Korean J. Chem. Eng., **22**(5), 682-686 (2005)

Removal of Freshwater Diatoms (*Synedra acus* and *Stephanodiscus* sp.) by Preozonation and Addition of Polyamine Coagulant-aid

Ju Dong Lee, Man Sig Lee*, Won Sik Shin*, Young-Hun Kim and Sang June Choi*,†**

Department of Chemical & Biological Engineering,
The University of British Columbia, 2216 Main Mall, Vancouver, BC, Canada V6T 1Z4
*Department of Environmental Engineering, Kyungpook National University,
1370 Sankyuk-dong, Buk-gu, Daegu 702-701, Korea
**Department of Environmental Engineering, Andong National University,
383 Seongcheon-dong, Andong City, Gyeongbuk 760-749, Korea
(*Received 20 April 2005 • accepted 10 June 2005*)

Abstract−Pilot studies were conducted for the removal of two freshwater diatoms (*Synedra acus* and *Stephanodiscus* sp.). Poly aluminum chloride (PAC), one of the coagulants commonly used in conventional potable water treatment, was found to be not effective in removing diatoms, especially for *Synedra*. In this work, preozonation and polyamine coagulant-aid in the presence of PAC were compared with each other and combined to investigate their performances on removing diatoms. It was found that the preozonation and polyamine coagulant-aid increased the removal rate significantly for both diatoms, better performance than PAC alone. When polyamine coagulant-aid and preozonation were combined with PAC, approximately 90% of *Synedra* and 100% of *Stephanodiscus* were eliminated. It can be concluded that the combination of preozonation and polyamine coagulant-aid in the presence of PAC could be a promising solution for removing resistant diatoms in water treatment.

Key words: Algae Removal, *Synedra acus*, *Stephanodiscus* sp., Preozonation, Polyamine, Freshwater Diatoms

INTRODUCTION

One of the most serious problems we are facing in this world is a shortage of water supply. The amount of usable clean water has become insufficient due to water pollution and natural eutrophic processes [Choe and Jung, 2002]. It is well known that algal blooming produces bad tastes and odors. It is also reported that algae-containing water causes high organic contents in raw water and thus seriously hinders the recreational use of water [Petrusevski et al., 1993; Vlaski et al., 1996; Choe and Jung, 2002]. Particularly in the spring, diatoms such as *Synedra acus* and *Stephanodiscus* sp. bloom in most rivers in Korea. Raw water has to pass through a preliminary treatment process where these specific diatoms are trapped in the interstices of the filter bed, which causes a gradual or rapid pressure drop. Although an effective coagulation and sedimentation process can remove up to 90-95% of the incoming diatoms, the remaining ones may be sufficient to significantly shorten filter life [Montgomery, 1985]. Water treatment plants in Korea such as Cheong-Ju, Mae-Gok and Sa-Chun could not remove most of the diatoms efficiently so the filter run times were rapidly decreased by the influx of diatoms [Jun et al., 1998]. Recently, the removal strategy of algae has been under intensive investigation.

In this pilot test, water samples from Nakdong River, which is a major source of potable water in Korea and covers an area of approximately 23,000 km^2, were used. *Synedra. acus* and *Stephanodiscus* sp. were the most abundant algal species during the test period. The effects of preozonation and a cationic polymer coagulant-aid in the presence of poly aluminum chloride (PAC) were investigated for the removal of *Synedra acus*, *Stephanodiscus* sp. and turbidity.

In conventional potable water treatment plants, the PAC has been extensively used, which can lead to high residual aluminum ions in water. In such a case, high concentrations of aluminum may cause neurological diseases such as Alzheimer's disease or presenile dementia [Crapper et al., 1973]. The residual aluminum ion has been regulated to below 0.2 mg/L because of that [Nilsson, 1992; Hlavacek and Remy, 1995]. For reducing the required PAC dose, the addition of preozonation or polyamine coagulant-aid in the presence of PAC was also evaluated.

