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HYDROLYTIC CHARACTERISTICS OF POLYFERRIC SULFATE AND ITS APPLICATION IN SURFACE WATER TREATMENT

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ABSTRACT

The hydrolysis and polymerization of polyferric sulfate (PFS) were characterized. Jar test experiments were conducted to evaluate the coagulations of PFS, ferric chloride, and polyaluminum chloride. A pilot water-treatment plant consisting of coagulation, sedimentation, and filtration processes at a capacity of 30 l/h was simulated to analyze the effect of coagulant types on their performances. Results show that PFS leaves less iron residual and yields more efficient removals of turbidity and color than equivalent doses of conventional coagulants.

Key Words: Polyferric sulfate; Polyaluminum chloride; Coagulant; Hydrolysis; Turbidity

INTRODUCTION

Polyaluminum chloride (PACl) and aluminum sulfate (AS) are in widespread use as coagulants for the removal of particles and dissolved materials from raw water. However, recent studies have shown that aluminum is harmful to humans and animals. Because the uptake and discharge of aluminum from tissues are hard to regulate, the toxic levels of accumulated aluminum can lead to maladies such as Alzheimer's syndrome, osteoporosis, anemia, and anorexia. By contrast, iron is essential for the formation of hemoglobin; adults need 10 mg per day. The use of iron as a water purification agent can prevent the accumulation of aluminum in human and animal tissues (1–2).

Polyferric sulfate (PFS), $[Fe_2(OH)_n(SO_4)_{3-n/2}]_m$ ($n < 2$, $m > 10$), is an inorganic, high molecular-weight chemical compound that differs from other metal-salt coagulants in several aspects (3–5). Due to prehydrolysis, PFS contains a range of species, including $[Fe_2(OH)_3]^{3+}$, $[Fe_2(OH)_3]^{6+}$, $[Fe_8(OH)_{20}]^{4+}$ and other polynuclear complexes of iron (III), resulting in higher positive charge than Al(III) coagulants. PFS also has a wider range of applicable pH and leaves less residual iron. Therefore, PFS is more applicable with respect to eliminating water turbidity and color. PFS is less corrosive requiring less equipment maintenance. The flocs produced by PFS coagulation separate more easily during filtration. Because of these many advantages, PFS has been extensively studied and applied to water treatment systems in recent years (6–8). This paper focuses on describing the characteristics of PFS through the use of the comprehensive parameter, $B^* = OH/Fe$, to characterize the extent of Fe(III) hydrolysis and polymerization from each preparation. Both jar test and laboratory-scale processes were studied on the Mingder Dam surface water. The coagulation and filtration treatment efficiencies of PFS were compared with those of $FeCl_3$ and PACl with respect to turbidity, color removal, and residual metal.

EXPERIMENTAL PROCEDURES

PFS Preparation

The PFS used in this study was prepared in our laboratory by catalytic oxidation of a solution containing concentrated sulfuric acid and ferrous sulfate. The molar ratio of sulfuric acid to ferrous sulfate was kept greater than 0.2 to prevent the formation of ferric oxide sediment. After catalysis and polymerization, the liquid product in the reactor vessel was dark brown and highly acidic. The preparation was completed with an aging period of 5 to 7 h at 50°C to achieve PFS stability. The PFS thus prepared was characterized as follows: $Fe(III) > 150$ mg/L; $Fe(II) < 1$ mg/L; $[OH^-]/[Fe] = 0.4$; it was reddish brown with consistent viscosity. Because $[OH^-]/[Fe]$ ratios are generally expressed as γ-ratios, this PFS is written as $PFS_{r\,=\,0.4}$.

Analysis of Water Samples

The aluminum concentration was analyzed by measuring the adsorption at 535 nm following the ECR (Eriochrome cyanide R) method (9). The iron content was determined by the atomic adsorption spectrophotometer (Shimadzu AA-680). The color of the pure sample was determined by a model HACH DR-2000 spectrophotometer via the Pt-Co method (9). Turbidity was determined by using a HACH model 2100 turbidity meter as unit of NTU (nephelometric turbidity unit).

