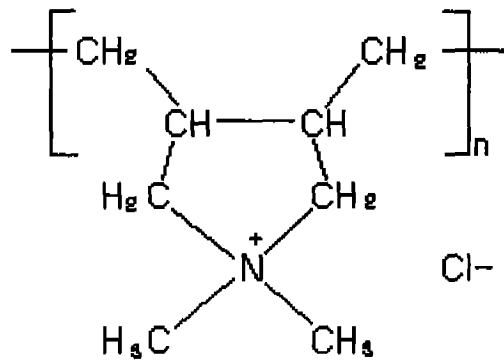
Fig. 5. The structure of copolymer of acrylamide and quaternary acrylic ester[a], polyamine[b] and polyDADMAC[c].

2. Methods
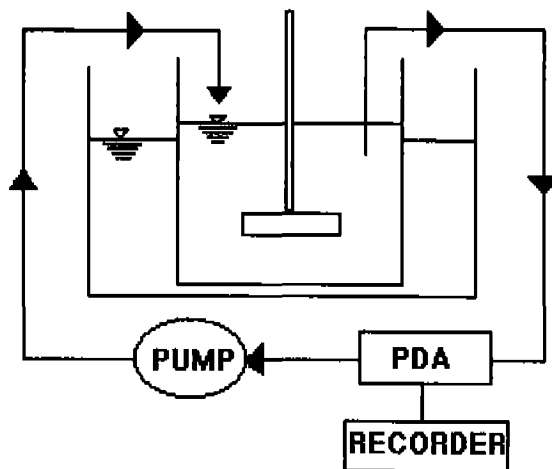
Fig. 6. Schematic diagram of experimental set-up.

5 ㎖ of humic acid(1 g/ℓ) and 2 ㎖ of 0.1N-Na₂CO₃ were added to the 300 ㎖ beaker containing about 193 ㎖ deionized water or kaolin solution and the pH of the solution was adjusted to pH 7 with 0.1N or 0.01N-HNO₃. With the content of kaolin particles, the solution was stirred additional 1 hr to give the chance to react humic acid with kaolin particles. The 300 ㎖ beaker was placed into a water bath to uniform solution temperature(25 ℃). Then, a predetermined amounts of cationic polymer was added into the suspension and the solution was stirred for a period of 1min at a speed of 150 rpm, followed by 60 rpm for 15 min. If the droplets of added polymer solution are not rapidly dispersed, they may act 'nuclei' for floc formation(Gregory, 1988). In the following results, we shall assume that complete mixing has been achieved during 1 min of rapid mixing. The solution pH was held constant at 7±0.1 throughout the operation period. Microtube pump(Eyla MP-3N; Japan) was used to re-circulate the sample continuously. It was placed after the sample had passed through the

PDA so as not to disrupt the flocs and their detection. The sampling tube to the PDA monitor was 2.65mm internal diameter and the flow rate was set at 15 ㎖/min Although there is a time lag between sampling from the beaker and response from the PDA, this is negligible.

The experimental set-up is shown schematically in Fig. 6. After a flocculation test, 50 ㎖ of the solution from the beaker was poured into the 50 ㎖ centrifuge tube with 27 mm internal diameter, settled for 2 hrs. Then the supernatant liquid(25 ㎖) was taken and used for the absorbance measurement at 254 nm(A_{254}) or turbidity (NTU). In order to compare the removal of humic acid by settling with that by centrifuge, 50 ㎖ of a sample in a solution was drawn off, placed in a centrifuge tube, and centrifuged at 3,000 rpm for 20 min. After that, the supernatant liquid(25 ㎖) from the centrifuge tube was taken and used for the absorbance measurement at 254 nm.

Zeta potentials were measured immediately after flocculation experiment. Also, the effects of adsorbed polymers on the zeta potential of humic acid with and without kaolin particles was determined with a ZM3+ Zeta Meter(USA).

Above experimental conditions were summarized in Table 4.

Table 4. Summary of experimental conditions

	Items	Value
Solution	Humic acid conc. (mg/ℓ)	25
	Turbidity(NTU)	15, 35, 55
	Ionic strength(mM)	0 ~ 311
	pH	7
	Temperature(℃)	25
Mixing	Rapid mixing(rpm, min)	150, 1
	Slow mixing(rpm, min)	60, 15
Tube	Internal diameter(mm)	2.65
	Length(mm)	950
Flowing	Flow rate(mℓ/min)	15
Separation	Settling(hr)	2
	Centrifuge(rpm, min)	3,000, 20

Ⅳ. Results and Discussion

1. Feature of flocculation curve

A recently developed technique, based on measurements of fluctuations in transmitted light intensity with flowing suspensions, gives a very sensitive indication of changes in the state of flocculation.

A typical flocculation experiments was carried out by adding a certain amount of polymer to a stirred suspension of humic acid with and without the presence of kaolin particles and withdrawing sample through the monitor as shown in Fig. 6. The state of flocculation was monitored after polymer addition. The value of Ratio(RMS/DC) can be adjusted by the DC Gain and the RMS Gain to enhance the sensitivity of the instrument to the state of flocculation of particles. In this study, DC Gain was set at 5.0 and RMS Gain was set at 0.9. Since Ratio value, R, gives a sensitive indication of the state of flocculation of particles, it is termed 'Flocculation Index' in the following results.

A characteristic curve resulting from such an experiment is shown in Fig. 7, which was obtained using P-A at a dosage of 23.9 mg/ℓ in salt-free solution. The curve can be arbitrarily divided into 4 regions. In regions A, there is little change in the Flocculation Index with time, which is a consequence of the relatively slow polymer adsorption. In this phase most particles have not yet acquired sufficient polymer to become destabilized and particle collisions do not result in flocculation. As more polymer is adsorbed, the particles become destabilized and thus collisions of particles will form stable flocs. As a results, the value of the Flocculation Index begin to show a distinct rise with time which marks the initiation of flocculation(Region B). In region C, the flocculation rate has become constant and Flocculation Index shows a nearly linear rate of
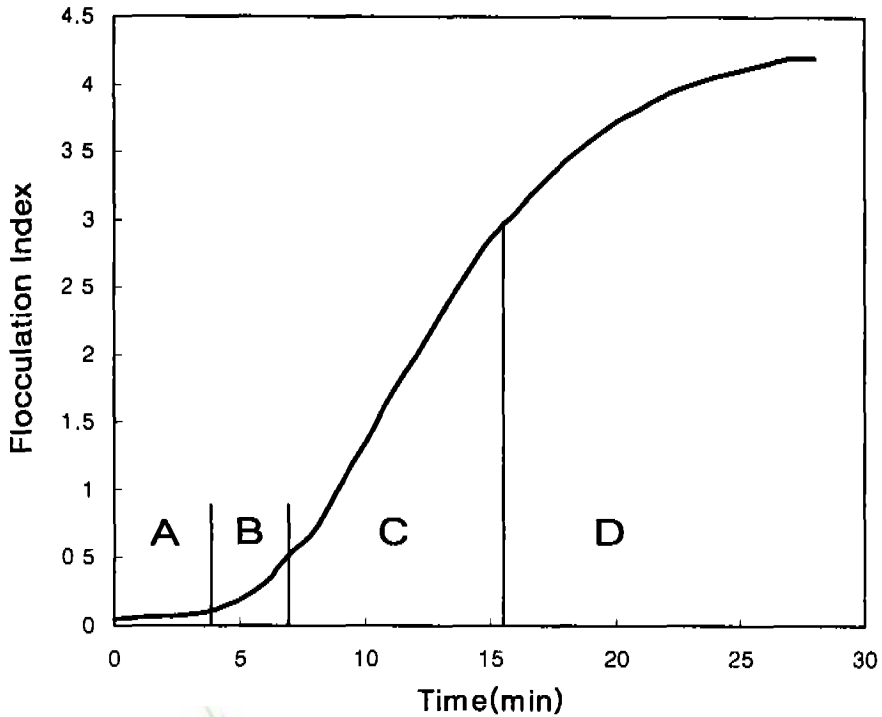
Fig. 7. A typical flocculation curve(P-A; 23.9 mg/ℓ,
humic acid; 25 mg/ℓ).

increase. The amount of adsorbed polymer required to bring about this maximum rate will depend on the characteristics of the polymer, the particle concentration and the ionic strength of the solution. Further adsorption of polymer may reduce collision efficiency and an excess coverage of polymer may lead to a reversal of surface charge. Under the given shear conditions where the dominant transport mechanism is orthokinetic collision, the larger collision radii of flocculated particles can enhance the collision rate of flocculating particles. The net effect of the enhanced particle collision rate and reduced collision efficiency seems to give a steady flocculation rate(Lee, 1991). In region D, there is a leveling-off of the Flocculation Index. Depending on the amount of polymer added, restabilization of particles is possible when excess polymer is

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adsorbed. This could lead to a declining flocculation rate. Even when the amount of polymer added is insufficient to restabilize the particles, the flocs will eventually reach a limiting size as determined by the polymer type, the stirring conditions and the floc strength(Lee, 1991; Lee and Gregory, 1990).

