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## EFFECT OF ALGAE PRE-OXIDATION WITH CHLORINE DIOXIDE ON THEIR REMOVAL BY DISSOLVED-AIR FLOTATION

The dissolved air flotation (DAF) experiments involving pre-oxidation of algae with chlorine dioxide and alum coagulation were carried out in a bench-scale unit under laboratory conditions. Such a procedure allows the removal of chosen green algae (*Chlorophyceae*) from water. The efficiency of the process under investigation was related to the parameters of algal particles agglomeration and separation. Destabilization of algal particles was necessary to provide favourable conditions for microagglomerate attachment to the collectors (air bubbles). The parameters of agglomeration can be itemized as follows: pre-oxidant ( $\text{ClO}_2$ ) and coagulant (alum) doses, pH, duration and rate of mixing during flocculation. The parameters of separation comprised recycle ratio and saturation pressure. DAF allows collisions between the destabilized particles and air bubbles and simultaneously reduces flocculation periods. DAF preceded by pre-oxidation, alum coagulation and flocculation of algae produced clear water with low algal content at significantly limited coagulant doses.

### 1. INTRODUCTION

Removal of algae during eutrophic surface water treatment is a seasonal but rather troublesome problem mainly when water is stored in the impoundment lake over prolonged periods [1]. Algae in water, even in small numbers, are responsible for the development of tastes and odours and are themselves susceptible to microbial attack since they form a substrate for further bacterial growth and biological aftergrowth in distribution systems and clear water storage tanks [2]. Analyses of various parameters of raw water quality suggest that algae are also responsible for a significant proportion of haloforms' precursor concentration [3]–[5]. The separation of algae from water has proved to be a difficult operation because of the small size of individual cells (from 3 to 15  $\mu\text{m}$ ) and the low specific gravity of the individual cells (1.05–1.20  $\text{g}/\text{cm}^3$ ), the latter being further reduced by the attachment of small bubbles of internally produced oxy-

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gen. The treatment of surface waters containing algae is also difficult since the suspensions in which algae occur are relatively dilute.

Discrete algal cells form stable microbial suspensions, possess a chemically reactive cellular surface and a net negative surface charge due to ionization of functional ionogenic groups. They can be considered as hydrophilic biocolloids. The stability of algal suspensions heavily depends on the forces interacting between the particles themselves and between the particles and the water. Effective agglomeration of algal particles requires surface charge neutralization. Destabilization of algae has been accomplished by various inorganic and organic coagulants. The effect of each coagulant depends on pH, algae concentration, and other parameters.

Algal agglomerates obtained during the coagulation/flocculation process as low-density particles and potential precursors of trihalomethanes (THMs) can be removed from water by dissolved-air flotation (DAF) [6]–[8]. This process represents a viable alternative to conventional sedimentation processes. DAF is based on the transfer of particles to the surface of a liquid through attachment of air bubbles to the particle surfaces. Schematic diagram of DAF plant is shown in figure 1. The treatment prior to the flotation consists in coagulant addition with rapid mixing followed by flocculation. Recycled water saturated with air under pressure is introduced following the flocculation stage. Following the release of pressure the air comes out of solution and forms tiny bubbles which attach to the floc and make it float to the surface. The floated sludge is then collected and removed by intermittent skimming. The flotation mechanism of separation is more effective with smaller and lighter particles [9]. It has been also stated that formation of large, dense flocs is not required as it would be in a sedimentation process.

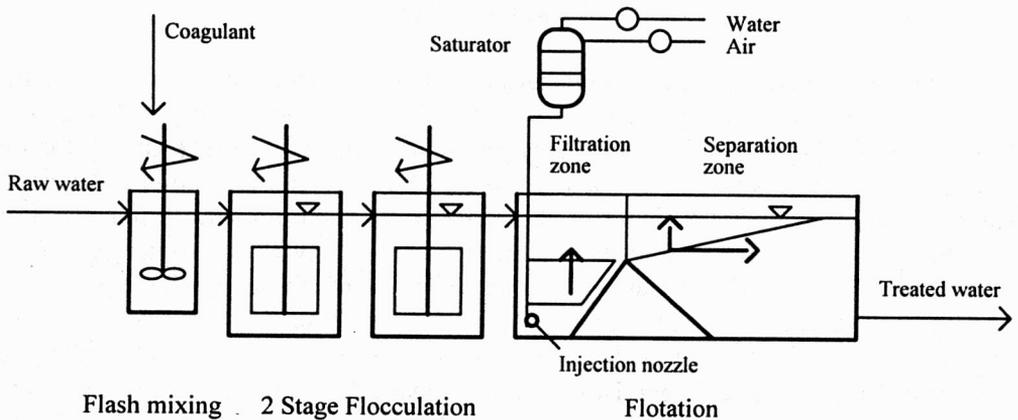


Fig. 1. Diagram of a dissolved-air flotation water treatment plant

Charge neutralization is an important step in promoting the attachment of hydrophobic particles to the surfaces of air bubbles and thus promoting removal of particles via

flotation. Pre-oxidation has been widely reported to assist algal coagulation [10], [11]. The chemicals used most commonly in municipal water treatment are chlorine and ozone. However, chlorine is responsible for THMs and other by-products formation, especially when water contains significant amounts of organics. Pre-ozonation instead of pre-chlorination can solve some problems of by-products. Another possible alternative is chlorine dioxide application at the head of the treatment line because although it is a strong oxidant it does not form THMs and other chlorinated organic compounds.

