Solid/liquid separation behavior of alum and polyaluminium chloride coagulation flocs

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Abstract Properties of alum and polyaluminium chloride (PACl) flocs were analyzed in order to explain solid/liquid separation behavior of these aggregates in dissolved air flotation and gravity settling. PACl flocs settle better and are less sensitive to changes in water temperature than alum flocs. Therefore, PACl flocs may be more suited for gravity separation, especially in cold waters, and alum flocs may be preferred for flotation. At an optimum coagulant dose for dissolved air flotation the logarithmic mean size of alum flocs was close to the size of the air bubbles (30 μm) and the proportion of flocs smaller than 20 μm was about 30.5%.

Keywords Alum; dissolved air flotation; flocs; gravity separation; polyaluminium chloride

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Introduction

Success of water treatment depends strongly on the effectiveness of solid–liquid separation process. In conventional water treatment plant flocs formed in the coagulation process are separated from the liquid in sedimentation and filtration. Removal of flocs can either be downwards due to gravity forces (gravity settling), or upwards by entraining air in the aggregates (flotation). Water sources often contain light or almost neutrally buoyant particles that cannot be efficiently removed by sedimentation. Therefore, in many cases dissolved air flotation (DAF) is replacing sedimentation. DAF process will be used, for example, to treat water from Shoal Lake supplying the city of Winnipeg, Manitoba (Canada) which has high algae content (Winnipeg Water Consortium, 1998).

Successful operation of the DAF process has been extremely challenging during cold water conditions which dominate in most Canadian plants. In the pilot water treatment study conducted by the City of Winnipeg, 40 mg/L of alum was used for warm water (15–22 °C), while for cool water (5–15 °C) an alum dosage of 60 mg/L was required to achieve filtered water turbidity less than 0.1 NTU (Winnipeg Water Consortium, 1998). The significant increase of coagulant dose with the decrease of water temperature calls for study of the factors affecting the optimum dosage of coagulant for DAF process.

Alum ($Al_2(SO_4)_{3*}14\,H_20$) is well known for its poor performance in cold temperatures. High alum dosages, coagulation aids and longer flocculation time have to be applied when the temperature drops to 5 °C. Many plants seek an alternative coagulant that would be less sensitive to cold temperatures than alum. Polyaluminium chloride (PACl) was found to have many advantages over conventional alum in water treatment practice. However, the PACl hydrolysis reaction is quite complex and its action is not fully understood (Pernitsky and Edzwald, 1999).

In this study, alum and PACl flocs were analyzed to identify flocs optimal for flotation and gravity separation. The specific objectives of the study were as follows:

1. Analyze properties of alum and polyaluminium chloride flocs in warm and cold water coagulation.

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2. Compare properties of alum flocs and polyaluminium chloride flocs.
3. Determine the optimum alum dosage and floc size distribution for a bench-scale DAF process operated with Winnipeg tap water.

Optimum floc properties for gravity separation

Gravity separation of individual flocs can be modeled using Stokes' law:

$$v^2 = \frac{4g(\rho_f - \rho_w)}{3\,C_D}\frac{d}{\rho_w} \tag{1}$$

Generally the bigger (d) and denser ($\rho_f - \rho_w$) the floc the higher its settling velocity v. Highly porous flocs experience lower drag force ($C_{D)}$ during settling due to the flow of liquid inside the floc. Lower drag force would also result in a higher settling velocity of the aggregate (Gorczyca and Ganczarczyk, 2001).

Optimum floc properties for DAF

There is universal agreement and experimental evidence that two conditions are necessary for favorable particle flotation: (1) particle charge neutralization; (2) particle hydrophobicity. These conditions can be achieved in the coagulation process.

Different opinions still exist as to the optimum floc size for DAF process and corresponding to it coagulation conditions. For example, some researchers emphasized that long flocculation times were not needed and pin-floc sizes between 10–30 μm were most favorable (Edzwald *et al.*, 1992). In their study, the flocculation time of 5–15 minutes and chemical dosage as low as 10 mg/L were sufficient for successful DAF operation. Han *et al.* (2001) reported that most efficient bubble particle collision was achieved when the flocs' size was close to the bubble size. Han *et al.* (2002) also showed that particles with diameters smaller than 20 μm were not removed easily in the DAF process; the reported removal of these particles was only 10% at the bubble size of 40 μm. Some researchers indicated that larger flocs are preferred in DAF separation process (Fukushi *et al.*, 1995). Large flocs could be removed if sufficient number of bubbles attach to them so that the buoyancy force is greater than the aggregate weight. Large flocs, therefore, require more bubbles and more air to be raised than small flocs. Since pressurizing air requires power, it does not seem economical to produce very large flocs in DAF.

