

Comparison of Flocculation-Spectrophotometry and Streaming Current Detector Method to the Control of Flocculants for the Removal of Humic Acid

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Flocculation-spectrophotometry and streaming current detector(SCD) method were investigated and compared in order to determine the optimum dosages of synthetic cationic polymers of different charge density and molecular mass for the removal of humic acid.

The optimum dosage for each of the polymers was determined with the dosage at which the lowest absorbance of humic acid was shown for the former and was determined with the dosage required during charge neutralization of humic acid for the latter. It was in good agreement between both methods and there is a strong inverse correlation between the optimum dosage and charge density of the polymers, with highly charged polymer giving the lowest optimum dosage, pointing out the importance the charge neutralization. By flocculation-spectrophotometry, it was found that the absorbance of humic acid with the amount of each of the polymers dosed, changes sharply for polymers of high charge density, but changes rather broadly for polymers of low and middle charge density. Both methods showed that a stoichiometric correlation exists between the optimum dosage of each of the cationic polymers and the negatively charged humic acid.

Key words : flocculation-spectrophotometry, streaming current detector(SCD) method, humic acid, cationic polymers, optimum dosage, charge density.

1. Introduction

In practical applications of polymers, their charge density is often great importance. This is especially the case for polymeric flocculants, in water and wastewater treatment, paper making and many other examples. Most dissolved material such as humic substances is anionic in character and can be effectively removed by cationic flocculants such as hydrolyzing metal salts and cationic polymers.

The flocculant dosage required for treating surface water by adsorption coagulation with

charge neutralization is strongly determined by the negative charge concentration of the raw water which is the sum of the negative surface charge of inorganic particles(clay and loam), organic particles(algal cells), and naturally occurring dissolved macromolecular organics, provided that these carry deprotonizable functional groups. Dissolved macromolecular organics are of allogenetic nature and consists for most part of acid polysaccharides and refractive organic acids with a high molecular weight(>3000).

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. Stoichiometric characteristics were also found to determine the flocculation of bacteria and algal cells (Ives, 1956; Tenney and Stumm, 1965; Bernhardt and Clasen, 1967; Tenney, 1969; Tilton, 1972).

Ives (1959) pointed out that the flocculation of algae is predominantly determined by the adsorption of positively charged flocculants to the surface of negatively charged particles, with optimum elimination results being obtained in the region of charge neutralization. Ives further indicates that the charge density of algal cells determines the flocculant amount required in relation to the algal surface.

Kawamura et al. (1966, 1967) presented a method to ascertain the charge concentration by means of a stoichiometric addition of oppositely charged polyelectrolytes and colorimetric end-point determination. At that time, however, little tribute was paid to this new approach by water scientists. It was only years later that Horn (1978) introduced a modified version of Kawamura's colloid titration process for determining both charge density and charge concentration. A selection of different flocculation test procedures is presented by Gregory (1983) who also underlines the utility of the zeta potential to control the dosage of positively charged flocculants (especially cationic polyelectrolytes) for neutralization of negatively charged particulate substances. Another flocculant control method according to the nature and extent of the floc formation that is based on measuring fluctuations in the intensity of light transmitted through a flowing suspension was developed by Gregory and Nelson (1986), Eisenlauer and Horn (1985), and Matsui et al. (1991).

In this study, the optimum dosages of the cationic polymers of different charge density and

molecular mass were determined and compared for removing humic acid, that is a major component of humic substances in natural water, using flocculation-spectrophotometry and streaming current detector (SCD) method.

2. Experimental

2.1. Reagents and Apparatus

Analar grade reagents were used and the solutions were prepared with deionized distilled water from an Elga 'Spectrum' unit.

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 mL of 0.1 N sodium hydroxide and the solution was filtered through a qualitative (Whatmann) filter paper. Working standard solution (1 g/L or 50 mg/L) was diluted five times or prepared by diluting 10 mL of this stock solution and 10 mL of 0.1 N sodium carbonate to 1 L with water. The sodium carbonate was used to fix the initial pH of the humic solution. The humic solution was then filtered under vacuum through the prewashed 0.45 μm cellulose nitrate membrane and adjusted to pH 7 with 0.01 N HNO_3/NaOH .

