

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

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The effects of pH (5, 7 and 9) and ionic strength of different salts on the flocculation characteristics of humic acid by inorganic (alum, polyaluminum chloride (PAC) with degree of neutralization, $r=(\text{OH}/\text{Al})$ of 1.7) and organic (cationic polyelectrolyte) coagulants, have been examined using a simple continuous optical technique, coupled with measurements of zeta potential. The results are compared mainly by the mechanisms of its destabilization and subsequent removal. The destabilization and subsequent removal of humic acid by PAC and cationic polyelectrolyte occur by a simple charge neutralization, regardless of pH of the solution. However, the mechanism of those by alum is greatly dependent on pH and coagulant dosage, i.e., both mechanisms of charge neutralization at lower dosages and sweep flocculation at higher dosages at pH 5, by sweep flocculation mechanism at pH 7, and little flocculation because of electrostatic repulsion between negatively charged humic acid and aluminum species at pH 9. The ionic strength also affects those greatly, mainly based on the charge of salts, and so is more evident for the salts of highly charged cationic species, such as CaCl_2 and MgCl_2 . However, it is found that the salts have no effect on those at the optimum dosage for alum acting by the mechanism of sweep flocculation at pH 7, regardless of their charge.

Key Words : Flocculation, Humic Acid, pH, Ionic strength, Inorganic and organic coagulants, Zeta potential

1. Introduction

Natural organic matter (NOM) in water may impart undesirable color to water and some constituents can form carcinogenic and mutagenic by-products when water is chlorinated^{1,2}. NOM consists of a huge variety of organic compounds including simple sugars, amino acids, organic acids, proteins and many others. In most cases, so-called 'humic substances' are major components of aquatic NOM³. Humic substances are complex, heterogeneous, refractory organic compounds with phenolic and alcoholic hydroxyl, carboxyl, keto and quinoid functional groups which may be protonated-deprotonated depending on pH that exist in all soil and water environments^{4~6}. They are thought to originate from decomposition of plant and animal re-

mains, their molecular weight ranges from several hundred to hundreds of thousands, and their predominant fractions are fulvic and humic acids in natural waters^{3,7}.

Since the presence of NOM in water makes unacceptable for drinking purposes because of undesirable color and the formation of carcinogenic and mutagenic by-products during chlorination as mentioned above, it should be removed during water treatment. Several techniques are used to remove NOM and a very common method is flocculation, followed by either filtration, sedimentation or flotation. Since NOM is nearly anionic over the natural waters, they can interact with cationic additives, such as inorganic (e.g., hydrolyzing metal salts and their pre-hydrolyzed materials) and organic coagulants (e.g., cationic polyelectrolytes).

The flocculation process operated in many water treatment plants in Korea and other countries, is optimized primarily for the removal of turbidity. Optimum

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conditions for turbidity removal are not always the same as those for NOM removal, but provided that the turbidity of the water is not excessive, the coagulant demand is governed by the concentration of NOM^{8,9)}, indicating that the treatment process should be optimized for NOM removal when NOM is the major contaminants. It is frequently found that the optimum dosage of the coagulant is close to that required to neutralize the surface charge carried by the impurities, although there are some important exceptions¹⁰⁾, and the charges of the coagulant and the impurities are dependent on pH of the solution^{11,12)}. Moreover, the dosage is variable depending on the ionic strength of the solution^{13,14)} and coagulants used because of impurities destabilization by different mechanisms⁷⁾.

It is well-known that metal salts, such as alum (aluminum sulfate), are rapidly hydrolyzed to form cationic hydroxide species and hydroxide precipitate, depending on pH of the solution. Cationic hydroxide species interacts with anionic impurities in water to form insoluble charge-neutral products (charge neutralization). Metal hydroxide precipitates tend to have a rather open structure, so that even a small mass can give a large effective volume concentration and, hence, a high probability of capturing impurities. This mechanism has become known as 'sweep flocculation' (entrapment or surface adsorption) since impurities are swept out of water by an amorphous hydroxide precipitate⁷⁾.

Pre-hydrolyzed materials are often found that to be considerably more effective than traditional coagulants¹⁵⁾, such as alum. In the case of aluminum, most materials are formed by controlled neutralization of aluminum chloride solutions and generally known as polyaluminum chloride (PAC). PAC products seem to be give better flocculation than alum at low temperature and are also claimed to produce lower volumes of residual solids (sludge). Because they are already partially neutralized, they have a smaller effect on pH of the water and so reduce the need for pH correction. However, the mechanisms of the action of PAC and similar products are still not well understood. Most explanation are in terms of the high charge associated with species such as $\text{Al}_{13}(\text{Al}_{13}\text{O}_4(\text{OH})_{24})^{7+}$ and the consequent effectiveness in neutralizing the negative charge of colloids in water. The relatively high

stability of PAC means that it should be more readily available for adsorption and charge neutralization at around neutral pH. However, charge neutralization cannot be the only mechanism of destabilization, which is less effective than sweep flocculation. It is still not clear what role hydroxide precipitation plays in the action of pre-hydrolyzed coagulants. It has been shown recently that the volume of sediment produced in flocculation of clay suspensions by commercial PAC products is proportional to the coagulant dosage¹⁶⁾. This implies that some form of sweep flocculation is operating, since the volume of hydroxide precipitate would be expected to depend on the amount of coagulant added.

In contrast to these inorganic coagulants, it is well-known that organic coagulants, such as cationic polyelectrolytes, destabilize impurities by the mechanism of bridging and neutralization of the surface charge and particle potential¹⁷⁻¹⁹⁾. It can be found that less amount is required to neutralize particle charge and less time is needed to achieve a certain degree of destabilization for the polyelectrolyte of high charge density¹⁹⁾. Also, electrostatic repulsion between polyelectrolyte segments becomes more significant at the higher charge density and this leads to a greater expansion of polyelectrolyte chain. The maximum floc size during the flocculation of particles by the low molecular weight polyelectrolyte is lower than that for the polyelectrolyte of high molecular weight, which is considered to be a weak bridging effect based on lower molecular weight^{17,19)}.

As mentioned above, the flocculation process in many water treatment plants is optimized for the removal of turbidity and the coagulants used are inorganic ones. The purpose of this study is to compare the flocculation characteristics of humic acid (which is a major component of humic substances) by inorganic and organic coagulants at different pH and ionic strength. This study is mainly focused on its flocculation mechanisms by each of the coagulants at different pH and ionic strength. The dynamic aggregation of humic acid solution was monitored by a simple technique, which involves the measurement of transmitted light (turbidity) fluctuations in flowing humic acid solution, and is very sensitive to the state of aggregation of particles^{19,20)}. Measurements of zeta potential (ZP) and residual humic acid concentration

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

provide valuable insights into the different mechanisms of flocculation by each of the coagulants^{21,22}.

2. Materials and Methods

2.1. Materials and equipment

Analytical grade reagents were used and the solutions were prepared with deionized water from a Branstead ultrapure water system.

