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Determination of Trace Polymer in Waste Water

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Polymeric flocculant plays an important role in sludge dehydration in sewage treatment plants. Slaked lime is currently used as a flocculant for dehydration in most sewage treatment plants in Japan. When slaked lime is added to the sludge for burning in a multi-stage incinerator, the calorific value of the cake is lowered and trivalent chromium is oxidized to the hexavalent form. The present authors have investigated the dehydration by some polymeric flocculants for prevention of environmental pollution and energy conservation. Since some polymeric flocculants are, however, toxic, the prevention of environmental pollution must be considered when their use is contemplated.

An accurate method of determination is required for the measurement of a trace polymeric flocculant. Recently, Seto and Saito (1977) reported a colloidal titration method for the determination of cationic flocculant. It can not , however, be accurately determined when soluble organic matter is present in the sample, and so the method can not be used for real waste water without modification. Attia and Rubio (1975) reported a method for direct determination of polyacrylamide and polyethylene oxide flocculants in dilute solution. The present authors have investigated this method, and used it to develop a new procedure for determining the level of flocculant in real waste water. Details of the procedure are presented in this paper.

MATERIALS AND METHODS

Tannic acid solution (0.1%) was used as a reagent for the experiment. Known quantities of flocculants listed in Table 1 were dissolved in distilled water, and a certain amount of each was put into a 50-ml volumetric flask to which 20 ml of an inorganic salt solution and successive 5-ml aliquots of tannic acid solution were added. The solution was then finally made up to volume with distilled water, the flask tightly stoppered, and

the contents stirred for approximately one minute. The sample was left to stand for one hour at room temperature except in the case of the experiment to investigated the influence of temperature. The reference solution was prepared using the same procedure and quantities of reagents as those in the test solutions. The transmittance was measured with a spectrophotometer at two wavelengths (Type 624, Hitachi Ltd., Japan). The cell used was 5 cm long. The polyelectrolytes used were supplied by the Konan Chemical Industry Company (Japan).

Table 1. Polyelectrolytes used

Polyelectrolyte	Character	Molecular weight
K-35	Polyacrylamide cation	5 million
K-111	Ester polyaminocarbonate cation	2 million
ZH-750S	Polyacrylamide nonion	7 million

RESULTS AND DISCUSSION

The transmittance of the tannic acid solution with cationic polyelectrolyte K-111 was measured with the spectrophotometer at 360 to 1000 nm in order to find the optimum wavelength. Cationic polyelectrolyte K-111 at a concentration of 10.8 mg/l was used as a coagulant. Minimum values of transmittance were found at both 554 nm and 830 nm, as shown in Fig. 1.

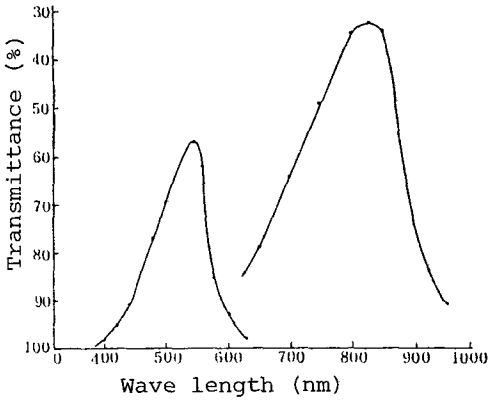

Figure 1. Transmittance of tannic acid solution with cationic polyelectrolyte K-111

Calibration curves of tannic acid with cationic polyelectrolyte K-111 were obtained at wavelengths of 554 and 830 nm, as shown in Fig. 2. Although both curves were linear, the calibration curve at 554 nm was more sensitive than that at 830 nm, and further measurement was therefore carried out at the former wavelength.

Colloidal titration can be used for determination of cationic and anionic flocculants. Attia and Rubio (1975) reported that the method using tannic acid described in this paper can be used for determination of both cationic and nonionic flocculants. Calibration curves for the flocculants listed in Table 1 were drawn up according to the determining procedure, and the results are shown in Fig. 3.

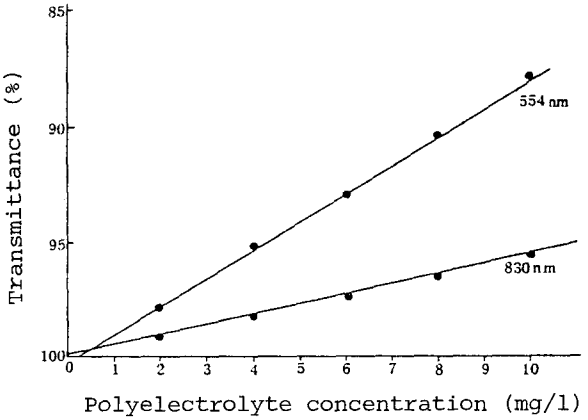

Figure 2. Calibration curves for tannic acid with cationic polyelectrolyte K-111 at wavelengths of 554 and 830 nm

