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Improvement of Sedimentation by the Coagulation using Poly-silicate Iron for the Removal of *Cryptosporidium* Oocyst

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Abstract: Poly-silicate iron coagulant (PSI) was a new coagulant for drinking water treatment. The performance of PSI for synthetic *Cryptosporidium* oocyst (S-Crypto) was higher than polyaluminum chloride (PAC) and ferric chloride (FC). The higher removal performance in Run-PSI (coagulation with PSI) was caused by both the biggest reduction of small particles and the higher sedimentation rate of residual particles and flocs produced. Before the sedimentation stage, PSI could reduce the numbers of the small particles and flocs up to half and one–third of that in Run-PAC and Run-FC, respectively. It becomes 10 and 7 times lower at maximum after 29 min sedimentation in the comparison with PSI and FC, respectively. The predominant mechanism for S-Crypto coagulation was charge neutralization and interparticle bridging in Run-PSI. The biggest reduction of small particles and the higher sedimentation rate of residual were caused by the polymerized silica, not by iron in PSI.

Keywords: Coagulant, drinking water, ferric chloride, polyaluminum chloride (PAC), PSI, sedimentation rate

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INTRODUCTION

Coagulation and sedimentation followed by rapid sand filtration is the most common drinking water treatment process. Coagulation is a process for combining colloid materials and small particles into larger aggregates (flocs), thereby facilitating their removal in the following sedimentation and filtration stages. Conventional chemicals used for coagulation are aluminum sulfate (alum), polyaluminum chloride (PAC), ferric chloride (FC), and ferric sulfate. Among them, PAC is the most widely used in Japan.

There have been outbreaks of Cryptosporidiosis in Japan (1) and worldwide (2). The U.S. EPA (United States Environmental Protection Agency) promulgated the "Interim Enhanced Surface Water Treatment Rule" (IESWTR) in 1998, as a means to control *Cryptosporidium* in drinking water. Within the regulation, compliance is defined by performance requirements for water treatment plants and by monitoring indices (e.g. turbidity, performance of individual filters) that aim to optimize the filtration process and in some cases the disinfection process (3). In Japan, the 1996 outbreak of cryptosporidiosis forced drinking water treatment authorities to make guidelines for the treatment and monitoring of *Giardia* and *Cryptosporidium* (4–6). The quality control of raw water and treated water (e.g., 0.1 mg-kaolin/L of turbidity in treated water) was urged by the guideline.

Therefore, the development of the process for the removal and/or inactivation of *Cryptosporidium* oocysts in drinking water treatment process is urgently needed (7, 8). Many researchers (9–12) reported that the removal efficiency of coagulation and sedimentation processes for *Cryptosporidium* oocysts was affected by treatment conditions and coagulant type and that its removal was not perfect and not easy because of their small size and low density.

Polysilicate-iron coagulant (PSI) is a new coagulant approved by the Center of Quality Certification of Japan Water Works Association in 2001. PSI is made from polymerized silica and iron (13). The higher performance for turbidity and phytoplankton removals than PAC and FC has been confirmed by jar tests and pilot plant experiments in the eutrophic reservoir water (14, 15). In comparison with PAC, PSI could reduce 15% and 55% of residual turbidity and phytoplankton, respectively. In comparison with FC, PSI could reduce about 30% of both residual turbidity and phytoplankton. PSI had the highest performance for phytoplankton irrespective of species.

In the past research, the removal performance of PSI for *Cryptosporidium* oocysts was also studied by using synthetic *Cryptosporidium* oocyst (S-Crypto), and PSI showed the higher performance than PAC and FC (16). In comparison with PAC, PSI could reduce 42% of residual S-Crypto. However, the mechanism of the higher performance in PSI was not studied. The mechanism analysis would be useful information on the further improvement of coagulation for *Cryptosporidium* oocysts. In this study, the mechanism of the higher performances of PSI than PAC was studied by batch experiments using the S-Crypto, especially in terms of the sedimentation stage. The comparison with FC was also conducted to evaluate the effect of the polymerized silica in PSI structure.

MATERIALS AND METHODS

Coagulants and Materials

PSI was produced by the polymerization of silicate and the mixing with ferric chloride. The polymerization was conducted by heating a diluted water glass solution (Sodium silicate solution; 28.7% SiO_2) and sulfuric acid solution with rapid mixing at 70°C. The average molecular weight of the PSI produced in this study was about 500,000 Da (14) and the 3-to-1 of silica-to-iron molar ratio was used in this study.

