Environ. Eng. Res. Vol. 11, No. 1, pp. 45~53, 2006
Korean Society of Environmental Engineers

CONTROL OF DIATOM BY PREOXIDATION AND COAGULATION IN WATER TREATMENT

Jeong-mi Seo[1], Dongsoo Kong[1], Seoungkoo Ahn[2], and Hyunook Kim[2†]
[1]National Institute of Environmental Research
[2]Department of Environmental Engineering, University of Seoul
(received February 2005, accepted February 2006)

Abstract : Conventional coagulation is still the main treatment process for algae removal in water treatment. The coagulation efficiency can be significantly improved by the preoxidation of algae-containing water. Jar test was conducted to determine the optimal condition for the removal of diatoms, especially *Cyclotella* sp. by preoxidation and the subsequent coagulation. The effects of various concentration of PAC (Polyaluminum chloride) on coagulation with and without preoxidation using chlorine or potassium permanganate at different pHs (7.7 and 9.0) were evaluated. At pH 7.7, preoxidation with 2ppm Cl_2 followed by coagulation with 7.5 ppm PAC coagulant could reduce *Cyclotella* sp. concentration by 86%. At pH 9.0, preoxidation with 1 mg $KMnO_4$/L followed by coagulation with 12.5 ppm PAC coagulant reduced *Cyclotella* sp. concentration by 85%. Non-linear regression was applied to determine the optimal condition. At pH 7.7 and 9.0, R was over 0.9, respectively. The pH of algal blooming water is over 9.0. Algae (diatom; *Cyclotella* sp.) can be controlled in the following ways: preoxidation with 1 mg $KMnO_4$ /L followed by coagulation with 12.5 ppm PAC coagulant can remove 80% algae from water. If water pH is adjusted to 7.7, it was expected that less amount of coagulant (7.5 or 10 mg PAC /L) after preoxidation (Cl_2 2 ppm or $KMnO_4$ 0.33, 1 ppm) would be needed to achieve similar level of algae removal. The oxidation with 0.33ppm $KMnO_4$ followed by coagulation with 7.5 ppm PAC coagulant was preferable due to cost-effectiveness of treatment condition and color problem after treatment.

Key Words : coagulation, preoxidation, jar-test, diatom, chlorine (Cl_2), potassium permanganate ($KMnO_4$)

INTRODUCTION

The algae blooming caused by the eutrophication of surface water is growing problem in the production of drinking water. Algae are negatively charged bio-particles that consume the coagulant demand in water treatment processes. It can have a negative impact on filtration; larger algae can cause filter clogging. Small and motile algae can penetrate into filter bed, which can lead to reduce filter runs and increase use of backwash water. Also, tastes and odors can arise from metabolic products of algae as well as the decay of dead cells. Algae is a precursor of disinfection by-products, including trihalomethanes,[1,2] haloacetic acids[2] and haloacetonitriles.[3]

Algae is known to have physically similar properties to *Cryptosporidium parvum* oocysts. Therefore, poor removal of algae, in addition to other inconveniences, also indicates that removal of other particles in the algal size range, such as oocysts of *C. parvum* may be inefficient as well.[4]

Conventional coagulation is still the main treatment process for algae removal in water treatment and preoxidation of water containing algae can significantly improve coagulation efficiency. Preoxidation can improve algal removal in direct filtration by immobilizing motile algae and causing the release of biopolymers from algae that act

† Corresponding author
E-mail: h_kim@uos.ac.kr
Tel: +82-2-2210-5624, Fax: +82-2-2210-2245

as a coagulant aid.

Prior research has shown that pre-treatment with oxidants, such as chlorine, chlorine dioxide and ozone enhance the coagulation process and the algae removal.[5] Potassium permanganate also has been investigated as an alternate preoxidant to improve the direct filtration of impounded surface water. The jar tests and experiments with a pilot plants showed that permanganate pre-treatment followed by coagulation significantly improved the particle and algae removal.[6]

The object of the current research is to determine optimal condition for algal removal by preoxidation and the subsequent coagulation of water containing diatoms, especially *Cyclotella* sp., in water treatment processes. Coagulant used in this study was PAC (Polyaluminum Chloride) of 17% w/w which known as more effective than alum for enhanced coagulation[7] and oxidants are chlorine and potassium permanganate.