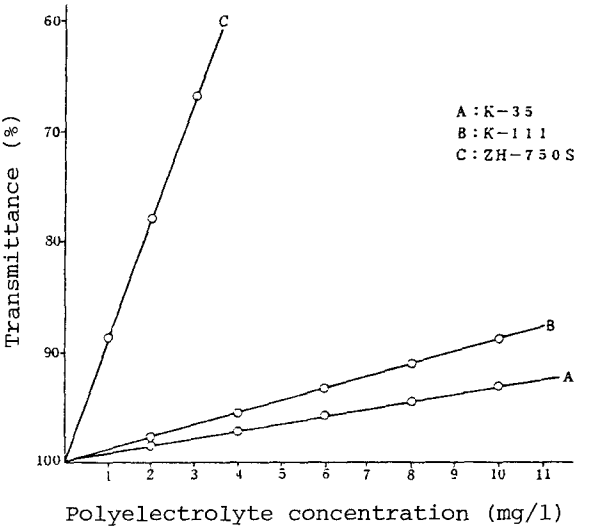

Figure 3. Calibration curves for tannic acid with different polyelectrolytes

It was revealed that all calibration curves showed linearity and nonionic flocculant (ZH-750S) in particular could be determined even at a low concentration because of the sensitivity of the calibration curve.

Since temperature, pH, and salt concentration are all known to affect turbidity, these parameters were investigated. Determinations were made under constant conditions except that the temperature was varied between 10°, 20°, and 30°C. The results are shown in Fig. 4. Since it was revealed that transmittance was independent of temperature in the range between 10° to 30°C, a further measurement was made at room temperature.

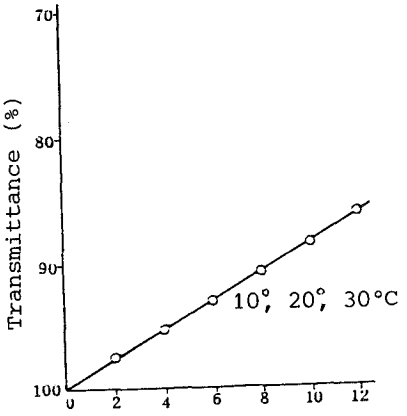

Figure 4. Effect of temperature on transmittance

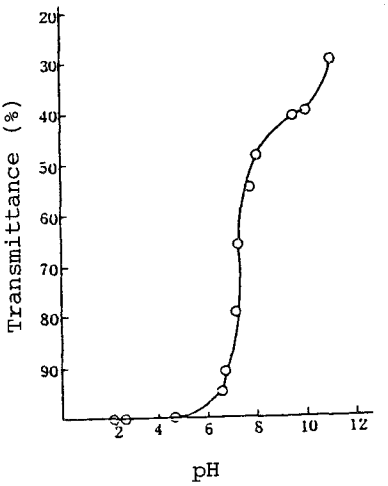

Figure 5. Effect of pH on transmittance

Investigations were then made as to how variation of pH value affected the transmittance. The experiment was carried out according to the normal determination procedure, except that the pH was varied using 0.1N NaOH and 0.1N HCl. The results are shown in Fig. 5. Transmittance was found to be high on the acidic side, while rapidly decreasing with shift from neutral to alkaline pH. The reason for this was considered to be that colloidal particles in tannic acid solution are large at acidic pH, while they are so small at alkaline pH that oxidation is accelerated, resulting in a darkening of the color. Figure 6 shows the oxidation of the phenolic portion of tannic acid to quinone by air or dissolved oxygen at alkaline pH.

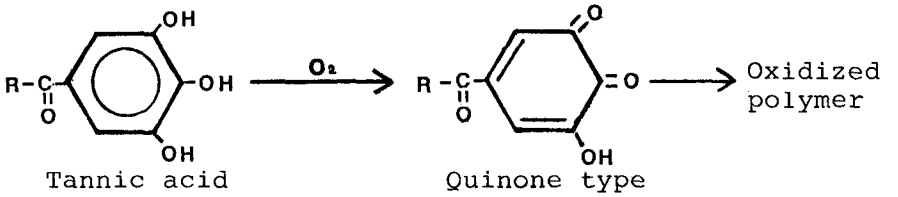

Figure 6. Oxidation of tannic acid at alkaline pH

It is therefore preferable that determinations are made at pH values lower than 7. Since tannic acid solution is a negatively charged colloid, it would be considered to form ionic bonds with cationic flocculants and hydrogen bonds with nonionic flocculants.