The coagulants used were inorganic (aluminum sulfate, PAC) and organic (poly(diallyldimethylammonium) chloride, PDDA) ones. A stock aluminum sulfate (alum, $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$, BDH Co., UK) solution was prepared at a concentration of 1,000 mg Al/L. PAC (Summit Research Lab, USA) had a degree of neutralization, $r(\text{OH}/\text{Al})$, of 1.7, and was supplied as a 10.2% Al_2O_3 solution. A stock PAC solution was prepared at a concentration of 100 mg Al/L. To prevent ageing effects of these stock solutions, fresh stock solutions were prepared for a sequence of experiments or renewed every two weeks. The stock solutions were kept in a refrigerator at 4°C. PDDA (Allied Colloids Ltd. (Now Ciba Speciality Chemicals), UK) with an intrinsic viscosity of about 0.2, corresponding to a molecular weight of about 14,000, and a high charge density (about 6 meq/g), was supplied as a 40% aqueous solution and was diluted to give a stock solution of 0.01% or 100 mg/L. This stock solution was used within one week of preparation.

Humic acid was obtained from Aldrich Chem. Co., USA. The stock solution (5 g/L) was prepared by dissolving 2.5 g of humic acid in 500 mL of 0.1 N NaOH and the solution was filtered through a qualitative (Whatmann) filter paper. A working standard solution (25 mg/L) was prepared by diluting 5 mL of this stock solution and 10 mL of 0.1 N Na_2CO_3 to 1 L with water. The Na_2CO_3 was used to fix the initial pH of the humic solution. The humic acid solution was then filtered under vacuum through the pre-washed 0.45 μm cellulose nitrate membrane and adjusted to pH 5, 7 and 9 with 0.1 N or 0.01 N HNO_3/NaOH .

Flocculation monitor is a Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK), the principles of which have been given by Gregory and Nelson²⁰. Basically, the intensity of nar-

row beam of light transmitted through a flowing suspension is monitored by a photodetector, the output of which consists of a steady (dc) component and a much smaller fluctuating (ac) component (The ac component arises from random variations in the number of particles in the suspensions and the fact that the sample is continuously being renewed by flow. The fluctuation follows the Poisson distribution, so that the root mean square (rms) value of the fluctuating signal increases markedly as particle aggregation occurs and provides a very sensitive measure of the extent of flocculation¹⁷).

The flocculating suspension was conveyed through PVC tubing of 2.65 mm internal diameter, by means of a microtube pump (Eyla MP-3N) at a rate of 15 mL/min. The sample continuously passed through the detector of PDA and the monitoring was carried out directly through the transparent tubing. The results were recorded in terms of ratio values ($R=\text{rms}/\text{dc}$), because the dc value may change only slightly as flocculation proceeds and the ratio value provides a signal which is largely immune to such problems as electronic drift and fouling of optical surfaces. The output of PDA 2000 was conveyed to digital form and logged by a chart recorder. The arrangement is systematically shown in Fig. 1.

Zeta potential of humic acid suspension flocculated under different conditions was measured by a Zeta Potential Meter (Sephzy Zetaphoremeter III, France).

The absorbance of humic acid solution was measured by a UV/Vis Spectrophotometer (HP 8452A, USA).

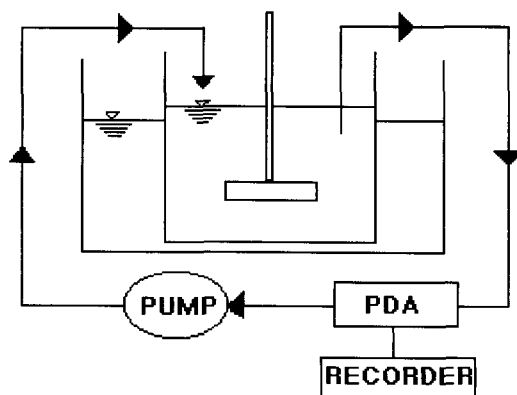


Fig. 1. Flocculation test arrangement.

2.2. Methods

Flocculation tests were carried out in a 300 mL Pyrex beaker with 200 mL of humic acid solutions at a concentration of 25 mg/L containing different concentrations (0, 0.5, 1.0 and 2.0 mM) of electrolytes (NaCl, CaCl₂, MgCl₂), which were placed into a water bath to maintain a constant temperature (20 °C). In these cases, the humic acid solutions were adjusted to pH 5, 7 and 9 with 0.1 N HNO₃/NaOH, as described above, in order to examine the effect of pH on flocculation of humic acid by each of the coagulants. However, prior to the addition of coagulants, the target pH for inorganic coagulants was adjusted by adding a predetermined amount of NaOH into the humic acid solution, with rapid stirring. This procedure was conducted because a sulfate ion based on its high acidic property for alum and a partial neutralization for PAC, lowered the target pH, even if a sodium sulfate solution used for the preparation of humic acid solution has a buffer capacity for the target pH to some extent. The pH changes were greater at pH 7 and 9 for alum and at pH 9 for PAC. However, the target pH changed little for organic coagulant, PDDA. Immediately after the addition of predetermined amount of NaOH and each of coagulants, the humic acid solution was stirred rapidly (200 rpm corresponding to about shear rate 869 s⁻¹) for 1 min, followed by slow stirring (50 rpm corresponding to about shear rate 109 s⁻¹) for 15 min, with a single flat blade (67 mm x 8 mm x 1 mm thick) with a clearance of 10 mm above the base of the beaker. This mixing condition was the optimum in terms of ratio values which show a sensitive indication of the state of aggregation of the particle, in a preliminary experiment. During the stirring, ratio values were logged for analysis. Immediately after flocculation test, 25 mL of the solution or suspension was taken from the beaker for zeta potential measurements. The sample was injected into the cell and the mean zeta potential was computed from 10 readings. Standard deviations ranged around 5% of the mean, or less. The other solution or suspension was centrifugated at 4000 rpm for 20 min, and the supernatant liquid was taken and used for the absorbance at 254 nm, in order to examine the removal efficiency of humic acid or residual humic acid concentration with the dosage of each of the coagulants. The removal efficiency of humic acid was determined by

the calibration curve obtained in a different concentrations (0-25 mg/L) at each pH.

3. Results and Discussion

3.1. Effect of pH

It is well-known that the pH of the solution or suspension affects the flocculation of organic matter or particles by the coagulants^{11,23}. The effect of pH on its flocculation is mainly by simple hydrolyzing metal salts, such as alum. In this study, the effect of pH on flocculation characteristics of humic acid (25 mg/L) by inorganic (alum, PAC) and organic (cationic polyelectrolytes) coagulants, was examined at pH 5, 7 and 9, and the results were compared. For this, the flocculation test at each pH was carried out in a wide range of each of the coagulant dosage.

The results of continuous monitoring with PDA 2000, using the arrangement shown in Fig. 1 for the flocculation of humic acid solution with the dosage of alum, PAC and PDDA at pH 5, 7 and 9, are shown in Fig. 2(a-c), Fig. 3(a-c) and Fig. 4(a-c), respectively, together with the results for the residual humic acid concentration (shown as residual UV absorbance at 254 nm) by centrifugation and zeta potential of flocculated material after flocculation test with the corresponding dosage of each coagulant at each pH. Results of continuous monitoring with PDA for the flocculation of humic acid for 16 min after the addition of each of the coagulants, are given in terms of the Ratio value (rms/dc), which is here referred to as Flocculation Index (FI) since the value is sensitive indication of the state of aggregation of the particle.