MATERIALS AND METHODS

Investigation of Diatom Concentration

In order to know diatom occurrence patterns in Seoul's Water Intake Plants, algal conc. data[8] of six Water Intake Plants (Paldang, Amsa, Guui, Jayang, Pungnap, Gangbuk) were collected and investigated. The followings were analyzed: yearly average, ratio to total algae, upper 5% occurrence, guideline of problem outbreak, days of problem outbreak per year and trend of diatom occurrence during the same period per year.

Algal Culturing

Raw water was taken from Guui Water Intake Plant in December 2003 and incubated in a 10 L batch reactor for 135hrs at a temperature of 17 ± 2°C and under light of 2000 lux (12-950 Lumilux® de Luxe ; Osram). The light-dark cycle was maintained at 14:10 hours, after adding culture medium (M. Chu No. 10)[9] to the water. Also, the reactor was agitated at 60 rpm.

The initial algae concentration was total 5,200 cells/mL (4,500 cells/mL of diatom and 3,500 cells/mL of *Cyclotella* sp.), pH was 7.8, and turbidity was 2 NTU. After culturing, the total algae concentration increased to 177,000 cells/mL (166,000 cells/mL of diatom and 162,000 cells/mL of *Cyclotella* sp.). Water pH was raised to 9.6, and turbidity was 13.2 NTU. In addition, microscopic green algae accounted for a part of algae. Algal cell counts followed low-magnification (up to 200×) method using Sedgwick-Rafter chamber (length 20 mm, width 50 mm, depth 1 mm ; volume 1 mL).

Sample Preparation

Sample water for the experiment was prepared by diluting the cultured solution in raw water. This sample was, then, measured for pH, turbidity, alkalinity, UV_{254}, DOC, algae conc., Cl_2 demand and $KMnO_4$ demand. Demand of oxidants was estimated after 30 minutes contact.

Coagulation-Sedimentation Test

Jar tests were conducted to evaluate algae removal efficiency by preoxidation followed by coagulation. Coagulant used in the tests was PAC (Polyaluminum chloride) of 17%w/w. PAC is being used in many water treatment plants. The PAC doses used in the experiment was 2.5~12.5 mg/L. The effects of various PAC conc. on coagulation with and without preoxidation (Cl_2 and $KMnO_4$) at different pHs (7.7 and 9.0) were evaluated with a jar tester apparatus (Phipps & Bird, USA) with six 2-L cylindrical jars. The water pH of each vessel was adjusted with 2N NaOH.

When the coagulant was added, samples were agitated at 100 rpm for 10 sec, at 60 rpm for 7.5 min, at 40 rpm for 7.5 min and then at 20 rpm for 5 min.[10] Afterward, it was allowed to settle for 16 min. Thereafter, sample aliquot was taken from 10 cm below the surface and was analyzed to determine residual algae cell concentration, UV_{254}, DOC and turbidity.

Settling Velocity

Sedimentation basins remove particles by gravity.

The particles can be removed in the form of either individual particles or the flocs formed during the coagulation process.

Theoretically, a tank designed with an overflow rate of 2.4 m/h can remove particles that settle faster than 4 cm/min. Particles settling at less than 4 cm/min, therefore, would not be removed. Jar test conducted to determine the percent of the turbidity at a certain settling velocity and thereby the efficiency of the sedimentation basin. For example, if the basin has an overflow rate of 1 gpd / ft^2 and 80 percent of the particles is found to settle faster than 4 cm/min, then one would predict 80 percent turbidity removal in the sedimentation basin. The particle settling velocities are estimated by procedures developed by Hudson.[11]

A typical alum or ferric coagulation sedimentation basin is designed for an overflow rate of 400 to 1000 gpd / ft^2 (0.67 to 1.67 m/h), corresponding to particle settling velocities of 1 to 3 cm/min.[12] Therefore, sample collections should be performed between about 2 and 10min.[13] Allowing the particles in water of a jar to settle for 30 min or 60 min and then taking a subsample from the jar for turbidity measurement do not give useful information in designing a full-scale sedimentation system. Therefore, samples for the turbidity measurement were taken 1, 2, 4, 8 and 16 min after the beginning of particle settlement.

