

Pilot plant evaluation of PFS from coal-fired power plant waste

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Abstract

Pilot plant studies were conducted to evaluate the performance of a polymeric ferric sulfate (PFS) coagulant synthesized from waste SO₂. Aluminum sulfate (alum), ferric sulfate and ferric chloride were compared with PFS. Preliminary jar tests were performed to determine coagulant dose range and expected turbidity removal. The studies were conducted at the City of Savannah Industrial and Domestic (I&D) Water Treatment Plant in Port Wentworth, GA. The raw water source, a tributary of the Savannah River, was high in organic content. Due to its proximity to the coast, the tributary is tidally affected resulting in continuous water quality changes. Of the three iron-based coagulants tested, all provided nearly 10% greater reductions in total organic carbon when compared to alum. The pH ranges using the iron-based coagulants were much lower than those experienced with alum. Turbidity removal was approximately 100% for all coagulants. Ferric sulfate required the highest average dosage for proper coagulation/flocculation with efficient turbidity removal at 110 ppm. The performance of the PFS was comparable to that of ferric sulfate. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Coagulation, a crucial unit process in the treatment of drinking water, primarily removes turbidity and color [1]. The most common coagulants used in the treatment of drinking water are aluminum and iron salts such as aluminum sulfate (alum), ferric sulfate (FS) and ferric chloride (FC). A drawback of these conventional coagulants is that the formation of metal hydrolysis species is uncontrolled. To avoid this drawback and form the desired optimum species coagulants, several pre-polymerized inorganic coagulants such as polyaluminum chloride, polymeric ferric chloride and polymeric ferric sulfate (PFS) have been developed [2]. Generally, performance of polymeric coagulants is better than conventional coagulants in the equivalent dose and

at a similar pH. Specifically, PFS shows more efficiency than FS for the removal of turbidity, algae, color and natural organic matter (NOM) [3].

The first PFS synthesis approach was developed by Japanese researchers in 1980s. In this process, ferrous sulfate and sulfuric acid were used as the major raw materials, and oxygen was used as the oxidant with sodium nitrite as a catalyst to oxidize Fe²⁺ into Fe³⁺ [4,5]. However, there are concerns with the health effects of sodium nitrite used in this process. Jiang and Graham [3] synthesized PFS using hydrogen peroxide and nitric acids as the oxidants and the same raw materials, ferrous sulfate and sulfuric acid. However, the use of hydrogen peroxide in this process increases the price of PFS and its marketability is affected. Furthermore, using nitric acid does not alleviate the problems associated with the presence of nitrates. To address the problems of PFS from these two production methods, a low cost, environmentally friendly method for the production of PFS has been developed using sodium chlorate as the alternative oxi-

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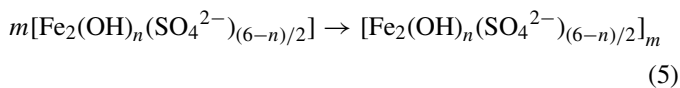
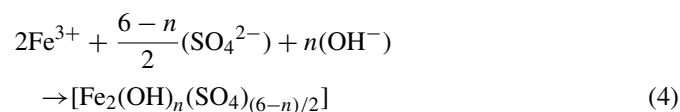
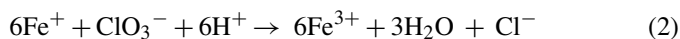
dant [6–8]. To further reduce the cost of PFS production, Fan et al. [9] explored the possibility of using SO₂, a by-product of many industries, as an alternative to sulfuric acid for the production of PFS. Because it integrates water treatment and air pollution control as well as waste material utilization, this new PFS production process has good prospects.

This work focuses on the performance evaluation of PFS synthesized from waste sulfur dioxide, ferrous sulfate and sodium chlorate. The performance assessment was based on the comparison of PFS, FS, FC and alum for the simultaneous removal of turbidity and total organic carbon (TOC) under different plant treatment conditions.

2. Materials and methods

2.1. Coagulants

The PFS used in this research was synthesized by the process of Fan et al. [9,10] from waste SO₂ (fly ash), ferrous sulfate and sodium chlorate. In this method, the fly ash is washed with hot water to remove the major metallic components present (CaO, MgO, K₂O, and Na₂O) with the exception of aluminum and iron. The primary reactions for synthesis are outlined in reactions (1)–(5):



where m is a function of n . The synthesized PFS contains 11.5 wt.% Fe, and its basicity (B value, mass of OH[−]/mass of total Fe) is 8.5 wt.%.

