Desalination and Water Treatment
www.deswater.com

10 (2009) 95–100

Utilization of floc characteristics for the evaluation of seawater coagulation process

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Received 2 October 2008; Accepted in revised form 17 August 2009

ABSTRACT

The principal aim of this study is to analyze a seawater coagulation process by means of the evaluation of flocculation index and fractal dimension of flocs. Floc size was evaluated by flocculation index (FI) and floc shape by fractal dimension. Two coagulation parameters of the coagulant type and the mixing condition were selected to evaluate a seawater coagulation process. The study results indicate that the coagulant type was important for seawater coagulation. The coagulant type affected the kinetics of floc formation, floc size and floc shape. Floc formed fast at use of ferric chloride, while it formed slowly at use of aluminum salts. Ferric chloride and titanium chloride produced bigger flocs than aluminum salts. Flocs formed by use of ferric chloride and titanium chloride were more spherical than Al floc. Fe floc was more insensitive to a change in the coagulant dose and the seawater pH than Al floc. Slow mixing was more important for seawater coagulation than rapid mixing. Tapered flocculation produced bigger flocs than constant flocculation. Increase in slow mixing speed from 20 rpm to 40 rpm resulted in formation of bigger flocs, which was reflected by lower settled turbidity value. On the base of the study results, it can be stated that the evaluation of floc characteristics could be a useful tool in order to optimize the seawater coagulation process.

Keywords: Seawater; Coagulation; Floc; Flocculation index; Fractal dimension

1. Introduction

Coagulation is important for seawater desalination using reverse osmosis (RO) membranes. Since RO membranes are susceptible for fouling caused by particles, a particle separation process is usually employed as pretreatment for protection especially when surface seawater is taken [1,2]. Media filtration is most frequently employed as pretreatment in seawater desalination using RO membrane mainly because of cost effectiveness and simple technology. The media life is long and the media is inexpensive. In addition, there is no fouling problem in media filtration and it has been used for long in drinking water treatment. Subsequently, dual media filtration (DMF) with sand and anthracite is commonly used for media filtration in seawater desalination. DMF provides high suspended solids removal efficiency for a substantial period of time [3].

Media filtration is generally supplemented by coagulation to improve the filtration performance. The important parameters of coagulation are the coagulant type and coagulation conditions. In seawater coagulation, coagulants are generally added just before filtration without sedimentation (direct filtration) or without flocculation and sedimentation (in-line filtration). Ferric salt

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Presented at EuroMed 2008, Desalination for Clean Water and Energy Cooperation among Mediterranean Countries of Europe and the MENA Region, 9–13 November 2008, King Hussein Bin Talal Convention Center, Dead Sea, Jordan.

such as ferric chloride is commonly selected as a coagulant in seawater desalination, while aluminum salt such as aluminum sulfate is the popular choice in drinking water treatment. Ferric salt is favored over aluminum salt mainly due to its low solubility [4]. Solubility of coagulant is important in seawater desalination because it is related to fouling of RO membranes. Soluble metal ions leaving media filtration process can penetrate into RO membranes and then form precipitates inside the membrane, which leads to fouling of RO membranes. Since ferric salt forms more insoluble precipitates than aluminum salt, it is commonly used in seawater desalination.

Rapid and slow mixing conditions such as mixing intensity and time are important for coagulation. An aim of rapid mixing is to help uniform dispersion of coagulants in aqueous solution, while that of slow mixing is to grow a floc in its size. Therefore, intensive mixing is required to bring coagulants in contact with colloidal particles in rapid mixing. Coagulation is a very rapid process requiring just a few seconds to complete [4]. A pin-point floc is produced after rapid mixing. It then grows in size while slow mixing is provided.

Since floc is the result of coagulation and flocculation, which is the combined process, it is logically to evaluate these processes by floc characteristics. However, there is no study available to evaluate seawater coagulation using floc characteristics. There are two important floc characteristics; floc size and shape. Floc size is closely related to the settling velocity of a floc, according to the Stoke's law [5]. If other conditions are identical, a larger floc settles faster. Floc shape is also related to the settling velocity. If other conditions are identical, a floc with a spherical shape settles faster [5]. Floc size is usually represented by flocculation index (FI) [6]. The higher the FI is, the bigger the floc is. The fractal dimension, which is a floc property representing floc shape, indicates a degree of occupation of the embedding space by particles composing aggregates [7]. If a floc is a perfect sphere, it has the fractal dimension value of three. As the floc shape deviates from a sphere, the fractal dimension value decreases. Subsequently, fractal dimension is related to the settling velocity of a floc. A floc with higher fractal dimension value settles faster than that with lower fractal dimension value.