Analytical Methods

Dissolved organic materials filtered with a 0.45 μm cellulose membrane were estimated with a spectrophotometer ($\lambda = 254$ nm) and a carbon analyzer (Shimadzu TOC-V_{CPH} & ASI-V, Japan). Turbidity was measured by a turbidometer (HACH 2100P, USA).

30 mins contact time was provided to each oxidant. Chlorine stock solution of 1,000 mg Cl_2/L used for chlorination study was prepared by dissolving sodium hypochlorite (NaOCl, YAKURI) in distilled water. It was, then, adjusted to pH 8 with 1 N HCl. The Cl_2 demand of algae-containing water was analyzed by Standard Method 2350B.[14] Also, stock solution of 1000 mg $KMnO_4$/L was prepared by potassium permanganate ($KMnO_4$, Hanawa). The stock solution was diluted to 0.1 ~0.5 mg $KMnO_4$/L before it was used. $KMnO_4$ demand of the algae-containing water was determined by monitoring color change over 10 min after 30 min contact time. Petruševski B. *et al.* reported that result from this method was comparable with that from the spectrophotometry with the absorbance of 525 nm which is proposed by Standard Methods 4500-$KMnO_4$ B.[15]

Trihalomethanes were measured by a gas chromatograph (5890 Series II, Hewlett Packard, USA).

RESULTS AND DISCUSSION

Diatom Occurrence

The patterns of diatom occurrence observed by six representative Water Intake Plants in Seoul are listed in Table 1. Generally, diatoms occupied about 90% of total algae observed by the plants. *Cyclotella* sp. accounts for about 75% of the diatoms. In addition, *Cyclotella* sp. was dominant in winter and early spring as illustrated in Figure 1; if *Cyclotella* sp. is over 20,000 cells/mL, its problematic outbreak can be assumed. In fact, the day of its outbreak was increasing gradually over years.

Water Quality of Samples

Water quality of samples used for this experiment was as follows: pH of 7.7, turbidity of 3.8 NTU, alkalinity of 43 mg $CaCO_3$/L, UV_{254} of 0.045, DOC of 4.91 mg/L, Cl_2 demand of 1 mg/L, $KMnO_4$ demand of 0.33 mg/L, and total algae of 24,008 (diatoms of 22,908, *Cyclotella* sp. of 22,325, green algae of 1,067 cells/mL). Other diatoms of small amount are included in the algae counting.

UV_{254} and DOC

UV absorption value has been used to characterize natural organic matter contents of natural water.[16] However, organic compounds commonly found in water, such as lignin, tannin, humic substances, and various aromatic compounds strongly absorb ultraviolet (UV) light, so UV absorption was used as a surrogate measure for these selected organic

Table 1. Diatom concentration of each Water Intake Plant (1998-2002)