The purpose of this research was to characterize and evaluate the effects of various parameters on the removal of algae from water by DAF method when chlorine dioxide was used as pre-oxidant. Effects of pre-oxidation of green algae cells with chlorine dioxide on their flocculation and final removal efficiency were investigated. The effects of alum dosage and flocculation time on algae agglomeration were studied. The influence of the recycling rate and saturation pressure on algae removal by DAF were also analysed.

## 2. ALGAL FLOCCULATION AND FLOTATION

Basically, removal of algae from water by means of chemical treatment follows the same principle as the removal of colloidal and dispersed particles although sometimes it is significantly different because of various shapes and sizes of algal cells [11]. Flocculation enables bringing the destabilized particles into contact which promotes floc formation. The equation that describes flocculation as the change in particle number with time under turbulent conditions was originally developed by Smoluchowski, and a simple form of this rate equation was proposed by O'MELIA [12]:

$$\ln \left( \frac{n}{n_0} \right) = - \left( \frac{4}{\pi} \right) \alpha \Phi G t_F, \quad (1)$$

where  $n$  is the number concentration of particles after flocculation,  $n_0$  is the initial number concentration of particles,  $\pi$  is the mathematical constant,  $\alpha$  is the efficiency factor of collisions,  $\Phi$  is the volume of solid material per unit volume of solution,  $G$  is the mean velocity gradient, and  $t_F$  is the flocculation time. Equation (1) allows predicting an increase in the efficiency of flocculation for an increased attachment of the particles, volume of solid material and flocculation time when velocity gradient is conserved.

For a steady-state performance of DAF in batch particle removal, MALLEY and EDZWALD [9] proposed the following equation:

$$\ln \left( \frac{N}{N_0} \right) = - \left( \frac{3}{2} \right) (\alpha_{pb} \eta_{tot}) \left( \frac{H}{d_b} \phi_b \right), \quad (2)$$

where  $N$  is the particle number concentration after flotation,  $N_0$  is the particle number concentration subjected to flotation,  $\alpha_{pb}$  is the attachment or adhesion efficiency of particle bubble collisions (fraction of successful collisions),  $\eta_{tot}$  is the total single collector (bubble) collision efficiency caused by transport of particles to the bubble surface,  $H$  is the depth of flotation tank,  $\phi_b$  is the bubble volume concentration, and  $d_b$  is the bubble diameter.

Parameters in the product ( $\alpha_{pb} \eta_{tot}$ ) are affected by coagulation and flocculation ahead of the flotation tank. The attachment factor ( $\alpha_{pb}$ ) suggests that good flotation performance should be obtained for such coagulation conditions that produce destabilized flocs. The total single-collector efficiency ( $\eta_{tot}$ ) is the sum of individual expressions of particle transport to the bubble surface formulated for the Brownian diffusion ( $\eta_D$ ), interception ( $\eta_I$ ) and gravity settling ( $\eta_G$ ). MALLEY and EDZWALD [9] proposed the following equations:

$$\eta_{tot} = \eta_D + \eta_I + \eta_G, \quad (3)$$

$$\eta_{tot} = 6.18(kT/g\rho_w)^{2/3}(1/d_p)^{2/3}(1/d_b)^2 + 1.5(d_p/d_b)^2 + [(\rho_p - \rho_w)/\rho_w](d_p/d_b)^2, \quad (4)$$

where  $k$  is Boltzmann's constant,  $T$  is an absolute temperature,  $d_p$  is the particle diameter, and  $\rho_p$  and  $\rho_w$  are the particle and water densities, respectively.

Model calculations of  $\eta_{tot}$  showed that large floc particles were inappropriate for DAF and a short time of flocculation could be applied before flotation [9]. Minimum values of  $\eta_{tot}$  were obtained for the particles whose size approaches 1  $\mu\text{m}$  suggesting that floc particles of the diameters of 10–30  $\mu\text{m}$  should be prepared for DAF, but larger flocs should be avoided. MALLEY and EDZWALD [9] found that particle density and water temperature had small effect on the total single collector efficiency. Some research indicates that in DAF plants designed in the last decade, the time of flocculation can be as short as some minutes only [9], [13].