Fig. 2(a-c) show the results for each of alum, PAC and PDDA at pH 5, respectively. It is reported that the flocculation curve can be arbitrarily divided into 4 regions^{17,19}: region A (where there is little change in FI value with time), region B (where FI value shows a distinct rise as flocculation begins), region C (where the flocculation rate has become constant and FI value shows a nearly linear rate of increase), and region D (where there is a levelling-off of the FI value). For PDDA (Fig. 2(c)), the value of FI shows essentially no change at the lowest dosage (5.5 mg/L) in this figure, indicating little or no flocculation in 16 min. With increasing dosages up to 7.5 mg/L, there is a reduced 'lag phase' (region A) before flocculation begins and the slope of the curve in region C becomes

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

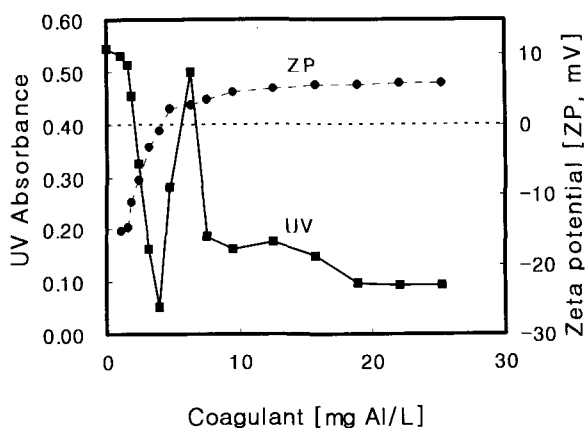
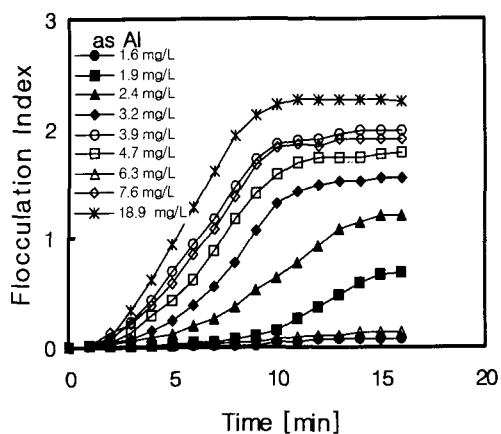
steeper, indicating more rapid flocculation. When a higher dosage than 7.5 mg/L was added, the humic acid solution rapidly acquire excess PDDA so that the collision efficiency is reduced because of restabilization. At the dosage of 10.5 mg/L and more dosages, the FI values also show little change like as at the lowest dosage (5.5 mg/L). In this case, the optimum dosage appears to be 7.5 mg/L, where the slope is the steepest and the maximum FI value is the greatest (i.e., where the most rapid flocculation occurs and the flocs reach the greatest size). In addition, it can be found that the removal of humic acid (shown as residual UV absorbance at 254 nm) is the highest at the dosage, which corresponds very well with the point at which the zeta potential of flocculated material approaches to near zero from the figure of the residual humic acid concentration and zeta potential of flocculated material, indicating that the flocculation and subsequent removal of humic acid at different coagulant dosages occur by a simple charge neutralization mechanism for PDDA at pH 5. The same results at pH 5 are obtained for PAC (Fig. 2(b)), except for the optimum dosage (1.1 mg Al/L), i.e., it can be found that the flocculation and subsequent removal of humic acid by PAC occur also by a simple charge neutralization mechanism.

However, its flocculation and removal by alum at pH 5 are a little different from those by PAC and PDDA (Fig. 2(a)). The value of FI shows essentially no change at the lowest dosage (1.6 mg Al/L) in this figure, indicating little or no flocculation in 16 min. With increasing dosages up to 3.9 mg Al/L, there is a reduced 'lag phase' and the slope of the curve in region C becomes steeper, indicating more rapid flocculation. With increasing the coagulant dosage from 3.9 mg Al/L up to 6.3 mg Al/L, the 'lag phase' increases and the slope of the curve in region C decreases because of restabilization. However, At the dosage of 7.6 mg Al/L, the 'lag phase' decreases and the slope of the curve in region C increases again. At the dosage of 18.9 mg Al/L (which is the highest dosage in this figure), the maximum FI value is higher than that at 3.9 mg Al/L. The reason why the maximum FI value increases again at the dosages above 7.6 mg Al/L may be the result of hydroxide precipitate formation at these high dosages²⁴⁾. This explanation becomes more evident by the Fig. 2(a)

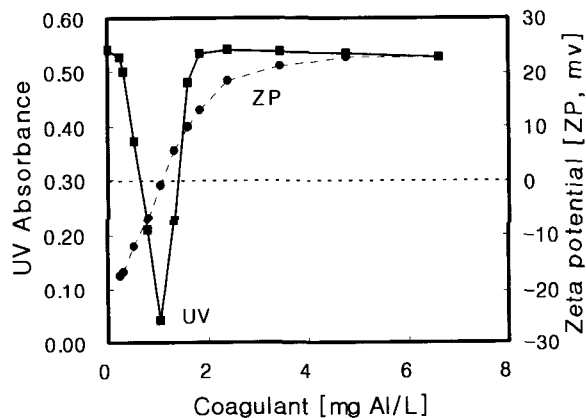
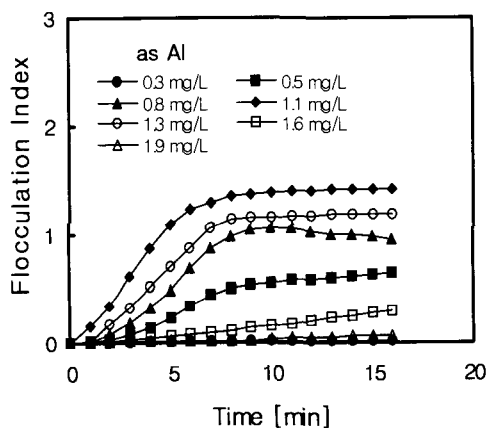
which shows the residual humic acid concentration and flocculated material with the alum dosage. When the coagulant dosage is increased up to 6.3 mg Al/L, the residual humic acid concentration decreases greatly and the zeta potential of flocculated material approaches to near zero from the negative value up to the dosage of 3.9 mg Al/L, and the residual humic acid concentration increases up to almost original humic acid concentration and the zeta potential of flocculated material changes from near zero to positive value, with increasing the coagulant dosage in the range of 3.9-6.3 mg Al/L. This is strong evidence for a simple charge neutralization mechanism under these conditions. When the dosage is increased at the dosages more than 6.3 mg Al/L, the residual humic acid concentration decreases and zeta potential of flocculated material remains positive, indicating that there is no correlation between two parameters and the removal of humic acid is due to the adsorption on a hydroxide precipitate (sweep flocculation) formed at these high alum dosages but not by its flocculation.

