Environment Protection Engineering

Vol. 28 2002 No. 2

ANDRZEJ JODŁOWSKI*

EFFECT OF PRE-OXIDATION ON FLOCCULATED ALGAL CELLS AUTOFLOTATION

Oxygen produced by algae can deteriorate their removal by conventional sedimentation process as a result of algal agglomerates autoflotation. Laboratory experiments were carried out to test the effect of water pre-oxidation on the improvement of algal removal by coagulation/flocculation process followed by sedimentation. The autoflotation of algal agglomerates was reduced as a result of chlorine, chlorine dioxide and potassium permanganate application before alum introduction. The autoflotation was partly reduced after pre-treating the algae with ozone and irradiating them with gamma rays. The chlorine demand (Cl.D.) of purified water, being used as a measure of water contamination with organics, was increased when hydrogen peroxide or gamma irradiation was used in the pre-oxidation step. That increase was due to the reaction between hypochlorous acid and hydrogen peroxide remaining in the water after pre-oxidation.

1. INTRODUCTION

Algae growing in surface waters used for municipal water supply form stable suspensions as a result of their morphological and cell surface properties. Algal removal during potable water treatment by the conventional coagulation/flocculation/filtration presents a serious problem because they interfere with the coagulation/flocculation, which makes sedimentation difficult and causes clogging of filters. Algae contribute to a remarkable portion of trihalomethanes (THMs) precursors in the water submitted to chlorine disinfection. They also impart unpleasant tastes and odors. Though the particles of fresh-water algae are larger than those of true colloids, they can be considered as biocolloids carrying a negative charge. Destabilization and agglomeration of algae can be accomplished by several coagulants. A high efficiency of algal removal from water can be achieved with alum and polyelectrolytes [1]–[3]. Better removal can be accomplished with ferric salts, and especially with lime, because of the formation of heavy flocs [4], [5]. Nevertheless the successful separation cannot always be obtained and the

* Faculty of Civil Engineering, Architecture and Environmental Engineering, Department of Water Management, Technical University of Łódź, 6 Politechniki Ave., 90-924 Łódź, Poland. E-mail: anjodl@ck-sg.p.lodz.pl

flotation of agglomerated algal particles is often observed.

It could be observed that such a partial flotation occurred naturally during sedimentation of flocculated algae [6]. Depending on the number concentration, growth phase and algae population composition, either sedimentation or flotation of agglomerates can be observed during treating the algal-laden water. The phenomenon of flotation occurs due to the entrapment of oxygen bubbles produced internally by algae within flocs structure.

The pre-oxidation can be applied in order to hamper an algal vital activity and to reduce the amount of oxygen produced [7], [8]. The application of oxidants results in an effective removal of algal cells together with other colloids and suspensions from treated water during sedimentation after coagulation/flocculation. It was stated that during the surface water treatment the pre-oxidation should be used for the process facilitation when the algae concentration approaches 500 cells/cm^3 [9]. The purpose of this study was to determine the effect of pre-oxidation with chosen oxidants on algal removal by the coagulation/flocculation process. Chlorine, chlorine dioxide, potassium permanganate, hydrogen peroxide, ozone and gamma irradiation were used as the pre-oxidation means. In the study, the autoflotation stoppage under certain test conditions was used as a criterion for the estimation of oxidants effect on the improvement of water treatment.

2. EFFECT OF THE OXYGEN PRODUCED BY ALGAE ON WATER TREATMENT

Algae are an oxygen source during daylight hours due to the process of photosynthesis. Higher levels of nutrients lead to high primary production with strong effect of biomass and dissolved oxygen on water quality and treatment. Biochemical reaction for photosynthesis resulting in the algal biomass and oxygen production is as follows [10]:

$$106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 122\,H_2O + 18\,H^+ + \text{microelements} + \text{energy}$$

$$\xrightarrow{\text{photosynthesis}} \{C_{106}H_{263}O_{110}N_{16}P\} + 138\,O_2\,. \qquad (1)$$

Algae use carbon dioxide in photosynthesis resulting in high pH, especially in waters of low alkalinity. Often some acid must be added to the purified algal-laden water to adjust pH which makes coagulation possible during water treatment with inorganic coagulants. Algal biomass and extracellular products create precursors of THMs during chlorination, especially in waters coming from eutrophic reservoirs.

Large amounts of oxygen produced by algae can interfere with the sedimentation of algal agglomerates. At a certain temperature and under certain pressure conditions the bubbles are secreted when the oxygen concentration exceeds the saturation level.

It was stated that the rate of oxygen evolution by an algal culture in the linear phase of growth was a logarithmic function of light intensity [11]. The rate of oxygen evolution per unit volume of suspension was linearly related to the reciprocal value of culture thickness. The amount of oxygen produced is approximately 1.65 g O_2/g of algal dry mass [12] and suffices to induce autoflotation of the algal agglomerates. The amount of oxygen can be so high that it might seem reasonable to apply the process of autoflotation during algal removal from high-rate algal ponds effluents [13].