Cationic polymers were obtained from Allied Colloid Ltd., UK. They 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 properties of the polymers, designated A-F, are given in Table 1. The molar portion of DMAEA determines the charge density. All these polymers were also prepared as 1 g/L or 0.1 g/L and used within a week.

The molecular mass ranges quoted are calculated from intrinsic viscosity values (given by the

Table 1. Properties of polymers used.

Polymer	Charge Density	Approximate Molecular Mass/10 ⁶
A	Low	11-16
B	Medium	11-16
C	High	11-16
D	Low	4-6
E	Medium	4-6
F	High	4-6

manufacturer) using the Mark-Houwink equation ($\eta = KM^\alpha$); with estimates of the constants K and α taken from Griebel and Kulicke(1992).

The low, medium, and high charge densities correspond to values in the ranges 0.5-1.5, 1.5-2.5, and 2.5-4.0 meq/g, respectively as determined by the manufacturer.

A CamSpec UV/Vis spectrophotometer and a Kontron scanning spectrophotometer were used for all absorbance measurements and absorption spectra. A Charge Analyzer II(Rank Brothers Ltd., UK) was used as a streaming current detector for streaming current measurements. A magnetic stirrer(Rank Brothers Ltd., UK) was used for variable speed setting.

2.2. Procedure

2.2.1. Flocculation-spectrophotometry

Each of the cationic polymer A-F was added to the 25 mL beaker containing 10 mL of humic acid(10-100 mg/L, pH 7) and the solution was stirred for a period of 15 min at a speed of 65 rpm. After that, 1.5 mL of a sample in a solution was drawn off, placed in a centrifuge capsule(1.5 mL), and centrifuged at 6,500 rpm for 20 min. The supernatant liquid from the centrifuge capsule was taken and used for the absorbance measurement at 300 nm.

2.2.2. SCD method

The plastic cup, containing a magnetic stirrer bar, was filled with water to about 3 mm above the ring of holes in the cylinder when placed on the stirrer system supplied with the Charge Analyzer II and stirred with the Dosimat stirrer at a moderate speed. When the cylinder of the measuring cell was completely clean(as shown by streaming current reading close to zero), each of the cationic polymers was dosed automatically to the solution containing 10 mL of humic acid(10-100 mg/L) adjusted to pH 7 with 0.1 N and 0.01 N HNO₃ or NaOH until the charge of the humic acid was neutralized and displayed the end point value(zero charge). The experimental set up is shown schematically in Fig. 1.

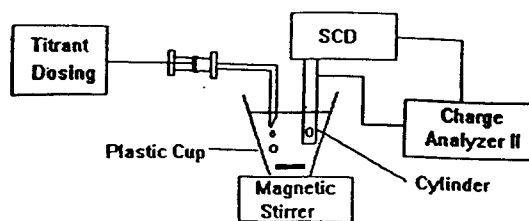


Fig. 1. Schematic diagram of experimental set-up for SCD method.

3. Results and Discussion

3.1. Flocculation-spectrophotometry

As humic acid is anionic in character and shows a strong absorption in the UV region because of its native yellow color(Fig. 2), the optimum dosage of the cationic flocculant can be determined in the UV region with the dosage at which the best color removal of humic acid occurs. It is frequently found that the optimum dosage of the flocculant is close to that required to neutralize the surface charge carried by the

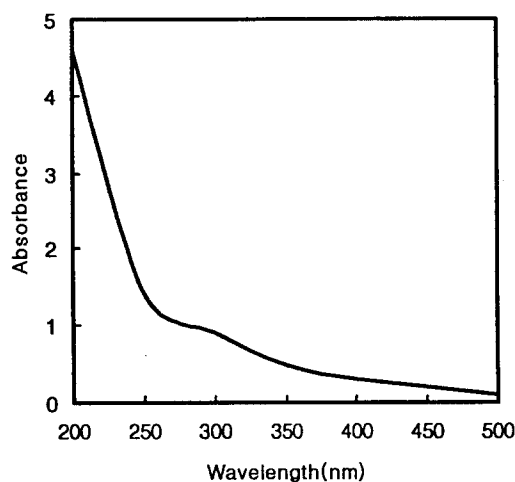


Fig. 2. Absorption spectrum of humic acid at pH 7 ($C_{\text{humic acid}} = 50\text{mg/L}$).