Fig. 3(a-c) show the results for alum, PAC and PDDA at pH 7, respectively. As shown in Fig. 3(b) and Fig. 3(c), the types of flocculation curve, and the residual humic acid concentration and zeta potential of its flocculated material with the coagulant dosage for PAC and PDDA are the same as those obtained at pH 5, except for each of the optimum coagulant dosage (2.3 mg Al/L and 9 mg/L for PAC and PDDA at pH 7, respectively), indicating that the flocculation and subsequent removal of humic acid occur by charge neutralization mechanism. This mechanism for the flocculation and subsequent removal of humic acid by PAC at pH 7 is different from that reported by Gregory and Dupont¹⁶⁾, who explains that some form of sweep flocculation is operating in flocculation of clay suspensions by commercial PAC products around neutral pH, since the volume of sediment produced is proportional to the coagulant dosage and the volume of hydroxide precipitate would be expected to depend on the amount of coagulant added. However, it is recently reported that the removal mechanism of particles by the PAC products with different degree of neutralization, $r(= \text{OH}/\text{Al})$ is different¹⁵⁾. And so, it is considered that the difference of removal mechanism between this study and the study by Gregory and Dupont is based on the fact that the PAC products

a) Alum



b) PAC



c) PDDA

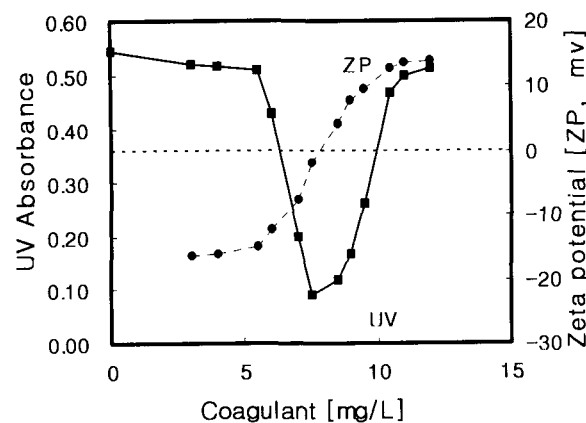
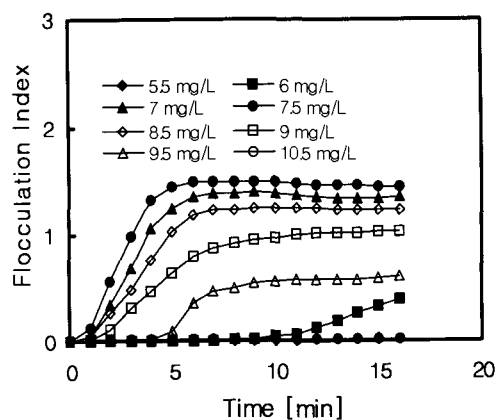
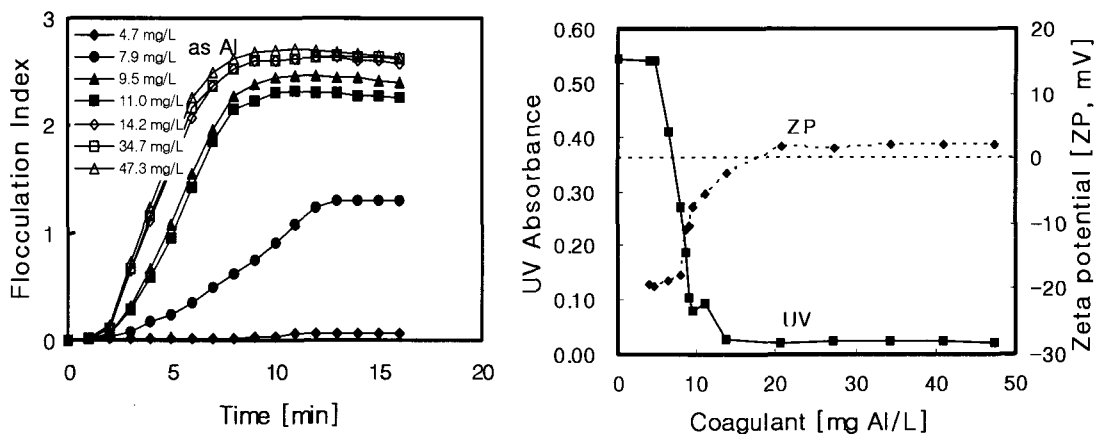


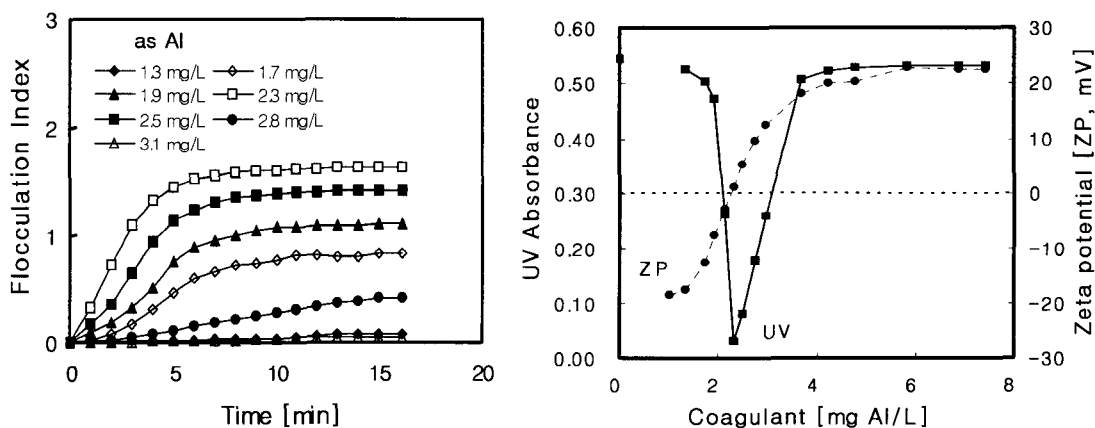
Fig. 2. The flocculation curves of humic acid solution, and residual humic acid concentration (shown as residual UV absorbance at 254 nm) by centrifugation and zeta potential of flocculated material after flocculation test, with the dosage of alum (a), PAC (b) and PDDA (c) at pH 5.