PAC and FC were obtained from the Central Glass Co., Ltd. and Tsurumi Soda Co., Ltd., respectively. The original concentrations of PSI, FC, and PAC were 7.33, 17.60, and 31.23 mg-metal/L, respectively.

S-Crypto is made from poly-methyl methacrylate (PMMA) and contains fluorescent materials in the polymer to help its determination using fluorescence microscope (Japan Water Research Center; “Crypto-Tracer”). Particle sizes and densities of kaolin, *Cryptosporidium* oocyst, and S-Crypto are shown in Table 1.

A eutrophic reservoir water (Hiroshima prefecture, Japan) was used as raw water. Turbidity of the reservoir water ranged from 11.4 to 26.0 mg-kaolin/L in the experimental period. The water temperature and pH ranged from 5.0 to 29.8°C and from 7.3 to 7.8, respectively. DOC and alkalinity ranged from 2.0 to 3.7 mg-C/L and 32 to 45 mg-$CaCO_3$/L, respectively.

Jar Test

Eight liters of raw water were coagulated in a 10 L jar tester with two paddles. Coagulants were added at the optimum dose for turbidity and the solution was

Table 1. Particle sizes and densities of kaolin, *Cryptosporidium* oocysts and synthetic *Cryptosporidium* oocyst (S-Crypto)

	Kaolin	*Cryptosporidium parvum* oocysts	S-Crypto
Particle size (μm)	4.79 (d_{50})	4.2–5.4	4.5–5.5
Density (g/cm^3)	2.6	1.05–1.10	1.2
References	Besra et al. (17)	Bustamante et al. (10); JWWA (1)	Japan Water Research Center

mixed at 100 rpm for 2 min. The optimum doses of PSI, FC, and PAC for the jar test were 4.4 mg-Fe/L, 4.5 mg-Fe/L and 2.2 mg-Al/L, respectively. Then the mixing speed was reduced to 30 rpm and was kept for 15 min. The optimum pH was 5.5, 5.5, and 6.0 for PSI, FC, and PAC, respectively, and kept during coagulation by adding hydrochloric acid and sodium hydroxide. The initial concentration of S-Crypto was adjusted to 1,000–5,000 oocysts/mL, and the samples for analysis were taken from 3 cm below the surface of water.

Analytical Methods

Dissolved organic carbon (DOC) was determined by total organic carbon analyzers (TOC-500 and TOC-5000, Shimadzu), and the pH was determined by a pH meter (F-8, Horiba). Alkalinity was determined by the titration method with automatic titrator (APB-410, Kyoto Electronics Manufacturing). Turbidity was determined using a turbidimeter (ANA-148, Tokyo Photoelectric). S-Crypto with fluorescent material was counted using a fluorescence microscope with UV irradiation (Optiphot-2 with HB-1010 AF, Nikon). The zeta potential was measured with a particle electrophoresis apparatus (mode1 Mark II, Rank Brothers).

Particle size distribution including flocs was determined after the slow mixing. A particle size analyzer (Hybrid Particle Counter equivalent of ZVL, Fuji Electric Systems) was used and it combined the forward scattering method and the optical blocking method for the particle size detection with flat intensity lens. The analyzer can detect particles with 0.35–500 μm of diameter.

RESULTS AND DISCUSSION

Table 2 shows the removal ratio of S-Crypto during sedimentation after coagulation with PSI, FC, and PAC (Run-PSI, Run-FC, and Run-PAC, respectively). The removal ratio in Run-PSI could be achieved to log 3 in 30 min, while 120 min were required in Run-PAC. It indicates that the coagulation with PSI requires shorter sedimentation time to obtain the same residual *Cryptosporidium* oocysts than PAC, that is, it can reduce the risk of *Cryptosporidium* oocysts residual in the treated water than PAC at the same sedimentation time.

The removal ratio in Run-FC was almost same as that in Run-PAC. The removal ratio in Run-FC could achieve to log 3 at 60 min, and they were 4 times longer than that in Run-PSI. Generally speaking, the higher sedimentation performance of the particle is caused by its bigger size or higher density.