materials, although there are many important exceptions. At higher dosages, excess flocculant is adsorbed and the solution becomes restabilized by excess charge. To achieve this, jar flocculation tests were carried out and a relatively slow speed of 65 rpm was chosen to provide a shear rate that was large enough to cause flocculation, but low enough to prevent subsequent floc break-up. As a solid/liquid separation process, filtration was performed firstly: each of the cationic polymers was added to the solution containing 10 mL of humic acid (50 mg/L) adjusted to pH 7 and the solution was stirred for a period of 15 min with 65 rpm, and was passed through a prewashed $0.45\ \mu\text{m}$ nitrate membrane. Each sample was measured at 300 nm spectrophotometrically. As shown in Fig. 3 for polymer A and B, the results indicate the gradual reduction in the absorbance of humic acid as the polymer dose is increased. However the optimum dosage could not be obtained from this study due to the interference by resulting precipitate and so another method of separating it from the liquid was required. Dolejs(1986) had stated that

separation by centrifugation is an efficient tool for the flocculation assessment of humic waters. Therefore centrifugation was used as the solid/liquid separation process.

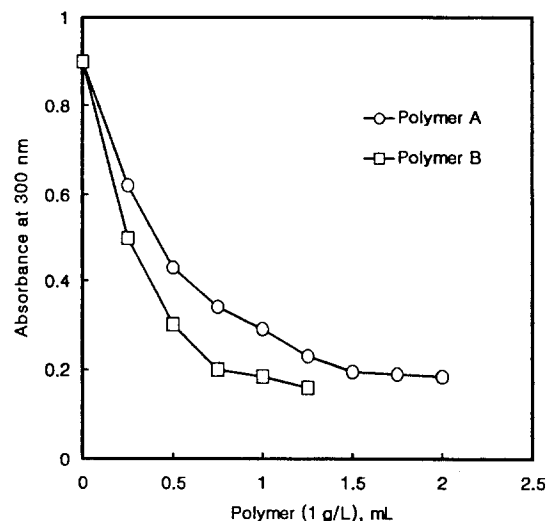


Fig. 3. The absorbance of humic acid with the dosages of polymer A and B by filtration ($C_{\text{humic acid}} = 50\ \text{mg/L}$, pH 7).

Fig. 4 shows the absorbance of humic acid with the dosage of each of the polymers. As shown in this figure, the absorbance with the amount dosed, changes very sharply for polymers of high charge density, but changes rather broadly for polymers of low and middle charge density. It is clear that there is a strong inverse correlation between the optimum dosage at which the lowest absorbance of humic acid is shown and charge density, with highly charged polymer giving the lowest optimum dosage. In fact, the results indicate that, in each case, the optimum dosage corresponds roughly with the same amount of cationic charge, pointing out the importance of charge neutralization. The optimum dosages of polymers in Fig. 4 and the removal efficiencies calculated from the calibration curve of humic acid (Fig. 5) are summarized in Table 2.

As shown in Table 2, with the polymers of higher charge density, the lower dosages were required to remove the humic acid and higher removal efficiencies were obtained.

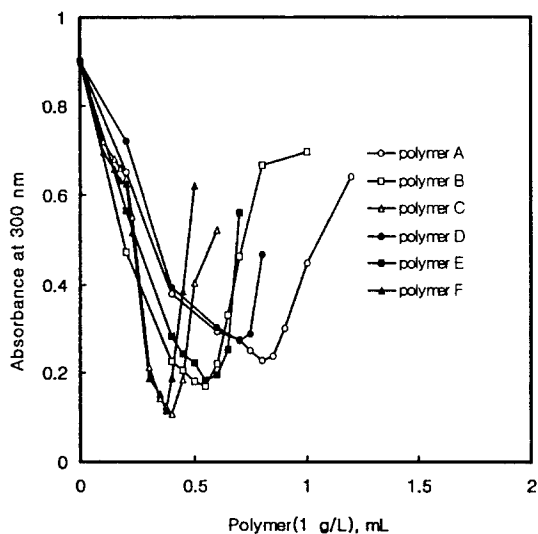


Fig. 4. The absorbance of humic acid with the dosage of each of the polymers by centrifugation ($C_{\text{humic acid}} = 50\text{mg/L}$, pH 7).