2. Effects of polymer dosage on the flocculation

1) Flocculation characteristics

Particles may undergo several collisions with other particles before acquiring sufficient amount of adsorbed polymer to be able to form stable flocs.

Fig. 8(a)～(d) shows the flocculation curves when different amounts of the polymers(P-A ～ P-D) are added to salt-free humic acid solutions (25 mg/ℓ).

Fig. 8(a) shows the flocculation curves for P-A of low charge density (20 %). At the lowest dosage, 22.0 mg/ℓ, the Flocculation Index is essentially unchanged which indicates little or no flocculation in the 16 minutes flocculation time.

Two distinct effects are observed with increasing polymer dosages. First, the lag time(Region A) reduces as the dosage increases up to 28.2 mg/ℓ of polymer dosage. It mean that the rate of particle-polymer collision is increased with an increase in polymer dosage. The higher the polymer dosage, the shorter the time required for the particles to acquire enough polymers to become destabilized. At 28.2 mg/ℓ of polymer dosage flocculation begins about 4 min after addition of polymer. This means that particles are not destabilized until about 4 min and thus collisions of particles did not result in flocculation of particles. The low charge density polymer may required a longer polymer adsorption time to acquire sufficient polymer to destabilize the particles(Lee,

1991). Although P-A did not achieve complete flocculation in 16 min of flocculation time, the flocculation is in progress and will lead to a higher-degree of flocculation if a longer flocculation time was allowed, as shown in Fig. 7.

The second effect is the slope of the flocculation curve in region C. Up to 28.2 mg/ℓ of polymer dosage, the slope becomes steeper with an increase in dosage. The steeper slope may be interpreted as a more rapid flocculation and the slope in Region C can be used as an empirical measure of the flocculation rate. Thereafter, the lag time increases and the slope decreases with an increase in polymer dosage. This indicates restabilization because of overdosing. .

The transition in flocculation behavior occurs at the point of near zero charge(PZC) of the humic acid(see Fig. 8(a) and Fig. 10).

An excess coverage of polymer may lead to a reversal of surface charge and the number of suitable vacant sites to allow for polymer bridging are also reduced At 34.7 mg/ℓ of polymer dosage, Flocculation Index is also unchanged.

As shown in Fig. 8(b)~(d), similar trends are found with flocculation tests performed with other polymers.

Fig. 8(b) shows the flocculation curves for P-B of medium charge density(40 %). At the lowest dosage, 16.7 mg/ℓ, the Flocculation Index is essentially unchanged which also indicates little or no flocculation in the 16 min flocculation time. The lag time(Region A) reduces as the dosage increases up to 19.6 mg/ℓ of polymer dosage. The higher the polymer dosage, the shorter the time required for the particles to acquire enough polymers to become destabilized. At 19.6 mg/ℓ of polymer dosage flocculation begins about 3 min after addition of polymer and the values of Flocculation Index has remained a little constant after 11 min flocculation time.

Up to 19.6 mg/ℓ of polymer dosage, the slope becomes steeper with an increase in dosage. Thereafter, the lag time increases and the slope decreases with an increase in polymer dosage because of restabilization due to overdosing. At 26.3 mg/ℓ of polymer dosage, Flocculation Index is also unchanged.
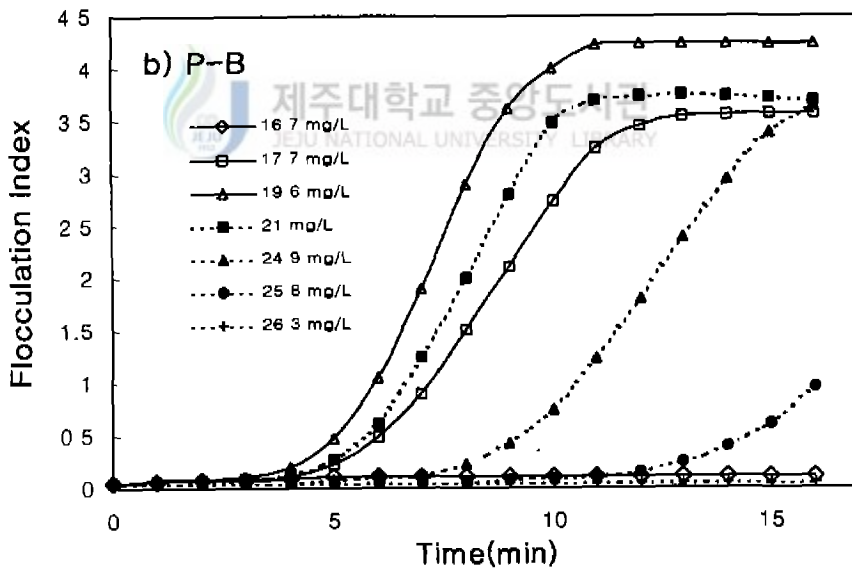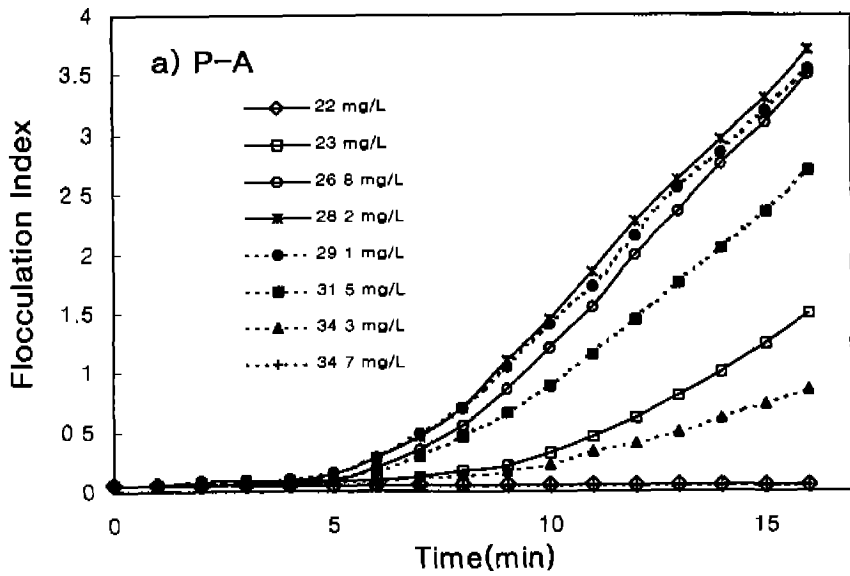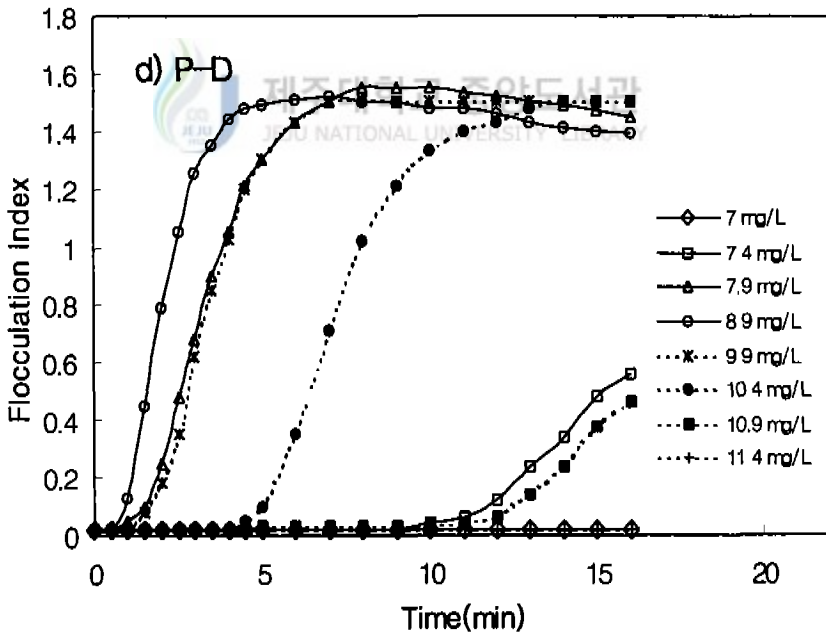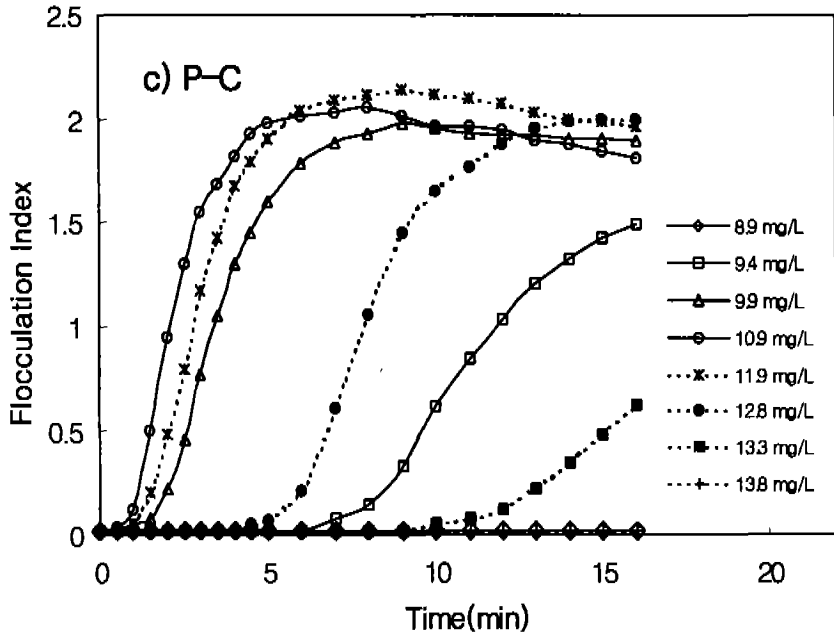
Fig. 8. The effects of dosage on the flocculation of humic acid
solution(25 mg/ℓ) using P-A(a), P-B(b), P-C(c) and
P-D(d).