Unit : cells/mL

Water intake plant		Paldang	Amsa	Guui	Jayang	Pungnap	Gangbuk
Avg. of Yearly diatom conc. (ratio to total algae, %)		4,612 ~5,882 (84.3~91.1)	5,246 ~7,298 (86.0~94.2)	5,299 ~7,604 (89.8~92.5)	5,860 ~8,578 (69.0~93.9)	6,094 ~9,640 (90.3~93.5)	2,460 ~6,273 (85.8~94.5)
Upper 5% occurrence (average)		15,832 ~28,852 (20,689)	19,150 ~36,780 (25,042)	21,540 ~44,190 (30,429)	28,983 ~44,926 (34,644)	30,300 ~48,431 (36,895)	15,468 ~28,155 (20,299)
Avg. of Yearly *Cyclotella* sp. Conc. (ratio to diatoms, %)		3,509 ~4,569 (68.3~82.1)	4,253 ~5,091 (68.2~82.5)	4,516 ~5,806 (68.1~85.2)	4,706 ~7,183 (69.8~84.3)	4,940 ~8,033 (69.3~86.6)	1,397 ~4,281 (56.8~81.5)
Upper 5% occurrence (average)		14,214 ~28,655 (19,459)	17,729 ~33,740 (23,774)	21,217 ~40,820 (29,100)	27,020 ~44,476 (33,174)	28,664 ~45,474 (35,174)	14,285 ~26,220 (19,155)
Guideline of *Cyclotella* sp. problem outbreak : 20,000 cell/mL							
Day of problem outbreak (day/yr)	1998	7	7	7	7	7	-
	1999	0	7	14	21	21	0
	2000	0	14	14	21	21	7
	2001	21	21	28	28	28	21
	2002	0	14	21	49	63	0
	Avg.	6	13	17	25	28	7

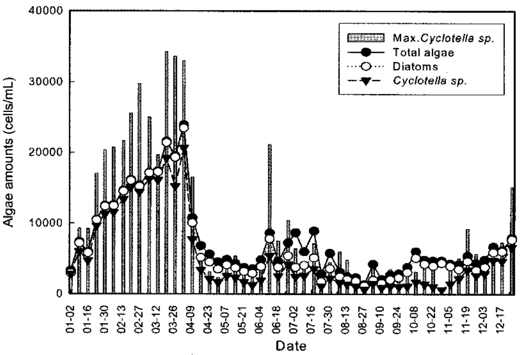

Figure 1. Trend of diatom occurrence from 1998 to 2002.

constituents. Strong correlations exist between UV absorption and organic carbon contents, color, and precursor levels of THMs and other disinfection by-products.

Figure 2 shows variance of UV_{254} and DOC concentrations at various preoxidation, and PAC coagulation. The UV_{254} of the water with preoxidation was lower than that without preoxidation. The destruction of aromatic compounds and other organics with carbon double bonds by chemical oxidation could cause reduction of UV absorption and increase of dissolved organic carbon (DOC). This is presumably due to both cell lyses and increased liberation of extracellular material by the oxidation. SUVA (Specific ultraviolet absorbance) can explain these UV_{254} and DOC concentration relations. SUVA is defined as the UV absorbance of a water sample at a given wavelength (usually λ = 254 nm) normalized for DOC concentration; SUVA(L/mg.m) = (UVA/DOC) × 100. If SUVA<3, DOCs in a water sample are considered of hydrophilic, non-aromatic and low molecular weight. In this case, organic carbons are not removed well by coagulation.

The water used in the current experiment contains a lot of algae, and the algae were decomposed by oxidation. The compounds from algae destruction were fulvic acid of low molecular weight and high negative charge.[17] Therefore, SUVA of this water was estimated to 0.3~0.9, implying other treatment processes such as enhanced water treatment is needed to control DOC concentration after coagulation.

THM

Figure 3 shows variation of THM concentration at various preoxidation and PAC coagulation.