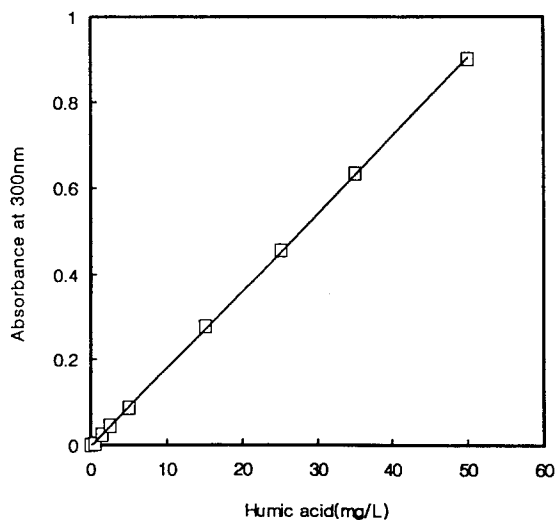


Fig. 5. Calibration graph of humic acid at pH 7.

Table 2. The optimum dosage and removal efficiency for each of the polymers by flocculation-spectrophotometry.

Polymer(g/L)	Optimum dosage*(mL)	Removal efficiency(%)
A	0.800	73
B	0.550	80
C	0.400	87
D	0.700	68
E	0.550	79
F	0.375	87

*obtained for 10 mL of humic acid(50 mg/L, pH 7)

In order to identify if the optimum dosage was obtained stoichiometrically, each of the polymer A, B, and C was dosed to the 10 mL of solutions containing 10, 25, 50, and 100 mg/L of humic acid, respectively. Fig. 6 shows the optimum dosages of polymer A, B, and C for different concentrations of humic acid. One can easily recognize that the optimum dosage increases proportionally to the concentration of humic acid, while the plot for each polymer is differently sloped.

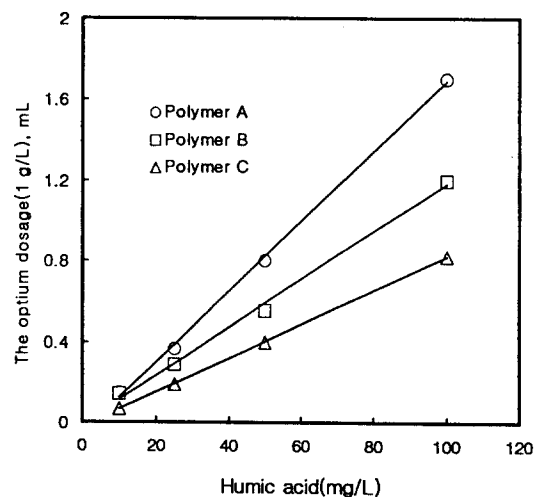


Fig. 6. The optimum dosages of polymer A, B, and C with different concentrations of humic acid by flocculation-spectrophotometry.

3.2. SCD method

In order to determine the optimum dosage of charged polymers more precisely, without using spectrophotometer, the SCD method can be utilized. SCD utilizes a capillary passage or porous plug of the material of concern, through which the bulk fluid can be forced by applied pressure. Counter ions in diffuse layer adjacent to the surface migrate with the fluid, creating an electrical potential or current, which can be measured. If the current is measured, it is termed the streaming current. This current can be mathematically related to the electrical potential at the surface of shear between stationary and mobile portions of the fluid(zeta potential). For a capillary tube, the relationship is expressed as(Heimenz, 1977):

$$I = \epsilon pr^2 \zeta / 4 \mu l$$

where I = streaming current, p = applied pressure, r = capillary radius, ζ = zeta potential, ϵ = permeability, μ = viscosity, and l = length of capillary.

