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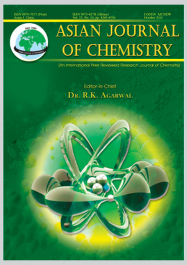

Humic Substances from Daecheung Lake Sediment and Their Removal Efficiency by Alum Coagulation†

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The humic substances from the sediment taken from Daecheung Lake of Korea were characterized and their removal efficiency by alum coagulation was investigated. And also the effects of coagulant doses and molecular weight distributions of humic substances on the coagulation performance were investigated. This study demonstrated that humic substances from Daecheung Lake sediment of Korea had the characteristics that were consistent with that of other humic substances sources; humic acid had high UV254-abs, specific UV-abs (SUVA) and THMFP values in comparison to that of fulvic acid. Alum coagulation can effectively remove more humic acid and higher apparent molecular weight fractions than fulvic acid and lower apparent molecular weight fractions of natural organic matter. The study results suggested that optimum alum coagulation could readily treat humic substances from Daecheung Lake sediment.

Key Words: Humic substances, Coagulation, Water treatment.

INTRODUCTION

Natural organic matter (NOM) is chemical and biological transformation products of animals and plants. They are created in large amounts in soil, sediments and water and are distributed ubiquitously. It is estimated that humic substances make up 60-70 % or 80 % of organic matters in soil and 30-50 % or 50-90 % of dissolved organic matters (DOMs) existing in fresh water[1-3].

Disinfection using chlorine has not only been adopted for disinfection processes to prevent water diseases in water treatment plants, it has also been expanded in application to remove ammoniac nitrogen, algae or manganese oxidation, prevent secondary contamination, *etc*. However, after the discovery of disinfections by-products (DBPs) in chlorination process, such as trihalomethane (THM) through reaction with natural organic matter in water, the focus of research has been set on the investigation of dissolved organics, mainly natural organic matter[4-7].

World Health Organization (WHO) has recommended the maximum concentrations of these D/DBPs and these parameters have been regulated in the D/DBPs Rule by the USEPA[8] and other developed countries' environmental agencies. In Korea, according to the water quality guidelines for drinking water, the maximum concentration of trihalomethanes has been regulated to 100 μg/L since June 1990.

It is assumed that in a lake's water environment aquatic natural organic matter and soil natural organic matter are in equilibrium[9], investigations on natural organic matter residing in lakebeds and its relationship with THMFP[10], along with evaluations on the efficiency of cohesion removal, have been taken into account for a great importance. In this context, Daechung Lake, which is a local drinking water resource for Korea's central region, was selected as a natural organic matter resource for this study.

This study aims to characterize the humic substances from the sediment taken from Daecheung Lake of Korea and investigate their removal efficiency by alum coagulation. And also to investigate the effects of coagulant doses and molecular weight distributions of humic substances on the coagulation performance was a one of aims in this study.

EXPERIMENTAL

Humic substances (HS) used in this study were isolated from the sediment of lake Daecheung in Daejon of Korea using an established procedure[1]. The isolated humic substance was then separated into two fractions, *i.e.*, humic and fulvic acids. The apparent molecular weight (AMW) distribution of humic substance was determined by an ultrafiltration procedure. The physicochemical parameters of humic and fulvic acids (*e.g.*, UV_{254}-abs, DOC, SUVA and THMFP) were measured following the AWWA standard procedures. Finally, a jar test apparatus

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was employed to assess the removal efficiency of humic and fulvic acids by coagulation using liquid aluminium sulfate (LAS). The detail in experimental material and procedures are follows:

Humic substance and preparation of raw water: Humic substance used in this study was extracted from the sediment in deep water in Daecheung Lake, Daejeon, Korea by the method in described in Fig. 1[11]. The 1:10 ratio of sediment (100 g) and 0.1N NaOH (1000 mL) was put into a 2 L of Elenmayer flask, then boiled it in water bath for 0.5 h. After that, it was extracted by rotary evaporator with 150 rpm for 24 h. After standing for a time, it was separated to fractions, *e.g.*, supernatant and precipitate by centrifuge with 2500 rpm for 20 min. $Na_2SO_4 \cdot 10H_2O$ (3 %) was added into supernatant, again it was separated supernatant from this solution by centrifuge with 2500 rpm for 20 min and filtrated with GF/C filter. Then, this supernatant was acidified with conc. HCl, separated in soluble fraction (fulvic acid) and insoluble fraction (humic acid) and neutralized in pH 7. These neutralized solutions were used as a stock solution for the preparation of raw water by dilution with purely distilled water in this experiment.