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

a) Alum



b) PAC



c) PDDA

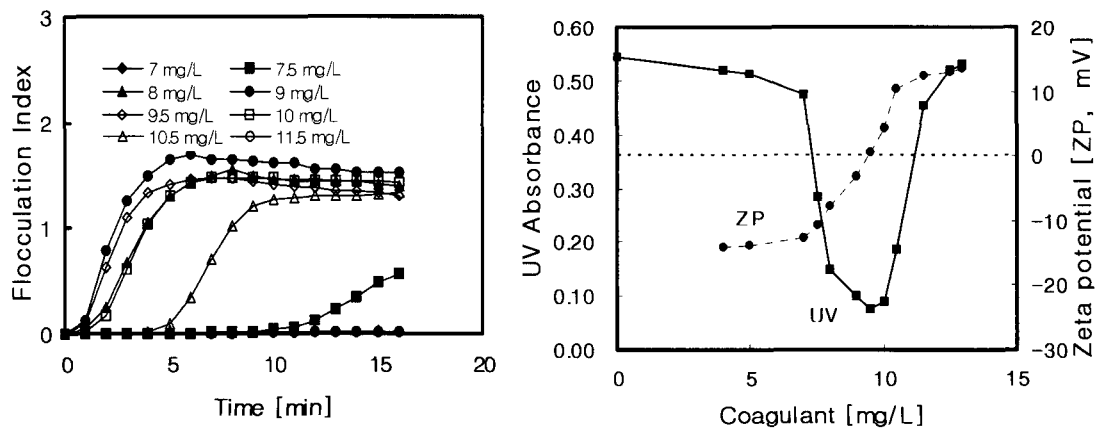
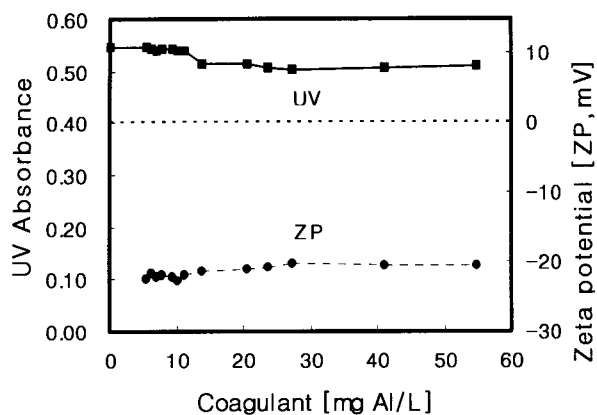
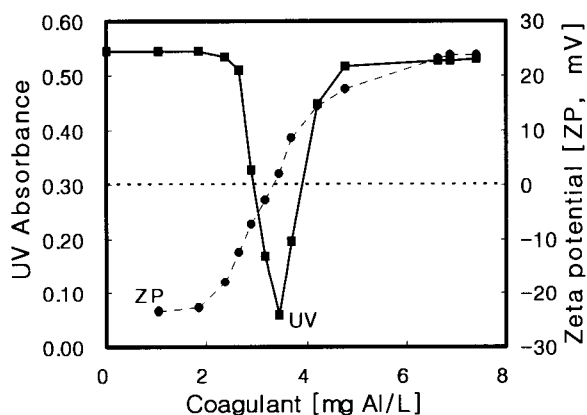
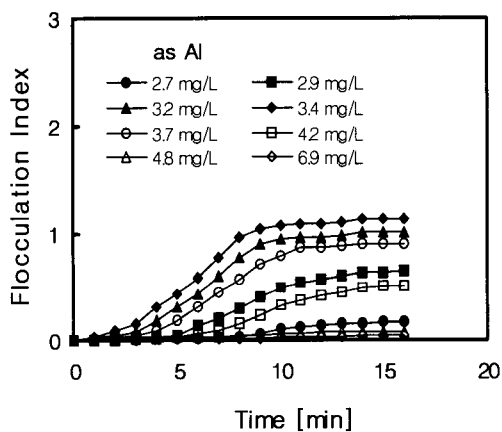


Fig. 3. As for Fig. 2, but for flocculation at pH 7.

a) Alum



b) PAC



c) PDDA

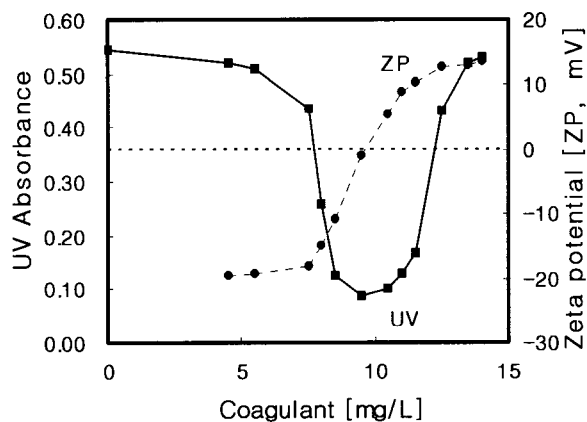
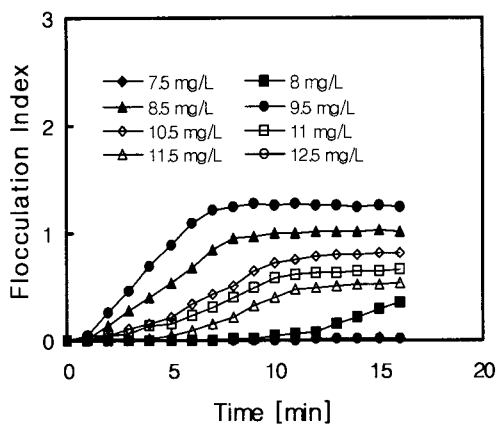


Fig. 4. As for Fig. 2, but for flocculation at pH 9.

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

used at each study have different degree of neutralization to some extent although it is not clear. And the reason why the optimum dosage at pH 7 is higher than that at pH 5 may be the increased deprotonation of humic acid and so its increased negative charge¹⁸⁾.

The types of flocculation curve and subsequent removal of humic acid, and zeta potential of flocculated material with the coagulant dosage for alum at pH 7 are different from those for alum at pH 5 shown in Fig. 2(a), as well as those for PAC and PDDA at pH 7. It can be seen that with increasing the coagulant dosage, the maximum FI value increases up to 9.5 mg Al/L, decreases slightly at the dosage of 11.0 mg Al/L, and increases at the dosages higher than 11.0 mg Al/L. With the results of flocculation test in the coagulant dosage range up to the 11.0 mg Al/L, there is an appreciable reduction of residual humic acid concentration at the dosage of 9.5 mg Al/L, which gradually improves at higher dosages, but the zeta potential of flocculated material remains negative up to around 15.0 mg Al/L. At the dosages higher than around 20 mg Al/L, it is slightly positive and changes little with increasing the dosage. This indicates strongly that the removal of humic acid under these conditions is entirely by adsorption on precipitated aluminum hydroxide (sweep flocculation). The reduction in residual humic acid concentration is slightly greater at pH 7 than pH 5, especially at the higher alum dosages.

Fig. 4(a-c) show the results for alum, PAC and PDDA at pH 9, respectively. As shown in Fig. 4(b) and Fig. 4(c), the types of flocculation curve, and the residual humic acid concentration and zeta potential of its flocculated material with the coagulant dosage for PAC and PDDA are the same as those obtained at pH 5 and pH 7, except for each of the optimum coagulant dosage (3.4 mg Al/L and 9.5 mg/L for PAC and PDDA, respectively), indicating that the flocculation and subsequent removal of humic acid occur by charge neutralization mechanism.

For alum, the FI values at pH 9 change little in a wide range of coagulant dosage (flocculation curves are not shown) and micro-flocs in the colloidal range are only formed, because of the electrostatic repulsion between negatively charged humic acid and negatively charged aluminum species ($\text{Al}(\text{OH})_4^-$)²⁵⁾ formed mainly at the pH. This result becomes more evident by the data of residual humic acid concentration and zeta po-

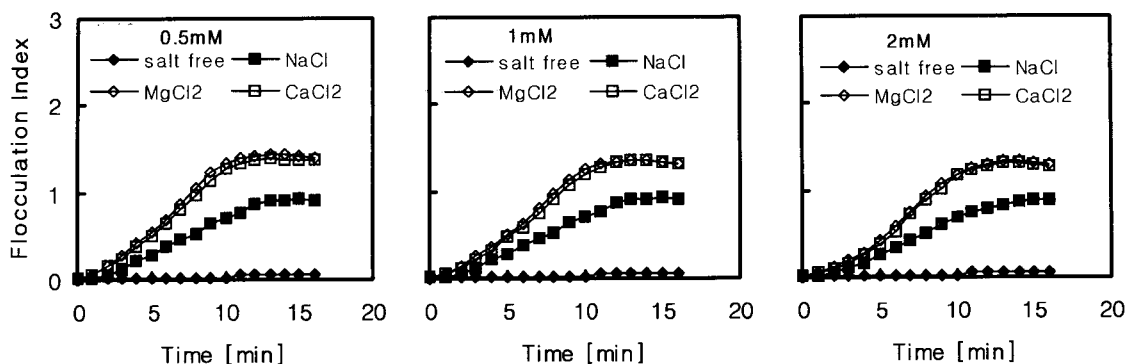
tential of flocculated material in a wide coagulant dosage up to about 60 mg Al/L, at which the two parameters change little.