A seawater coagulation process was evaluated utilizing floc characteristics of size and shape in this study. Floc size and shape were selected for floc characteristics. Two parameters of the coagulant type and the mixing condition were selected because they can affect a coagulation process. The effectiveness of each coagulant and the mixing condition was evaluated using floc characteristics.

2. Materials and methods

Seawater was taken from Masan Bay in Korea. Masan Bay is a closed bay and notorious for seasonal red-tide bloom. Its water quality parameters in 2008 are summarized in Table 1. In terms of chemical oxygen demand (COD) and UV254 values, the organic concentration of this seawater is relatively higher than those of other seawaters. According to Xu et al. [1], the COD concentration of China seawater was 1.15–1.76 mg/L. The conductivity of China seawater was 39.0–47.7 mS/cm and pH was 7.82–8.05. The UV254 values of Oman Bay and Persian Bay seawaters were 0.6–1.46 1/m and 0.9–2.2 1/m, respectively [8]. This seawater also contained many particles with high turbidity value. The number of particles greater than 2 μm was about 5,000 particles per mL and turbidity was slight less than 2 NTU. On the other hand, there were 1,633–3,296 particles per mL in the Oman bay seawater, while its turbidity was 0.12–0.56 NTU [8]. During the study period, there was no red-tide bloom. The chlorophyll-a concentration remained relatively low. All tests were conducted in accordance with Standard Methods [9].

A change in floc size after coagulant addition was monitored by the photometric dispersion analyzer (PDA). Narrow light beam illuminates flowing suspension of particles in PDA. Then, random variation of number and size of particles in light beam causes the fluctuation in the transmitted light intensity. The transmitted light intensity consists of large component (DC) and small fluctuating

Table 1
Water qualities of Masan Bay seawater in 2008

Parameters	Winter	Spring	Summer
pH	7.7–8.4 (8.0)	7.5–8.4 (7.8)	7.6–8.0 (7.8)
Conductivity, mS/cm	—	43.6~51.8 (49.7)	41.6~49.3 (45.8)
Turbidity, NTU	0.7–2.3 (1.3)	1.0–2.9 (1.7)	0.9–7.7(2.6)
Particles number > 2 μm, 1000/mL	1.6–7.9 (3.9)	5.0–8.1 (5.5)	2.4–8.7 (5.7)
Suspended solids, mg/L	—	4–30 (12)	—
COD, mg/L	—	3.2–13.6 (6.1)	1.6–9.2 (4.5)
UV254, 1/m	5.5–9.5 (6.6)	1.0–6.7 (3.0)	1.0–6.4 (2.0)
Chlorophyll-a, μg/L	0.9–5.5 (2.9)	1.0–11.1 (4.2)	0.9–16.3 (5.3)

component (AC). The root mean square value of AC divided by DC is termed as FI. FI value increases with aggregation. Detailed information about FI and PDA can be found elsewhere [6]. Fractal dimension is measured by the small angle laser light scattering (SALLS) technique using the Malvern Mastersizer/E. According to this method, fractal dimension of a floc is closely related to the scatter light intensity, $I(Q)$, and light wave function, Q. Fractal dimension is calculated from a log-log plat of $I(Q)$ and Q. Detailed information about the SALLS technique can be found elsewhere [10].

Four coagulants were used in this study. They are ferric chloride, alum, PACl (poly aluminum chloride) and titanium chloride. The dose was varied in the range of 10–80 mg/L. After coagulants were added to seawater, floc characteristics were monitored and measured using PDA and the Malvern Mastersizer/E while rapid and slow mixing were provided. Two mixing speeds (100 and 300 rpm) were evaluated for rapid mixing. The mixing time was adjusted so that both rapid mixing conditions have the similar $G{\cdot}t$ values. The mixing time of 20 s was provided at 300 rpm, while 60 s at 100 rpm. Two kinds of flocculation were provided; constant flocculation and tapered flocculation. Mixing intensity remained constant at constant flocculation, while it varied at tapered flocculation. Two different mixing speeds (20 and 40 rpm) were evaluated during constant flocculation. During tapered flocculation, mixing speed was gradually reduced from 60 rpm for 7.5 min to 40 rpm for 7.5 min to 20 rpm for 5 min. The same mixing time of 20 min was provided at both conditions. Samples were taken after rapid mixing and slow mixing for measurement of FI and fractal dimension values.