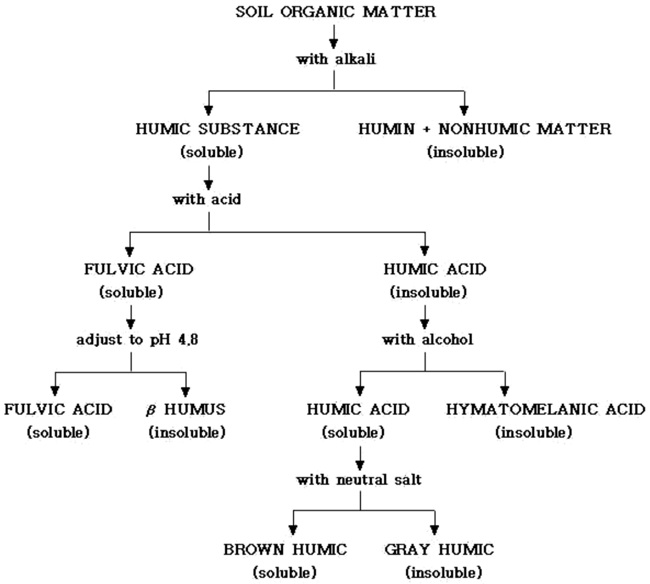

Fig. 1. Extraction method of humic substances from sediment

Coagulant: Coagulant used in this study was liquid aluminium sulfate (LAS) for water treatment produced in Hanbat Chemicals Co., Daejeon, Korea. The quantity of aluminium oxide in liquid aluminium sulfate was 10.1 % and it was diluted with purely distilled water in 100 times. This diluted liquid aluminium sulfate had a 0.711 mg Al^{3+} per a 1 mL. Physicochemical properties and composition of liquid aluminium sulfate used in this study was described in Table-1 and was met in Korean regulation and specification of chemicals for water treatment.

TABLE-1
PHYSICOCHEMICAL PROPERTIES OF COAGULANT

Item	Liquid aluminium sulfate
Al_2O_3 (%)	10.1
pH	3.8
Density	1.33
Al^{3+} (mg/mL)	71.19

Procedure

Analysis of apparent molecular weight distributions of humic substance: To identify the apparent molecular weight distributions in humic and fulvic acid solutions isolated from sediment, a cut off range was fixed in 3,000, 10,000 and 30,000 daltons and cut off by using the corresponding ultra fine filtration membrane, which was YM series with 62 mm diameter and 28.7 cm^2 of area and made of cellulose acetate and ultrafiltration stirred cell (Amicon Co. USA). The membrane were washed in a certain procedure before use it. 150 mL of sample water was put into the cell, then pressure of 55 psi was added the cell and filtration was done until 75 mL of permeate was obtained. After this cutting off, corresponding fractions were analyzed in terms of DOC, UV_{254} and THMFP.

Water quality analysis: The physicochemical parameters of humic and fulvic acids (*e.g.*, UV_{254}-abs, DOC, SUVA and THMFP) and of jar tested water were measured following the AWWA[12] and Korea standard procedures[13]. The experimental apparatus and analytical conditions of GC for THMFP used in this work can be seen in Tables 2 and 3, respectively.

TABLE-2
INSTRUMENTS FOR ANALYSIS

Item	Unit	Apparatus and its model
DOC	mg/L	TOC Analyzer (Dohrmann DC-180)
UV_{254}	cm^{-1}	UV/VIS spectrophotometer (Milton Roy Spectronic 3000)
pH		pH meter (TOA HM 30V)
Turbidity	NTU	Turbidimeter (HACH 2100 AN)
THMFP	mg/L	GC (Perkin Elmer Auto System)

TABLE-3
ANALYTICAL CONDITIONS OF GC

Column: Vocol 0.32 mm × 60 m	Initial temp.: 35 ºC
Carrier gas: N_2	Final temp.: 220 ºC
Detector: FID	Analysis time: 43.5 min
Detector temp.: 230 ºC	Injection volume: 25 mL