Figure 1 shows zeta potential of S-Crypto particle as a function of PAC and PSI coagulant dose after 3 min rapid mixing. There was an increase in

Table 2. The removal ratio of S-Crypto during the sedimentation. (Initial turbidity, 11.7 mg-kaolin/L; initial S-Crypto concentration, about 1,140 oocysts/mL)

Sedimentation time (min)	0	10	20	30	40	60	120	180
Run-PSI	0.0000	0.9968	0.9984	0.9991	0.9991	0.9992	0.9998	0.9998
Run-PAC	0.0000	0.9808	0.9881	0.9968	0.9971	0.9986	0.9991	0.9997
Run-FC	0.0000	0.9753	0.9843	0.9928	0.9961	0.9991	0.9997	0.9997

zeta potential with the increase in PAC and PSI dose. Zeta potential in Run-PAC become zero around 2 mg-metal/L, which is the same as optimum PAC dose. On the other hand, the zeta potential was less than −5 mV in Run-PSI around its optimum dose, 4.4 mg-metal/L. It indicates that the predominant mechanism for S-Crypto coagulation is charge neutralization in Run-PAC, and that is not only charge neutralization in Run-PSI. Hasegawa et al. (13, 18) reported that the coagulation of turbid materials were conducted by charge neutralization and interparticle bridging in Run-PSI, indicating that mechanism for S-Crypto would be also both them in Run-PSI.

Figure 2 shows the particle size distributions of the flocculated water with three coagulants at 0 min after slow mixing stage. We focused on the size above 3 μm in this research, because S-Crypto had approximately 5 μm diameter. The sample water was taken carefully and flowed into the particle size analyzer to prevent the crash of flocs. There would be some change of floc size during the sampling and injection, however, it would be not so

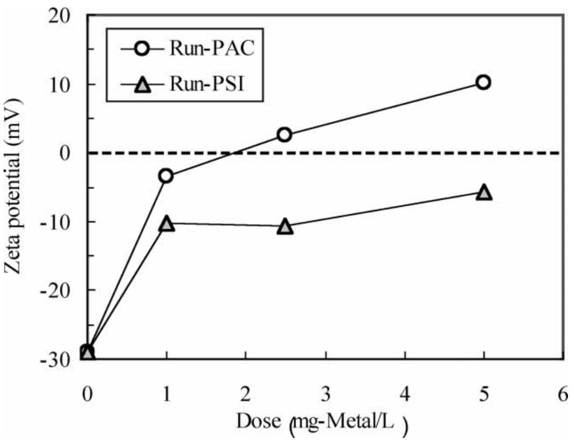


Figure 1. Zeta potential changes of S-Crypto particle with coagulant dose. (Initial turbidity, 11.2 mg-kaolin/L; initial number of S-Crypto, about 2,000 oocysts/mL).

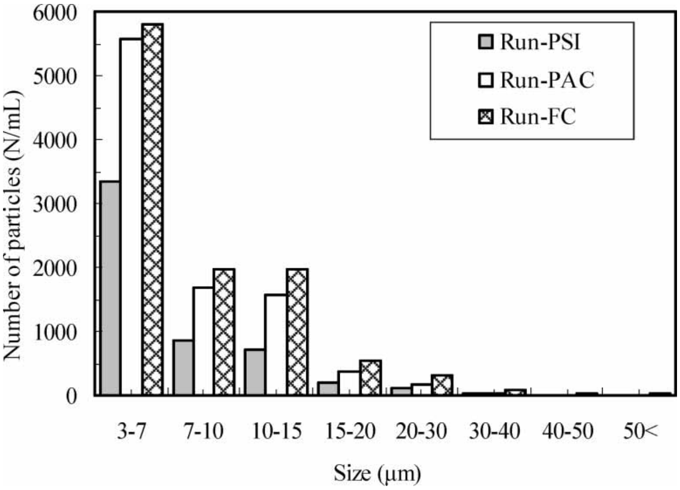


Figure 2. The residual particle size distributions in 0 min after the slow mixing with three coagulants. (Initial turbidity, 12.6 mg-kaolin/L; initial number of S-Crypto, about 1,000 oocysts/mL).