Fig. 8(c) shows the flocculation curves for P-C of high charge density(100 %). At the lowest dosage, 8.9 mg/ℓ, the Flocculation Index is essentially unchanged which also indicates little or no flocculation in the 16 min flocculation time. The lag time(Region A) reduces as the dosage increases up to 10.9 mg/ℓ of polymer dosage. The higher the polymer dosage, the shorter the time required for the particles to acquire enough polymers to become destabilized At 10.9 mg/ℓ of polymer dosage, flocculation begins about 1 min after addition of polymer and the values of Flocculation Index has remained constant or a little decrease after 5 min flocculation time.

Up to 10.9 mg/ℓ of polymer dosage, the slope becomes steeper with an increase in dosage. Thereafter, the lag time increases and the slope decreases with an increase in polymer dosage.

Fig 8(d) shows the flocculation curves for P-D of high charge density(100 %) At the lowest dosage, 7.0 mg/ℓ, the Flocculation Index is essentially unchanged which also indicates little or no flocculation in the 16 min flocculation time. The lag time(Region A) reduces as the dosage increases up to 8.9 mg/ℓ of polymer dosage. The higher the polymer dosage, the shorter the time required for the particles to acquire enough polymers to become destabilized. At 8.9 mg/ℓ of polymer dosage flocculation begins about 1 min after addition of polymer and the values of Flocculation Index has remained constant or a little decrease after 4 min flocculation time.

Up to 8.9 mg/ℓ of polymer dosage, the slope becomes steeper with an increase in dosage. Thereafter, the lag time increases and the slope decreases with an increase in polymer dosage.

The use of P-C and P-D gives a relatively lower value of Flocculation Index than P-A and P-B. The highest Flocculation Index recorded by P-C and P-D do not exceed 2.2 and 1.6 respectively. The highest Flocculation Index recorded by other polymers are mostly greater than 3. In the case of P-B, it can be as high as 4 25. A combination of factors, such as the low molecular mass, high

charge density and different chemical nature of the polymers, can contribute to the relatively low Flocculation Index of P-C and P-D. It is found that highly charged polymer adsorbed adopts a very flat conformation under low ionic strength(Kjellin et al., 1997). Another consideration is the effect of the size of the adsorbed polymer patches on the attraction between colliding particles. The size of P-B is considerably larger than those of P-C and P-D(shown in Table 3) and the length of the loops and tails of adsorbed polymer molecules may be longer for the larger molecules and this will enhance the capture of particles.

There are virtually short lag time with higher charge density polymers(P-C, P-D). This indicates the destabilization of the particles are rapid for a polymer of higher charge density.

The rate of polymer molecules re-conformation on particle surface may be more rapid with a higher charge density polymer. The attraction between oppositely charged polymer and particles may be stronger for a polymer of high charge density because the number of charges per polymer molecule will be higher. As a result, the interaction between oppositely charged particles and polymer is expected to be higher for the polymer of higher charge density and thus will result in a more effective particle destabilization.

It is thought by the value of Flocculation Index that P-A and P-B are a more effective flocculant than P-C and P-D. However, residual fraction of humic acid did not agree with the order of the value of Flocculation Index.

2) Removal efficiency

Fig. 9 shows the residual fraction of humic acid after flocculation test as shown in Fig. 7 then settling for 2 hrs(a) or centrifuging(b). The residual fraction of humic acid was measured as the absorbance ratio at 254 nm between the residual and initial humic acid solution(25mg/ℓ).
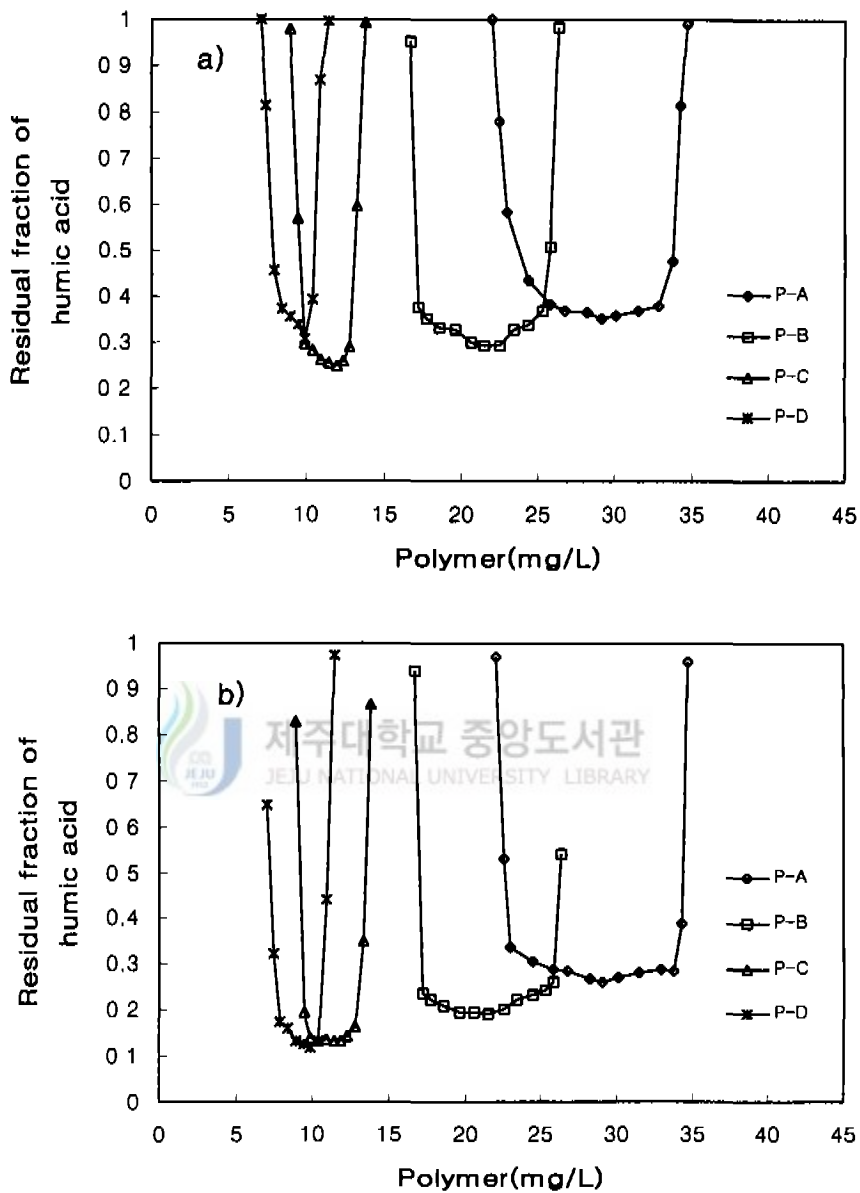
Fig. 9. The effects of dosage on the residual fraction of humic acid
solution(25 mg/ℓ) after flocculation tests and settling for
2 hrs(a) or centrifuging(b).