Hydrolysis of PFS

In each experiment, PFS was first diluted to the desired concentration using double-distilled water containing 0.1 M $NaClO_4$. The pH values of the mixtures were determined by a digital pH meter. The B* calculated from the pH of the solution immediately after the dilution represents the initial extent of hydrolysis of the solution at various concentrations.

Jar Tests

The untreated surface water from the Mingder Dam (Miaoli, Taiwan) was used as the test solution in the jar tests for coagulation. The turbidity of the surface water was less than 10 NTU. A 6-beaker jar test was set up for each trial. Each beaker contained 900 ml of surface water, and the initial pH value and turbidity were measured at room temperature. After the coagulants were added to the beakers, the samples were rapidly stirred at 120 rpm for 2 min, followed by a 20-min flocculation period at 30 rpm and a 30-min settling period. At the end of the settling time, the pH of the sample was recorded. Water samples at 3 cm below the water surface were collected and filtered through 0.45 μm membranes. The turbidity and metal-ion concentrations of the filtrates and the unfiltered samples were determined.

Pilot Studies

Equipment used in the pilot studies is shown in Fig. 1. Coagulants (PFS, $FeCl_3$, PACl) were added to the coagulation tank at iron and aluminum concen-

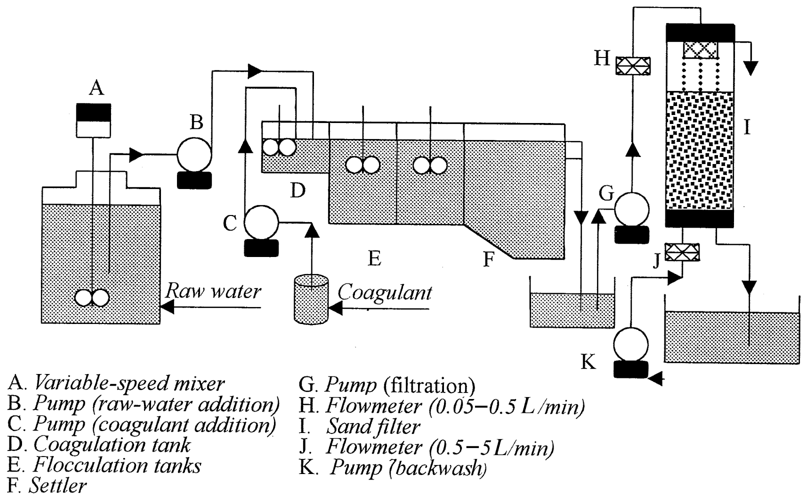

Figure 1. Pilot plant schematic.

trations ranging from 1 to 6 mg/L, and the flow rate was maintained at 30 l/h. Mixing was provided by mechanical stirrers. The rotational speeds were set at 200 rpm and 60 rpm for the coagulation tank and the flocculation tank, respectively. The retention times in the coagulation, flocculation, and sedimentation tanks were set at 1, 10, and 48 min, respectively. The sand filter was washed at the beginning of each run by draining the level of water to the top of the media and then backflushing it with water for about 10 min. The filtration capacity of the sand filter was maintained at 120 m^3/m^2 per day. Samples were taken from the sedimentation and filtration units for the analysis of turbidity, color, pH, and residual metal concentration after the operation had stabilized.

RESULTS AND DISCUSSION

Hydrolysis and Polymerization Characteristics of PFS

In coagulation, the hydrolysis of the added inorganic coagulant would consume the alkalinity of the water sample. Base is needed to compensate for this loss in alkalinity; however, its addition increases the cost of operation and is also detrimental to the quality of the finished water. Because PFS is a prehydrolyzed polymeric coagulant, less alkalinity is used than with the monomeric iron salt (e.g., $FeCl_3$). To determine the difference between the compounded $PFS_{r\,=\,0.4}$ and the monomeric iron salt, we applied the following function developed by Tang and

Stumm (10–11) to characterize the extent of Fe(III) hydrolysis and polymerization:

$$B^* = B_H + B - A \qquad (1)$$

In the equation,

$B^* = [OH^-]_{bond}/\ [Fe]_T$
$B_H = [H^+]/\ [Fe]_T = 10^{-pH}/\ [Fe]_T$
$B = [OH^-]_{add}/\ [Fe]_T$
$A = [H^+]_{add}/\ [Fe]_T$