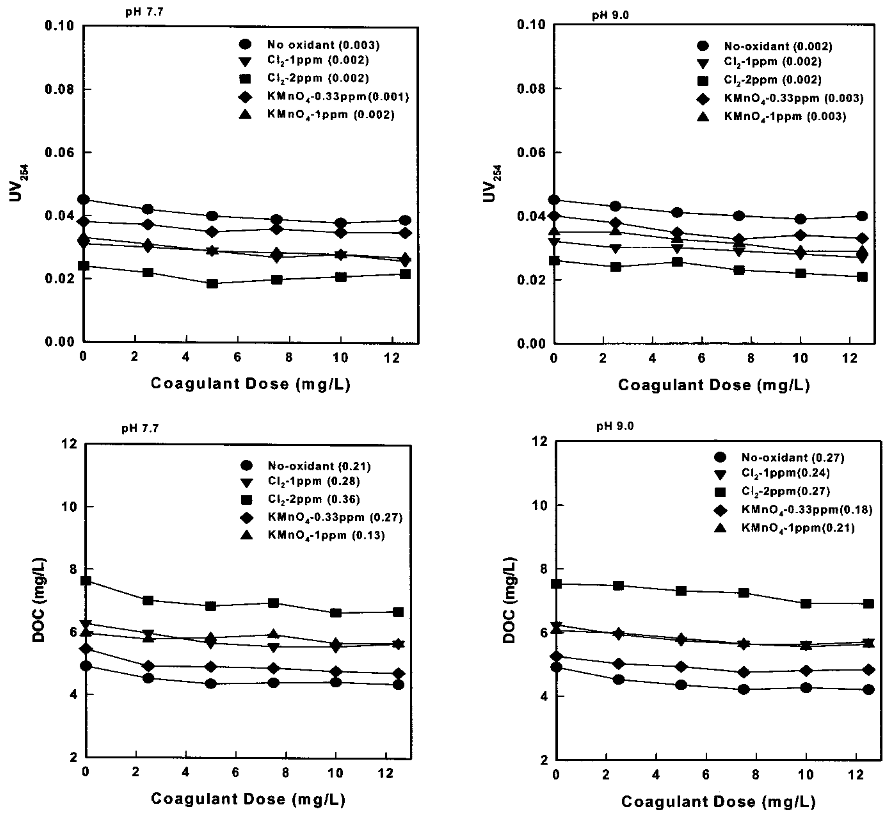

Figure 2. Variance of UV_{254} and DOC on preoxidation and PAC coagulation (( ): standard deviation).

The generation of THMs is due to the reaction between chlorine and DOC. At pH 7.7, 8.2~12.3 times more THMs were produced by the Cl_2-preoxidation than the control (no-oxidant: 3.7 μg/L), while 1.2~1.3 times more THMs were produced by the $KMnO_4$preoxidation. At pH 9.0, THM levels increased 7.2~10.7 times with Cl_2-preoxidation and 1.1 times with $KMnO_4$preoxidation. Generally, coagulation treatment processes with prechlorination can lead to higher production of THM in the downstream processes.[16] Thus, other treatment processes such as intermediate chlorination and coagulation or postchlorination after the $KMnO_4$ preoxidation and coagulation can be considered to minimize THM formation.

Settling Velocity & Algae Removal

Settling velocity was calculated through regression

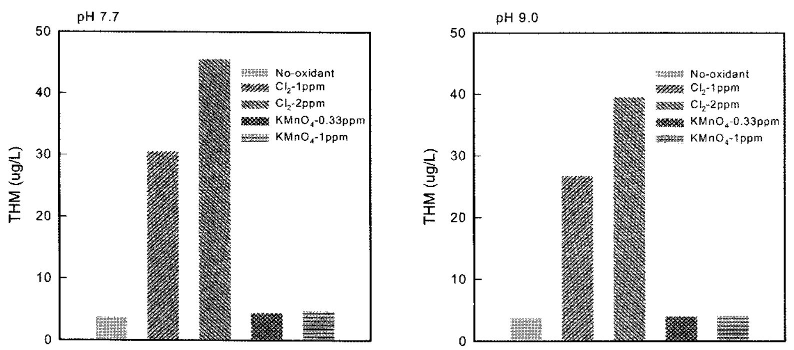

Figure 3. Variance of THM generation on preoxidation and PAC coagulation.