3. EXPERIMENTAL PROCEDURES AND MATERIALS

3.1. ALGAL CULTIVATION

The experiments were carried out using the water contaminated by algal suspensions prepared under laboratory conditions. Algae for the experiments were collected from the Sulejów reservoir which serves as a source of water supply for the city of Łódź. Algae were then cultivated in 10 dm^3 bell jars in a medium containing nutrients. A medium with 40 mg of CaO, 0.4 cm^3 of 5% $MgSO_4$ solution, 0.5 cm^3 of 1% $Ca(NO_3)$ solution and 0.5 cm^3 of 1% KH_2PO_4 solution in 1 dm^3 of distilled water was used as the source inorganic nutrients [14].

The contents of the cultivation reactors were mixed by means of compressed air. In this way, the culture was also enriched with carbon dioxide. "Coolwhite" fluorescent lamps with the intensity of 200–250 lm/m^2 served as the light source. Algae were cultured at a temperature of 20–22 °C.

3.2. PRE-OXIDATION AND COAGULATION

Pre-oxidation was used for algal activity control. Aqueous solutions of chlorine gas of a concentration of 500 mg Cl_2/ dm^3, chlorine dioxide of a concentration of 350 mg ClO_2/dm^3, 0.05% aqueous solution of potassium permanganate and 1.5% aqueous solution of hydrogen peroxide were applied during pre-oxidation. Aqueous solution of chlorine was prepared by saturation of distilled water with chlorine gas from a cylinder. Chlorine dioxide was produced in the laboratory from potassium chlorate. Aqueous solutions of potassium permanganate and hydrogen peroxide were prepared by dissolving the reagents in distilled water. All solutions were titrated before application to determine their concentration. The pre-oxidation of the oxidants listed above was carried out in reaction vessels of 250 cm^3 for 60 minutes at a pH of approximately 7.0 at 20 °C. The contents of reaction vessels were mechanically agitated with a constant velocity of about 100 rpm.

Pre-ozonation was applied as a process that enabled algal cells to diminish their

vital activity. The contact time of raw water with ozone–air mixture ranged from 2 to 20 minutes. Ozone was generated by water cooling apparatus produced by Instytut Mechaniki Precyzyjnej in Warsaw. Ozone doses ranged from 2 to 17 mg O_3/dm^3.

The purified water was also exposed to gamma irradiation before coagulation. The irradiation of water samples containing algae was conducted in an irradiation chamber equipped with a ^{60}Co energy source (Międzyresortowy Instytut Techniki Radiacyjnej, Politechnika Łódzka). Samples were placed in the irradiaton chamber for the appropriate time to be irradiated with a desired dose. Dose rate applied to samples was of 5 kGy/h. The exposure time varied from 6 to 120 minutes.

Aluminium sulfate of commercial grade in the form of 5% aqueous solution was introduced into the treated water after its pre-oxidation. Coagulation tests were carried out in a multiple stirrer unit. The coagulant dose of 100 mg/dm^3 established during preliminary investigations was kept constant throughout the entire experiment. A three-minute period of rapid mixing at 200 rpm was followed by a 15-minute period of flocculation at 30 rpm. Period of rapid mixing allowed pH measurement and its adjustment by HCl solution in each of the ten 0.5 dm^3 beakers.

3.3. SEPARATION OF ALGAL AGGLOMERATE SUSPENSION

At the end of the flocculation period, samples were transferred to a test stand in order to assess floc settleability. Separation of algal agglomerate suspension was observed on a set of ten separatory funnels exposed to a 300 lm/m^2 light source. The flow-diagram of the laboratory investigations is shown in figure 1.

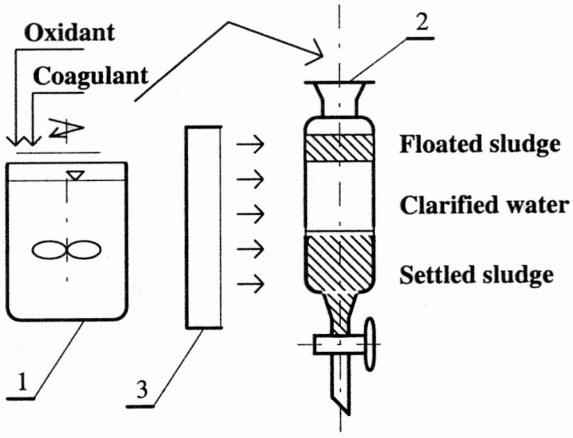

Fig. 1. Experimental setup for separation of agglomerated algal suspension:
1 – reaction chamber, 2 – separatory funnel, 3 – light screen