The FS and FC were purchased from Kemiron. The FC used contains 13.8 wt.% iron(III) while the FS used contains 12.78 wt.% iron(III). Both solutions met or exceeded the American Water Works Association (AWWA) standards and were ANSI/NSF Standard 60 certified. The alum used in the study was provided by General Chemical (Syracuse, NY) and contained 7.66 wt.% aluminum.

2.2. Raw water

The raw water used in the study was surface water obtained from a tributary of the Savannah River. The water was not pre-treated in any manner before the initial feed into the pilot plant. Because of the tidal effects experienced in the tributary, typical water quality determinants are not available; however, ranges of the raw water parameters can be found in Table 1.

Table 1
Typical raw water quality

Determinants	Range
TOC (mg/L)	5–8
TSS ^a (mg/L)	1–10
TDS ^b (mg/L)	55–85
Nitrate (mg/L)	0–1
Sulfate (mg/L)	0–15
Iron (mg/L)	1–2
Aluminum residual (mg/L)	0.03–0.05
True color	55–110
Total hardness (mg/L CaCO ₃)	24–30
Specific conductance	85–125
Alkalinity (mg/L CaCO ₃)	19–30
CO ₂ (mg/L)	9–20
Chloride (mg/L)	8–15
Turbidity (NTU)	12–16

^a Total suspended solids.

^b Total dissolved solids.

2.3. Sample collection

Samples were collected from the pilot plant at either 6-h or 12-h intervals. The frequency depended on the length of the experimental run, which was a function of the volume of coagulant available for testing. Analytical samples were collected in sterile 1 L bottles. Samples for TOC analysis were collected separately and stored in dark bottles containing sulfuric acid for preservation until analysis.

2.4. Analysis

All of the water samples in the pilot plant were analyzed for iron, aluminum, sulfate, nitrate, total organic carbon, alkalinity, total suspended solids (TSS), total dissolved solids (TDS), true color, hardness, specific conductance, and chlorides (where appropriate). The analyses were conducted by the laboratory personnel at the City of Savannah Industrial and Domestic (I&D) Water Treatment Plant (Port Wentworth, GA) using EPA approved methods [11].

3. Experimental

Before initial startup of the pilot plant, jar tests were conducted to determine the dosage required to adequately treat the water as it passes through the pilot plant. Due to frequent changes in the water quality, jar tests were also conducted periodically during the experiment. This was required to maintain the proper dosage for adequate treatment and mirrors the process followed for the associated operating plant. The study compared the iron-based coagulants to the traditional coagulant – aluminum sulfate – in an effort to determine differences in final water quality.

3.1. Jar-tests description

Jar tests were conducted using a six paddle jar-test apparatus (Phipps & Bird, Model 7790-400, Richmond, VA) at room temperature (~20 °C). The six beakers were filled with 1 L sam-

ples of the raw water and the appropriate volume of coagulant was added using a pipette. After coagulant addition, the samples were subjected to rapid mixing at approximately 200 rpm ($G=230\text{ s}^{-1}$) for 1 min followed by a three stage slow mix consisting of 5-min intervals at speeds of 60 ($G=56\text{ s}^{-1}$), 40 ($G=32\text{ s}^{-1}$), and 20 ($G=14\text{ s}^{-1}$) rpm, respectively. Slow mixing was followed by a 20 min settling period. After settling, the supernatant was withdrawn from a depth approximately 2 in. below the surface. Turbidity was measured on a HACH Model 2100A turbidimeter (Loveland, CO), and pH values were measured using a pocket calorimeter.

To determine the proper dosage, a two-step method was performed. The initial step involved testing a wide range of doses typically ranging from 20 to 70 mg/L. The dosage used in the second step was a spread of 6–9 mg/L above and below the best jar dosage obtained in the first step.

3.2. Pilot plant description

Pilot plant studies were conducted at a pilot facility owned and operated by the City of Savannah Industrial and Domestic Water Treatment Plant. The pilot plant consists of two identical treatment trains that include a rapid mix basin (76 L), rectangular settling basin (15.141 L) and filter (1135 L). The rapid mix basins consist of three stages each that are approximately $0.2\text{ m} \times 0.2\text{ m}$. The settling basins are approximately 9.1 m (30 ft) long, 1.5 m (5 ft) wide and 1.2 m (4 ft) deep. The first 1.5 m (5 ft) of each settling basin is designed for flocculation. Fig. 1 is a schematic of a single treatment train of the pilot plant used for the study. The rapid mix basins and the settling basins were designed with serpentine flow to minimize short-circuiting.