Jar test: Jar tests were carried out using the jar tester with 6 paddle type impeller and jar of (9.2 cm)W × (9.2 cm)L × (11.5 cm)H size. 1 L of a certain constant DOC concentration of the raw water (4.61 mg/L DOC of humic acid or 3.62 mg/L DOC of fulvic acid) adjusted in pH 7 and 20 ºC was put into each jars, tests were carried with rapid agitation (150 rpm) 1 min, slow agitation (30 rpm) 0.5 h. Then after 1 h standing, about 600 mL of supernatants were drawn through sampling port located in below 7 cm from the surface of water. pH and turbidity were measured directly and DOC, UV_{254}, apparent molecular weight distribution were measured after filtering with 0.45 μm cellulose membrane filter paper. Tests under different liquid aluminium sulfate dosages were also carried out and the final pH was about 4.6.

RESULTS AND DISCUSSION

Characteristics of humic substance isolated from sediment in deep water: The results from the analysis of humic substance extracts in term of TOC per g-sediment and the portions of DOC and UV_{254} can be seen in Table-4.

TABLE-4
PROPERTIES OF HUMIC SUBSTANCE EXTRACTED FROM SEDIMENT

Item	Humic acid	Fulvic acid
mg TOC/g sediment	2.12	3.63
DOC (%)	35.7	64.3
UV_{254} (%)	69.3	30.7

Humic acid and fulvic acid were 2.12 and 3.63 mg TOC per g-sediment, respectively. And the portions of humic acid and fulvic acid were 35.7 and 64.3 % in term of DOC and 69.3 and 30.7% in term of UV_{254}, respectively. It represents that the portion of humic acid in total organic carbon concentration of humic substance is lower than that of fulvic acid, but the UV_{254} per DOC so called SUVA value of humic acid is about 2, because of portions of unsaturated double bond linkages (UV_{254} absorbance) in compounds is about double times higher than that of fulvic acid.

Table-5 is showed that the water qualities of various rivers and lakes in Korea. This table was made for the determination of proper working concentration of humic substance solution in laboratory. There are approximately 1.8-4.8 mg/L of TOC concentration range and 0.03-0.1 cm^{-1} of UV_{254} absorbance range and the TOC portion of humic acid were 30-50 % was reported. Therefore, the working concentration of humic substance was decided within the range of concentration of raw water or little bit higher concentration in reason with having correctness in analysis.

TABLE-5
CHARACTERISTICS OF SURFACE WATER IN KOREA[14,15]

Site	TOC (mg/L)	UV_{254} (cm^{-1})	pH	Turbidity (NTU)
Daecheung lake (Cheungju)	1.83-3.18	0.029-0.098	–	1.07-5.09
Ilsan lake	3.6	0.034	7.3	3.1-3.3
Kum river (Puyo)	2.46-4.79	0.055-0.098	–	3.06-18.40
Nakdong river (Mulgem)	2.4-4.8	0.056-0.089	6.5-9.5	1.5-35.0
Han river (Jamsil)	1.87	0.030	7.5	5.5-5.6

Therefore, humic acid and fulvic acid solution sample for the experiments was prepared by the dilution of 500 and 100 times with purely distilled water to get into the concentration range of raw surface water. Then, their water qualities were analyzed and represented in Table-6. Humic acid has unsaturated double bond linkages in compounds and a great trihalomethanes formation potential. Then, to identify the apparent molecular weight distributions in humic and fulvic acid solutions, a cut off range was fixed in 3,000, 10,000 and 30,000 daltons, cut off by using the corresponding ultrafine filtration membrane according to the methods described in experimental methods section. After cutting off, corresponding fractions were analyzed in terms of DOC, UV_{254} and THMFP.

4.61 mg/L DOC of humic acid solution was cut off in molecular weight fractions and the fractions were analyzed in terms of DOC, UV_{254} and THMFP. Their results are shown in Fig. 2. This apparent molecular weight distribution is consisted of 64 % of > 30 K daltons, 12 % of 30-10 K Daltons, 3 % of 10-3 K daltons and 21 % of < 3 K daltons. In term of UV_{254}, there are 85 % of > 30 K daltons, 12 % of 30-10 K daltons, 1 % of 10-3 K daltons, 2 % of < 3 K daltons, in term of THMFP, 78 % of > 30 K daltons, 11 % of 30-10 K daltons, 2 % of 10-3 K daltons, 9 % of < 3 K daltons are obtained.