3.2. Effect of ionic strength

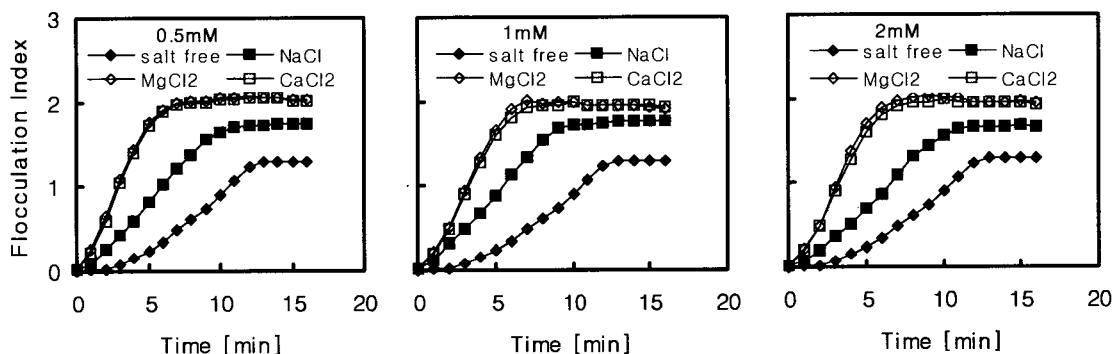
The ionic strength of the solution can affect the flocculation of impurities in water in several ways^{12~14)}. The destabilization and restabilization of negatively charged impurities by cationic coagulants occur primarily by charge neutralization, in particular, when the concentration of the impurities is low. The destabilization is caused by each of the mechanisms of charge neutralization due to the adsorbed coagulant and sweep flocculation due to the entrapment or surface adsorption on a amorphous hydroxide precipitate formed at neutral pH in case of hydrolyzing metal salts, or by reduction of electrical repulsion due to the salt effect. A reduction in the effective range of the electric double layer also encourages the bridging of impurities by adsorbed polyelectrolyte molecules or precipitated hydroxide, giving stronger aggregates. In the presence of a moderate amount of inert electrolyte, less coagulant dosage is needed to bring about flocculation and flocculation occurs over a broader range of coagulant concentration. An increase in ionic strength reduces the repulsion between charged segments of the polymerized coagulant chain (the polymerized coagulant chain adopts a more compact conformation) as well as reducing the range of inter-impurity repulsion. These effects may affect the coagulant adsorption and flocculation efficiency, leading to an optimum ionic strength at which the use of coagulants is most effective.

In this study, the effect of ionic strength on flocculation characteristics of humic acid by alum, PAC and PDDA, was examined for humic acid solution at a concentration of 25 mg/L containing different concentrations (0, 0.5, 1.0 and 2.0 mM) of electrolytes (NaCl , CaCl_2 , MgCl_2) (which are generally found in natural waters) using three coagulant dosages (i.e., the maximum dosage not forming humic flocs, the intermediate dosage forming humic flocs to some extent and optimum dosage showing the maximum FI value and removal efficiency in the absence of electrolytes) from the results of flocculation curves and subsequent residual removal of humic acid with the dosage at pH 7 in the 3.1 section. The coagulant dosages used are 4.7, 7.9 and 13.7 mg Al/L for alum, 1.3, 1.7 and 2.3

a) 4.7 Al mg/L



b) 7.9 Al mg/L



c) 13.7 Al mg/L

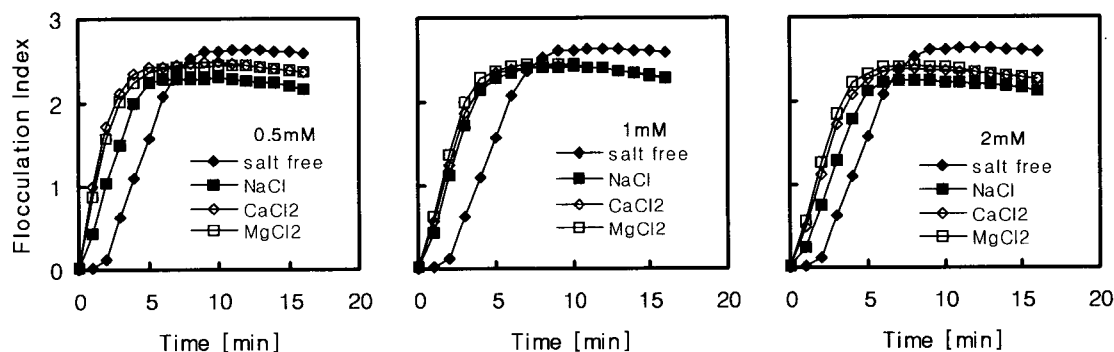


Fig. 5. The effect of ionic strength on flocculation of humic acid (25 mg/L) by alum at pH 7. Each of the three alum dosages shown in (a), (b) and (c) is the maximum dosage not forming humic flocs, the intermediate dosage forming humic flocs to some extent, and optimum dosage showing the maximum FI value and removal efficiency at pH 7 in the absence of electrolytes, respectively.

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants:
Effects of pH and Ionic Strength

mg Al/L for PAC, and 7, 7.5 and 9.0 mg/L. The results are given in terms of flocculation curves (Fig. 5(a-c)~Fig. 7(a-c)), together with the comparison of zeta potential and removal efficiency of humic acid (Table 1).

Fig. 5(a-c) show the results for alum. At the dosage of 4.7 mg Al/L, a significant flocculation of humic acid occurs when an electrolyte (salt) is present, although there is no or little flocculation in a salt-free solution (Fig. 5(a)). Its effect is greater for CaCl_2 and MgCl_2 of divalent cationic charge than NaCl of monovalent one, but the FI value and the type of flocculation curve are similar at salt concentrations used in this study, indicating that these concentrations have