much because flow rates for samplings and injections were kept to be less than 1 mL/sec (50 mL/min). The initial turbidity was 12.6 mg-kaolin/L in the raw water, and the initial number of S-Crypto was adjusted around 1,000 oocysts/mL. The number of particles (and flocs; particles/flocs) in Run-PSI was lower than that in Run-PAC during all size ranges above 3 μm. Small particles in Run-PSI would be aggregated with bigger flocs, because bigger floc production was observed in Run-PSI than Run-PAC on visual evaluations in

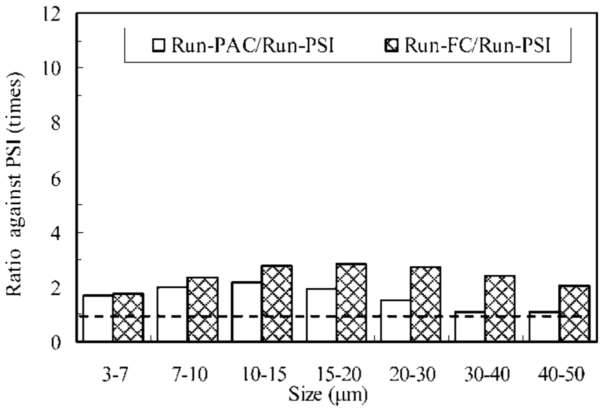
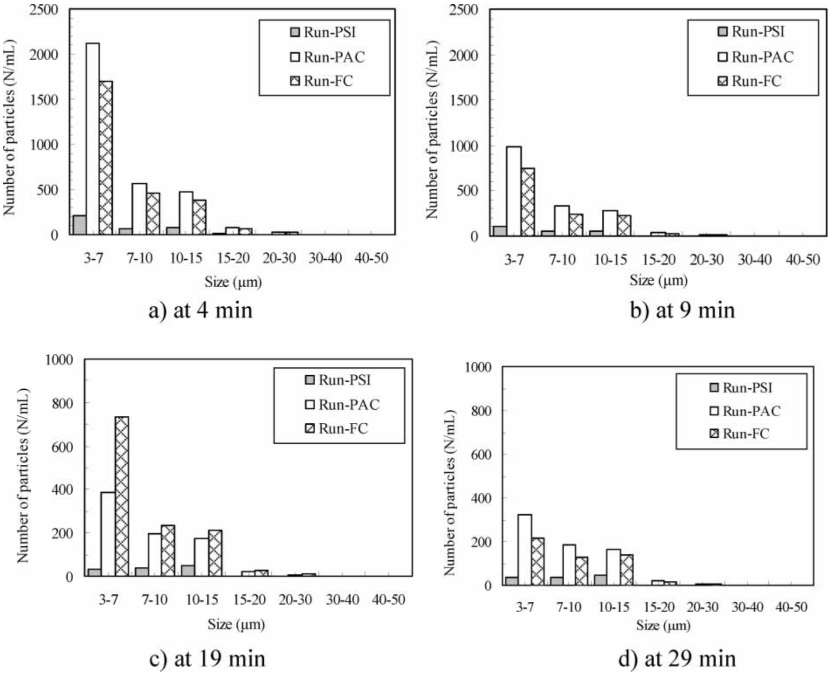


Figure 3. The ratio of particle/floc concentration in Run-FC and Run-PAC against Run-PSI at 0 min sedimentation.

this research as well as past research (13). The bigger flocs were already precipitated in slow mixing (flocculation) stage, resulting in the lower residual particles/flocs number of Run-PSI in all size range, even above 50 μm. In addition, it was well known that the sedimentation stage in full-scale drinking water treatment plant can remove the particle/floc with larger size than 50 μm even with a conventional coagulant (19, 20). Therefore, the sedimentation performance of particle/floc ranging until 50 μm was investigated in the following studies.

Figure 3 summarized the ratio difference of particle/floc concentration in Run-PAC against Run-PSI. The numbers of residual particles/flocs in Run-PAC were 10–120% larger than those in Run-PSI through the size, especially it was about 100% larger in 3–20 μm. These results indicate that the PSI could reduce the numbers of small particles/flocs during flocculation stage and it would be one of the reasons for the higher removal performance of PSI for S-Crypto in sedimentation stage.

The particle size distribution in Run-FC and the ratio difference against Run-PSI are also shown in Figs. 2 and 3, respectively. The residual numbers of particles/flocs ranging 3–50 μm in Run-FC were also about



a) at 4 min b) at 9 min

c) at 19 min d) at 29 min

Figure 4. The residual particle size distributions at 4, 9, 19, and 29 min after the slow mixing with three coagulants. (Initial turbidity, 12.6 mg-kaolin/L; initial number of S-Crypto, about 1,000 oocysts/mL).