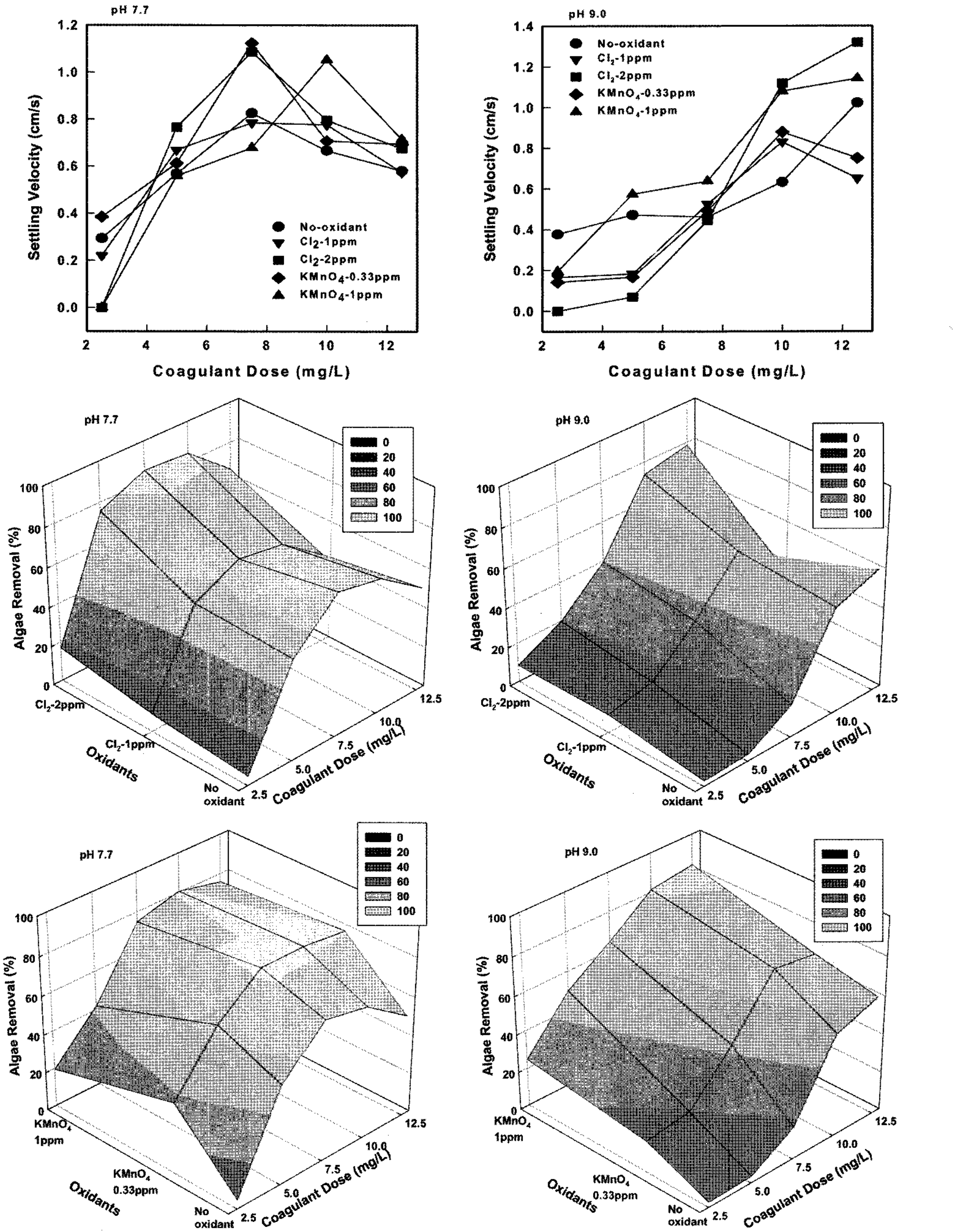

Figure 4. Variation of settling velocity and algal removal at different preoxdation, pH and PAC coagulation.

of sampling time versus measured turbidity. Figure 4 shows variations of settling velocity and algal removal ratio after preoxidation and PAC coagulation. It illustrates low residual algae concentration could be observed at high settling velocity. In all the treatment conditions, high removal of algae (*Cyclotella* sp.) was achieved.