As shown in residual fraction of humic acid in Fig. 9, flocculation is found to occur over a wide range of polymer dosages. Gregory(1973) has shown that the range of polymer dosages was dependent on the characteristics of the polymer and the range became broader with increasing molecular mass for a fixed ionic strength.

The optimum dosage for a given system is very difficult to define. In the case of P-A as shown in flocculation curve in Fig. 8(a), the optimum dosage appears to be about 28.2 mg/ℓ of polymer dosage where the slope is steepest and the maximum value of Flocculation Index is highest. However, it can easily be observed that almost same degree of removal of humic acid over a broad range of polymer dosage was shown in residual fraction of humic acid in Fig. 9

Because of the very low density of flocs, their settling rate in water is experimently low and removal by sedimentation would not be significant, even after 2 hrs of settling time.

The removal efficiencies of humic acid after settling for 2 hrs shown in Fig. 9(a) were in this order ; P-C > P-B≥ P-D > P-A. However, the removal efficiencies of humic acid after centrifuging in 3,000 rpm for 20 min were in this order , P-D ≥ P-C > P-B > P-A. This strangeness seems to be caused by the relative settling rate of flocs induced by the difference of floc size and floc density. Parazak et al.(1988) thought that polymers, having the smallest molecular weight and size, has by far the greatest adsorption density.

In many of the flocculation tests, a settleable floc was not formed. Instead, flocculation produced a colloidal solution that proved to be stable and remained in suspension after the designated period of settling. However, this sol will be effectively removed by the subsequent filtration step, leading to near or same removal efficiency that of centrifuging. Actually, the removal efficiencies of humic acid after settling for 24 hrs show no or a little differences with that after centrifuging in 3,000 rpm for 20 min.

The results(presented in Fig. 9) show a strong inverse correlation between the flocculation range and the charge density, with the most highly charged polymer giving the shortest flocculation range. In fact, the results indicate that, in each case, the flocculation range corresponds roughly with the same amount of cationic charge, pointing the importance of charge neutralization, as shown in Fig. 10.

Zeta potential can be used to give an indication of the double-layer repulsive forces of the particle and have been used successfully to obtain useful information in many investigations on the stability of colloids(Chandrakanth and Amy, 1996; Fairhurst and Warwick, 1998; Fairhurst et al., 1995; Kretzschmar et al., 1998; Okubo and Suda, 1999; Schwarz et al., 1998; Tsuruta et al., 1995). The adsorption of cationic polymer may neutralize the surface charge of the negatively charged particles and a reversal of particle charge will occur if an excess amount of polymer is adsorbed.
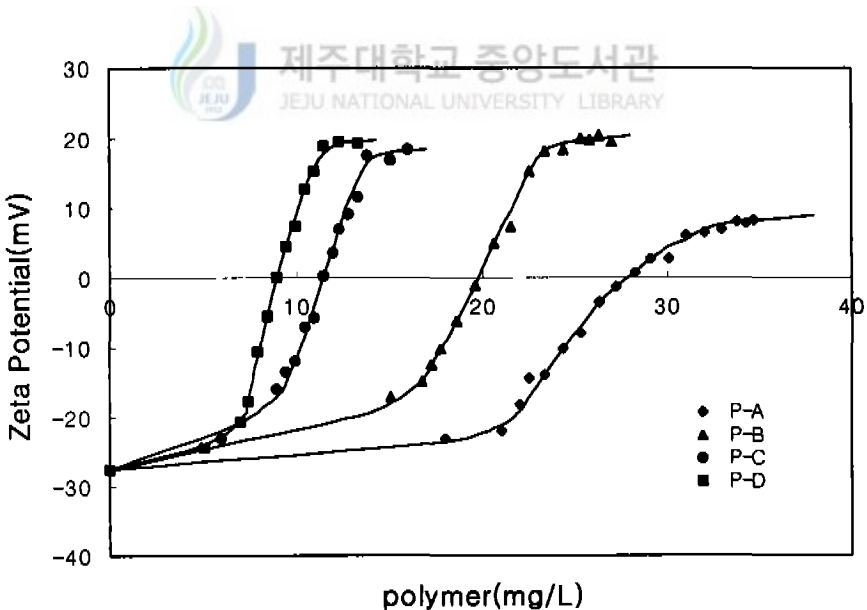

Fig. 10. The effects of dosage on the zeta potential of humic acid solution(25 mg/ℓ).

Fig. 10 shows the zeta potential of humic acid solution(25 mg/ℓ) for four polymers and with an excess amount of polymer the zeta potential reaches a plateau value which represents the maximum positive charge attained by the particles. Maximum positive charge of the particle is primarily determined by the amount of cationic charge residing on polymer in the adsorbed state when the coverage of the particle surface is completed. The ultimate amount of adsorbed polymer is independent of the molecular mass but dependent on the surface available(Lee, 1991). The amount of positive charge gained at complete surface coverage depends quite strongly on the charge density of the polymer. P-B(a 40 % charged polymer) gives a positive charge about two or three times higher than P-A(a 20 % charged polymer). The respective maximum positive zeta potential of these two polymers shows a good correlation with the ratio of their charge densities. The maximum positive zeta potential for the 100 % charged polymers(P-C, P-D) are lower than expected. This is because the lateral repulsion among charged segments of polymer molecules for highly charged polymer is higher than that for polymers of low charge density. Also, P-C and P-D are expected to adsorb in a rather "flattened" conformation because of the high charge density and low molecular mass of the polymers(Lee, 1991). Therefore, the amount of polymer adsorbed at full polymer coverage is less for P-C and P-D than for those polymers which can adsorb in a more extended conformation. As a results, the amount of excess positive charge remaining is also less, giving a lower maximum positive zeta potential than expected. It should also be mentioned that care should be taken when comparing the results of P-C and P-D with other polymers because these polymers are made from different types of monomers.

As shown in Fig. 10, the lower dosage were required to flocculate the humic acid solution(25 mg/ℓ) with the polymers of higher charge density, indicating the amount of adsorbed polymer molecules required to destabilize the particles are less for a polymer of higher charge density and also reinforce the

importance of charge neutralization.

3. Effects of the content of kaolin particles


1) Flocculation characteristics

Mineral and organic particles may be stable in water due to electrostatic charge interactions, hydrophilic effects or to steric interactions from adsorbed macromolecules.

Humic substances and clay are negatively charged and so, on average, electrostatic repulsion would be expected, but humic substances are adsorbed to clay surfaces by a variety of mechanisms including electrostatic attractive forces, specific adsorption via ligand exchange with protonated surface hydroxyl groups(surface $-OH_2^+$ or $-OH$ groups exchange with anionic groups on the humic acid), cation bridging, water bridging in the presence of hydrated cations on the surfaces, and hydrophobic adsorption of uncharged parts of humic acid macromolecules(Fairhurst and Warwick, 1998; Jekel, 1991; Kretzschmar et al., 1998; Zhou et al., 1994). It is almost certain that, due to the heterogeneous nature of humic acid, the wide range of mineral surface chemistries in the environment and the complex nature of groundwaters, adsorption of humic acid will be a combination of some, or all, of the above forces

Edzwald(1993) thought that natural organic matter(NOM) rather than particles initially in water supplies can control coagulat dosages and selection.