Several commercial versions of a streaming current detector(SCD) are available, intended mainly for coagulant dosage control(Dentel, 1991). A typical arrangement has a sampling chamber, a reciprocating piston in a cylinder, with electrodes and a signal amplifier. A continuous sample taken from a point immediately downstream of flocculant addition, flows through the sampling chamber. Colloids in the chamber momentarily adhere to the piston and cylinder surfaces. Because one end of the cylinder is closed, the piston acts as a displacement pump, imparting motion to the fluid in the annular gap between piston and cylinder. This causes motion of counter ions relative to the attached colloids. Movement of charge is equivalent to an electrical current and, although this current is quite small,

it can be detected by ring-shaped electrodes at opposite ends of the annulus and then amplified. The Charge Analyzer II(Rank Brothers Ltd., UK), used in the present work, employs the SCD technique and is able to carry out a fully automatic polyelectrolytes titration of a sample, using the streaming current signal to detect the equivalence point. This may be taken as the point where the streaming current becomes zero.

By using an electrokinetic technique for end-point detection, most of the problems associated with the indicator method(Kam, 1996) for determining the optimum dosages of the flocculants are avoided. The precise nature of the SCD response in the region of the equivalence point is not easy to predict, not least because of a lack of fundamental understanding of the technique. Nevertheless, there is little doubt that a zero value of the streaming current corresponds to the point of charge neutralization.

In order to determine the optimum dosage of each of the polymers required to neutralize the charge of humic acid by SCD method, the solution containing 10 mL of humic acid(50 mg/L, pH 7) was titrated against each of the polymers. Table 3 shows the polymer consumption during charge neutralization of humic acid. The results from Table 2 and 3 indicate that nearly identical optimum dosage values were obtained by both methods and the optimum dosage is equivalent to the charge of humic acid.

Table 3. The optimum dosage of each of the polymers by SCD method.

Polymer(g/L)	Optimum dosage*(mL)
A	0.772
B	0.587
C	0.401
D	0.708
E	0.528
F	0.358

*obtained for 10 mL of humic acid(50 mg/L, pH 7)

Stoichiometric relationship between the optimum dosage of each of the polymers and different concentration of humic acid was investigated by SCD method. Fig. 7 shows the polymer consumption during charge neutralization of different concentrations of humic acid. As shown in this figure, the neutralization of negatively charged humic acid with each of the polymers appears to proceed stoichiometrically. Also it was found that the optimum dosages of the polymers by SCD method were almost identical to those by flocculation-spectrophotometry for different concentrations of humic acid.

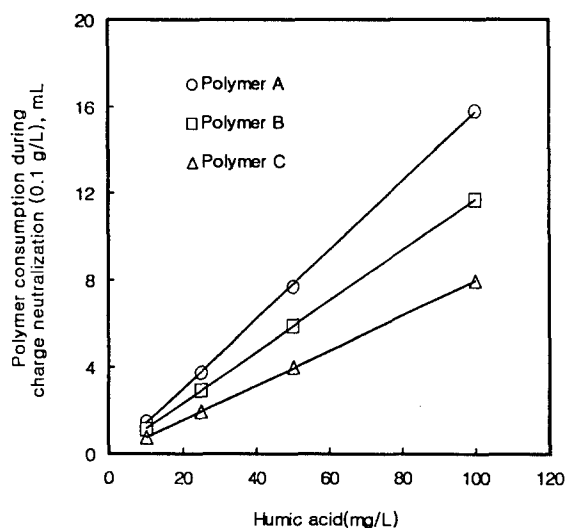


Fig. 7. Stoichiometric consumption of polymer A, B, and C during charge neutralization of different concentrations of humic acid by SCD method.

4. Conclusions

Using flocculation-spectrophotometry and SCD method, the optimum dosages of synthetic cationic polymers of different charge density and molecular mass for removing humic acid were determined

and compared.

By flocculation-spectrophotometry, it was found that the absorbance of humic acid with the amount of each of the polymers dosed, changes sharply for polymers of high charge density, but changes rather broadly for polymers of low and middle charge density.