With flocculation with 7.5 ppm PAC at pH 7.7 and without preoxidation, *Cyclotella* sp. was reduced from 22,000 cells/mL to 6,000 cells/mL (removal efficiency of 73%). Prechlorination with 2 ppm Cl_2 and preoxidation with 0.33 ppm

$KMnO_4$ at pH 7.7 (each case was followed by coagulation with 7.5 ppm PAC) could reduce *Cyclotella* sp. counts by 86% and 83%, respectively. After Flocculation with 12.5 ppm PAC at pH 9.0 and without preoxidation, *Cyclotella* sp. concentration was reduced from 22,000 cells/mL to 8,500 cells/mL (removal efficiency of 62%). Prechlorination with 2 ppm Cl_2 and preoxidation with 1 ppm $KMnO_4$ followed by coagulation with 12.5 ppm PAC at pH 9.0 reduced *Cyclotella* sp. counts by 79% and 85%, respectively. Also, preoxidation with 1 ppm $KMnO_4$ followed by coagulation with 10 ppm PAC reduced cell counts by 81%. From the result, it was presumed that preoxidation enhanced coagulation by immobilizing motile algae and causing the release of biopolymers to release from cells and to aid coagulation.

The pH of water with algal blooming usually is over 9.0. At pH 9.0, preoxidation with 1 ppm $KMnO_4$ followed by coagulation with 12.5 ppm PAC could remove about 80% algae from the water. If pH was lowered to 7.7 from 9.0, smaller coagulant doses were required; 7.5 or 10.0 mg PAC /L was required for the water with prechlorination with 2 ppm Cl_2 and with preoxidation with 0.33 ppm or 1 ppm $KMnO_4$.

Table 2. Cost-effectiveness of oxidants $KMnO_4$ and Cl_2

Oxidants	Cost (won/kg)	Ratio	Dosage (mg/L)	Ratio
$KMnO_4$	8000	6	0.33	1.0
Cl_2	1500	1	2.00	6.1

In Table 2, oxidation with $KMnO_4$ and with Cl_2 was compared in terms of chemical cost for similar level of treatment efficiency at pH 7.7. It shows that $KMnO_4$ oxidation had similar cost-effectiveness with chlorination since the higher price of the former than the latter could be offset by the smaller dosage of the former. Considering chemical cost, water color, and potential of THM formation, preoxidation with 0.33 mg $KMnO_4$/L was preferred.

Non-liner regression using the following *Gaussian* equation (eq. 1) was performed to fit the observed data and the fitting result is presented in Table 3.

$$z = a \times e^{-0.5\left[\left(\frac{x-x_0}{b}\right)^2 + \left(\frac{y-y_0}{c}\right)^2\right]} \quad (1)$$

where z is algae removal; x is PAC concentration; y is oxidant concentration.

In short, the data could be fitted well with the Gaussian model; the R values were 0.92 to 0.95. The model predicted values and the observed ones are compared in Figure 5. Most data points are located on the surface of the fitted Gaussian model. Through the model prediction, it was expected that the best algae removal efficiency be obtained by preoxidation with 2 ppm Cl_2 or with 0.50 ppm $KMnO_4$ followed by coagulation with 10 ppm PAC at pH 7.7. At pH 9.0, preoxidation with 2 ppm Cl_2 or 1 ppm $KMnO_4$ followed by coagulation with 12.5 ppm PAC would result in the good algae removal.

CONCLUSIONS

Jar tests were conducted to find out the optimal operational condition to remove algae (diatoms, especially *Cyclotella* sp.) from water by preoxidation and the subsequent coagulation in a water treatment plant. The effects of various amounts of PAC addition with and without preoxidation (Cl_2 and $KMnO_4$) at different pH (7.7 and 9.0) were evaluated by measuring UV_{254}, DOC, THM, turbidity and algae counts.

At pH 7.7, prechlorination with 2 ppm Cl_2

Table 3. R values, P values and coefficients of *Gaussian* equation obtained from regression 9.0

pH	Oxidant	R	P	x_0	y_0	a	b	c
7.7	Cl_2	0.92	0.0005	8.77	19.93	276.18	3.91	11.97
	$KMnO_4$	0.94	<0.0001	9.61	0.57	98.43	4.66	0.71
9.0	Cl_2	0.95	<0.0001	11.39	15.53	262.82	3.48	8.60
	$KMnO_4$	0.94	0.0001	12.46	1.39	93.57	5.46	1.33