Fig. 11(a)~(d) show the effects of the content of kaolin particles on the flocculation of salt-free humic acid solution using P-A(29.1 mg/ℓ, a), P-B(20.6 mg/ℓ, b), P-C(11.9 mg/ℓ, c) and P-D(9.9 mg/ℓ, d), each dosage shows maximum removal efficiencies of humic acid solutions(25 mg/ℓ) in the UV
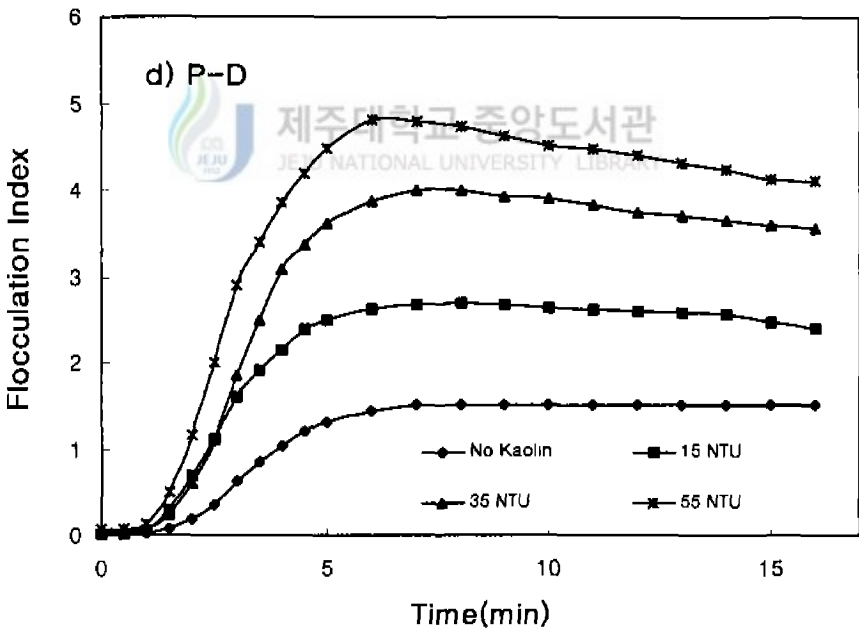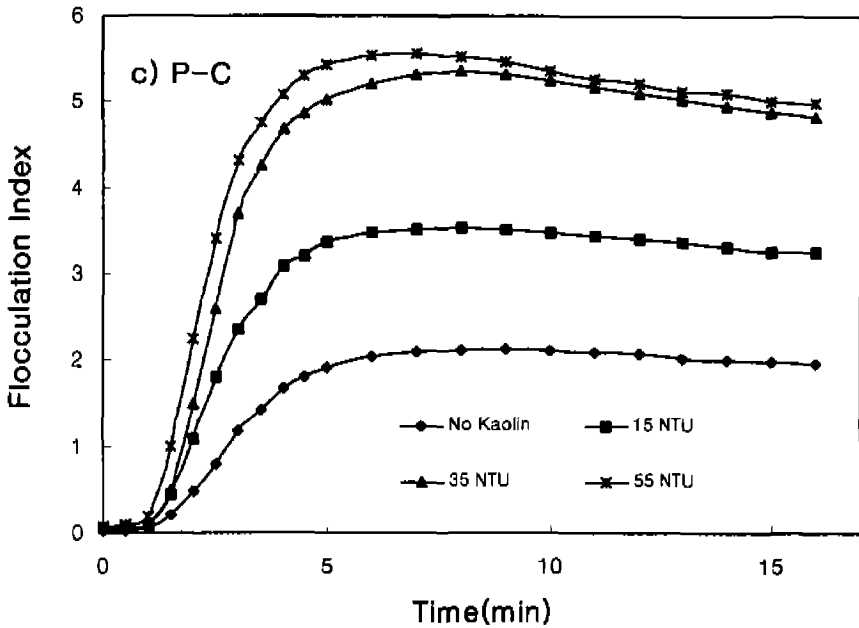
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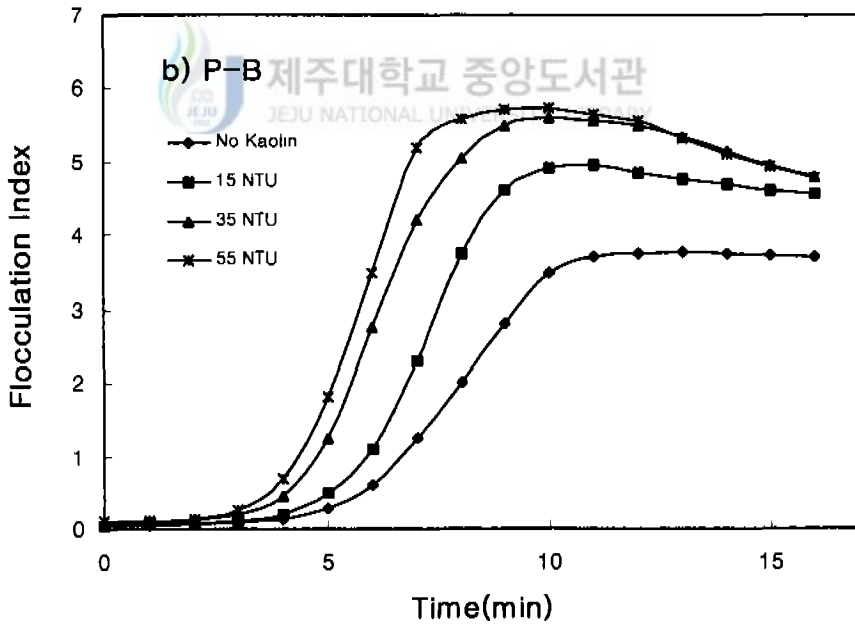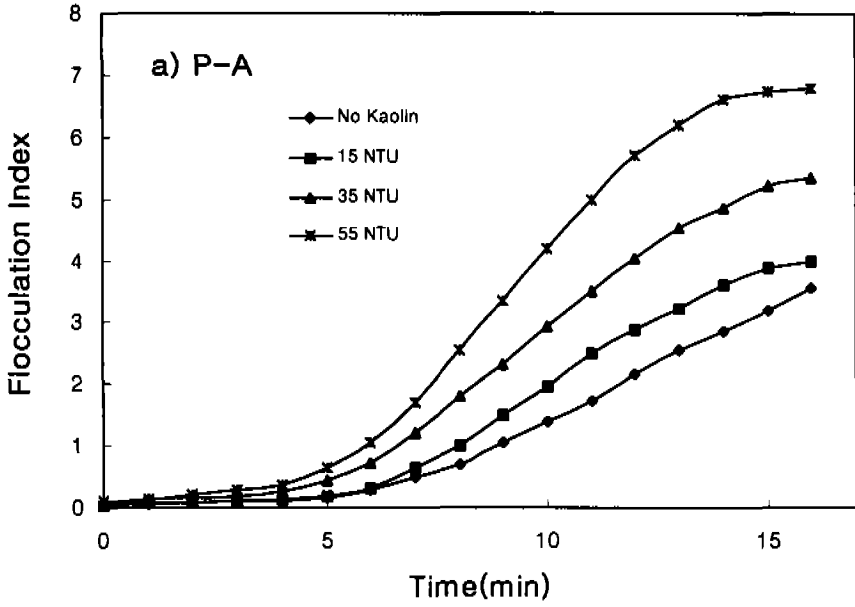
Fig. 11. The effects of the content of kaolin particles on the flocculation of humic acid solution using P-A(29.1 mg/ℓ, a), P-B(20.6 mg/ℓ, b), P-C(11.9 mg/ℓ, c) and P-D(9.9 mg/ℓ, d).

In the presence of kaolin particles, flocculation is also found to occur over a wide range of polymer dosages and it is observed that almost same degree of removal of humic acid was shown over a broad range of polymer dosages.

With increasing the content of kaolin particles however, the lag time reduces and the slope of the flocculation curve becomes steeper followed by higher value of Flocculation Index.

2) Removal efficiency

Fig. 12 shows the maximum removal efficiencies of humic acid solution with the presence of kaolin particles using P-A~P-D by UV absorbance(a) and turbidity(b). Fig. 12(a) shows a distinct rise in the maximum removal efficiencies with increasing the content of kaolin particles by highly charged polymers(P-C and P-D). It is probably thought that the kaolin particles provide nucleation sites for floc formation leading to short settling time resulted in a much stronger and denser floc. Floc density is known to increase with increase in mineral particle content. Density and strength of flocs affects both the flocculation-settling process and the contact coagulation-filtration process. Poorer settling of flocs formed in highly colored low turbidity waters(Rebhun and Lurie, 1993). Another reason is that the polymers are firmly bound to the kaolin surfaces due to the many attachments which is a consequence of their large size.