Each individual treatment train is rated for a maximum influent flow of 68 L/min with a retention time of approximately 4 h through the settling basin at maximum flow. The pilot plant filters are anthracite (0.25 m), sand (0.45 m), and gravel (0.30 m). The filters are rated for a flow of $234.7\text{ m}^3/\text{m}^2\text{ d}$ ($4\text{ gpm}/\text{ft}^2$).

The pilot plant is equipped with online instrumentation that provides real-time measurements. Each treatment train is

equipped with a pH electrode, two particle counters and two laser light turbidimeters. The pH electrode is positioned to analyze the pH after rapid mixing has occurred. The particle counters and light turbidimeters are positioned to analyze the particle counts and turbidity of the settled water and the finished filter water. The raw water line entering the pilot plant is also equipped with a pH electrode and a laser light turbidimeter to determine the raw water quality. The flows into the rapid mix basins and through the filter are measured by online magnetic (MAG) meters.

4. Results and discussion

Each of the iron-based coagulants was compared directly with alum in the pilot plant tests. The pilot plant was continuously operated for periods of 52–96 h for each of the three experimental runs. Due to the tidal influences previously mentioned, the raw water quality fluctuates temporally in an unpredictable manner. Therefore, the coagulant dosages were optimized based on jar tests conducted every 4 h with raw water taken upstream from the pilot plant intake. This is a standard practice for both the pilot plant and the associated production facility. The average coagulant dosage and mixed water pH for each experimental run are outlined in Table 2. Although the water quality changed between experimental runs, some information regarding the dosage required to achieve effective turbidity removal in comparison to alum can be obtained. The alum dosage for the three experimental runs was consistent at an average concentration of about 46 mg/L. FS required the highest average dosage in comparison to alum while FC required the lowest average dosage for effective treatment. The iron-based coagulants resulted in a much lower mixed water pH in comparison to the alum coagulant. The PFS and FS reduced the pH to a low of approximately 4.0.

As shown in Fig. 2, greater reductions in TOC and TSS are observed with PFS than with alum. However, alum produces greater reductions in nitrate, iron, and TDS. The aluminum residual when using PFS increases 137% compared to an increase of only 61% when using alum. A significant aluminum residual is expected in the PFS because the source material contains aluminum. Fan et al. [10] reported an average of 21% aluminum by weight in the source fly ash, and concentrations ranging from 0.008 to 0.93 mol/L in PFS depending on reaction conditions. In addition, water treated with PFS shows a greater increase in specific conductance when compared to water treated with alum. All of the alkalinity was removed from the water when using PFS as the coagulant while 24% of the initial alkalinity

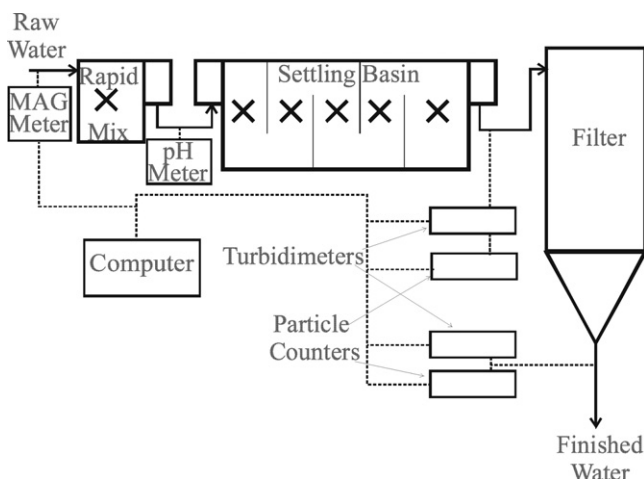


Fig. 1. Schematic of the pilot plant.

Table 2
Coagulant dosage and pH comparisons

	Experimental run conditions					
	PFS		Ferric chloride		Ferric sulfate	
	Alum	PFS	Alum	Ferric chloride	Alum	Ferric sulfate
Dosage (mg/L)	48	65	45	40	46	110
Average pH	5.40	4.00	5.73	4.70	5.70	4.02