Volume concentration of the air released ( $\phi_b$ ) and the size of the air bubbles ( $d_b$ ) are important parameters of flotation tank [14]. High values of  $\phi_b$  enhance collisions between the particles and the bubbles and guarantee a sufficient bubble volume that lowers the density of particles being subjected to flotation. Model calculations of  $\eta_{tot}$  suggest that small air bubbles (less than 100  $\mu\text{m}$ ) should be most effective. Mean size of a bubble approaches 40  $\mu\text{m}$  and is established from noticeable difference in the pressure of saturator and the atmosphere of flotation tank.

### 3. MATERIALS AND METHODS

#### 3.1. RAW WATER PREPARATION

The tests were conducted on small planktonic green algae (*Scenedesmus quadricauda*, *Ankistrodesmus longissimus*, and *Selenastrum capricornutum*). The algae

were cultivated under tubular fluorescent lamps in 20 dm<sup>3</sup> bottles at a temperature of about 20 °C. A modified Bold's Basal Medium (table 1) served as the inorganic nutrient source. Algae were provided with CO<sub>2</sub>, the sole carbon source, by bubbling air through the media. Two bottles were initially inoculated with a pure culture of *Scenedesmus quadricauda* and *Selenastrum capricornutum*, while the third one – with a mixture of algae inhabiting water impoundment lake which serves as a drinking water source. After a few weeks *Ankistrodesmus longissimus* dominated that culture.

Table 1

Modified Bold's Basal Medium

Compound	Concentration (mg/dm <sup>3</sup> )
NaNO <sub>3</sub>	476
Ca(NO <sub>3</sub> ) <sub>2</sub> × 4H <sub>2</sub> O	59
MgSO <sub>4</sub> × 4H <sub>2</sub> O	25
NaHCO <sub>3</sub>	84
KH <sub>2</sub> PO <sub>4</sub>	24
FeEDTA	10
Microelements	10

10 cm<sup>3</sup> of each of the following micro-element solutions were added per liter of solution: FeEDTA solution dissolved in 1 dm<sup>3</sup> H<sub>2</sub>O, the following compounds in the amounts indicated, all dissolved in 1 dm<sup>3</sup> of distilled water: (NH<sub>4</sub>)Mo<sub>7</sub>O<sub>24</sub>, 0.9 mg; KBr, 1.2 mg; KI, 0.8 mg; ZnSO<sub>4</sub> × 7H<sub>2</sub>O, 2.9 mg; Co(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O, 1.5 mg; CuSO<sub>4</sub>, 1.3 mg; NiSO<sub>4</sub>(NH<sub>4</sub>)SO<sub>4</sub> × 6H<sub>2</sub>O, 2.0 mg; KAl(SO<sub>4</sub>)<sub>2</sub> × 12H<sub>2</sub>O, 4.7 mg; Cr(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O, 0.4 mg; H<sub>3</sub>BO<sub>3</sub>, 31.0 mg.

In order to investigate raw water, a defined volume of algal culture at a stationary growth phase (e.g. 7 days) containing algal cells and extracellular organic matter was thoroughly mixed with a certain volume of tap water. The algal concentration obtained ranged from 8 × 10<sup>4</sup> to 4 × 10<sup>5</sup> org/cm<sup>3</sup>.

### 3.2. ANALYTICAL METHODS

The number of algae in suspension was determined in a Fusch–Rosenthal counting chamber using a biological light microscope. The electrophoretic mobility of algae was measured by means of the apparatus manufactured by Zeta-Meter Inc. A total of at least 20 measurements was made for each test run. Half way through the trials the polarity of direct current was reversed so that the particle moved in the opposite direction. Zeta potential was calculated based on the velocity of particles.

## 3.3. WATER TREATMENT PROCEDURE

Flocculation tests were carried out with aluminium sulphate ( $\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ ) at pH level of 6.5–7.0. Chlorine dioxide ( $\text{ClO}_2$ ) obtained from the reaction between sodium chlorite and hydrochloric acid was used as a pre-oxidant in the doses from 0.1 to 0.5  $\text{mg}/\text{dm}^3$ . Pre-oxidation and rapid mixing were conducted in the beaker which served as a reaction chamber.