MATERIALS AND METHODS

1. Pilot Plant

A scheme of the pilot plant is presented in Fig. 1. The pilot plant (50 m^3/day) was designed for two parallel experiments. The raw water

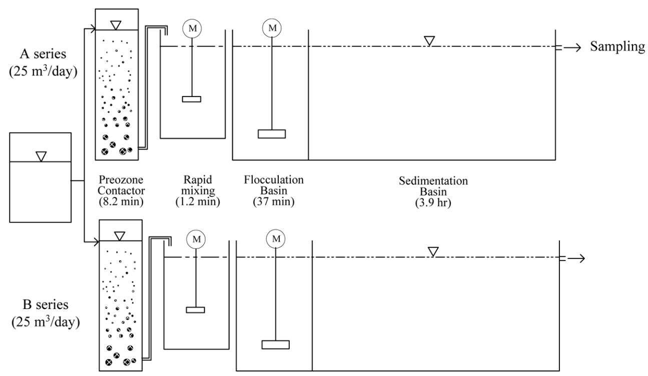


Fig. 1. Schematic diagram of the pilot plant.

†To whom correspondence should be addressed.
E-mail: sjchoi@mail.knu.ac.kr

Table 1. Average raw water quality of the Nakdong River during test period

	Minimum	Maximum
pH	8.3	8.8
Turbidity (NTU)	4.95	5.04
Synedra acus (cells/mL)	270	308
Stephanodiscus sp. (cells/mL)	17,510	18,050

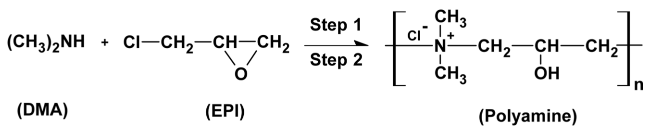


Fig. 2. Synthesis of polyamine coagulant aid by polycondensation of dimethylamine and epichlorohydrin.

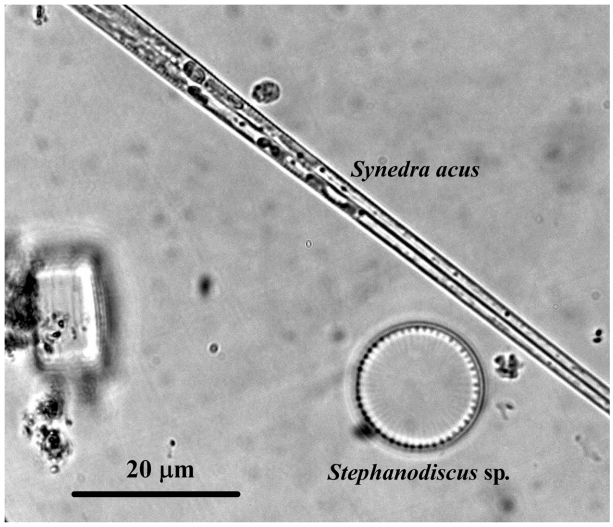


Fig. 3. The picture of *Synedra acus* and *Stephanodiscus* sp. from the Nakdong River. Notes: *Synedra acus* were 150-200 mm in length and *Stephanodiscus* sp. were 8-18 μm in diameter.

for both experiments (25 m^3/day) was collected from the Nakdong River. The average raw water quality is shown in Table 1. Each preozonation column was 4.5 m in height and 0.25 m in inside diameter. Ozonated air was introduced at the bottom of the column through a porous glass diffuser and ozone contact time was 8.2 minutes. A rapid mixing chamber (0.25×0.25×0.8 m), two flocculation basins (0.6×0.6×1.2 m), a sedimentation basin (1.2×3.8×1.9 m) and sample port were placed in series. The basic coagulant was PAC, which has the chemical structure $[Al_2(OH)_nCl_{6-n}]_m$ containing average of 17% aluminum by weight. A dose of 13 mg/L of PAC was determined for the maximum turbidity removal in the jar test of dose versus turbidity removal (data not shown). The optimal dose of PAC (13 mg/L) and 70% of the optimal dose (9.1 mg/L) were applied for pilot plant test.

The polyamine coagulant-aid was a cationic polymer, which was synthesized by the polycondensation of dimethylamine and epichlorohydrin as shown in Fig. 2 [Lee et al., 1998]. The intrinsic viscosity $[\eta]$ of the polyamine coagulant-aid was 0.065 dL/g, which is equal to molecular weight of about 13,000 g/mol. This coagulant (PAC) and coagulant-aid (polyamine) were mixed with water after preozonation and the process was allowed to attain a steady state before water samples were collected for analysis.