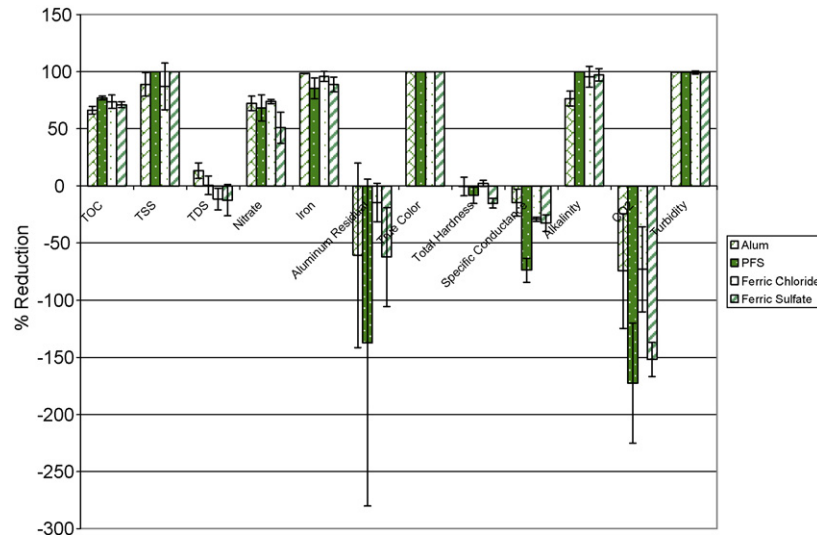


Fig. 2. Comparison of PFS performance relative to alum, ferric chloride and FS.

remains when using alum. The CO₂ increases by 75% when using alum compared to an increase of 173% when using PFS as the coagulant. As shown in Fig. 3, the sulfate concentration increased when using both coagulants; however, no initial concentration of sulfate could be measured and therefore the percentage increase could not be effectively calculated. The sulfate concentrations increased from a value of 0 to average values of 27.9 and 39.7 mg/L for alum and PFS, respectively.

FS also produced a greater reduction in TOC and TSS when compared to alum (Fig. 2). Greater reductions are observed in nitrate and iron when using alum as the coagulant as compared to FS. A slight increase in TDS is observed with both coagulants, although FS causes a much greater increase in sulfate concentration. A slight reduction of the aluminum concentration, nearly 2%, is observed with alum in comparison to an increase of 62% observed when using FS. An increase in specific conductance of nearly 14% is observed when treating with alum as opposed to an increase of nearly 33% observed when using FS as the coagu-

lant. In addition, a small reduction in the chloride concentration was observed for both coagulants.

Fig. 2 illustrates a greater reduction in TOC and nitrate with FC as opposed to alum. However, slightly greater reductions in TSS and iron are observed when using alum as the coagulant. A 5% reduction in TDS is observed when using alum as the coagulant in comparison to an increase of 12% when using FC as the coagulant. The aluminum residual for the two coagulants shows a greater increase at 15% for the FC in comparison to a 10% increase with alum. Nearly 95% of the alkalinity is removed from the water when using FC as opposed to 75% reduction observed when treating with alum. In addition, a reduction in chloride is observed when using alum in comparison to an increase of nearly 210% observed when using FC; this outcome is expected with the use of a chloride-based coagulant. The sulfate concentration (Fig. 3) increased for water treated with both coagulants. Water treated with alum showed the greatest increase, increasing from a value of 1.6 mg/L in the raw water to a value of 27.1 mg/L in

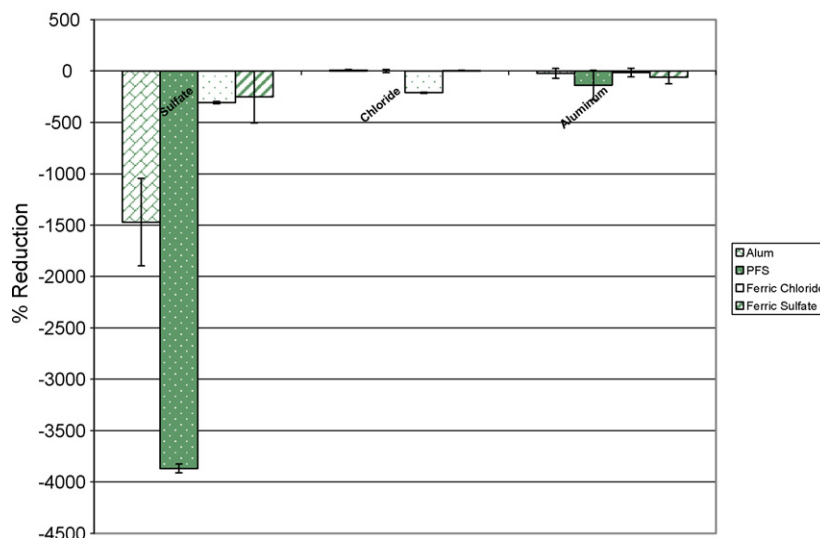


Fig. 3. Comparison of aluminum, sulfate and chloride residuals for all four coagulants.

the filtered water (1593% increase). While water treated with FC showed an increase from 1.6 mg/L to a value of 6.6 mg/L (312% increase), a greater increase in specific conductance is observed in water treated with FC than that observed when using alum as the coagulant.