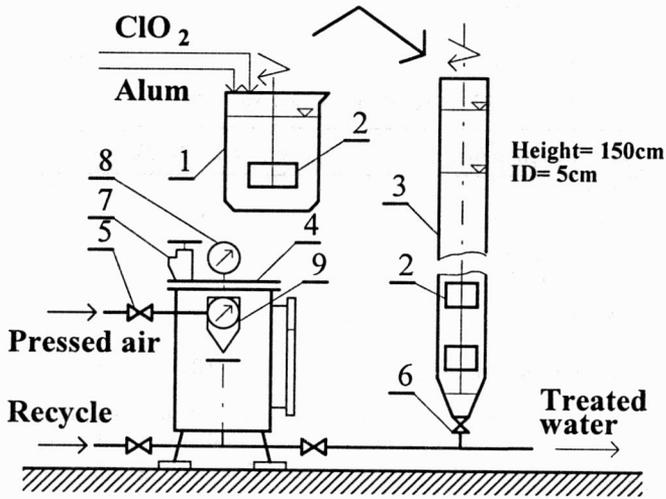


Fig. 2. Experimental set-up of the flocculation/flotation unit:  
 1 – reaction chamber, 2 – mixing paddle, 3 – flocculation/flotation column,  
 4 – saturation chamber, 5 – stop valve, 6 – recycle valve,  
 7 – vent valve, 8 – manometer, 9 – pressure-reducing valve

The laboratory flotation tests were conducted using a batch flocculation/flotation unit shown in figure 2. It consisted of pre-oxidation/rapid mixing chamber, flocculation/flotation column, and a pressure tank, which was initially filled approximately half-full with tap water. The air pressure in the tank was then raised to 0.42 MPa and the tank was allowed to stand for 10 min to supersaturate water with air.

The samples of water containing destabilized algal particles were poured into the flocculation/flotation column where the suspension was flocculated. Having the flocculation time completed, a stream of supersaturated water was released from the pressure tank to the base of the flotation column. Following 8 min of flotation time, a sample was withdrawn for algal concentration measurement.

## 4. RESULTS AND DISCUSSION

### 4.1. ALGAE REMOVAL BY DAF METHOD

Coagulation was a pretreatment step in the DAF process which aimed at destabilizing algal particles. Experiments were conducted on an algal suspension (*Scenedesmus* and *Ankistrodesmus*) of  $10^5$  cell/cm<sup>3</sup> which was coagulated by alum at pH of 6.8. Algal cells in the untreated water were negatively charged and showed a zeta potential of  $-47$  mV in the case of *Ankistrodesmus* and  $-27$  mV in the case of *Scenedesmus*. With an increase in the alum doses, a negative charge was reduced at the doses of  $60$  mg/dm<sup>3</sup> and  $40$  mg/dm<sup>3</sup> for *Ankistrodesmus* and *Scenedesmus* cells, respectively. Larger alum doses entailed the reversal of algal cells' charge into the positive range (figure 3).

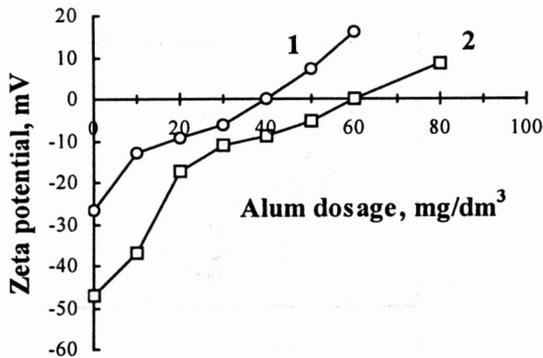


Fig. 3. Change of the zeta potential of *Scenedesmus* (1) and *Ankistrodesmus* (2) cells due to increasing the alum dosage

Table 2

Effect of alum coagulation on the removal of *Selenastrum capricornutum* cells ( $n_0$  of  $5.4 \times 10^5$ ) during DAF process at pH of 7.0,  $t_F$  of 10 min,  $P_{sat}$  of 0.4 MPa, and  $R$  of 10%

Alum dosage (mg/dm <sup>3</sup> )	Removal (%)	$A_{420}$ (m <sup>-1</sup> )
0	9.5	5.20
10	11.1	5.00
20	24.4	4.56
30	90.1	1.10
40	91.7	0.60
60	89.7	1.20
80	89.4	1.80

The data presented in table 2 show that the proper alum dosage is necessary to maximize the rate of algal removal, while the coagulant overdosage causes the proc-

ess deterioration. This can be attributed to the effects of the reversal of particle charge.

The recycle ratio and the saturation pressure had essential effect on the flotation efficiency of destabilized particles. Results of the investigation with *Selenastrum capricornutum* cells showed that algal removal of 69.2% to 91.2% could be obtained at the alum doses of 30 and 40 mg/dm<sup>3</sup>, respectively, and at the recycle ratio of 5% (figure 4). Larger alum doses resulted in particle destabilization. Separation of algal cells was improved for increased (10–15%) recycle ratio at the alum dose of 40 mg/dm<sup>3</sup> when the particle removal reached 95.9%.