The B_H is the initial ratio, a counterpart to the free H^+ in the iron solution that can be calculated from the pH values. $[OH^-]_{add}$ and $[H^+]_{add}$ are the strong base and acid added, and B* represents the number of OH^-resulting from Fe(III) hydrolysis. The pH values of the stock and diluted solutions of $PFS_{r\,=\,0.4}$ or $FeCl_3$ were measured under equilibrium conditions to determine the values of A and B_H, and the B* values were calculated using Eq. 1. The results are shown in Fig. 2. The differences of B* values of $PFS_{r\,=\,0.4}$ and $FeCl_3$ at the same concentration were always within 0.3 and 0.4. This is because 0.4 OH^- ions have already bonded to each Fe(III) ion during the production according to the $Fe_2(OH)_{0.8}(SO_4)_{2.6}$ formula that characterizes $PFS_{r\,=\,0.4}$. Consequently, PFS undergoes a lessened degree of hy-

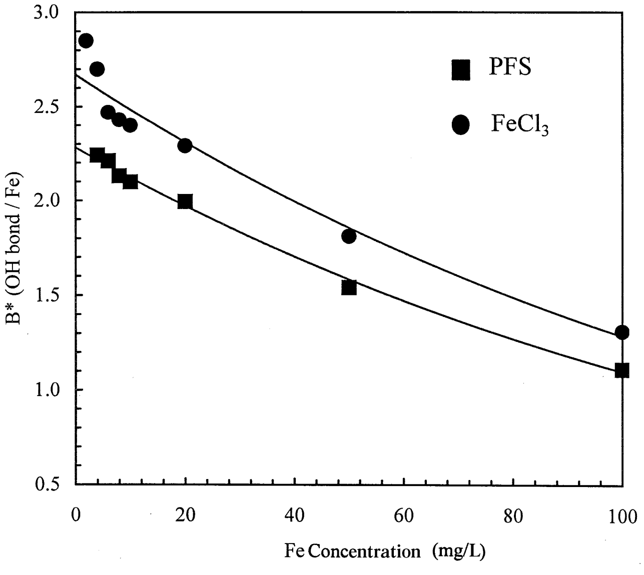

Figure 2. The relationship between B* and coagulant dosage.

drolysis when contacted with the water. The above result indicates that the alkalinity consumption of PFS is lower than that of monomeric ferric chloride. This property of $PFS_{r\,=\,0.4}$ increases the production of flocs and results in less residual iron.

Figure 3 shows the results of distilled water turbidity measurements at various doses of coagulants with controlled ionic strength (0.01M $NaClO_4$) but uncontrolled pH levels. It was found that the colloid particles formed with the addition of $PFS_{r\,=\,0.4}$ exhibited a greater turbidity than that of $FeCl_3$. This indicates that ferric hydroxide precipitated at lower concentration of $PFS_{r\,=\,0.4}$, proving that $PFS_{r\,=\,0.4}$ consumed less alkalinity than $FeCl_3$ during coagulation.

Figure 4 shows the residual iron concentrations in the filtrate and suspension after coagulation. The filtration process was able to remove the flocs formed from $PFS_{r\,=\,0.4}$ coagulation, as indicated by the extremely low residual iron in the filtrate. However, the ferric hydroxide precipitates formed by $FeCl_3$ were nearly all less than 0.45 μm, making the filtration process useless in preventing the iron ions from entering the water stream. This is why $FeCl_3$ is not widely accepted for processing drinking water in Taiwan, and choosing $PFS_{r\,=\,0.4}$ as a coagulant may solve the problem associated with high iron levels in household water.