However, the maximum removal efficiencies by UV absorbance are the same or a little decrease in the humic acid solution with 55 NTU kaolin particles than that in the humic acid solution with 35 NTU kaolin particles using low charge density polymers(P-A and P-B), although using a P-A and P-B show a distinct rise in the maximum removal efficiencies with increasing the content of kaolin particles up to 35 NTU. Since, there is no information available on the polymer segment density distribution with increasing the content of kaolin

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particles for the system studied, it is not possible to verify this point, leaving a room for more study.
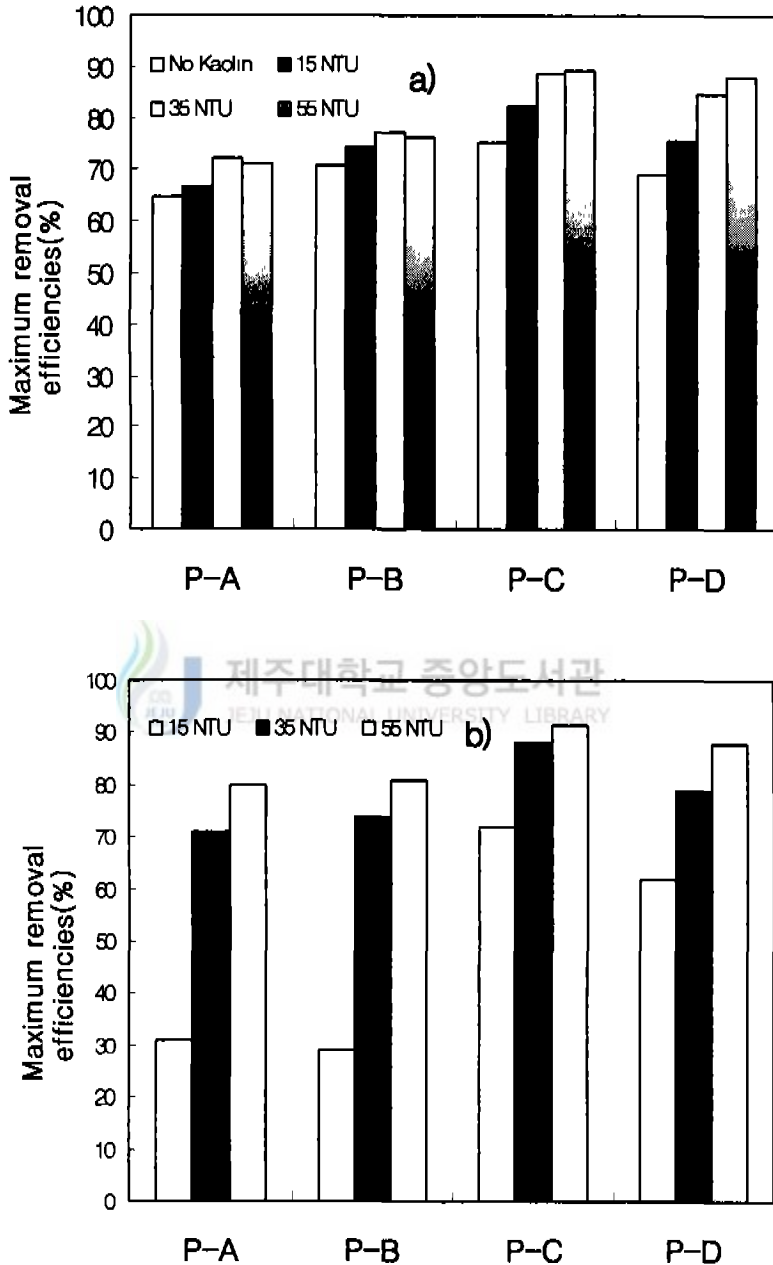
Fig. 12. The effects of the content of kaolin particles on the maximum removal efficiencies by UV absorbance(a) and turbidity(b).

We have not been able to measure the binding isotherm and thus do not know the free kaolin concentration. So we measure the turbidity of the solution before and after flocculation test and shows the maximum removal efficiencies of the turbidity in Fig. 12(b) between the residual and initial humic acid solution with the presence of kaolin particles. A distinct rise in the maximum removal efficiencies was shown with increasing the content of kaolin particles by four polymers. However, the removal efficiencies of the humic acid with the presence of 15 NTU kaolin particles show poorer efficiencies by low charge density polymers than that by high charge density polymers.

Fig. 13. The effects of the content of kaolin particles on the zeta potential of humic acid solution(25 mg/ℓ with 35 NTU) (four solid lines show the zeta potential of humic acid solution without the presence of kaolin particles by each polymer).

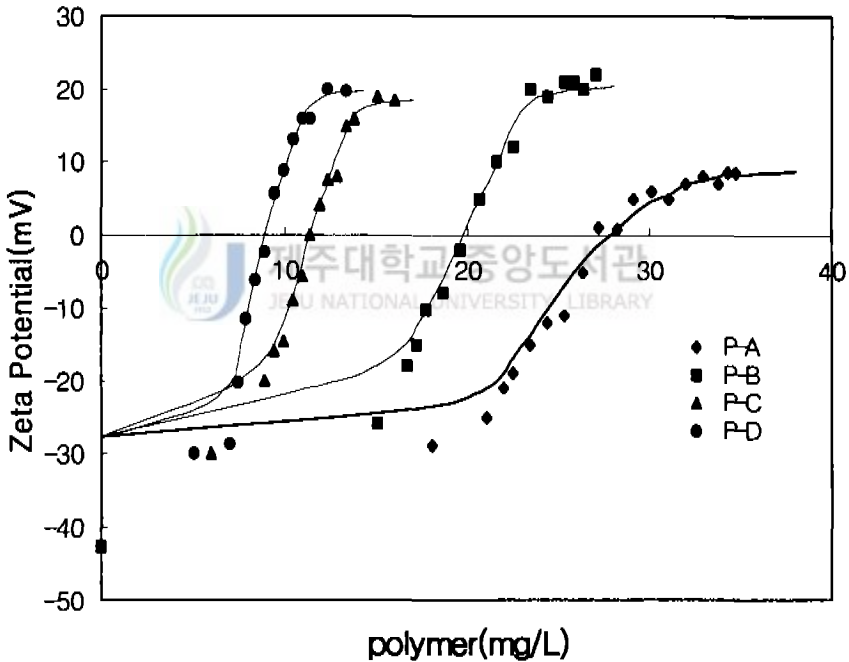Fig. 13 shows the zeta potential of humic acid solution(25 mg/ℓ) with 35 NTU kaolin particles. In the presence of kaolin particles, the strong shift is observed in zeta potential as a result of adsorption of the particles by humic acid. Four solid lines represent the zeta potential of humic acid solution without the presence of kaolin particles At low polymer dosages, the value of zeta potential are lower than that in the humic acid solution without the presence of kaolin particles. However, with increasing the polymer dosages, the value of zeta potential are somewhat in accordance with the solid lines, giving the maximum positive value likes humic acid solution without the presence of kaolin particles.

4. Effects of ionic strength

1) Flocculation characteristics

The ionic strength of the solution can affect polymeric flocculation in several ways. The destabilization and restabilization of negatively charged particles by cationic polymers occur primarily by charge neutralization.

In order to certify the effect of ionic strength, flocculation curves and residual fraction of humic acid at different concentration of NaCl are presented for different polymers.

Fig. 14(a)~(d) show the flocculation curves of humic acid solution(25 mg/ℓ) for each polymer dosages at a range of salt concentrations from deionized water to 311mM NaCl.

In the presence of a moderate amount of electrolyte, less polymer is needed to bring about flocculation(Lee, 1991).

The polymer used in Fig. 14(a) was P-A and show that there is no

flocculation at a polymer dosage of 22 mg/ℓ in a salt-free solution. However, significant flocculation occurs when salt is present.

Two distinct effects are also observed with increasing NaCl concentration. First, the lag time(Region A) reduces as the NaCl concentration increases up to 5.1 mM. At 5.1 mM of NaCl concentration flocculation begins about 4 min after addition of polymer. This also means that particles are not destabilized until about 4 min and thus collisions of particles did not result in flocculation of particles.

The second effect is the slope of the flocculation curve in region C. Up to 5.1 mM of NaCl concentration, the slope becomes steeper with an increase in NaCl concentration. The steeper slope may be interpreted as a more rapid flocculation. Thereafter, the lag time increases and the slope decreases with an increase in NaCl concentration.

At 17 mM of NaCl concentration, Flocculation Index is also unchanged which indicates restabilization because of overdosing.

As shown in Fig. 14(b)～(d), similar trends are found with flocculation tests performed with other polymers.

The polymer used in Fig. 14(b) was P-B and show that there is no flocculation at a polymer dosage of 16.7 mg/ℓ in a salt-free solution. However, significant flocculation occurs when salt is present. The lag time(Region A) reduces as the NaCl concentration increases up to 8.5 mM. At 8.5 mM of NaCl concentration flocculation begins about 3 min after addition of polymer and the values of Flocculation Index has remained a little constant after 13 min flocculation time.