2. Counting Cells

There are a few methods to measure the amount of algae. Several studies employed photosynthetic pigments to estimate algal biomass, using optical methods such as spectrophotometric and fluorometric techniques. However, these optical methods can significantly under- or overestimate chlorophyll concentrations, in part because of the overlap of the absorption and fluorescence bands of co-occurring accessory pigments and chlorophyll degradation products [Gieskes and Kraay, 1984; Berman et al., 1984; Hallegraeff and Jeffrey, 1985]. Moreover, it is not possible to count separately for each algal species. To overcome these limitations, a direct method with a microscope for algal identification and enumeration was used in this study.

Microscopic analysis was conducted for algal enumeration. The sample (1 L) was fixed with 1% formalin and transfused in a mess-cylinder for concentration. After precipitating for 24 hours, the upper part of water (900 mL) was removed by siphon and the remaining volume from the lower part of the cylinder was re-mixed for cell counting. 1 mL of the concentrated sample was transferred to Sedgwick-Rafter cell and *Synedra acus* and *Stephanodiscus* sp. were counted by microscope (Olympus, BH2) after 15 minutes [APHA, 1995]. More than three measurements were conducted and their average values were reported. The error bar in the results stands for twice the standard deviations. In order to calculate real number of algae species in the original sample, the following equation was used.

$$N = \frac{Nc \cdot 1{,}000\ mm^3}{A \cdot D \cdot F} \cdot C_1 \cdot C_2$$

where N is the number of algae species in original sample (cells/mL), Nc is the number of algae species counted, A is the area of field (mm^2), D is the depth of a field (mm), F is the number of fields counted, C_1 is a concentration factor and C_2 is dilution factor.

Fig. 3 shows the picture of *Synedra acus* and *Stephanodiscus* sp. photographed by a digital camera (Fujifilm, Finepix 1700Z).

RESULTS AND DISCUSSION

1. Effect of Preozonation

The effects of preozonation on the removal efficiency of algae and turbidity were investigated. Fig. 4 shows experimental results of the pilot test. Using PAC alone, the removal efficiency was 36.5% for *Synedra acus* and 88.9% for *Stephanodiscus* sp. *Synedra acus* was not sufficiently removed by a conventional water treatment process. When preozonation was performed with optimal coagulant dose (13 mg/L of PAC), the removal efficiencies were highly improved and the efficiencies were increased as the concentration of ozone increased. The maximum removal was 91.1% for *Synedra acus*, 99.0% for *Stephanodiscus* sp., and 86.5% for turbidity removal, respectively. However, the turbidity removal was better at the 1.0 mg/L of ozone than at 2.0 mg/L. This is probably due to excessive oxidation by ozone. Oxidation might induce damage on algae cellular surface and lead to a release of cell contents [Sukenik et al., 1987; Edzwald and Reckhow, 1992]. These materials (cell contents) seem to cause the effect of turbidity increase.

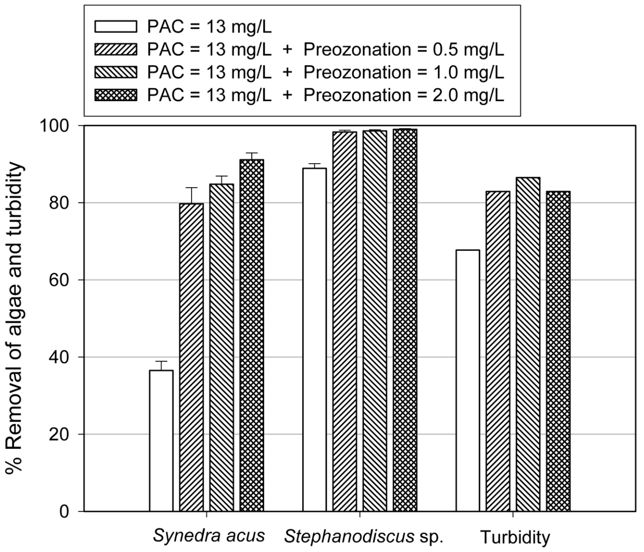


Fig. 4. Effects of preozonation on algal and turbidity removal at optimal PAC dose.