3. Results and discussion

3.1. Comparison of different coagulants

Floc characteristics obtained by using four different coagulants are summarized in Table 2. According to

Table 2
Comparison of floc characteristics by different coagulants

Coagulant	Time to complete the floc formation, min	FIocculation index*	Fractal dimension
$FeCl_3$	5	0.15	2.59
$TiCl_4$	10	0.70	2.58
Alum	15	0.09	2.40
PACl	15	0.07	2.39

*Maximum FI values are shown

Table 2, the coagulant type affected the kinetics of floc formation. The kinetics was also affected by the coagulant dose. A floc formed faster as the dose increased. After coagulant was added, the FI value increased with time until it reached a plateau and then, it decreased (Figs. 1, 2). This result indicates that a floc grew with time until it reached the maximum size. After the plateau, the FI value decreased because big flocs settled, leaving small flocs in the solution. The time to complete the floc formation in Table 2 means the time required for the FI value to reach the plateau. When 10 mg/L of $FeCl_3$ was added, approximately 10 min was required to complete the floc formation. As the dose was increased, the time of floc formation was reduced. It was 5 min at 20 mg/L of $FeCl_3$. This result means that increasing ferric chloride dose expedited the floc formation. Similar results were obtained with other coagulants, but the kinetics was slower. The complete floc formation required about 15 min at the addition of 20 mg/L of alum, and 20 min at other doses. The kinetics was a little faster with titanium chloride, which required about 10 min. Unlike ferric chloride and aluminum salts, the kinetics of floc formation was unaffected by titanium dose. This result indicates that the coagulant type was important for seawater coagulation and that ferric chloride caused the fastest floc formation.

The coagulant type also affected floc size. According to Table 2, the largest FI value (0.70) was obtained when

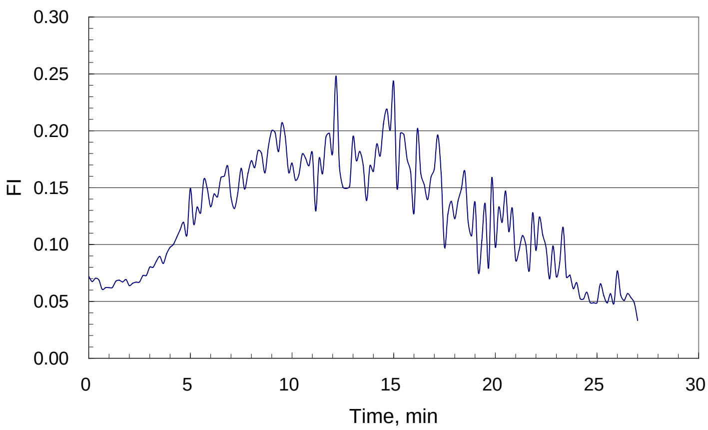

Fig. 1. FI monitoring results during tapered flocculation (rapid mixing at 100 rpm).

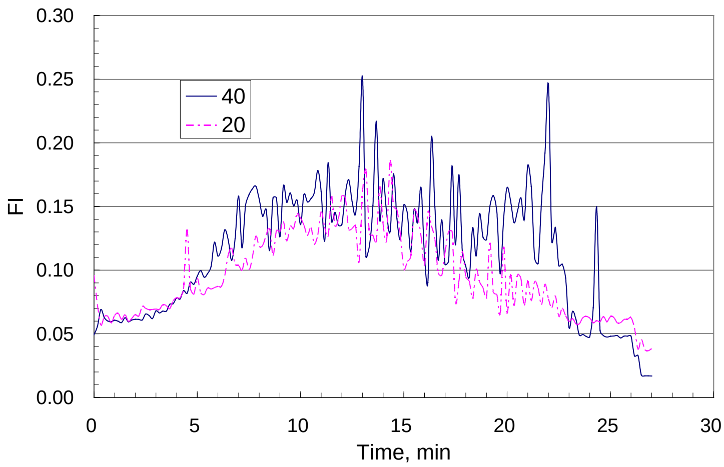

Fig. 2. FI monitoring results during constant flocculation (rapid mixing at 100 rpm).

titanium chloride was added to raw seawater. The FI value was 0.15 for the floc obtained by $FeCl_3$ (Fe floc), but less than 0.10 for the floc by aluminum salts of alum and PACl (Al floc). This result means that the biggest floc was produced by titanium chloride, and that ferric chloride produced bigger floc than aluminum salts. Subsequently, it is suggested that Ti floc and Fe floc could settle faster than Al floc.