Experimental methods

Raw water quality

Waters from two Canadian lakes: Split Lake and Shoal Lake were coagulated and flocs separated in DAF or gravity settling.

Split Lake water. The Tataskweyak Cree Nations community is located approximately 120 km northeast of Thompson, Manitoba (Canada) on the northwest shore of Split Lake. Tataskweyak community utilizes the Split Lake as its drinking water source. The water treatment plant with a capacity of 14.5 L/s was built in 1987. The existing treatment process consists of alum coagulation with polymer aid, flocculation, sedimentation, rapid sand filtration and disinfection with chlorine. Alum dosages applied vary from 50–100 mg/L and polymer aid (about 2 mg/L) is added continuously to aid cold water coagulation (the cold water season at Split Lake may sometimes last more than six months). There is a need for an alternative coagulant which would eliminate the use of coagulation aids and simplify the work of unskilled operators, typically working at these remote plants. With less coagulation chemicals the cost of transport (often by air only) may be reduced.

Shoal Lake water (water supply for the city of Winnipeg). The city of Winnipeg's drinking water comes from Shoal Lake located on the border of Manitoba and Ontario (Canada). The water is continuously chlorinated at the Shoal Lake headwork before flowing through a closed aqueduct to the four-cell open-air Deacon Reservoir located east of Winnipeg. At Deacon Reservoir the water is re-chlorinated. The water then flows by gravity to the City's three distribution system reservoirs where chlorine is added again. The water in Deacon Reservoir is characterized by low turbidity (0.25–1.9 NTU, with average of 0.80 NTU), and moderate to high total organic carbon (TOC, 4–11 mg/L, with average of 8.9 mg/L) and moderate to high algae levels. Unpleasant taste and odour (T and O) events normally coincide with or follow the elevated algae levels in Deacon Reservoir and/or Shoal Lake (Winnipeg Water Consortium, 2001). The Winnipeg tap water contains significant levels of disinfection by-products (THM, 50–205 μg/L), frequently above the Canadian Drinking Water Quality Guidelines.

A pilot-scale water treatment plant (WTP) was designed to define a state-of-the-art and cost-effective water treatment process for the City of Winnipeg. It was operated continuously from June 1996 through four different Shoal Lake water quality seasons (16 months). Direct filtration and DAF processes were investigated in the pilot studies. The finished water quality goals used in the pilot study are listed below:

Filtered water turbidity $<$ 0.1 N.T.U.

Particles $>$ 2 μm $<$ 20 particles/mL

Total organic carbon (TOC) removal $>$ 40%

Taste and odor control $<$ 10 Threshold odor number

Filter water production rate $>$ 200 m^3/m^2

Direct filtration did not meet all the performance goals, primarily due to the unacceptable filter loading rate, water production volumes and TOC reduction. Also, when plankton counts exceeded 30,000/mL direct filtration could not meet the turbidity, particle and water production targets simultaneously. The DAF process was found to be superior in all the experimental categories investigated. A four-step water treatment process was developed and recommended for Winnipeg: (1) DAF for suspended solids, mainly algae removal; (2) ozonation for primary disinfection and taste and odor control; (3) biological activated carbon (BAC) filters as a second barrier for pathogen and organics removal, and (4) chloramination for disinfection throughout the distribution system (Winnipeg Water Consortium, 2002).

Gravity separation of alum and polyaluminium chloride flocs

Coagulation jar tests were conducted at the Split Lake Plant between July 29 and August 1, 2002. The raw water at that time had a turbidity of 44 NTU, color 70 ACU, alkalinity 89 mg/L $CaCO_3$, pH 7.7 and temperature 19 °C. Alum and polyaluminium chloride (PACl) were used in coagulation of warm water. The optimum dosages were found to be 100 and 80 mg/L respectively.

Cold water coagulation of Split Lake water was conducted at 5 °C in the temperature controlled chamber at the University of Manitoba Environmental Laboratory. The raw water was delivered to the University in September, 2002. The water turbidity was 38 NTU, color 70 TCU and temperature 5 °C. Alum dosage of 100 mg/L and 80 mg/L of PACl were applied. The formed flocs were collected from the bottom of the jars after 30 minutes of settling and embedded in agar according to the procedure described elsewhere (Gorczyca and Ganczarczyk, 2001).