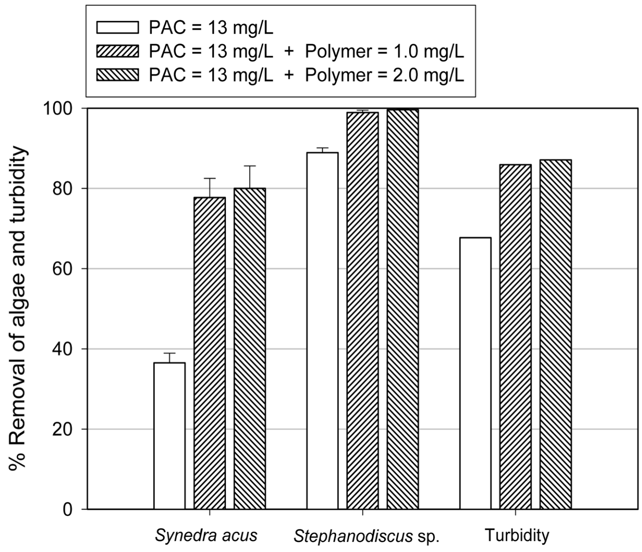


Fig. 6. Effects of polyamine coagulant-aid on algae and turbidity removal at optimal PAC dose.

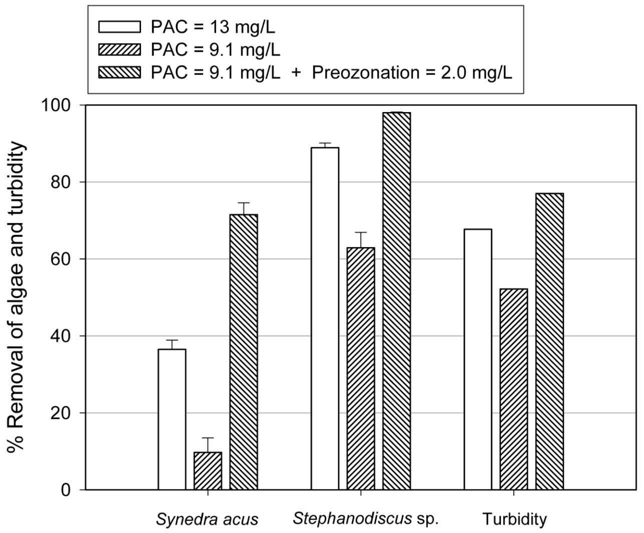


Fig. 5. Effects of preozonation in combination with reduced PAC dose.

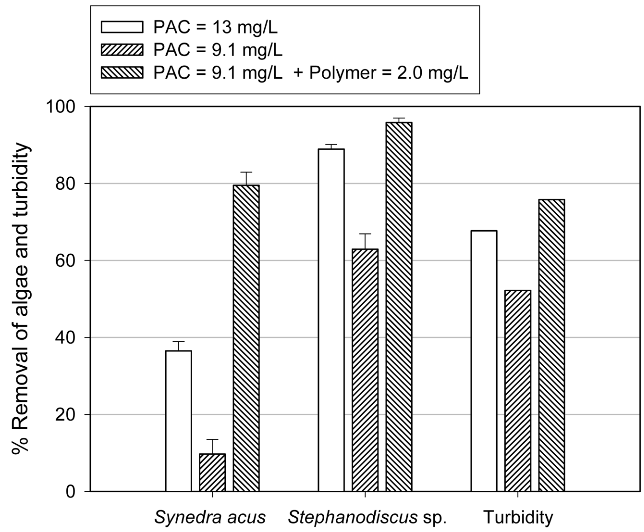


Fig. 7. Effects of polyamine coagulant-aid in combination with reduced PAC dose.

A set of pilot tests was performed to reduce the metal salt-type coagulant (PAC) dose with preozonation. Fig. 5 shows the effect of preozonation in combination with reduced PAC dose. It is noticed that the performance of preozonation can reduce the PAC dose by 30% while improving algae and turbidity removal efficiencies.

The detailed mechanism of the enhanced coagulation by preozonation is not well understood; however, numerous mechanistic explanations have been proposed [Edzwald and Benjamin, 1992]. Among those explanations, one theory states that ozone modifies the algal cellular surface and then causes the release of biopolymers, which may act as coagulant aids to promote inter-particle bridging [Sukenik et al., 1987; Edzwald and Reckhow, 1992].