Up to 8.5 mM of NaCl concentration, the slope becomes steeper with an increase in NaCl concentration. Thereafter, the lag time increases and the slope decreases with an increase in NaCl concentration.
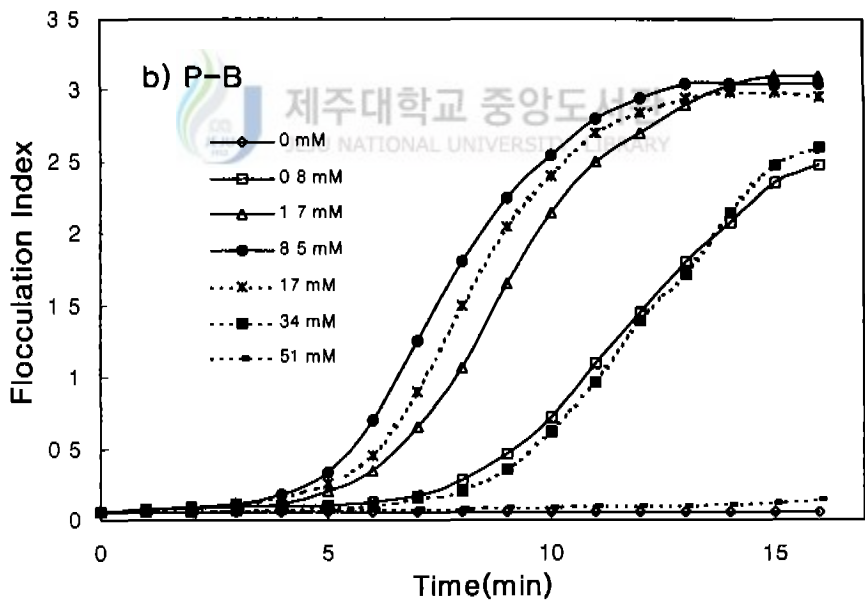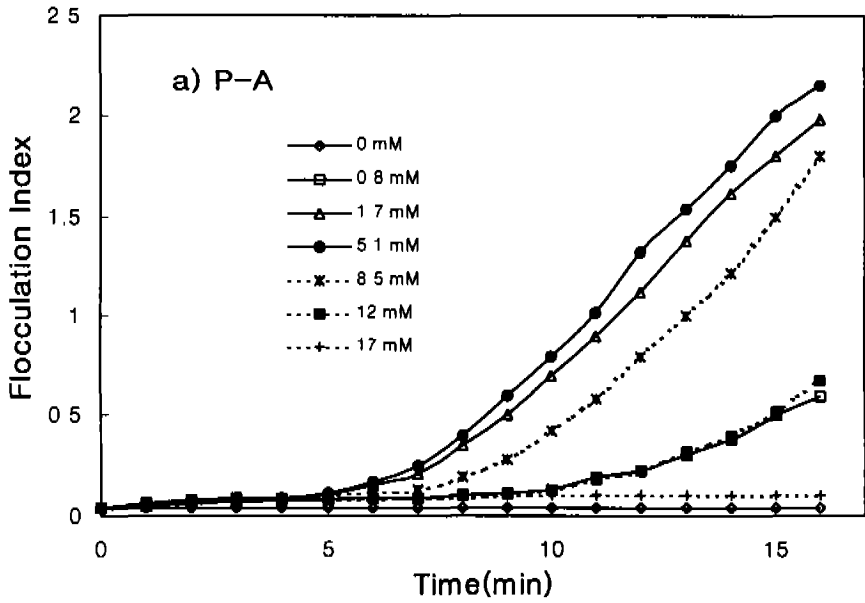
At 51 mM of NaCl concentration, Flocculation Index is also unchanged which indicates restabilization because of overdosing.

a) P-A

Flocculation Index vs Time(min)

- 0 mM
- 0 8 mM
- 1 7 mM
- 5 1 mM
- 8 5 mM
- 12 mM
- 17 mM

b) P-B

Flocculation Index vs Time(min)
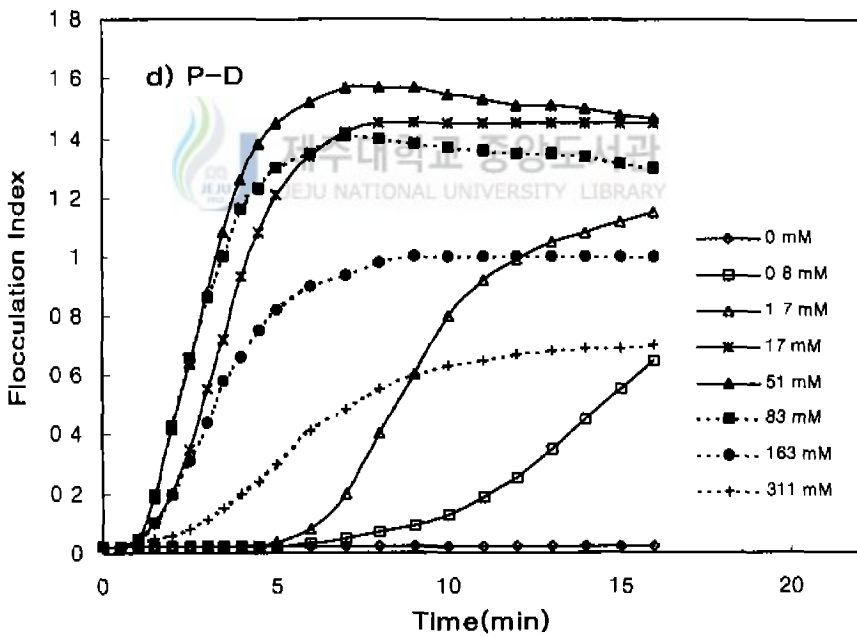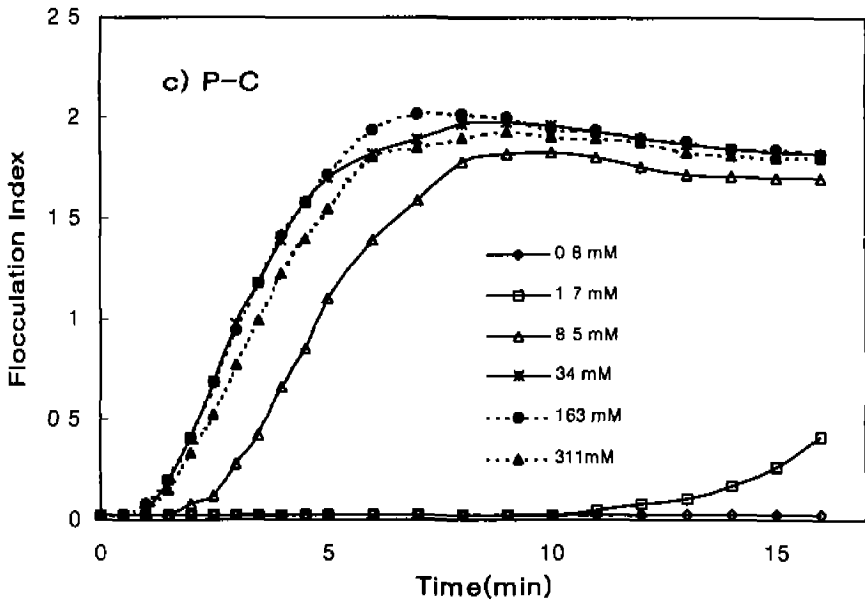
- 0 mM
- 0 8 mM
- 1 7 mM
- 8 5 mM
- 17 mM
- 34 mM
- 51 mM

Fig. 14. The effects of ionic strength on the flocculation of humic acid solution(25 mg/ℓ) using P-A(22 mg/ℓ, a), P-B(16.7 mg/ℓ, b), P-C(8.9 mg/ℓ, c) and P-D(7 mg/ℓ, d).

The polymer used in Fig. 14(c) was P-C and show that there is no flocculation at a polymer dosage of 8.9 mg/ℓ in a 0.8 mM NaCl concentration. However, significant flocculation occurs when NaCl concentration increases. The lag time(Region A) reduces as the NaCl concentration increases up to 163 mM. At the range of 34 mM~163 mM of NaCl concentration, flocculation begins about 1 min after addition of polymer and the values of Flocculation Index has remained constant or a little decrease after 6 min flocculation time.

Up to 163 mM of NaCl concentration, the slope becomes steeper with an increase in NaCl concentration. Thereafter, the lag time increases and the slope decreases with an increase in NaCl concentration.

At higher NaCl concentration(up to 311 mM), flocculation is still effective for the experiment conditions.

The polymer used in Fig. 14(d) was P-D and show that there is no flocculation at a polymer dosage of 7 mg/ℓ in a salt-free solution. However, significant flocculation occurs when NaCl concentration increases. The lag time(Region A) reduces as the NaCl concentration increases up to 51 mM. At 51 mM of NaCl concentration, flocculation begins about 1 min after addition of polymer and the values of Flocculation Index has remained constant or a little decrease after 7 min flocculation time.

Up to 51 mM of NaCl concentration, the slope becomes steeper with an increase in NaCl concentration. Thereafter, the lag time increases and the slope decreases with an increase in NaCl concentration.

At higher NaCl concentration(up to 311 mM), flocculation is still effective for the experiment conditions.

The response of polymer towards the effect of ionic strength of the solution depends on the characteristics of the polymer and the charge density of the polymer is an important parameter as the destabilization is essentially due to charge neutralization.