The coagulant dose and the seawater pH influenced the FI values and subsequently, floc size. When alum was added to seawater, the largest flocs were produced at 20 mg/L (pH 7.62) and at 30 mg/L (pH 7.48). Flocs became smaller at other doses. Ferric chloride was less sensitive to a change in the coagulant dose and the seawater pH. Similar FI values obtained when ferric chloride was added at 10–80 mg/L and the seawater pH was decreased from around 8.00 to 5.82. Titanium chloride showed different behavior. The FI value kept increasing with the dose when titanium chloride was added to seawater. The largest FI value was obtained at 80 mg/L (pH 5.91).

The coagulant type also affected floc shape. According to Table 2, Fe floc (2.59) and Ti floc (2.58) had higher fractal dimension values than Al flocs (2.40, 2.39). This result means that Fe and Ti flocs were more regular-shaped than Al flocs. In other words, Fe and Ti flocs were more spherical than Al flocs, which means that Fe floc and Ti floc could settle faster than Al floc. Use of ferric chloride and titanium chloride produced flocs, which were easy to settle, in terms of floc characteristics, while use of aluminum salts did not.

3.2. Comparison of different flocculation conditions

The comparison results of two rapid mixing conditions (100 rpm and 300 rpm) are summarized in Table 3. According to Table 3, floc characteristics and settled water qualities were not affected by a change in rapid mixing condition. This result suggests that effects of rapid mixing condition were insignificant in seawater coagulation.

The comparison results of four different slow mixing conditions are summarized in Table 4. According to Table 4, slow mixing condition affected the floc characteristics. When slow mixing was provided at low speed (20 rpm), floc formed was small (FI of 0.10–0.15). As the mixing speed was increased to 40 rpm, the FI value increased to 0.15–0.20, indicating formation of bigger flocs. Subsequently, lower settled turbidities were obtained at high speed (1.0, 0.9 NTU) than at low speed (1.3 NTU). The filtrate particle numbers were also lower at high speed than at low speed. However, effects of slow mixing were not reflected in settled particle number and filtrate turbidity. The particle numbers of settled seawater were similar. The filtrate turbidity remained same (0.2 NTU) under all conditions of slow mixing. There was no definite

Table 3
Effects of rapid mixing

Conditions*	Flocculation index	Fractal dimension	Turbidity**, NTU	Particle number > 2 μm**, 1000/mL
100 rpm	0.20–0.25	2.60	0.9	1.7
300 rpm	0.20–0.25	2.52	0.8	1.7

*Mixing speed of rapid mixing
**Settled seawater qualities

Table 4
Effects of slow mixing

Conditions*	Flocculation index	Fractal dimension	Residual turbidity**, NTU	Particle number > 2 μm**, 1000/mL
100–40	0.15–0.20	2.65	1.0 (0.2)	2.7 (0.5)
100–20	0.10–0.15	2.54	1.3 (0.2)	2.8 (0.6)
300–40	0.15–0.20	2.50	0.9 (0.2)	2.8 (0.3)
300–20	0.10–0.15	2.54	1.3 (0.2)	2.8 (0.4)

* 100–40 means 100 rpm of rapid mixing followed by 40 rpm of slow mixing;
100–20 means 100 rpm of rapid mixing followed by 20 rpm of slow mixing;
300–40 means 300 rpm of rapid mixing followed by 40 rpm of slow mixing;
300–20 means 300 rpm of rapid mixing followed by 20 rpm of slow mixing
** Values in parentheses indicate filtered water qualities with 0.45 mm filter paper, while other values indicate settled seawater qualities

pattern found in fractal dimension values, which suggests that floc shape might be unaffected by mixing speed.