70–180% larger than those in Run-PSI. The effect of the silicate polymerized in the PSI structure could be evaluated from the comparison between Run-PSI and Run-FC because the PSI was produced by the binding with polymerized silicate and ferric chloride (FC). The lower residual particles/flocs in Run-PSI than Run-FC suggested that the bound polymerized silica in PSI structure enhanced the aggregation of the small particles before sedimentation stage.

Figure 4a – 4d shows the particle size distributions in each coagulant at 4, 9, 19, and 29 min of sedimentation time, respectively. It was found that the residual number of particles/flocs in Run-PSI was always much lower than that in Run-PAC and Run-FC at all particle size.

Figure 5 summarized the ratio of particle/floc concentration in Run-FC and Run-PAC against Run-PSI after 29 min sedimentation. The sedimentation time of 10–30 min have been ordinarily used by jar-test in past research to simulate the real flow sedimentation stage. In Run-PAC, the difference was approximately 2 times for 3–20 μm at 0 min sedimentation as shown in Fig 3, however it become 3–10 times at 29 min. The increase of difference means faster sedimentation rate in Run-PSI than Run-PAC, indicating that the sedimentation rate of the small particles/flocs produced by PSI is faster than that by PAC.

The ratio of residual particle/floc number in Run-FC against that in Run-PSI at 29 min was also summarized in Fig. 5, and the difference in 3–20 μm also increased to 3–7 times from 2–3 times at 0 min sedimentation. This result indicates that the sedimentation rate of the small particles/flocs produced by PSI is faster than that by FC. Because the bound polymerized silica was the only difference between PSI and FC, it would increases the sedimentation rate,

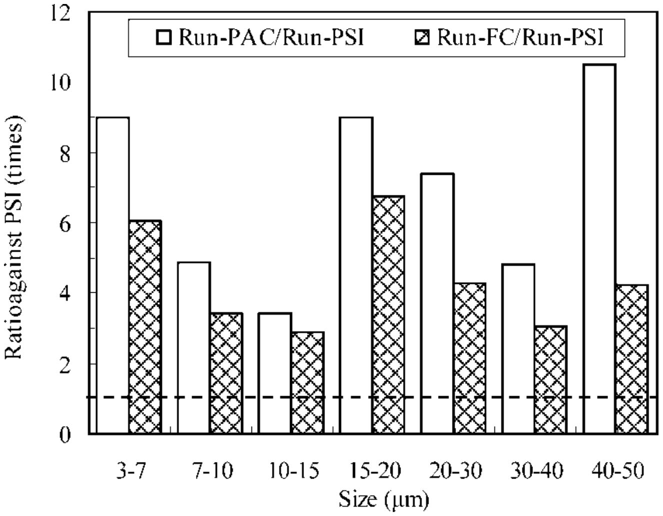


Figure 5. Ratio of particle/floc concentration in Run-FC and Run-PAC against Run-PSI at 29 min sedimentation.

that is, the faster sedimentation rate of small particles/flocs was caused by the polymerized silica in PSI, and not by iron. The higher density would be caused by the adsorbed polymerized silica itself and/or the larger amount of adsorbed iron on particles/flocs promoted by the polymerized silica in PSI.

CONCLUSIONS

The purpose of this study was to investigate the mechanism of high performances of PSI for S-Crypto (synthetic *Cryptosporidium* oocysts). The removal percentage of S-Crypto in Run-PSI could be achieved to log 3 in 30 min, the predominant mechanism for S-Crypto coagulation was charge neutralization and interparticle bridging in coagulation with PSI (Run-PSI). The high removal performance in Run-PSI was caused by both the biggest reduction of small particles during coagulation (flocculation) and the higher sedimentation rate of flocs. PSI could reduce the numbers of the small particles and flocs before sedimentation stage up to half and one third of that in Run-PAC and Run-FC, respectively. It becomes 10 and 7 times lower in Run-PSI and Run-FC, respectively, at maximum after 29 min sedimentation. The biggest reduction of small particles and flocs and their higher sedimentation rate was caused by the polymerized silica in PSI, not by iron.

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