2. Effect of Polyamine as a Coagulant-aid

In comparison to the use of PAC alone, the addition of polyamine improved the water quality in proportion to amount of polyamine added to PAC, which is shown in Fig. 6. These improvements are similar to Fig. 4. The maximum removal was 80.0% for *Synedra acus*, 99.6% for *Stephanodiscus* sp., and 87.1% for turbidity removal, respectively. As seen in Fig. 7, turbidity removal was 67.7% when 13 mg/L of PAC was used. The turbidity decreased from 5.01 to 1.63 NTU (the regulation limit in South Korea is 2.0 NTU). However, with a PAC dose of 9.1 mg/L, the regulation limit was not able to be met (the turbidity was 2.41 NTU). This is probably due to insufficient floc formation and subsequent dispersion of fine particles at the lower PAC dose. When 2 mg/L of polymer was added, the removal efficiency of algae and turbidity was improved. These results also indicate that the use of 2 mg/L of polyamine can sufficiently improve water quality while reducing the required PAC dose.

Most suspended particles (clays, humic acid and bacteria) have negative surface charges and so does *Synedra acus*. One paper re-

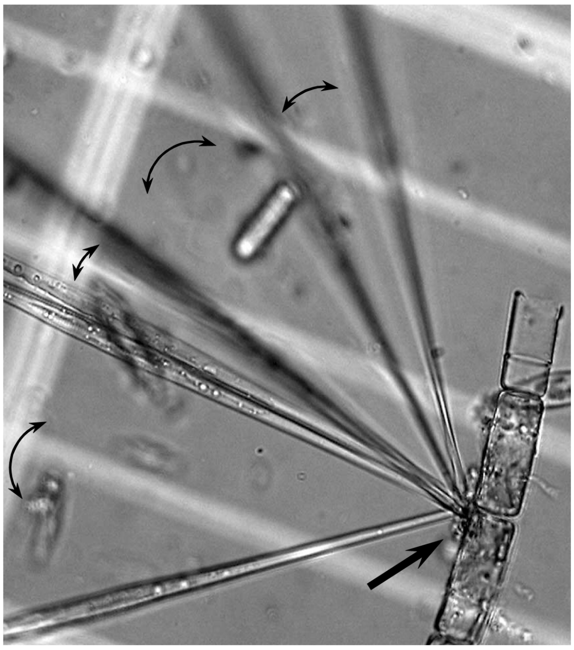
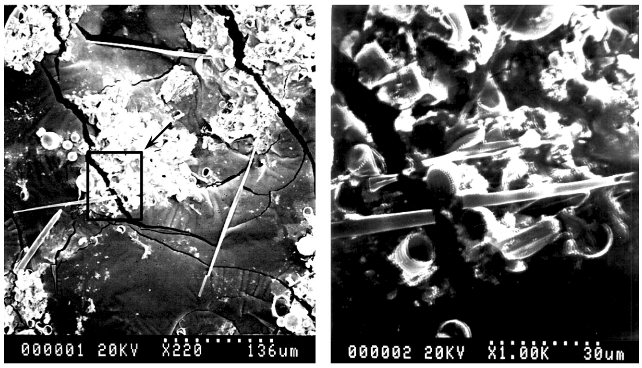


Fig. 8. The pictures of *Synedra acus* forming colony. Notes: The arrow represents secreted-mucilage and the sticky materials adhere to a moving organism (*Melosira varians*).

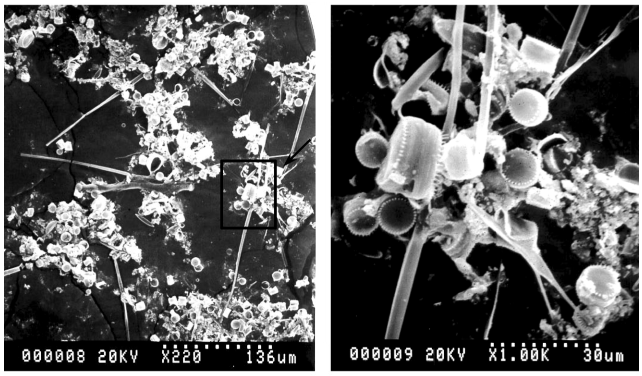
ported that water containing diatoms have relatively high values of zeta potentials, about −30 to −40 mV [Konno, 1993]. In most cases, *Synedra acus* occurs individually in fresh water but few form stellate-like colonies (Fig. 8). Although many factors might be associated with this type of colony formation, one possible reason is that secreted mucilage is employed to hold different cells together tightly. Simultaneously, *Synedra acus* has a strong repulsive force, thereby keeping the end of the cells away from other cells. Considering that most *Synedra acus* cells are suspended individually in natural water, each one might be kept separated by the high surface potential.