TABLE-6
WATER QUALITY CHARACTERISTICS OF HUMIC SUBSTANCE EXTRACTS DILUTED WITH PURELY DISTILLED WATER

Proportion item	Humic acid (× 500)	Fulvic acid (× 100)
DOC (mg/L)	4.610	3.629
UV_{254} (cm^{-1})	0.456	0.094
THMFP (μg/L)	444.4	236.2
Turbidity (NTU)	2.09	0.25
SUVA (cm^{-1}/(mg/L))	0.099	0.026
STHMFP ((μg/L)/(mg/L))*	96.4	65.1

*STHMFP: Specific trihalomethane formation potential (THMFP/DOC).

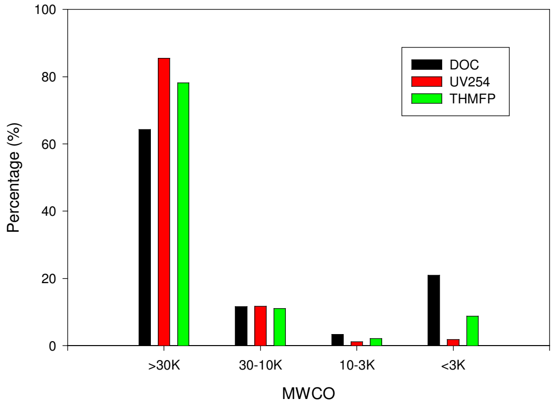

Fig. 2. Apparent molecular weight distributions of humic acid (as DOC, UV_{254} and THMFP)

In the same procedure, apparent molecular weight distribution of 3.63 mg/L DOC of fulvic acid solution was obtained in terms of DOC, UV_{254} and THMFP and the results can be seen in Fig. 3. The apparent molecular weight distribution is consisted of 23 % of > 30 K daltons, 43 % of 30-10 K daltons, 3 % of 10-3 K daltons and 31 % of < 3 K daltons. In term of UV_{254}, there are 35 % of > 30 K daltons, 46 % of 30-10 K daltons, 5 % of 10-3 K daltons, 14 % of < 3 K daltons. In term of THMFP, 27 % of > 30 K daltons, 49 % of 30-10 K daltons, 2 % of 10-3 K daltons, 22 % of < 3 K daltons are obtained.

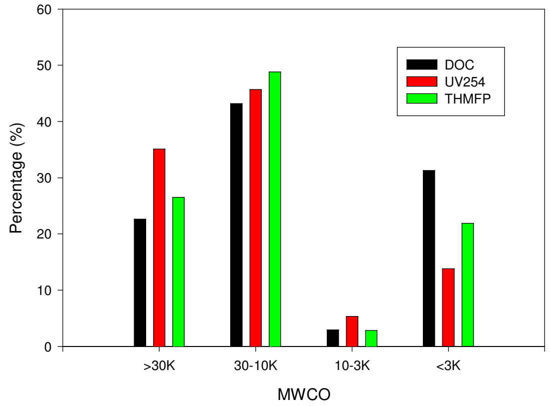

Fig. 3. Apparent molecular weight distributions of fulvic acid (as DOC, UV_{254} and THMFP)

SUVA value, which is a ratio of UV_{254} absorbance and DOC concentration, of different molecular weight fractions of humic substance are presented in Fig. 4. It can be seen that humic acid has a distribution of 0.1285 of > 30 K daltons, 0.0972 of 30-10 K daltons, 0.0329 of 10-3 K daltons and 0.0083 of < 3 K daltons and fulvic acid has a distribution of 0.046 of > 30 K daltons, 0.0274 of 30-10 K daltons, 0.0481 of 10-3 K daltons, 0.0114 of < 3 K daltons.

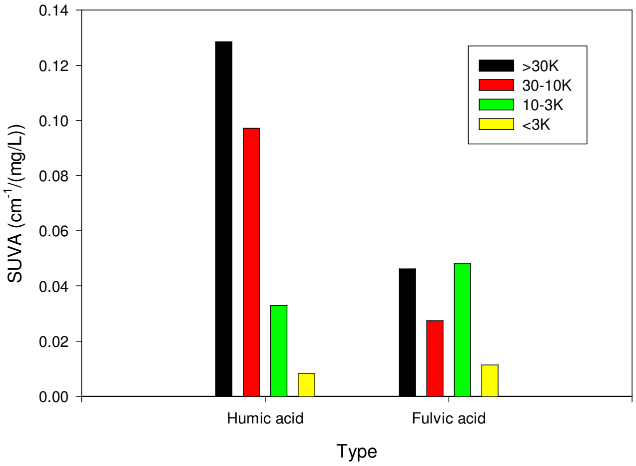

Fig. 4. SUVA Values of humic substance on apparent molecular weight distributions