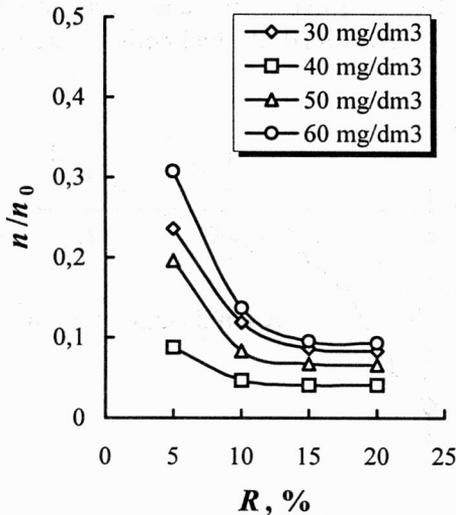


Fig. 4. Effect of recycle ratio on the removal of *Selenastrum* cells at different alum dosage ( $n_0 = 5.53 \times 10^5$  org/cm<sup>3</sup>;  $G = 10$  s<sup>-1</sup>;  $P_{\text{sat}} = 0.42$  MPa)

The contribution of the air-bubble volume fraction to the efficiency of the DAF process was investigated by varying the saturator pressure and maintaining a constant recycle ratio. The effect of saturation pressure on the efficiency of algal removal is shown in figure 5. Alum dosage, mixing intensity and recycle ratio were constant during that part of investigation. The most efficient algal removals, i.e. 99.2% of the *Scenedesmus* cells and 87.4% of the *Ankistrodesmus* cells, were obtained at the saturation pressure exceeding 0.45 MPa although further pressure increase did not cause significantly better results. Both the recycle ratio and the saturation pressure influenced the bubble volume concentration  $\Phi_b$ . Particle destabilization and large value of  $\Phi_b$  enabled a successful particle–air bubble attachment. It was shown that for the values typical of DAF practice, i.e. 0.48 MPa, 70% of saturator efficiency and 10% recycle, a large bubble-volume concentration of 5600 ppm was produced at 20 °C [9].

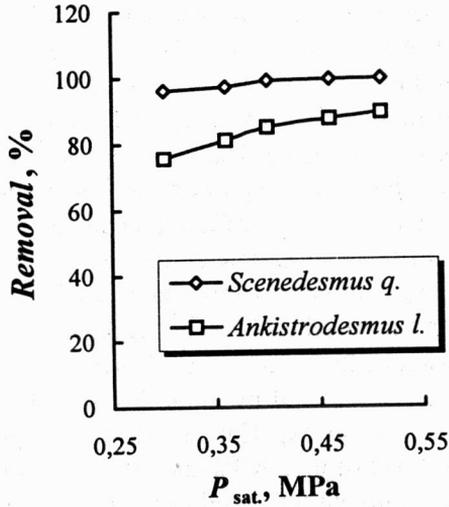


Fig. 5. Effect of saturation pressure on algal removal efficiency by DAF after alum coagulation ( $n_0$  of  $2.1 \times 10^4$ ; alum dosage,  $40 \text{ mg/dm}^3$ ;  $t_F$  of 10 min;  $G$  of  $10 \text{ s}^{-1}$ ;  $R$  of 15%)

Effect of flocculation time on the process efficiency was under investigation for different concentrations of *Ankistrodesmus* cells. Experiments were conducted in the very same hydrodynamic conditions ( $G$  value was about  $10 \text{ s}^{-1}$ ). Samples were withdrawn from flocculation column in certain time intervals and counted under the microscope and using the Fusch–Rosenthal chamber. The results obtained are shown in figure 6.

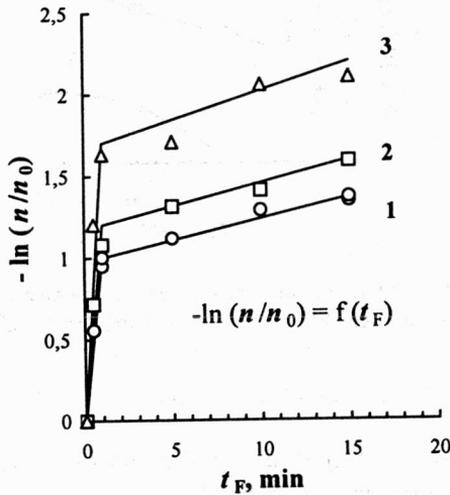


Fig. 6. Kinetics of the flocculation of *Ankistrodesmus* cells at different concentrations of algae and alum: 1 –  $1 \times 10^5 \text{ org/cm}^3$ , alum dosage,  $35 \text{ mg/dm}^3$ , 2 –  $2 \times 10^5 \text{ org/cm}^3$ , alum dosage,  $40 \text{ mg/dm}^3$ , 3 –  $4 \times 10^5 \text{ org/cm}^3$ , alum dosage,  $45 \text{ mg/dm}^3$

It was noticed that flocculation was a two-phase process. Initial 2–3 minutes of the operation were most important since during that time distinct algal agglomerates formation took place. Agglomeration rate was much slower in the second phase of the process. It was also observed that flocculation efficiency was higher in the case of greater algal cells concentrations since the value of  $\phi$  increased. That increase was caused not only by the greater density of algal suspensions, but also by higher alumn dosage strictly linked to them.