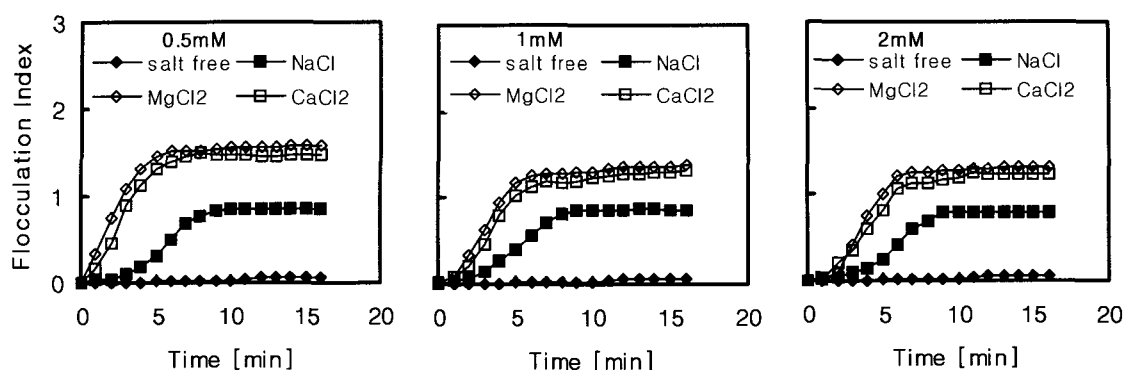
little effect on those. The effects of salt and its concentration become more evident by the data of removal efficiency of humic acid and zeta potential of flocculated material in Table 1. Its removal efficiency of 1% in a salt-free solution increases to about 23% for NaCl and to about 60% for CaCl_2 and MgCl_2 , regardless of their concentrations. Its zeta potential of -19.7 mV in a salt-free solution increases to about -15~-14 mV for NaCl and to about -14~-12 mV for CaCl_2 and MgCl_2 with the result of interaction between negatively charged humic acid and cationic charge of salt and a strong interaction for high charged cationic species. However, its removal efficiency changes little, although its negative zeta potential de

Table 1. Effect of salt (electrolyte) and its concentration on zeta potential of flocculated material and removal efficiency of humic acid by each of alum, PAC and PDDA and its dosage

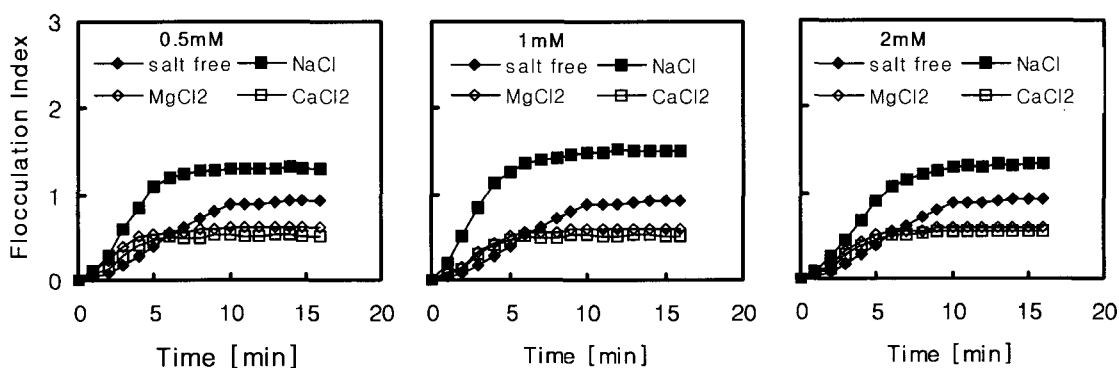
Coagulant	Dosage	In the absence of salt		In the presence of salt						
				Conc. (mM) ³⁾	NaCl		CaCl ₂		MgCl ₂	
		ZP (mV) ¹⁾	RE (%) ²⁾		ZP (mV) ¹⁾	RE (%) ²⁾	ZP (mV) ¹⁾	RE (%) ²⁾	ZP (mV) ¹⁾	RE (%) ²⁾
Alum	4.8	-19.7	1	0.5	-14.8	23	-13.8	60	-13.1	60
				1	-14.7	26	-13.2	58	-12.7	60
				2	-13.8	22	-12.8	58	-11.7	59
	7.9	-17.9	50	0.5	-9.9	68	-7.9	84	-7.9	85
				1	-9.6	69	-7.8	83	-7.2	83
				2	-8.8	67	-7.1	82	-6.9	83
	13.7	-2.3	95	0.5	-6.4	95	-5.9	96	-5.4	96
				1	-6.1	96	-5.3	96	-5.2	96
				2	-5.9	95	-4.7	96	-4.4	96
PAC	1.3	-17.5	4	0.5	-10.7	26	-4.9	93	-5.9	93
				1	-9.7	30	-4.3	92	-3.8	92
				2	-9.3	22	-3.4	91	-3.1	92
	1.7	-8.7	50	0.5	-5.1	70	2.8	45	3.2	46
				1	-4.2	71	3.4	45	4.1	45
				2	-3.0	67	4.6	45	4.6	45
	2.3	1.1	94	0.5	1.4	95	6.3	19	6.9	15
				1	1.6	95	7.2	14	7.0	14
				2	2.2	94	8.7	12	7.4	13
PDDA	7	-12.7	13	0.5	-3.2	77	2.1	83	2.0	83
				1	-3.1	77	3.0	82	3.0	82
				2	-3	76	4.2	80	4.2	80
	7.5	-10.7	48	0.5	-2.6	82	4.5	54	4.1	55
				1	-2.0	82	5.3	54	5.1	54
				2	-1.7	81	6.1	53	5.9	53
	9	1.2	86	0.5	1.3	77	7.9	27	7.8	27
				1	1.5	77	8.2	26	8.0	26
				2	1.9	76	9.7	24	9.6	25

¹⁾zeta potential of flocculated material; ²⁾removal efficiency of humic acid; ³⁾salt concentration.

a) 1.3 Al mg/L



b) 1.7 Al mg/L



c) 2.3 Al mg/L

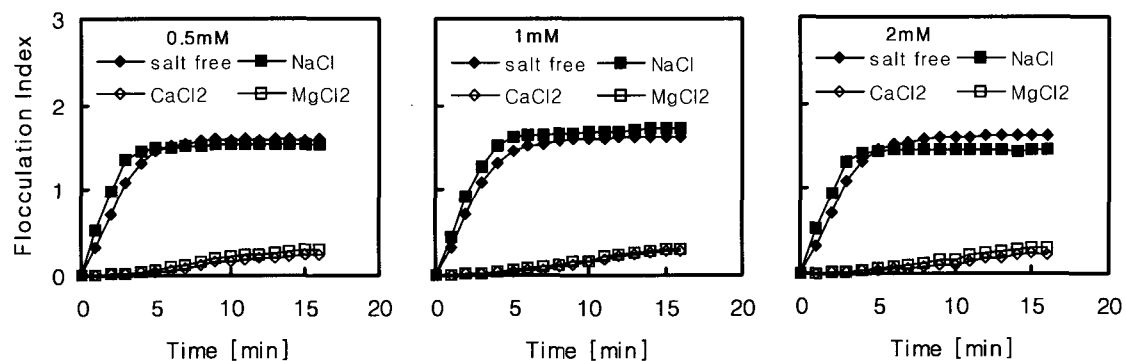
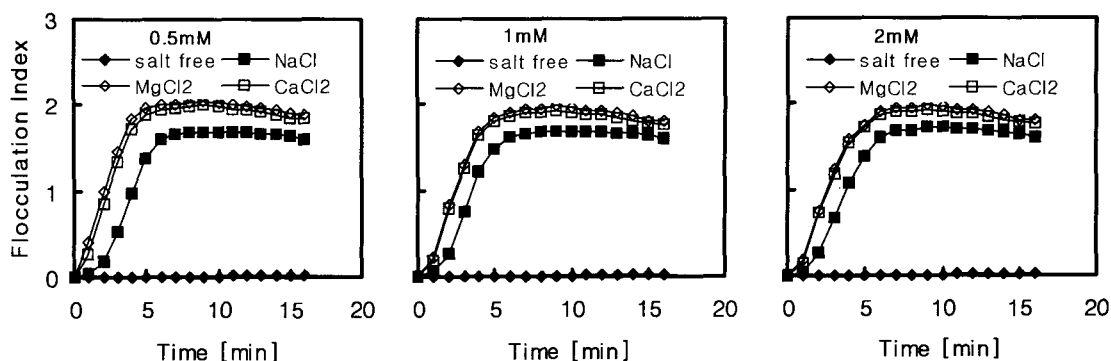