The optimum dosage for each of the polymers by this method was determined with the dosage at which the lowest absorbance of humic acid was shown and was in good agreement with that required during the charge neutralization of humic acid by SCD method. Also it was found that there is a strong inverse correlation between the optimum dosage and charge density of the polymers, with highly charged polymer giving the lowest optimum dosage. These results indicate that, in each case, the optimum dosage corresponds roughly with the extent of cationic charge, pointing out the importance of charge neutralization. Both methods showed that a stoichiometric correlation exists between the optimum dosage of each of the cationic polymers and the negatively charged humic acid.

References

- Bernhardt, H. and J. Clasen, 1967, Probleme der entfennung von mikroorganismen durch flockung in der trinkwasser aufbereitung, *Veroffentl. Abt Lehrstuhls. Wasserchem. Univ. Karlsruhe* 3, 294-338.
- Dentel, S. K., 1991, Coagulant control in water treatment, *Critical Reviews in Environmental Control* 21, 41-135.
- Dolejs, P., 1986, Centrifugation study of humic water coagulation by brownian motion, In: Pawlowski, L., G. Alaerts and W.J. Lacy(eds.), *Chemistry for Protection of the Environment 1985 Studies in Environ-*

- mental Science 29, Elsevier Pub., Amsterdam, pp 297-310.
- Eisenlauer, J. and D. Horn, 1985, Fibre-optic sensor technique for flocculant dose control in flowing suspensions, *Colloids Surface* 14, 121-134.
- Gregory, J., 1983, Flocculation test methods, *Effluent Water Treat. J.* 23, 199-205.
- Gregory, J. and D. W. Nelson, 1986, Monitoring of aggregates in flowing suspensions, *Colloid Surfaces* 18, 175-188.
- Griebel, T. and W. M. Kulicke, 1992, Molecular characterization of water-soluble cationic polyelectrolytes, *Makromol. Chem.* 193, 811-821.
- Heimenz, P. C., 1977, Principles of Colloid and Surface chemistry, Marcel Dekker Inc., New York.
- Horn, D., 1978, Optisches zweistrahlverfahren zur bestimmung von polyelektrolyten in wasser und zur messung der polymer adsorption an grenzflächen, *Progr. Colloid polymer Sci.* 65, 251-264.
- Ives, K. J., 1956, Electrokinetic phenomena of planktonic algae, *Proceed. Soc. Water Treat. Examin.* 5, 41-58.
- Ives, K. J., 1959, The significance of surface electric charge on algae in water purification, *J. Biochem. Microbiol. Technol. Eng.* 1, 37-47.
- Kam, S. K., 1996, Charge determination of synthetic and natural polyelectrolytes by colloid titration, Proc. 4th Joint Symposium of Cheju Nat'l Univ. and Nagasaki Univ. on Sci. and High Technol., Cheju, April 11-13, pp 189-197.
- Kawamura, S. and Y. Tanaka, 1966, Applying of colloid titration technique to coagulant dosage control, *Water Sewage Works* 113, 348-357.
- Kawamura, S., G. P. Hanna and K. S. Shumate, 1967, Application of colloid titration technique to flocculation control, *J. Am. Water Works Assoc.* 59, 1003-1013.
- Matsui, Y., N. Tambo, K. Abe, Y. Zaitso and T. Ohto, 1991, Evaluation of color colloid removal after coagulation by way of dual wavelength adsorption, *J. Jap. Water Works Assoc.* 60, 2-9.
- Stumm, W. and C. R. O'Melia, 1968, Stoichiometry of coagulation, *J. Am. Water works Assoc.* 60, 514-539.
- Tenney, M. W., W. F. Eichelberger, R. G. Schussler and J. L. Pavoni, 1969, Algal flocculation with synthetic organic polyelectrolytes, *Appl. Microbiol.* 18, 965-971.
- Tenney, M. W. and W. Stumm, 1965, Chemical flocculation of microorganisms in biological waste treatment, *J. Water Pollut. Control Fed.* 37, 1370-1388.
- Tilton, R. C., J. Murphy and J. K. Dixon, 1972, The flocculation of algae with synthetic polymer flocculants, *Water Res.* 6, 155-164.