Behavior of alum coagulation flocs in DAF

The bench-scale DAF unit used in the experiments was composed of two parts: pre-treatment unit and DAF clarification unit, as was shown in Figure 1. The operating conditions

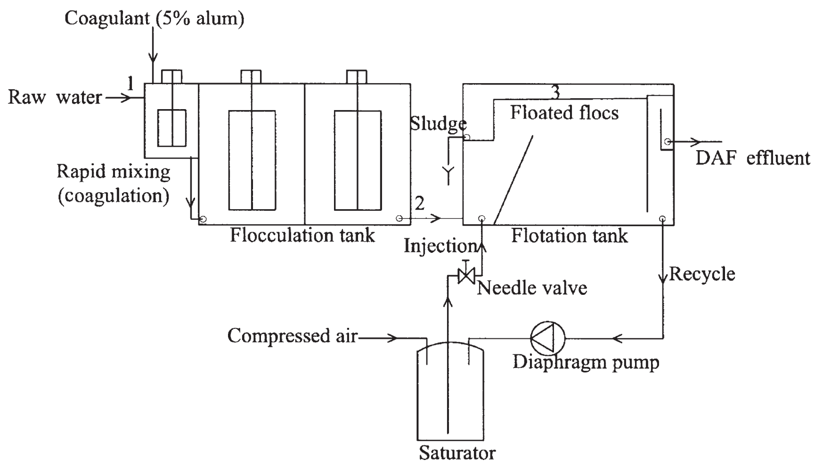

Figure 1 Laboratory DAF unit

for the DAF system are summarized and listed in Table 1. The data for the pilot-scale study by the City of Winnipeg are also listed for comparison. Tap water in The University of Manitoba Environmental Laboratory was used in the experiments. The water had an average turbidity of 0.47 NTU, color of 4.0 TCU, pH of 7 and alkalinity 65 mg/L $CaCO_3$.

Initial coagulant dosage could not be selected in the standard jar test because the formed flocs did not settle well and remained in suspension for sometimes more than one hour. The first coagulant dosage (41.7 mg/L) was selected based on the results of pilot studies conducted with the same water at temperature 15–22 °C. It was realized during the experiments that the water temperature in the coagulation chamber never actually reached warm temperatures and the unit was operating in the cool water conditions (5–15 °C). A total of three alum dosages were tested on the bench-scale DAF system. Each experiment was run for about four hours. The DAF effluent was analyzed for turbidity, color, and pH every 30 min during each test. The samples for floc size analysis were collected only when the steady DAF effluent quality was reached. It was reported earlier that the number and volume of flocs in the coagulation chamber and those entering the DAF tank are almost the same (Edzwald *et al.*, 1992). Hence in this study, the sample

Table 1 Laboratory DAF unit operating conditions

Parameter	Experiment			Pilot study result from Winnipeg
	1	2	3	
Raw water flow rate (L/h)		61.5[1]		~ 20,000[2]
Raw water temperature (°C)		7–11		4–15
Alum dosage (mg/L)	41.7	25.5	15.5	60[3]
Coagulation time (min)		2		In-line mixing
Flocculation time (min)		16		10
Velocity gradient in the flocculation tank G (s^{-1})		40		40–100
DAF hydraulic loading rate (m/h)		2.2		20
DAF saturator pressure (psi)		90		70–80
Air bubble size (μm)		30		32
Recycle ratio (%)		8		10
pH		7.0		6.6

[1]Winnipeg tap water
[2]Water from Deacon Reservoir
[3]Polymer CatFloc2 dose of 3 mg/L was also added

collected at the sample cock installed at the bottom of the second flocculation chamber (location 2 as indicated in Figure 1) was considered representative of the sample entering the DAF process. The diameter of the sample cock was 10 mm (10,000 μm) which is much larger than the size of flocs. Floc samples were embedded in agar.

Particle size measurement

The coagulation flocs ranging from 5–1,000 μm in diameter were observed under the microscope (Leitz Laborlux S) with 4× magnification objective. The projected areas (cross-sectional area) of flocs were measured with an image analysis system. The system was composed of the microscope coupled with a high-resolution video monitor, a high-resolution digital camera (Sony Exwave HAD) and a computer with an image analysis software (*Image Pro Plus version 4.5* Media Cybernetics Inc.). The floc equivalent diameter was calculated as the diameter of a circle having the same projected area as the particle image:

$$\text{Equivalent diameter} = (4 \times \text{projected area}/\pi)^{1/2} \tag{2}$$

The floc size data was further processed using statistical software SPSS. More details about the floc sizing procedure can be found elsewhere (Zhang, 2004).