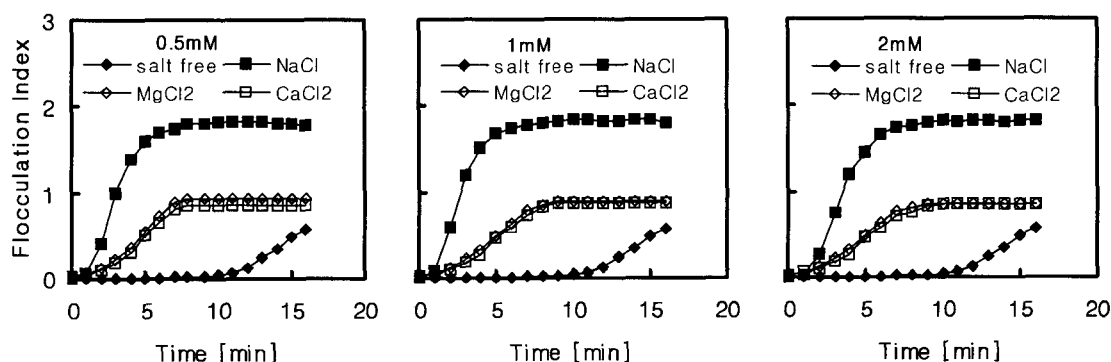
Fig. 6. As for Fig. 5, but for PAC.

Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

a) 7 mg/L



b) 7.5 mg/L



c) 9 mg/L

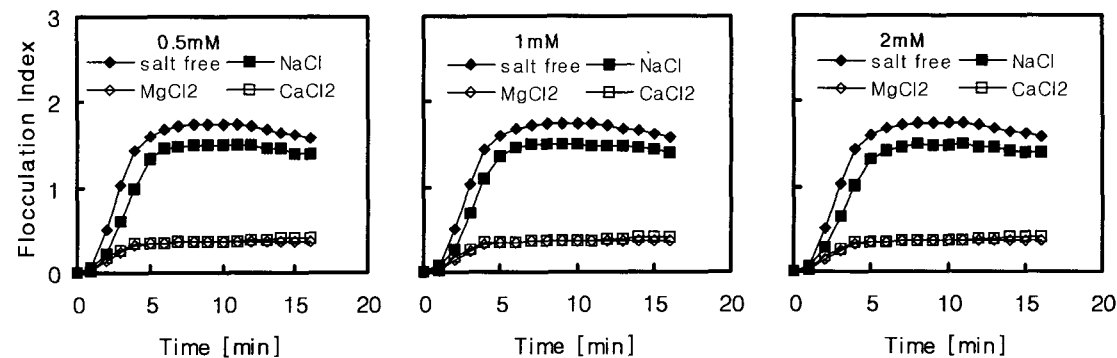


Fig. 7. As for Fig. 5, but for PDDA.

creases a little more with increase in salt concentration. The similar results are obtained at the dosage of 7.9 mg Al/L (Fig. 5(b)). At the dosage of 13.7 mg Al/L, a little different results are obtained (Fig. 5(c)). In the presence of salt, the flocculation occurs more rapidly, but maximum FI value decreases than in the absence of salt. In addition, the effect among the salts has little difference, differently from that in the other dosages, indicating that the salts at this dosage affect the flocculation and removal of humic acid in different ways. This conclusion is reinforced by the data of the removal efficiency of humic acid and zeta potential, i.e., the removal efficiency of humic acid changes little in the absence and presence of salt, although the maximum FI value in the presence of salt is lower than that in the absence of salt. The zeta potential in the presence of salt is more negative, differently from those in the other dosages. The effect of salt can generally be explained by its cationic charge effect, leading to the reduction of negatively charged impurities and the reversal of their charge, depending on the added salt concentration. In conclusion, it is considered that the charges of these salts at this dosage have little effect on the removal of humic acid for alum acting by sweep flocculation mechanism for its removal at pH 7, as mentioned in 3.1 section.

The effect of salt for PAC is shown in Fig. 6(a-c). It can be found that the charge effect among the salts is more evident, i.e., for NaCl of monovalent cationic charge, the FI value increases gradually with the increase in the dosages of 1.3 and 1.7 mg Al/L, compared with that in the absence of its salt, and is nearly the same as that in its absence at 2.3 mg Al/L. However, for CaCl_2 and MgCl_2 of divalent cationic charge, the FI values increase greatly at the dosage of 1.3 mg Al/L, but decrease gradually at the dosages of 1.7 and 2.3 mg Al/L, which may be due to the restabilization of flocculated material by virtue of acquired excess charge, pointing out the importance of charge neutralization. This conclusion is reinforced by the data of zeta potential and the removal of humic acid (Table 1). The similar results are obtained for PDDA (Fig. 7(a-c)). For CaCl_2 and MgCl_2 of divalent cationic charge, the FI values of flocculated materials and the removal efficiencies at the dosage of 7 mg/L where there is little flocculation in the absence of

salt, are nearly the same as those obtained at the optimum dosage in the absence of salt, and the above two values decrease at higher dosages. Their effects for NaCl of monovalent cationic charge are lower than those for CaCl_2 and MgCl_2 of divalent cationic charge, indicating that the destabilization and restabilization of humic acid occur by charge neutralization.

4. Conclusions

The flocculation characteristics of humic acid by inorganic (alum and PAC with degree of neutralization, $r=(\text{OH}/\text{Al})$ of 1.7) and organic (PDDA) coagulants is examined at different pH (5, 7 and 9) and ionic strength, and the results are compared using a simple monitoring technique. The method gives useful insight into the behavior of coagulant in stirred suspensions (i.e., this method gives information on the state of aggregation of particles and colloidal or dissolved organic materials from the moment of coagulant addition).

It has been shown that the flocculation and subsequent removal of humic acid by the coagulants are dependent on pH. For PAC and PDDA, they occur by a simple charge neutralization mechanism, regardless of pH used in this study. However, for alum, at pH 5, they occur by both mechanisms of charge neutralization at lower dosages and sweep flocculation at higher dosages, occur by sweep flocculation mechanism at pH 7, and there is little flocculation at pH 9, because of the electrostatic repulsion between negatively charged humic acid and negatively charged aluminum species ($\text{Al}(\text{OH})_4^-$) formed mainly at this pH.

It has been found that the flocculation and subsequent removal of humic acid are also affected by ionic strength and its effect is caused on its charge and so is more evident for the salts of highly charged cationic species, such as CaCl_2 and MgCl_2 . However, it has been observed that the salts have no effect on those at the optimum dosage for alum acting by the mechanism of sweep flocculation at pH 7, regardless of their charge.

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Comparison of Flocculation Characteristics of Humic Acid by Inorganic and Organic Coagulants: Effects of pH and Ionic Strength

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