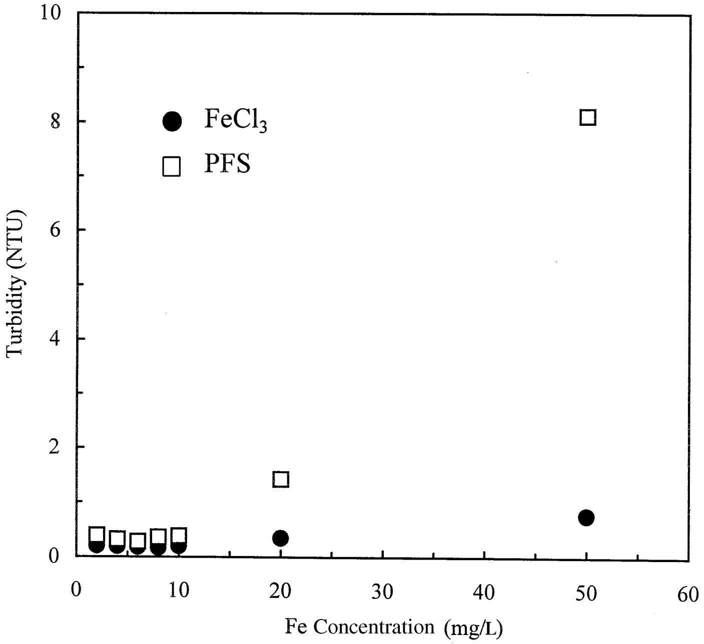

Figure 3. Solution turbidity as a function of iron dosage.

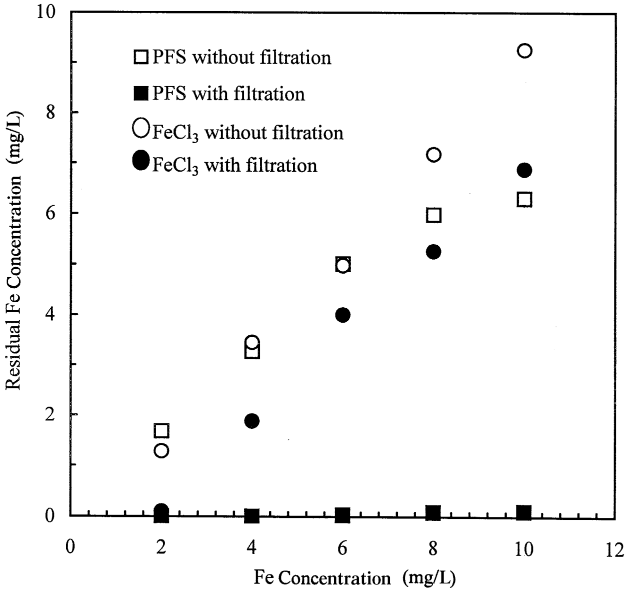

Figure 4. Residual iron concentration after jar mixing. Settling is shown as a function of coagulant dosage.

Jar Test Experiments for Mingder Dam Surface Water

To generate information for plant studies, jar testing was performed on the surface water of Mingder Dam. Various amounts of $FeCl_3$, $PFS_{r\,=\,0.4}$, and PACl were added while the pH was controlled at 7. The turbidity removal efficiencies for the three coagulants are shown in Fig. 5. At 2 mg/L, 75–82% turbidity removal levels were achieved for all three coagulants. To understand the relationship between the coagulation efficiency and the pH of the raw water, jar tests were also performed at various pH while 2 mg/L coagulant was used for all three coagulants. The turbidity removal as a function of pH is shown in Fig. 6. The removal efficiency of PACl dropped dramatically at pH higher than 8, proving that $PFS_{r\,=\,0.4}$ or $FeCl_3$ are more applicable at relatively high pH.

Laboratory-Scale Pilot Studies on the Mingder Dam Surface Water

Various dosages of $PFS_{r\,=\,0.4}$, PACl, and $FeCl_3$ coagulants were tested on the Mingder Dam surface water in this experiment. The turbidity removals of the