As discussed above, when PAC is used alone, *Synedra acus* is difficult to remove from the raw water, whereas *Stephanodiscus* sp. can be successfully removed by coagulation. To see the microscopic phenomena of the coagulation of *Synedra acus* in the presence of polyamine coagulation-aid, SEM (Scanning Electron Microscopy) examinations were conducted as shown in the Fig. 9. The figures on the right side show higher magnification as indicated by an arrow on the left-hand side. From the SEM examination of the algal floc after the sedimentation process by PAC (Fig. 9a on the left), each *Synedra acus* cell was separated by nearly equal spaces, probably due to strong electrostatic repulsion, but the *Stephanodiscus* sp. and other diatom species formed dense flocs. In Fig. 9a on the right-hand side, the SEM specimen with higher magnification indicates that some parts of *Synedra acus* cells are not sufficiently combined with other particles. On the contrary, when 1 mg/L of polyamine was added to the same dose of PAC, which is shown in Fig. 9b on the right-hand side, *Synedra acus* were tightly captured by other algal flocs. These observations can account for the previous results of higher removal rate with polyamine. Moreover, this mutual repulsive behavior can give a physical interpretation of the *Synedra acus* removal mechanism.

In water treatment processes, organic polymers have two principal functions: destabilization by charge neutralization and polymer-bridging effects [Montgomery, 1985]. From the observations in Fig. 8, *Synedra acus* has a strong electrostatic repulsion in the water system. Therefore, the surface potential must be lowered by some means. PAC was not sufficient to reduce the surface potential and thus it could not form dense flocs. However, the use of polyamine improved *Synedra acus* floc formation and strength. The polymer has cationic functional groups, which may act to reduce surface potential through charge neutralization and combine algal cells together through the bridging effect.



(a)



(b)

Fig. 9. The SEM pictures of PAC floc with and without coagulant-aid; (a) PAC 13 mg/L and (b) PAC 13 mg/L with polyamine 1.0 mg/L.

3. Comparison and Combination of Preozonation and Polyamine

A good approach for algal removal can be formulated from the data in Figs. 4 and 6. When 2.0 mg/L of preozonation and 13 mg/L of PAC were used, the maximum removal was 91.1% for *Synedra acus* and 99.0% for *Stephanodiscus* sp. (Fig. 4). When 2.0 mg/L of polyamine coagulant-aid and same dose of PAC were used, the maximum removal was 80.0% for *Synedra acus* and 99.6% of *Stephanodiscus* sp. (Fig. 6). Considering the algal removal efficiency, the relatively high dose of ozone was more useful for the removal of *Synedra acus.* Considering the removal efficiency of *Stephanodiscus* sp., the use of polyamine coagulant-aid gave a slightly better result than the performance of preozonation. Further studies, such as economic factor or residual products from preozonation, would be required to evaluate practical methods.

Preozonation and polyamine were combined to investigate the

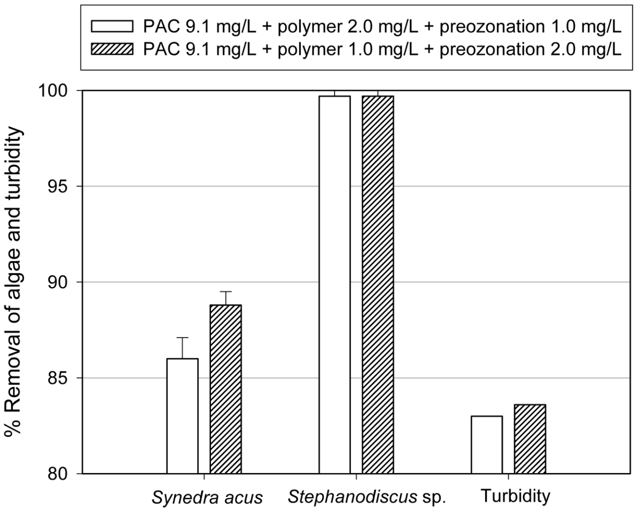


Fig. 10. Comparison of preozonation and polyamine in combination with PAC.

performance on removing diatoms as shown in Fig. 10. This result also showed that a relatively high dose of preozonation was more useful for *Synedra acus* removal. Fig. 10 also shows that the primary coagulant (PAC) can be reduced by preozonation and addition of polyamine, which in turn substantially reduces the residual aluminum ion.