Determination of destabilization conditions enabled the undertaking of the experiments on the effect of flocculation time on the separation efficiency. Two kinds of raw water were used during that part of investigations. The first contained *Scenedesmus* cells whose concentration reached  $1.3 \times 10^5$  org/cm<sup>3</sup> and the other *Ankistrodesmus* cells with the concentration of  $2 \times 10^5$  org/cm<sup>3</sup>. Water samples with *Scenedesmus* and *Ankistrodesmus* cells were coagulated by alum doses of 40 mg/dm<sup>3</sup> and 50 mg/dm<sup>3</sup>, respectively. During the flotation experiments, saturation pressure and recycle ratio were kept at the constant level of 0.42 MPa and 10%, respectively. High volume fractions of air bubbles created favourable conditions for particle–bubble collisions. Figure 7 indicates that DAF enables entire removal of *Scenedesmus* cells after a short period of agglomeration lasting 2 to 3 min.

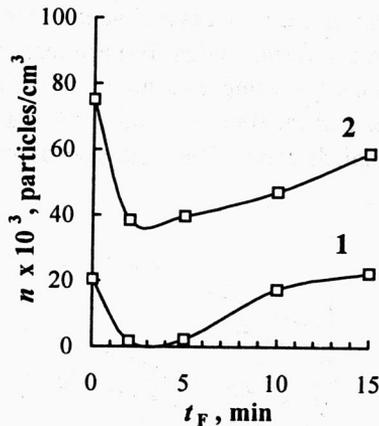


Fig. 7. Effect of flocculation time on algal cell number after flotation:  
 1 – *Scenedesmus*, alum dosage, 40 mg/dm<sup>3</sup>, 2 – *Ankistrodesmus*, alum dosage, 50 mg/dm<sup>3</sup>

#### 4.2. RESULTS OF ALGAE REMOVAL BY DAF WITH PRE-OXIDATION

The effects of flotation of agglomerated algal cells were amplified by the pre-oxidation treatment. Pre-oxidation with a low ClO<sub>2</sub> dose of 0.3 mg/dm<sup>3</sup> at the contact time of 30 minutes made algal particles destabilization easier and had a beneficial influence on the kinetics of the agglomeration. By adding ClO<sub>2</sub>, the negative charge of the *Ankistrodesmus* cells was reduced from –47 mV to –17 mV. Neutrali-

zation of particle charges (zeta potential equal to 0 mV) required 60 mg/dm<sup>3</sup> of alum if pre-oxidation was not applied and only 20 mg/dm<sup>3</sup> after ClO<sub>2</sub> introduction (figure 8).

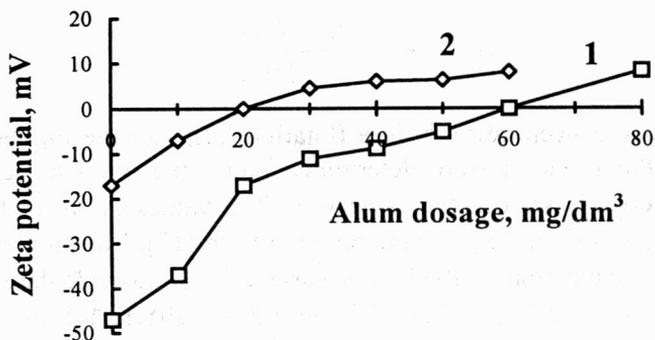


Fig. 8. Effect of alum dosage on zeta potential change of *Ankistrodesmus* cells without pre-oxidant application (1) and after introduction of ClO<sub>2</sub> in the dose of 0.3 mg/dm<sup>3</sup> (2)

Also kinetic studies of algal flocculation (see figure 9) showed that chlorine dioxide pre-treatment was useful in enhancing flocculation. ClO<sub>2</sub> attacked and modified the microalgal envelopes and thus enhanced flocculation by reducing colloidal stability of algal particles. The elongated cells of *Ankistrodesmus* were more susceptible to chlorine dioxide attack than *Scenedesmus* coenobia regarded as more resistant to algicide action.