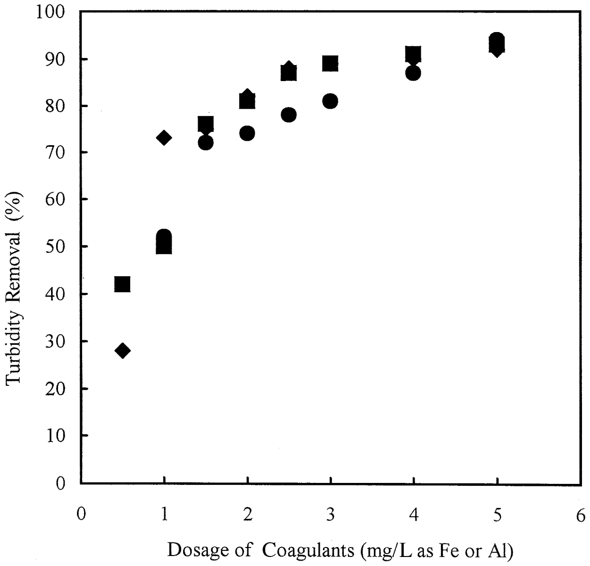

Figure 5. Turbidity removal percentage after jar mixing and settling for various coagulant dosages at pH 7. ■ $\mathrm{PFS}_{r=0.4}$; ● $\mathrm{FeCl_3}$; ♦ PACl

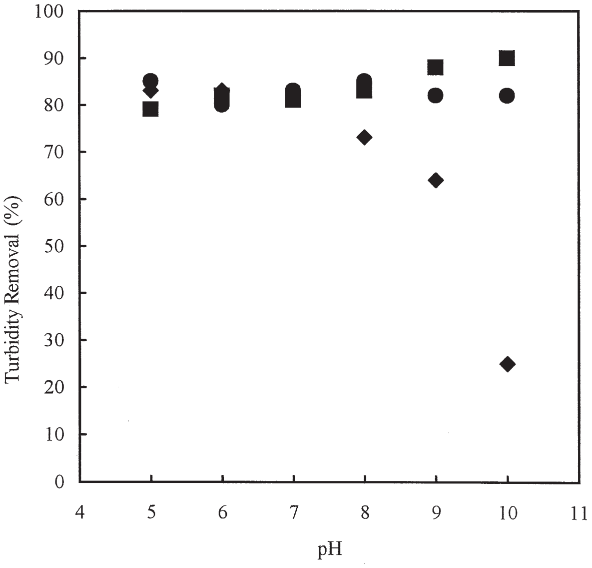

Figure 6. Turbidity removal after mixing and settling for various pH values in jar tests (2 mg/L) as Fe or Al. ■ $\mathrm{PFS}_{r=0.4}$; ● $\mathrm{FeCl_3}$; ♦ PACl

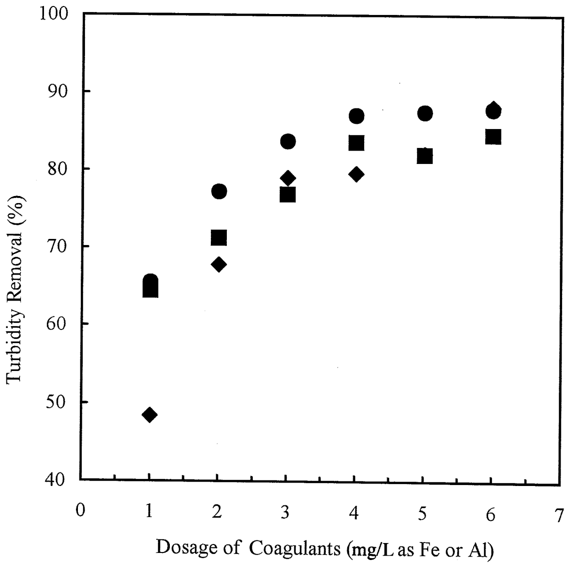

Figure 7. Turbidity removal after mixing and settling in pilot studies. ■ PFS$_{r\,=\,0.4}$; ● FeCl$_3$; ◆ PACl

samples (measurements taken after the settling process) are shown in Fig. 7. The results are consistent with those of the jar test; that is, the turbidity removal reached about 70–85% at concentrations of 2–3 mg/L for all three coagulants. However, as shown in Fig. 8, when the samples taken after filtration were analyzed, more PFS and FeCl$_3$ were removed at identical coagulation conditions. This result suggests that larger and more compact particles were formed during coagulation of iron salts (PFS and FeCl$_3$). Because the Fe(OH)$_3$ colloid is denser than that of Al(OH)$_3$, the flocs formed from the iron-salt coagulation were expected to settle much faster in the water treatment system, and as a consequence, to result in more efficient turbidity and color removal.