Total SUVA value of humic acids is 0.2669 cm^{-1} and it is a double time of that of fulvic acids. It seems that humic acids have a more functional groups *e.g.*, carbon double bond, carboxyl and phenolic OH and so on in their structure of compounds than fulvic acids and resulted in higher UV_{254} absorbance per a unit DOC. And generally, high molecular weight humic acids have a higher SUVA values.

It is shown that fulvic acids exist in relatively lower molecular weight than humic acid, the portions of its unsaturated linkages in structure proportionate generally the portions of molecular weights and have a lower trihalomethanes formation potential than humic acid. Whilst humic acids in general have a relatively higher molecular weight than fulvic acid, high molecular weight humic acids are more unsaturated and have a higher trihalomethanes formation potential than low molecular weight humic acids.

To know it more clearly, data can be rearranged in term of STHMFP, which is a ratio of THMFP value and DOC concentration; it can be seen in Fig. 5. It is the similar results as SUVA values for humic acids to be higher in the high molecular weight fractions and also higher in total than fulvic acids. It means that when humic acids drive into disinfection process in water treatment plant, they can be able to make a much more trihalomethanes.

Change of molecular weight distributions of humic substance by coagulation: The changes of molecular weight distributions of humic acids and fulvic acids by coagulation using liquid aluminum sulfate (LAS) were investigated to identify the removal efficiency in coagulation process of water treatment plant.

DOC concentration changes of different fraction of fulvic acids in different doses of liquid aluminium sulfate are plotted in Fig. 6. According to the increasing of liquid aluminium sulfate dose to 2.1 mg/L, total 3.629 mg/L of fulvic acids was reduced in 2.417 mg/L corresponded to 66.6 %, therefore, about 34 % of DOC corresponded to 1.212 mg/L was removed. 22.6 % of more than 30 K daltons fraction corresponded to 0.820 mg/L was reduced in 3.9 % corresponded to 0.141 mg/L. 30-10 K daltons fraction was also reduced from 43.2 % corresponded to 1.568 mg/L to 8.5 % corresponded to 0.308 mg/L. However, low molecular weight fraction, for example 10-3 K daltons fraction was quite slightly increased from 2.9 % corresponded to 0.104 mg/L to 3.7 % corresponded to 0.133 mg/L, less than 3 K daltons fraction was increased of *ca.* 20 % from 31.3 % corresponded to 1.137 mg/L to 50.6 % corresponded to 1.835 mg/L.

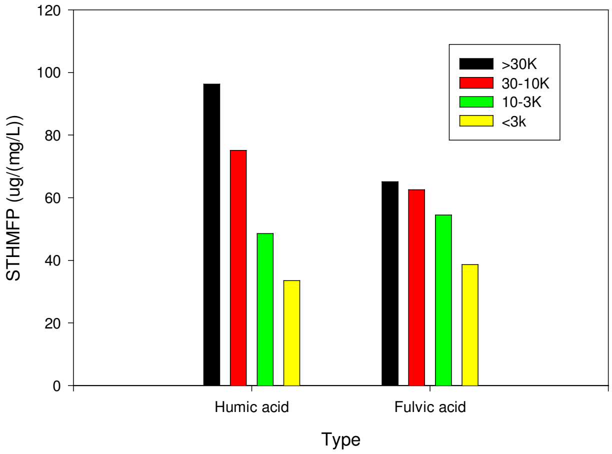

Fig. 5. STHMFP Values of humic substance on apparent molecular weight distributions