Tapered flocculation was compared to constant flocculation while rapid mixing was provided at 100 rpm. The results are summarized in Figs. 1 and 2. According to these figures, the FI value was higher at tapered flocculation than at constant flocculation, and higher FI value was obtained at 40 rpm than at 20 rpm during constant flocculation. This result suggests that tapered flocculation was more advantageous than constant flocculation for formation of big floc. It is advisable not to provide too low speed in slow mixing of seawater coagulation because floc size could become small. Mixing speed is related to velocity gradient; larger velocity gradient at higher mixing speed. Velocity gradient is important for orthokinetic flocculation. As velocity gradient increases, the rate constant of orthokinetic flocculation becomes larger, resulting in faster flocculation [5]. There is also possibility of floc break-up at large velocity gradient, suggesting an optimum mixing speed. In coagulation of seawater used in this study, mixing speed of 40 rpm corresponded to the optimum condition.

4. Conclusion

In this study, floc characteristics of size and shape were utilized in the evaluation of a seawater coagulation process. For this purpose, flocculation index was used to represent floc size and fractal dimension was used to represent floc shape. Two parameters of the coagulant type and the mixing condition were selected in order to evaluate a seawater coagulation process.

The study results indicate that the coagulant type was important for a seawater coagulation process. Firstly, the coagulant type affected the kinetics of floc formation. The fastest floc formation was obtained with ferric chloride, while the slowest formation with aluminum salts. Secondly, the coagulant type affected floc size. Ferric chloride and titanium chloride produced bigger flocs than aluminum salts. Thirdly, the coagulant type affected floc shape. Flocs formed from use of ferric chloride (Fe floc) and titanium chloride (Ti floc) were more spherical than Al floc. Subsequently, Fe and Ti flocs could settle faster than Al flocs. Unlike Al floc, Fe floc was insensitive to a change in the coagulant dose and the seawater pH. These results suggest that ferric chloride is preferred over aluminum salts in terms of floc characteristics in a seawater coagulation process. Slow mixing was more important for a seawater coagulation process than rapid mixing. Tapered flocculation produced bigger flocs than constant flocculation. At constant flocculation, slow mixing at 40 rpm produced bigger flocs than that at 20 rpm, with lower settled turbidity values. On the base of the obtained results, it can be stated that the evaluation of floc characteristics could be a useful tool in order to optimize a seawater coagulation process.

Acknowledgements

This research was supported by a grant (07seaheroB01-02-03) from Plant Technology Advancement Program funded by Ministry of Construction and Transportation of Korean government.

References

[1] J. Xu, G.L. Ruan, X.Z. Chu, Y. Yao, B.W. Su and C.J. Gao, A pilot study of UF pretreatment without any chemicals for SWRO desalination in China. Desalination, 207 (2007) 216–226.

[2] M. Pontié, S. Rapenne, A. Thekkedath, J. Duchesne, V. Jacquemet, J. Leparc and H. Suty, Tools for membrane autopsies and antifouling strategies in seawater feeds: a review. Desalination, 181 (2005) 75–90.

[3] J.Y. Shin and C.R. O'Melia, Pretreatment chemistry for dual media filtration: Model simulations and experiment studies. Wat. Sci. Technol., 53(7) (2006) 167–175.

[4] M. Wilf, The Guidebook to Membrane Desalination Technology. Balaban Desalination Publications, L'Aquila, Italy, 2007.

[5] AWWA, Water Quality and Treatment, 5th ed., R.D. Letterman, ed., McGraw-Hill, US, 1999.

[6] J. Gregory and D.W. Nelson, A new optical method for flocculation monitoring. Solid–Liquid Separation. J. Gregory, ed., Ellis Horwood, Chichester, UK, 1984.

[7] B.B. Mandelbrot, The Fractal Geometry. Wiley, New York, 1983.

[8] V. Bonneyle, M.A. Sanz, J. Durand, L. Plasse, F. Gueguen and P. Mazounie, Reverse osmosis on open intake seawater: pretreatment strategy. Desalination, 167 (2004) 191–200.

[9] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 19th ed., A.D. Eaton, L.S. Clesceri and A.E. Greenberg, eds., Washington, 1995.

[10] J.W. Guan, T.D. Waites and R. Amal, Rapid determination of fractal dimension of bacterial assemblages in wastewater-implications to process optimization. Wat. Sci. Technol., 38(2) (1988) 9–15.