In Fig. 9, for both polynuclear species, color removal efficiency obtained with PFS$_{r\,=\,0.4}$ was clearly superior to that achieved with PACl. The lower dosages of PFS$_{r\,=\,0.4}$ needed to achieve the complete color removal suggests that PACl has less cationic charge than PFS.

The residual metals before and after filtration are presented in Figs. 10 and 11. The figures show that the PFS$_{r\,=\,0.4}$ performed equally well with or without filtration; after filtration, the residual Fe concentrations were undetectable. In contrast, high iron residual was detected when FeCl$_3$ was used and the amount increased with the coagulant dosage. The results reported by Hahn and Stumn

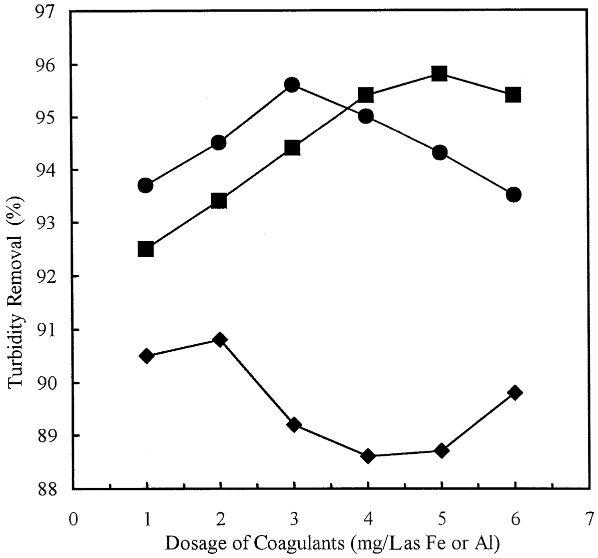

Figure 8. Turbidity removal after mixing, settling, and filtration in pilot studies. ■ $PFS_{r=0.4}$; ● $FeCl_3$; ◆ PACl

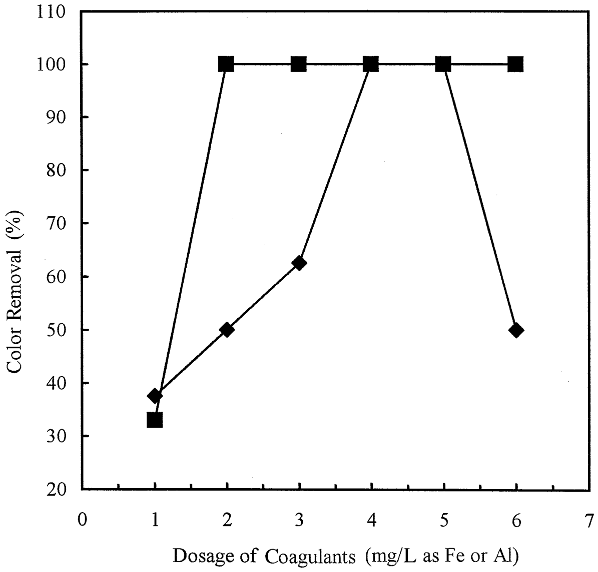

Figure 9. Color removal after mixing, settling, and filtration in pilot studies (■ PFS, ◆ PACl) (the initial surface water color was 8 Pt-Co unit).