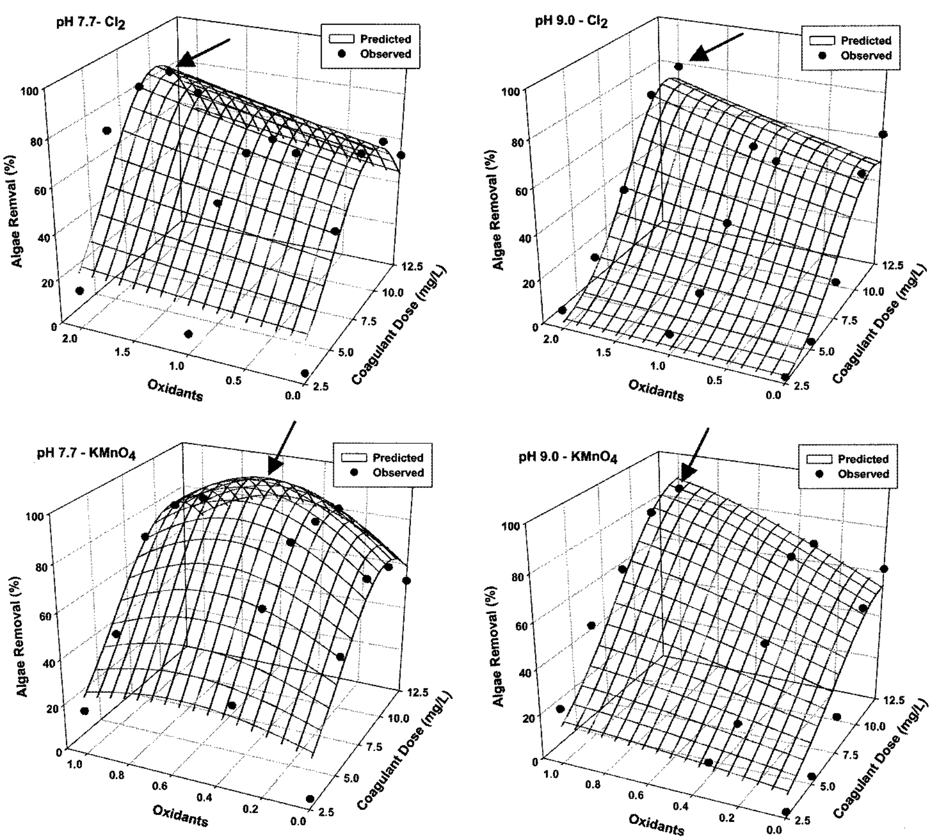

Figure 5. Comparison between predicted values and observed ones about algae removal. (→ indicates the operating condition where the best performance is expected)

followed by coagulation with 7.5 ppm PAC could reduce *Cyclotella* sp. concentration by 86%. At pH 9.0, preoxidation with 1 mg $KMnO_4$/L followed by coagulation with 12.5 ppm PAC also could reduce *Cyclotella* sp. by 85%. From the result, it was assumed that preoxidation could enhance coagulation by immobilizing motile algae and causing biopolymers to release from the cells and to act as a coagulant.

Non-linear regression using the Gaussian equation was performed to determine the optimal condition of preoxidation and coagulation for algae removal. At pH 7.7 and 9.0, R values were over 0.9. The pH of algal blooming water is over 9.0 and preoxidation with 1 mg $KMnO_4$ /L followed by coagulation with 12.5 ppm PAC can be used for algae removal. Also, if water pH is adjusted to 7.7, less amount of coagulant (7.5 or 10 mg PAC/L) after preoxidation (Cl_2 2 ppm or $KMnO_4$ 0.33, 1 ppm) can be alternated for similar level of algae removal. Among these treatment conditions, if its cost-effectiveness and color problem after treatment is considered, the oxidation with 0.33 ppm $KMnO_4$ followed by coagulation with 7.5 ppm PAC coagulant will be preferable. Because most coagulation treatment processes are using Cl_2 preoxidation, intermediate or post-chlorination after algae removal by $KMnO_4$ preoxidation and coagulation can be suggested considering THM formation potential.

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