CONCLUSIONS

Direct microscopic analysis was conducted for algae counting in the pilot tests. The results showed that *Synedra acus* has poor settling behavior; thereby its removal efficiency was not as good as *Stephanodiscus* sp. Compared to PAC alone treatment, the combined treatment of preozonation and polyamine coagulant-aid showed better performance in the removal of the two freshwater diatoms and turbidity. Although both processes highly enhanced algal removal, different removal patterns were found. Relatively high dose of ozone could be more useful for *Synedra acus* removal. Considering the removal efficiency of *Stephanodiscus* sp. and turbidity, the use of polyamine coagulant-aid gave a slightly better result than the performance of preozonation.

The combination of preozonation and polyamine coagulant-aid could be a promising solution for the removing diatoms and reducing the required PAC dose.

REFERENCES

APHA, *Standard Methods for the Examination of Water and Wastewater*, 19th ed., American Public Health Association, Washington, D.C., USA (1995).

Berman, T., Townsend, D. W., El Sayed, S. Z., Trees, C. C. and Azov, Y., "Optical Transparency, Chlorophyll and Primary Productivity in the Eastern Mediterranean near the Israeli Coast," *Oceanol. Acta*, **7**, 367 (1984).

Choe, S. and Jung, I., "Growth Inhibition of Freshwater Algae by Ester Compounds Released from Rotted Plants," *J. Ind. Eng. Chem.*, **8**, 297 (2002).

Crapper, D. R., Krishnan, S. S. and Dalton, A. J., "Brian Aluminum Distribution in Alzheimer's Disease and Experimental Neurofibrillary Degeneration," *Science*, **180**(4085), 511 (1973).

Edzwald, J. K. and Reckhow, D. A., "Ozone Effects on Algae and Tastes and Odors for Boston's Drinking Water Supply," AWWA Water Quality Technology Conference, Toronto, Canada, November 15-19 (1992).

Edzwald, M. and Benjamin, M. N., "Effect of Preozonation on Coagulation-NOM Interactions," *J. Am. Water Works Assoc.*, **84**, 63 (1992).

Gieskes, W. W. C. and Kraay, G. W., "Phytoplankton, its Pigments, and Primary Production at a Central North Sea Station in May, July and September 1981," *Neth. J. Sea Res.*, **18**, 51 (1984).

Hallegraeff, G. M. and Jeffrey, S. W., "Description of New Chlorophyll a Alteration Products in Marine Phytoplankton," *Deep-Sea Res., Part A*, **32**, 697 (1985).

Hlavacek, M. and Remy, J. F., "Simple Relationships among Zeta Potential, Particle Size Distribution, and Cake Specific Resistance for Colloid Suspensions Coagulated with Ferric Chloride," *Sep. Sci. Technol.*, **30**, 549 (1995).

Jun, H. B., Lee, Y. J., Lee, D. J. and Lee, B. D., "Optimal Combination of Coagulants for Removal of the Filter Clogging Algae," *J. Korean Soc. Environ. Eng.*, **20**, 1803 (1998).

Konno, H., "Settling and Coagulation of Slender Type Diatoms," *Wat. Sci. Technol.*, **27**, 231 (1993).

Lee, S. H., Shin, M. C., Choi, S. J., Shin, J. H. and Park, L. S., "Improvement of Flocculating Efficiency of Water Treatment by using Polymer Flocculants," *Environ. Technol.*, **19**, 431 (1998)

Montgomery, M. M., *Water Treatment Principles and Design*, John Wiley & Sons, Inc., New York (1985).

Nilsson, R., "Residual Aluminum Concentration in Drinking Water after Treatment with Aluminum or Iron Salts or Apatite - Health Aspects," *Water Supply*, **10**, 55 (1992).

Petrusevski, B., Vlaski, A., van Breeman, A. N. and Alaerts, G. J., "Influence of Algal Species and Cultivation Conditions on Algal Removal in Direct Filtration," *Water Sci. Technol.*, **27**, 211 (1993).

Sukenik, A., Teltch, B., Wachs, A. W., Shelef, G., Nir, I. and Levanon, D., "Effect of Oxidants on Microalgal Flocculation," *Water Res.*, **2**, 533 (1987).

Vlaski, A., van Breemen, A. N. and Alaerts, G. J., "The Algae Problem in the Netherlands from a Water Treatment Perspective," *Aqua* (London), **45**, 184 (1996).