In comparison, the results acquired when using FS and PFS are similar. Both coagulants cause a greater reduction in TOC and TSS when compared to that achieved in alum. Greater reductions in nitrate and iron are achieved with alum when comparing PFS and FS with alum. The specific conductance and CO₂ showed an increase over that observed with alum in water treated with both PFS and FS; however, the differential was greater with PFS.

Increases in both sulfate and aluminum after treatment were seen with all four coagulants, coupled with the observance of higher specific conductance and lower TOC. This suggests that both sulfate and aluminum are present in the raw water as organically bound species, and therefore undetectable by the methods used. The treatment process results in the reduction of the organic matter and destruction of the complexes. The ligands are then detected as ionic species, resulting in higher sulfate and aluminum concentrations as well as a higher specific conductance. The lower pH required for all of the iron-based coagulants would favor the dissolution of the complexed species. This coupled with the presence of sulfate in the iron-based coagulants results in significantly higher sulfate concentrations in the treated water than that of the raw water.

5. Conclusions

In comparing the three iron-based coagulants with alum, the study indicates that overall better reductions in TOC will be achieved with iron-based coagulants when compared to aluminum sulfate. Also, the specific conductance of water treated with iron-based coagulants is typically greater than water treated with alum. The iron-based coagulants have a higher demand on the alkalinity and therefore reduce the alkalinity in the treated water to much lower values than those experienced when using alum as the coagulant. Accordingly, the CO₂ observed in water treated with iron-based coagulants is higher than that observed in water treated with alum. Second, the ferric-based coagulants caused a much lower mixed water pH in comparison to the alum coagulant.

The use of a polymerized coagulant such as PFS provides an ability to form coagulants with the desired optimum species by control of the metal hydrolysis. The use of the waste SO₂ for the synthesis of the PFS avoids the presence of nitrates and the costs

associated when using hydrogen peroxide with other methods. In addition, it allows for the avoidance of both the economic and environmental costs if the waste was placed in a landfill, as is normal practice.

PFS compares extremely well with results achieved when using FS and FC. As expected, the results show that PFS correlates more closely to FS than FC, but overall PFS possesses the typical qualities of iron-based coagulants.

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References

- [1] C. Volk, K. Bell, E. Ibrahim, D. Verges, G. Amy, M. Lechevallier, Impact of enhanced and optimized coagulation on removal of organic matter and its biodegradable fraction in drinking water, *Water Res.* 34 (2000) 3247–3257.
- [2] J.-Q. Jiang, Development of coagulation theory and new coagulants for water treatment: its past, current and future trend, *Water Sci. Technol.: Water Supply* 1 (2001) 57–64.
- [3] J.Q. Jiang, N.J.D. Graham, Preparation and characterisation of an optimal polyferric sulphate (pfs) as a coagulant for water treatment, *J. Chem. Technol. Biotechnol.* 73 (1998) 351–358.
- [4] Y. Mikami, M. Yanayi, H. Molita, T. Tonaiyama, The manufacturing method of polymeric ferric sulfate liquid, *PPM* 5 (1980) 22–32.
- [5] Y. Mikami, M. Yanayi, The manufacturing method of polymeric ferric sulfate liquid, Japan, Patent No. 842085, 1984.
- [6] M. Fan, S. Sung, R.C. Brown, T.D. Wheelock, F.C. Laabs, Synthesis, characterization and coagulation performance of polymeric ferric sulfate, *J. Environ. Eng.* 128 (2002) 483–490.
- [7] S. Hendrich, M. Fan, S. Sung, R.C. Brown, M.L. Mazur, R. Myers, G.S. Osweiler, Toxic evaluation of polymeric ferric sulphate, *Int. J. Environ. Technol. Manage.* 1 (2001) 464–471.
- [8] M. Fan, R.C. Brown, S.W. Sung, C.P. Huang, S.K. Ong, J.H. van Leeuwen, Comparison of polymeric and conventional coagulants in arsenic(V) removal, *Water Environ. Res.* 75 (2003) 308–312.
- [9] M. Fan, R.C. Brown, S. Sung, Y. Zhuang, A process for synthesizing polymeric ferric sulfate using sulfur dioxide from coal combustion, *Int. J. Environ. Pollut.* 17 (2002) 102–109.
- [10] M.H. Fan, R.C. Brown, T.D. Wheelock, A.T. Cooper, M. Nomura, Y.H. Zhuang, Production of a complex coagulant from fly ash, *Chem. Eng. J.* 106 (2005) 269–277.
- [11] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, M.A.H. Franson (Eds.), *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC, 1998.