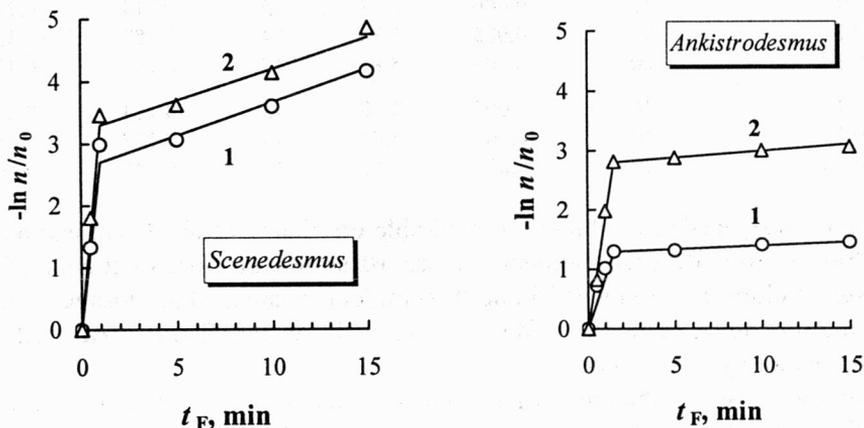


Fig. 9. Effect of pre-oxidation on flocculation efficiency of algal cells: 1 – without pre-oxidation, 2 – with application of ClO<sub>2</sub> at the dose of 0.3 mg/dm<sup>3</sup> and 30 min of contact time

The beneficial effect of pre-oxidation on algal agglomerate deposition at the air bubbles surface was evidenced by the increase in the coefficient  $\alpha_{pb}$ . The value of  $\alpha_{pb}$  was calculated according to equation (2) rearranged to the form:

$$\alpha_{pb} = \frac{-\ln(N/N_0)}{1.5 \phi_b \eta_{tot} (H/d_b)} \quad (5)$$

Particle number concentration before flotation ( $N_0$ ) and the number of particles remaining after the flotation were determined under the microscope. The particle diameters ( $d_p$ ) were assessed in the same way. The values of  $\Phi_p$  of 0.003 (at  $R$  of 10%),  $H$  of 1.0 m and  $d_b$  of 50  $\mu\text{m}$  were adopted from [19]. The single collector efficiency for particle deposition on the bubble surface ( $\eta_{tot}$ ) was calculated for  $kT$  of  $4.1 \times 10^{-21}$ ,  $g$  of  $9.81 \text{ m/s}^2$ , and  $\rho_w$  of  $998.23 \text{ kg/m}^3$  (at  $T = 298.13 \text{ K}$ ). Results of the calculations are shown in table 3. Pre-oxidation with  $\text{ClO}_2$  at the constant alum dosage assured the increase in separation efficiency entailing the increase in the value of  $\ln(N/N_0)$ . Pre-oxidation causing agglomerate diameters to diminish decreased the value of  $\eta_{tot}$ . As a result an increase of the value of  $\alpha_{pb}$  could be obtained.

Table 3

Effect of  $\text{ClO}_2$  dose on *Scenedesmus* agglomerates' attachment to air bubbles after alum coagulation

Pre-oxidant dosage (mg $\text{ClO}_2/\text{dm}^3$ )	Alum dosage (mg/ $\text{dm}^3$ )	$N/N_0$	$\ln(N/N_0)$	$d_p$ ( $\mu\text{m}$ )	$\eta_{tot}$	$\alpha_{pb}$
0	20	0.006	-5.12	15	0.214	0.27
0.15	20	0.005	-5.30	14	0.187	0.32
0.30	20	0.003	-5.81	12	0.137	0.47
0	30	0.005	-5.30	15	0.214	0.28
0.15	30	0.003	-5.81	14	0.187	0.35
0.30	30	0.001	-6.91	12	0.137	0.56

Less alum was needed to obtain a remarkable efficiency of algal removal as a result of chlorine dioxide pre-treatment. Figure 10 shows that pre-treatment with as small doses of chlorine dioxide 0.15 and 0.30 mg/ $\text{dm}^3$  enables alum dosage reduction from 40 mg/ $\text{dm}^3$  to 35 and 25 mg/ $\text{dm}^3$ , respectively during *Scenedesmus* cells' removal from water by DAF process.

Similar results were obtained when pre-ozonation was applied during investigations carried out in the potable water treatment plant in Moulle (France) [15]. The raw water was particularly rich in organic matter, with also algal blooms, so the coagulant doses were very high. Pre-ozonation improved the quality of clarified water and decreased the necessary coagulant doses.

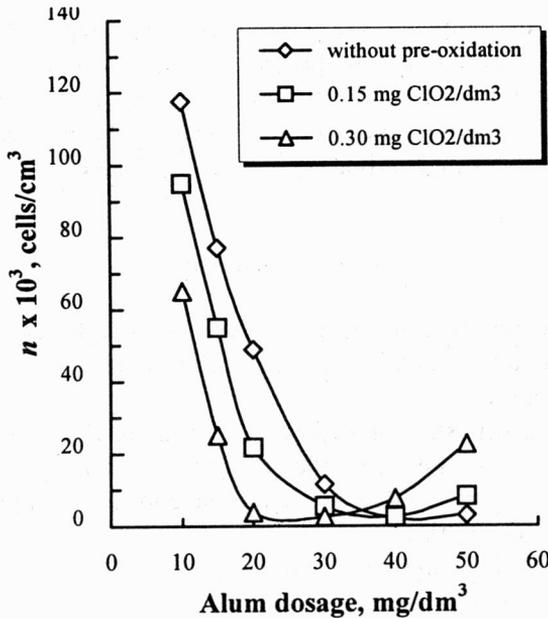


Fig.10. Effect of alum dosage on the removal of *Scenedesmus* cells after ClO<sub>2</sub> pre-oxidation during DAF treatment ( $P_{sat} = 0.42$  MPa,  $R = 10\%$ )