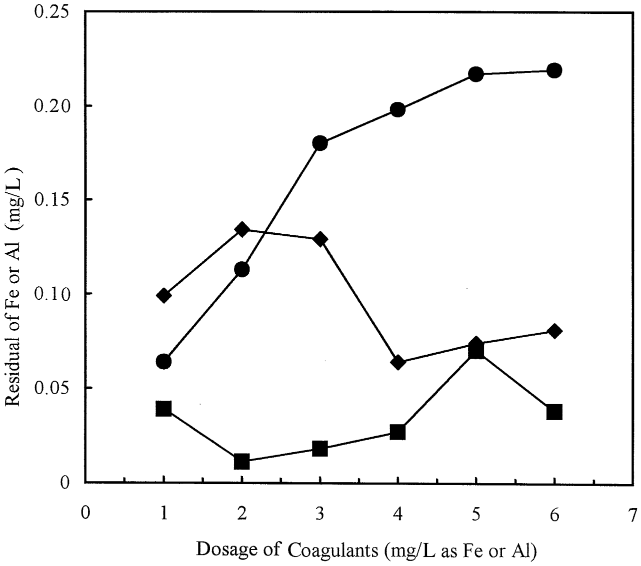

Figure 10. Residual metal after mixing and settling in pilot studies. ■ $PFS_{r=0.4}$; ● $FeCl_3$; ◆ PACl

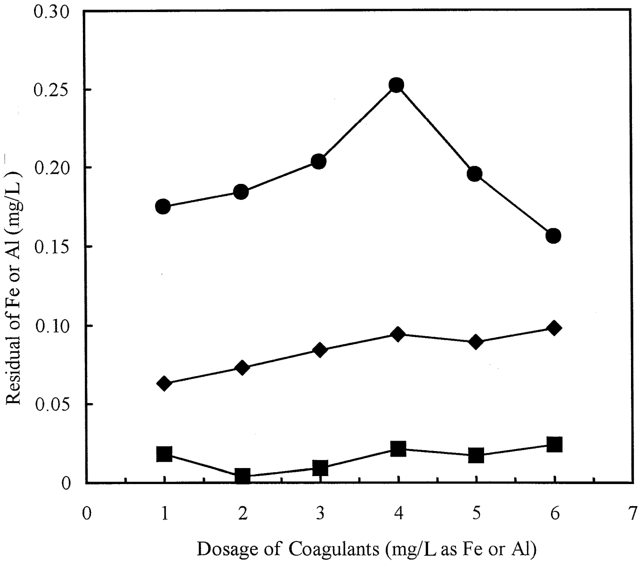

Figure 11. Residual metal after mixing, settling, and filtration in pilot studies. ■ $PFS_{r=0.4}$; ● $FeCl_3$; ◆ PACl

indicated that if polynuclear species are used as a coagulant, it can be absorbed to turbidity particles before any further modification. Because $PFS_{r\,=\,0.4}$ is a prehydrolysis coagulant, it contained the largest portion of high-charged polycations and greater molecular weight. Therefore, in water, $PFS_{r\,=\,0.4}$ might be readily adsorbed on particles and neutralize their negative charges by chemical interaction and cause the minimum coagulant residual. In contrast, direct addition of a monomeric iron salt, such as $FeCl_3$, to water may cause extremely rapid and uncontrolled hydrolysis that forms small hydrolysis products and promotes the possibility of Fe(III) ions residual in water. Therefore, these results support the hypothesis that the Fe(III) hydrolytic species are preformed from $PFS_{r\,=\,0.4.}$ These hydrolysis products give $PFS_{r\,=\,0.4}$ higher positive charges, faster rate of chemical interactions (e.g. charge neutralization and chemical complex creation), greater molecular weights, and more efficient coagulation than those attained by conventional low-nuclear coagulants (13).

CONCLUSION

PFS prepared in our laboratory was tested on the coagulation of the Mingder Dam source water by jar tests and continuous flow experiments. Results show that at room temperature, $PFS_{r\,=\,0.4}$ was more effective than conventional coagulants in color and turbidity removals. Coagulation using $PFS_{r\,=\,0.4}$ also yielded significantly less coagulant residual after filtration than $FeCl_3$ or PACl. Results support the theory that the characteristically high positive charge and large molecular weight of the $PFS_{r\,=\,0.4}$ cause more adsorption on the dissolved components in the raw water and form more compact flocs for easy separation during filtration. Because less alkalinity was consumed by $PFS_{r\,=\,0.4}$ during the coagulation process, the residual iron did not increase with the dosage of the coagulant. The result suggests that to reduce the potential hazard caused by aluminum accumulation in human bodies, $PFS_{r\,=\,0.4}$ may be an alternative to the popular aluminum coagulants for treating water.

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