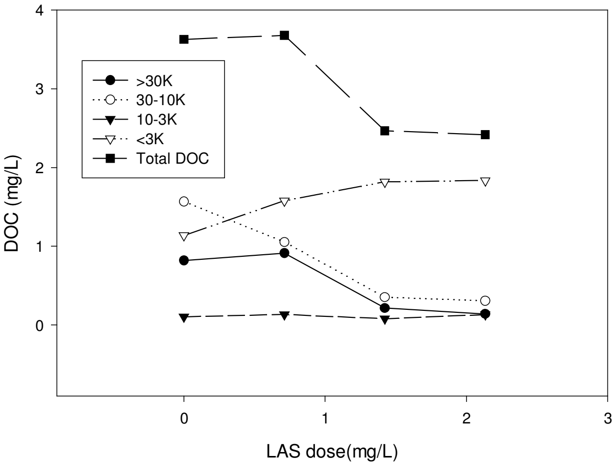

Fig. 6. Variation of different fulvic acid apparent molecular weight fractions (as DOC) *vs.* liquid aluminium sulfate dosage (as mg Al/L)

It seems that the phenomena for the increases of low molecular weight fractions is not simply derived from the breaking of particles by collision with paddle or by the addition of acid included in coagulant, when they are compared with the results of humic acids (Fig. 6). But it is true that this increase was derived from the conversion of large particles to small ones in any unknown way and stabilization of these will be established with positive charge on particles in coagulation process of jar tester.

Fig. 7 showed that the UV$_{254}$ absorbance changes of different fraction of fulvic acids in different doses of liquid aluminium sulfate. According to the increasing of liquid aluminium sulfate dose to 2.133 mg/L, initial 0.094 cm^{-1} absorbance of fulvic acids was reduced in 0.07094 cm^{-1} corresponded to 25.5 %. Therefore, about 74.5 % of UV$_{254}$ absorbance material was removed. The more than 30 K daltons fraction was reduced of 34 % from 35.1 % corresponded to 0.033094 cm^{-1} to 1.1 % corresponded to 0.001094 cm^{-1}. The 30-10 K daltons fraction was also reduced of 36.1 % from 45.7 % corresponded to 0.043094 cm^{-1} to 9.6 % corresponded to 0.009094 cm^{-1}. The 10-3 K daltons fraction was also reduced of 3 % from 5.3 % corresponded to 0.005094 cm^{-1} to 2.1 % corresponded to 0.002094 cm^{-1}, the less than 3 K daltons fraction was reduced of *ca.* 1 % from 13.83 % corresponded to 0.013094 cm^{-1} to 12.8 % corresponded to 0.012094 cm^{-1}.

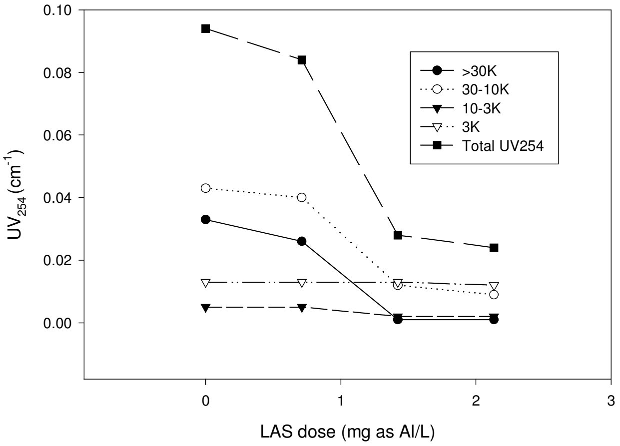

Fig. 7. Variation of different fulvic acid apparent molecular weight fractions (as UV$_{254}$-abs.) *vs.* liquid aluminium sulfate dosage (as mg Al/L)

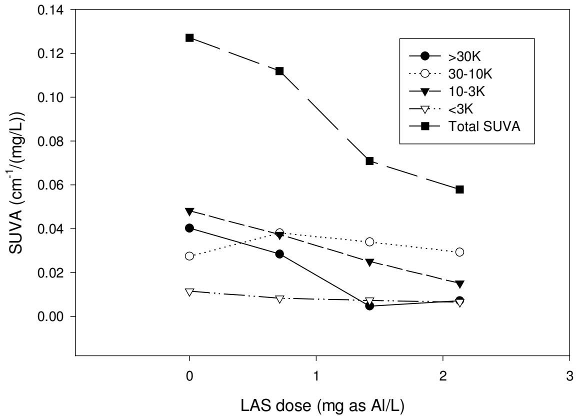

Fig. 8. Variation of different fulvic acid apparent molecular weight fractions (as SUVA) *vs.* liquid aluminium sulfate dosage (as mg Al/L)