#### 4.3. OVERCOMING POSSIBLE CHLORINE DIOXIDE DRAWBACKS

Chlorine dioxide as a strong oxidant can be considered as an excellent alternative to pre-oxidation of drinking water for several reasons. The oxidative efficiency of chlorine dioxide is not impaired over a wide pH range. It does not react with such chlorine-demanding materials as ammonia and other nitrogenous compounds. It destroys taste-producing phenolic compounds, and also serves as an algicide. Chlorine dioxide readily dissolves in water to form solution that is biocidal to a wide range of microorganisms [16]. The use of chlorine dioxide as a pre-oxidant minimizes the formation of THMs that are common with chlorination [17].

Nevertheless, chlorine dioxide like ozone is a very unstable oxidant and must be generated on site from sodium chlorite. What is more important, some inorganic by-products of ClO<sub>2</sub> are known to be unhealthy, namely chlorite ion (ClO<sub>2</sub><sup>-</sup>) and chlorate ion (ClO<sub>3</sub><sup>-</sup>). Effective use of chlorine dioxide as an alternative pre-oxidant in water treatment may require removal of by-product, i.e. chlorite ion (ClO<sub>2</sub><sup>-</sup>). Ferrous iron appears to be extremely effective in removing undesirable ClO<sub>2</sub> and ClO<sub>2</sub><sup>-</sup> residuals from finished water. The use of ferrous iron following ClO<sub>2</sub> treatment will greatly minimize residual oxidant levels in the finished water [18], [19].

Finally, pre-oxidation with  $\text{ClO}_2$  may be regarded as a step for the enhancement of algal cell removal, but this requires the protections against breakthrough of dissolved organic carbon (DOC) produced during its attack on organic material. Safe and effective purification of algal-laden waters is possible if DOC barriers, such as further oxidation or a granular activated carbon (GAC), are available.

## 5. CONCLUSIONS

From the data presented the following conclusions were drawn:

1. Dissolved-air flotation (DAF) can be applied in treating eutrophic waters of high algal concentrations.
2. Flocculation time was short in order to avoid large flocs' formation. Flocculation periods shorter than 5 minutes provided a good performance of the DAF process.
3. Alum doses were lower than those used in the conventional process as there was no need to produce large-size flocs.
4. Pre-oxidation with chlorine dioxide dose of  $0.2\text{--}0.3 \text{ mg/dm}^3$  improved algal agglomeration during flocculation step.
5. The short detention time of water to be treated in flotation unit (5–15 min) can reduce the capital costs of treatment that would typically require the detention time of up to 4 h if conventional settling tanks were used.
6. It was found that saturation pressure should exceed 0.4 MPa so as not to deteriorate the efficiency of the process.
7. Ferrous iron can be used for removing undesirable  $\text{ClO}_2$  and  $\text{ClO}_2^-$  residuals from finished water.

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WPLYW WSTĘPNEGO UTLENIANIA GLONÓW  
DWUTLENKIEM CHLORU  
NA ICH USUWANIE METODĄ FLOTACJI CIŚNIENIOWEJ

Przeprowadzono doświadczenia nad usuwaniem zielenic (*Chlorophyceae*) z wody metodą flotacji ciśnieniowej obejmujące ich wstępne utlenianie dwutlenkiem chloru i koagulację siarczanem glinu. Badania prowadzono w laboratorium, używając instalacji porcjowej. Skuteczność tej metody była związana z parametrami procesów aglomeracji i separacji. Aby stworzyć warunki sprzyjające przyłączeniu się mikroaglomeratów do kolektorów (pęcherzyków powietrza), należy zdestabilizować cząstki. Parametry aglomeracji to: dawki wstępnego utleniacza ( $\text{ClO}_2$ ) i koagulantu (siarczanu glinu), pH, jak również czas i intensywność mieszania podczas flokulacji, a parametry separacji to: stopień recyrkulacji i ciśnienie saturacji. Flotacja ciśnieniowa umożliwia zderzenia pomiędzy zdestabilizowanymi cząstkami i pęcherzykami powietrza, skracając długi czas flokulacji. Dzięki flotacji ciśnieniowej poprzedzonej wstępnym utlenianiem i koagulacją za pomocą siarczanu glinu otrzymuje się klarowną wodę, która zawiera tylko niewielką ilość glonów przy znacznie ograniczonych dawkach koagulantu.

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