For P-A and P-B, the Flocculation Index achieved in salt solution are lower

than the corresponding Flocculation Index achieved in salt-free solutions for the range of polymer dosages. However, the flocculation curve in Fig. 14(c)~(d) show that P-C and P-D do not fit in with the above results.

The adsorption of polymer involves the desorption of adsorbed counter ions ; sodium ions for the negatively charged particles and chloride ions for the cationic polymer. The need to displace these weakly adsorbed ions for flocculation to take place may be responsible for the lowering of Flocculation Index in salt solutions. The extent of the displacement of adsorbed counter-ions depends on the characteristics of the polymer and of the particles, such as how strongly are the respective counter-ions adsorbed and the degree of the polymer-particle interaction(Lee, 1991).

The destabilization is caused by charge neutralization due to adsorbed polymer and partly by reduction of electrical repulsion due to the salt effect. Based on the Gouy-Chapman theory of the diffuse double layer, the thickness can be significantly compressed by the presence of NaCl(Müller et al., 1980 ; Rashid et al., 1972). A reduction in the effective range of the electric double layer also encourages the flocculation of particles by adsorbed polymer molecules.

An increase in ionic strength reduces the repulsion between charged segments of the polymer chain(the polymer chain adopts a more compact conformation) as well as reducing the range of inter-particle repulsion. These effects may affect the polymer adsorption and flocculation efficiency, leading to an optimum ionic strength(Lee,1991).

2) Removal efficiency

The results(presented in Fig. 15(a)) show that flocculation of humic acid by highly charged polymers(P-C, P-D) occurs over a broad range of ionic strength than that of lower charge density polymers(P-A, P-B).
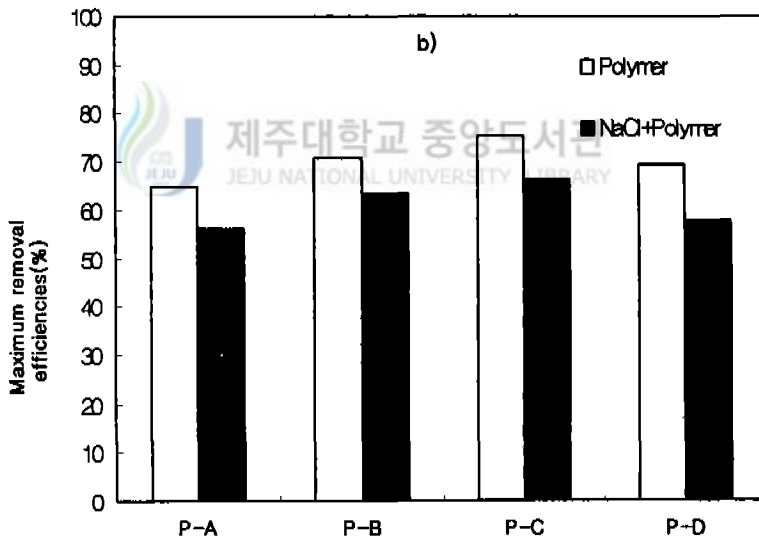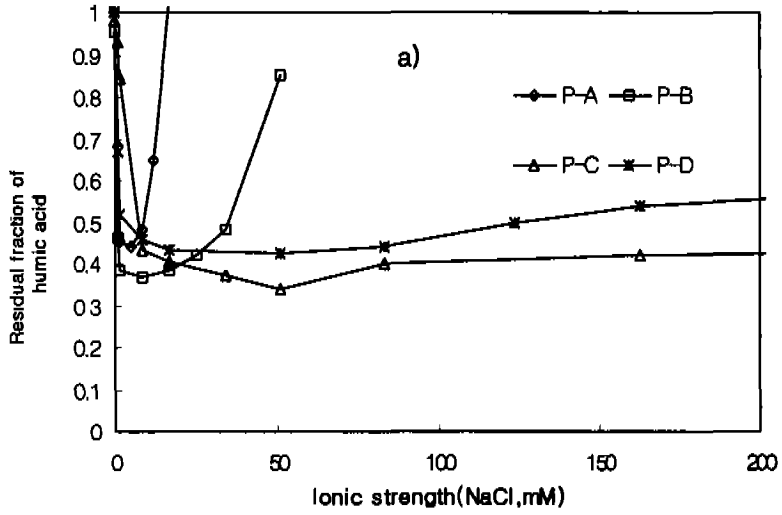
Fig. 15. The effects of ionic strength on the residual fraction of humic acid solution(25 mg/ℓ) after flocculation tests and settling for 2 hrs(a) and on the maximum removal efficiencies by UV absorbance(b).

Although flocculation of humic acid by P-A and P-B occurs within 17 mM and 51 mM of NaCl concentration respectively, P-C and P-D does not show the maximum NaCl concentration for the experiment conditions.

Although P-C and P-D show no distinct differences in the value of Flocculation Index in salt solution, poor removal efficiencies of humic acid in salt solution were acquired than in salt-free solutions, as presented in Fig. 15(b). It is possible that particles are destabilized by low polymer dosage in the presence of added salt but the ultimate removal efficiencies may be lower than in salt-free solutions.

The optimum ionic strength for a polymer of a given cationic charge density is difficult to establish. This is because the molecular mass and the chemical nature of the polymer, as well as the charge density should be taken into account.

The influence of the salt effects on the value of Flocculation Index, flocculation efficiency and the range of ionic strength still remains to be elucidated.

Ⅴ. Conclusions

In order to remove humic acid solutions containing different content of kaolin particles and ionic strength by flocculation method, four cationic polymers of different charge density and molecular mass were used, and the flocculation characteristics and the subsequent removal of humic acid were investigated with the dosage of each polymer, the content of kaolin particles and ionic strength.

The lag time between the addition of polymer and the onset of flocculation of humic acid was shorter and the flocculation rate was faster for polymers of high charge density(P-C and P-D) than that for polymers of low and middle charge density(P-A and P-B), indicating the destabilization of humic acid occurs rapidly when the polymers of higher charge density were used.

There is a strong inverse correlation between the charge density of the polymers and the range of polymer dosages required to flocculate humic acid, with highly charged polymers giving the shorter dosage ranges. Also it was found that the lower dosages were required and the higher removal efficiencies was obtained with the polymers of higher charge density, indicating the importance of charge neutralization.

The flocculation extent and removal efficiencies of humic acid by each of the polymers were increased by the presence of kaolin particles, which is considered to be due to a larger and denser floc formation by the act of kaolin particles as nuclei.

The zeta potential data show the charge effect of adsorbed polymer on the destabilization of humic acid solution with and without the presence of kaolin particles. The dosages required to give zero zeta potential somewhat correlate with the maximum removal efficiency.

The ionic strength of the solution can affect the polymer dosage and flocculation efficiency. Particles are destabilized by low polymer dosage in the

flocculation efficiency. Particles are destabilized by low polymer dosage in the presence of added salt but ultimate removal efficiencies may be lower than that in salt-free solutions by each of the polymers.

There is a correlation between the ionic strength range of the solution and charge density of the polymers, with highly charged polymer giving the broader flocculation range than that with low charged polymer.

However, the influence of the content of kaolin particles and ionic strength effects on flocculation of humic acid still remains to be elucidated.

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감사의 글

대학생활 동안 저를 지켜봐 주시고 학문적 가르침으로 지도해 주신 감상규 교수님께 진심으로 감사를 드립니다. 그리고 바쁘신 중에도 저의 논문을 세심하게 검토해 주신 허철구 교수님과 이용두 교수님, 항상 깊은 관심과 조언을 아끼지 않으셨던 오윤근 교수님, 허목 교수님, 이기호 교수님, 조은일 교수님께도 깊이 감사드립니다.

짧은 시간동안이나마 실험을 할 수 있도록 도와주신 곽종운 박사님과 워테크 기술 연구소 내 모든 분들과 여러모로 조언을 주신 보건환경 연구원 송영철 선배님께 감사드리고, 대학원 생활을 하면서 어려움을 나눴던 김경훈, 류성필, 오희부, 이명훈, 한지용, 고민철, 김승건, 김현희, 양순미, 이정미, 김지영, 김병현, 강병낭, 강춘희, 강진영, 송희경 학형과 김창영 교수님, 박용이 교수님, 조영우 선생님, 문창성 선생님께도 이 자리를 빌어 고마움을 전합니다.

실험실 생활을 하면서 많은 힘이 되어준 김길성, 장원재, 김재성, 오승희, 변경미, 오재영 선배님께 감사드리고, 항상 옆에서 도와준 혜림, 은경, 현정, 경훈, 경호, 유경, 정호, 병건, 또 논문을 준비하느라 바쁜 중에도 도움을 준 성수 형에게도 감사드립니다.

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