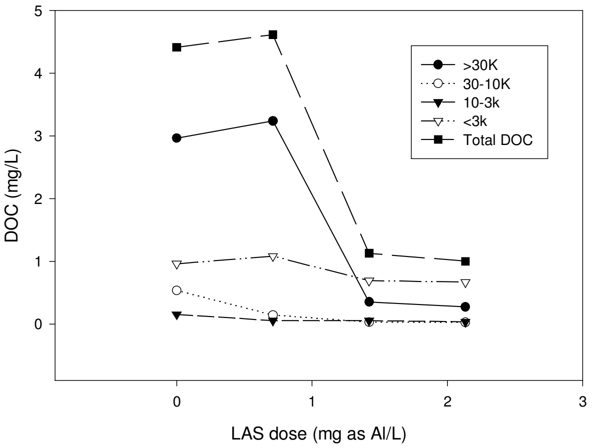

Fig. 9. Variation of different humic acid apparent molecular weight fractions (as DOC) *vs.* liquid aluminium sulfate dosage (as mg Al/L)

It can be shown that the removal efficiency of UV$_{254}$ absorbance by coagulation is higher than that of DOC concentration; it indicates that unsaturated portions of fulvic acids may be able to be removed in coagulation process.

SUVA values of the different apparent molecular weight fractions of fulvic acids were drew against the liquid aluminium sulfate dosage in Fig. 8. For a liquid aluminium sulfate dose of 2.133 mg/L and at coagulation pH 6, 55.5 % of initial SUVA value of fulvic acids was reduced from 0.1271 cm^{-1}/(mg/L) to 0.0578 cm^{-1}/(mg/L) corresponded to 45.5 %. 26 % of SUVA value of the more than 30 K daltons fraction was reduced from 31.6 % corresponded to 0.04021271 cm^{-1}/(mg/L) to 5.9 % corresponded to 0.00711271 cm^{-1}/(mg/L). The 30-10 K daltons fraction was slightly increased from 21.6 % corresponded to 0.02741271 cm^{-1}/(mg/L) to 23.0 % corresponded to 0.02921271 cm^{-1}/(mg/L). The 10-3 K daltons fraction was also reduced of 26 % from 37.8 % corresponded to 0.04811271 cm^{-1}/(mg/L) to 11.8 % corresponded to 0.01501271 cm^{-1}/(mg/L), the less than 3 K daltons fraction was reduced of *ca.* 4 % from 9.0 % corresponded to 0.01141271 cm^{-1}/(mg/L) to 5.1 % corresponded to 0.00651271 cm^{-1}/(mg/L).

Then, the changes of apparent molecular weight distributions of humic acids by liquid aluminium sulfate coagulation were also investigated. Variations of DOC concentrations in different fractions are represented in Fig. 9. According to the increasing of liquid aluminium sulfate dose to 2.133 mg/L, Totally 77 % of initial 4.412 mg/L DOC of humic acids was reduced in about 23 % corresponded to 1.000 mg/L. About 58 % of more than 30 K daltons fraction was reduced from 64.3 % corresponded to 2.964 mg/L to 6.2 % corresponded to 0.272 mg/L. 11 % of 30-10 K daltons fraction was also reduced from 11.6 % corresponded to 0.535 mg/L to 0.6 % corresponded to 0.026 mg/L. In unlike low molecular weight fractions of fulvic acids, the fractions of humic acids were reduced, for example 10-3 K daltons fraction was reduced from 3.3 % corresponded to 0.152 mg/L to 0.8 % corresponded to 0.035 mg/L, less than 3 K daltons fraction was reduced from 20.9 % corresponded to 0.961 mg/L to 15.1 % corresponded to 0.667 mg/L.

Fig. 10 shows the results for the variations of UV$_{254}$ absorbance in different fractions of humic acids by the different liquid aluminium sulfate dosages.