Results

All floc size distributions were logarithmic; therefore, logarithmic means are discussed in the results. Sizes of alum and PACl flocs formed in coagulation of Split Lake water at two water temperatures are shown in Table 2.

Mean sizes of flocs formed in alum coagulation of Winnipeg tap water and DAF effluent quality are listed in Table 3. Since the highest dosage of 41.7 mg/L resulted in the average floc size larger than 30 μm, which was the size of the air bubbles produced by the saturator, two lower dosages (25.5 and 15.5 mg/L) were tested.

Discussion

Gravity separation of alum and PACl flocs. Settled water turbidity was consistently better for PACl coagulation regardless of the small size of the flocs. This indicates that settling properties of PACl flocs are superior to alum flocs, which may be due to higher density of the PACl flocs (Equation 1). From a variety of hydrolyzed aluminium (III) species polymeric $Al_{13}(OH)_{32}^{7+}$ is reported to have the strongest coagulation properties and significantly higher molecular weight than monomer aluminium hydroxides. Solubility diagrams for alum show that at pH 6.2 almost no polymer species are found when alum is dissolved in water. Polyaluminium chloride coagulants, on the other hand, may contain up to 90% of the polymeric aluminium (Parthasarthy and Buffle, 1985). This may explain the possible high density of PACl flocs and their superior settling properties.

Table 2 Sizes of alum and PACl flocs – coagulation conducted on Split Lake water

Coagulant	Temperature 19 °C		Temperature 5 °C	
	Turbidity [NTU]	Mean floc size [μm]	Turbidity [NTU]	Mean floc size [μm]
PACl[1] 80 (4.32 as Al)	1.2	78	1.3	82
Alum 100 (9.09 as Al)	1.5	104	1.8	83

[1]SternPAC (Eaglebrook Inc.)

Table 3 Sizes of alum flocs and DAF effluent quality – coagulation conducted on Winnipeg tap water (Shoal Lake)

Alum dosage [mg/L]	DAF effluent turbidity (average) [NTU]	DAF effluent color [TCU]	Mean particle size in flocculated water [μm]	Particles smaller than 20 μm in flocculated water [%]
41.7	0.25	3.8	45	14.2
25.5	0.25	3.8	27	30.5
15.5	0.52	4.0	21	40.5
Raw	0.47	4.0	9	94

DAF separation of alum flocs. The successful flotation at the alum dosage of 25.5 mg/L could be attributed to the log mean size of the floc particles of 27 μm, which was close to the bubble size (30 μm). Further increase of the alum dose showed limited benefit for the DAF effluent quality. At the higher alum dosage, i.e. 41.7 mg/L, the mean size of the coagulation flocs was 45 μm, which is significantly larger than the bubble size. Therefore, the logarithmic mean size of flocs is the most important parameter for flotation. This is in agreement with the theory developed earlier (Han *et al*., 2000; Han *et al*., 2002).

Many factors influence the scale-up of the DAF process; however, it is quite surprising that optimum dose in our study (25.5 mg/L) was 57% lower than the optimum alum dose in the pilot study conducted with the same water (Table 1). The flocs in the pilot study were not analyzed; however, our study showed that higher alum dose forms larger flocs. It is reasonable to expect that at the dose of 60 mg/L flocs larger than those formed at 25.5 mg/L (Table 2) would be formed. Comparison of velocity gradients applied in the two studies may provide some explanation to this observation. Velocity gradients for the coagulation and flocculation in this study were equal to $240\,s^{-1}$ and $40\,s^{-1}$ respectively. The velocity gradients for coagulation and flocculation in the pilot study were higher and equal to $400\,s^{-1}$ and $60–80\,s^{-1}$ respectively (Table 1). In the pilot study, therefore, although the high alum dose produced large flocs their size was kept small by applying high velocity gradients. This condition not only causes unnecessary higher chemical dosing but also increases power demand. In our study we were able to achieve good effluent turbidity with a much lower dosage of alum (25.5 mg/L) and lower flocculation intensity.

It should be emphasized that there are many other factors not discussed in this paper that could influence the scale-up of the DAF process.

Conclusions

First, we concluded that PACl always settled better than alum flocs. Abundance of polymer alum hydroxides may be responsible for higher density and better settling properties of PACl floc compared to alum flocs. PACl flocs may be more suited for gravity separation and alum flocs may have properties more favorable for flotation.

Secondly, at the optimum dosage of 25.5 mg/L of alum in the bench-scale DAF test, the logarithmic mean diameter of coagulation flocs was equal to 27 μm and was close to the bubble size. Floc size distribution control in the DAF process may allow for significant reduction in coagulant dose.

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