Although Attia and Rubio (1975) carried out their determination of flocculant at different concentrations of 0.1M and 0.5M NaCl, the present authors used $NaNO_3$ and $NaClO_3$.

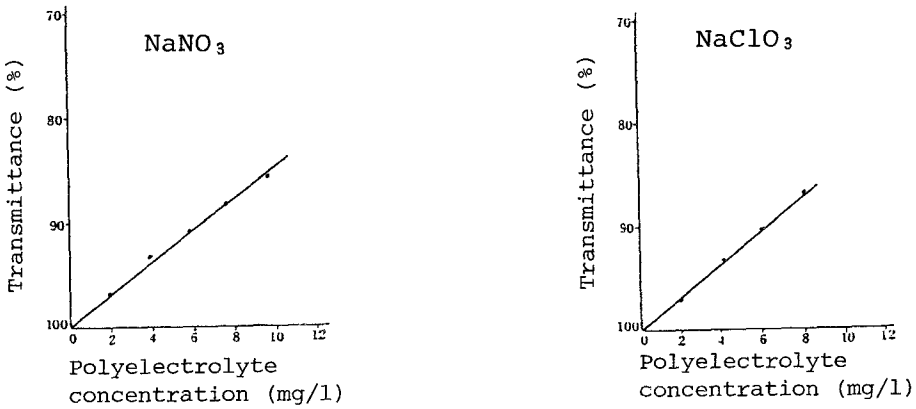

Figure 7. Effect of salt on transmittance

The calibration curves for these salts are shown in Fig. 7, in which it can be seen that the respective slopes obtained are almost the same as that of NaCl (Attia and Rubio 1975). When no salt solution was added, calibration curves could not be obtained because no suspensoid was produced.

Tannic acid produces precipitates by reacting with certain metals, alkaloids or proteins. Since samples containing large quantities of these materials are considered to affect determination, heavy metals present in the filtrate from a dehydrator at a polymer injecting plant were analyzed. As a result, ferric ions were found to be prevalent in various quantities. A further determination of transmittance was therefore made by adding standard solutions of ferric ions to polymeric flocculant. At ferric ion concentrations of 0, 50, 100, and 200 mg/l, the transmittance was 69.0%, 64.1%, 64.3%, and 67.5%, respectively. Ferric ions, therefore, do not seem to affect transmittance significantly, when their concentration is 200 mg/l or less.

An investigation was then conducted as to how organic matter in real waste water sludge affects the determination and how to remove it. The experimental procedure was as follows: 1 ml of polymeric flocculant solution at a concentration of 100 mg/l was put into a color comparison tube; concentrated sludge was separated by centrifugation at 800 rpm for 30 minutes; the separated liquid was filtered through 1-μm filter paper; finally, 2 ml of the filtrate was added to the color comparison tube and a calibration curve obtained according to the usual determination procedure. This was compared with a calibration curve obtained without addition of the filtrate. Ethylenediamine tetrasodium acetate (EDTA) was added to the sample prepared by the above procedure to prevent interference. The effect of EDTA on transmittance was determined as shown in Fig. 8. It reveals that in the calibration curve obtained by the addition of the filtrate, although the slope is not changed so much, the transmittance

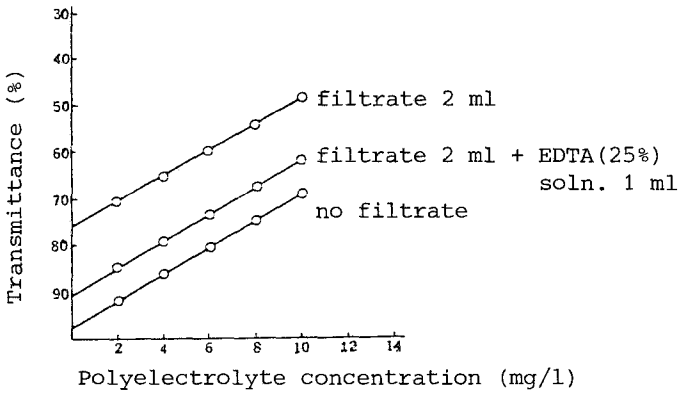

Figure 8. Effect of filtrate and EDTA on transmittance

decreases. The calibration curve obtained by the addition of EDTA solution shows that the transmittance is remarkably improved compared with that obtained by the addition of sludge, but is a little poorer than that without addition of the filtrate. This is because the heavy metal contained in the filtrate is affected by masking of the EDTA solution but a small quantity of salts unaffected by masking remains It was, therefore, understood that masking by EDTA solution would be applicable for the determination of real waste water. From these experiments for determining low concentr tions of cationic and nonionic flocculants and screening real waste water using the supernatant liquid from sludge, was found that the addition of EDTA could be applied for determination of the flocculant contained in real waste water.

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