By increasing of liquid aluminium sulfate dose to 2.133 mg/L, initial 0.094 cm^{-1} absorbance of fulvic acids was reduced in 0.023 cm^{-1} corresponded to *ca.* 5 %, therefore about 95 % of unsaturated, UV$_{254}$ absorbance material was removed. About 84 % of the more than 30 K daltons fraction was reduced from 85.4 % corresponded to 0.381 cm^{-1} to 1.1 % corresponded to 0.005 cm^{-1}. The 30-10 K daltons fraction was reduced of *ca.* 10 % from 11.7 % corresponded to 0.052 cm^{-1} to 1.3 % corresponded to 0.006 cm^{-1}. The 10-3 K daltons fraction was also reduced from 1.1 % corresponded to 0.005 cm^{-1} to 0.4 %

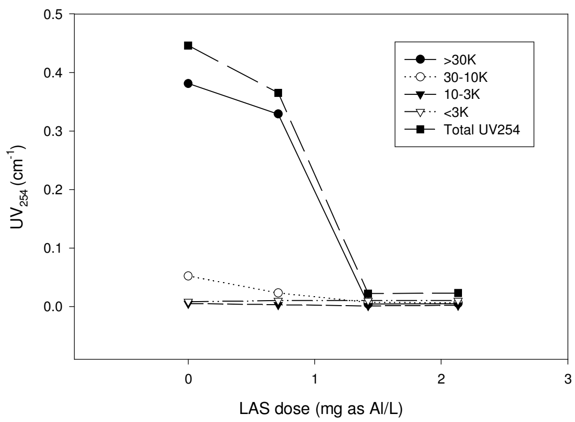

Fig. 10. Variation of different humic acid apparent molecular weight fractions (as UV_{254}) *vs*. liquid aluminium sulfate dosage (as mg Al/L)

corresponded to 0.002 cm^{-1}, the less than 3 K daltons fraction was increased slightly.

It can be seen that SUVA values of the different apparent molecular weight fractions of humic acids against the liquid aluminium sulfate dosage in Fig. 11. For a liquid aluminium sulfate dose of 2.133 mg/L, totally SUVA value of humic acids was increased of 20 % from 0.2669 cm^{-1}/(mg/L) to 0.3213 cm^{-1}/(mg/L). About 41 % of SUVA value of the more than 30 K daltons fraction was reduced from 48.1 % corresponded to 0.1285 cm^{-1}/(mg/L) to 6.9 % corresponded to 0.0184 cm^{-1}/(mg/L). However, the portion of UV_{254} per a DOC was increased in small molecular weight fractions; it was not in line with those of fulvic acids. The 30-10 K daltons fraction was dramatically increased of *ca*. 50 % from 36.4 % corresponded to 0.0972 cm^{-1}/(mg/L) to 86.5 % corresponded to 0.2308 cm^{-1}/(mg/L). The 10-3 K daltons fraction was also increased of *ca*. 9 % from 12.3 % corresponded to 0.0329 cm^{-1}/(mg/L) to 21.4 % corresponded to 0.0571 cm^{-1}/(mg/L), the less than 3 K daltons fraction was increased of *ca*. 2 % from 3.1 % corresponded to 0.0083 cm^{-1}/(mg/L) to 5.6 % corresponded to 0.0150 cm^{-1}/(mg/L).

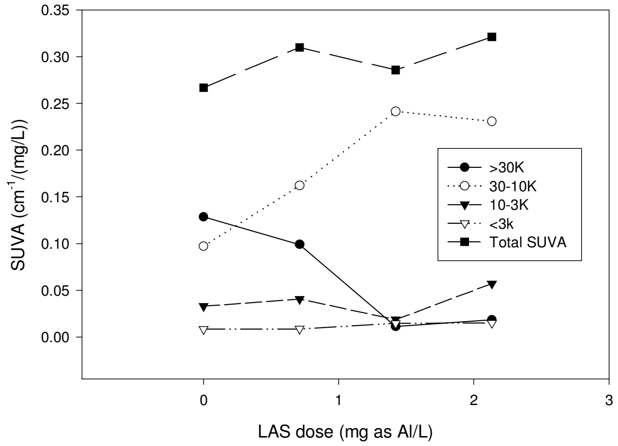

Fig. 11. Variation of different humic acid apparent molecular weight fractions (as SUVA) *vs*. liquid aluminium sulfate dosage (as mg Al/L)

Conclusion

This study demonstrated that humic substances (HS) from Daecheung Lake sediment of Korea had the characteristics that were consistent with that of other humic substances sources; humic acid had high UV_{254}-abs, specific UV-abs (SUVA) and THMFP values in comparison to that of fulvic acid. Alum coagulation can effectively remove more humic acid and higher apparent molecular weight fractions than fulvic acid and lower apparent molecular weight fractions of natural organic matter. The study results suggested that optimum alum coagulation could readily treat humic substances from Daecheung Lake sediment.

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