Flocculated algal cells were exposed to light for a constant period of 60 minutes and no separation was observed. Two or three zones could be distinguished in the water column (clarified water, sedimented sludge and/or floated sludge), depending on the oxidant applied and its dose. Fifty cm^3 samples of clarified water were taken from the middle zone for physical-chemical and hydrobiological analyses. Then 200 cm^3 sample was extracted from the lower layer. The remainder of the sample (250 cm^3) was used to assess suspended solids (SS) concentration. The fraction of algal suspension being subjected to autoflotation was used to calculate the rate of autoflotation (A) according to the formula:

$$A = \frac{c_f \, V_f}{c_0 \, V_0}, \tag{2}$$

where c_f and c_0 are the concentrations of the floating sludge suspension and the initial suspension, respectively (mg SS/dm^3), V_f and V_0 are the volumes of the floating sludge zone and the sample, respectively (dm^3).

Having $V_f = 0.25$ dm^3 and $V_0 = 0.50$ dm^3, the autoflotation rate A could be obtained from the formula:

$$A = 0.5 \, c_f / c_0 \, . \tag{3}$$

Some water samples were subjected to a coagulation/flocculation/separation process and then to paper filtration. The water treatment efficiency was determined on the basis of algal cells' elimination.

Hydrobiological analyses were carried out using an inverted light microscope following sample fixation using Lugol fluid and sedimentation over 24-hour period. Chlorophyll-a was identified in raw water samples by the extractive/colorimetric method.

3.4. ASSESSMENT OF PURIFIED WATER CHLORINE DEMAND

In order to define conditions necessary for the removal of algal suspensions, the chlorine demand (Cl.D.) of the water being treated had to be determined. Cl.D. was used as a measure of organics' concentration in the purified water. Three raw water samples of the volume of 3 dm^3 were treated. Different doses of pre-oxidants were added to the two water samples. The third sample being a control was subjected to coagulation only. For the clarified water the Cl.D. was determined for a 30-minute reaction time and chlorine doses of 1–7 mg Cl_2/ dm^3 after sludge separation.

4. RESULTS AND DISCUSSION

The water being treated was polluted with algae and their metabolites. The composition of algal species in the water under investigation is shown in table 1. *Scene-*

desmus quadricauda, *Anabena flos-aquae* and *Dictyosphaerium* sp. were recognised as the dominant algal species. The number of cells ranged from 726×10^3 to 1255×10^3 per 1 cm^3, while the concentration of the chlorophyll-a was in the range of 135–370 μg/ dm^3. The concentration of suspended solids ranged from 100 to 270 mg/dm^3, water colour, from 120 to 245 mg Pt/dm^3, turbidity, from 110 to 190 mg/dm^3.

Table 1

Algal species in the water under investigation

Taxons	Percentage in total algal number, %
Cyanophyta	
Oscilatoria sp.	+
Anabena flos-aquae	9–33
Microcystis wesenbergii	+
Gloecapsa sp.	+
Bacillariophyceae	
Synedra ulna	+
Melosira varians	+
Stephanodiscus sp. 11	
Cyclotella sp.	17
Fragilaria sp.	+
Navicula sp. +	+
Nitzschia acicularis	+
Chlorophyta	
Scenedesmus quadricauda	36–80
Scenedesmus acurninautus	+
Scenedesmus ecornis +	
Pediastrum boryanum +	+
Pediastrum duplex	+
Dictyosphaerium sp.	8–28
Filamentous green algae	3–7
Separated green algae	+
Dinophyceae	
Ceratium hirundinella	+
Total cell count in 1 cm^3, $\times 10^3$	726–1255

(+) too small number of algal cells for counting.

The flotation test revealed that a sludge had a tendency to floate despite an efficient algal agglomeration during the coagulation/flocculation run. The value *A* calculated for algal-laden water after coagulation/flocculation was in the range from 50 to 75%. The efficiency of algal removal, assessed by a comparison of the concentration of suspended solids in the clarified zone with their initial concentration, varied from 76 to 87%. The coagulation/flocculation efficiency expressed as the difference be-

tween the cell number logarithms before and after treatment was in the range of 0.62 log–0.90 log (table 2).

Table 2

Logs of algal removal within treatment trains

Oxidants and their doses (mg/mg SS)	Treatment train			
	Coagulation/ flocculation	Pre-oxidation/ coagulation/ flocculation	Coagulation/ flocculation filtration	Pre-oxidation/ coagulation/ flocculation/ filtration
Chlorine, 0.025 mg Cl_2/mg SS	0.72	0.92	3.79	4.52
Chlorine dioxide, 0.015 mg ClO_2/mg SS	0.90	2.61	3.56	5.74
Potassium permanganate, 0.050 mg/mg SS	0.62	1.05	3.56	5.49
Hydrogen peroxide, 0.100 mg/mg SS	0.82	1.09	3.69	4.04
Ozone, 0.040 mg/mg SS	0.94	1.12	3.40	4.10
Gamma irradiation, 1.5 kGy	0.90	1.31	3.04	5.56

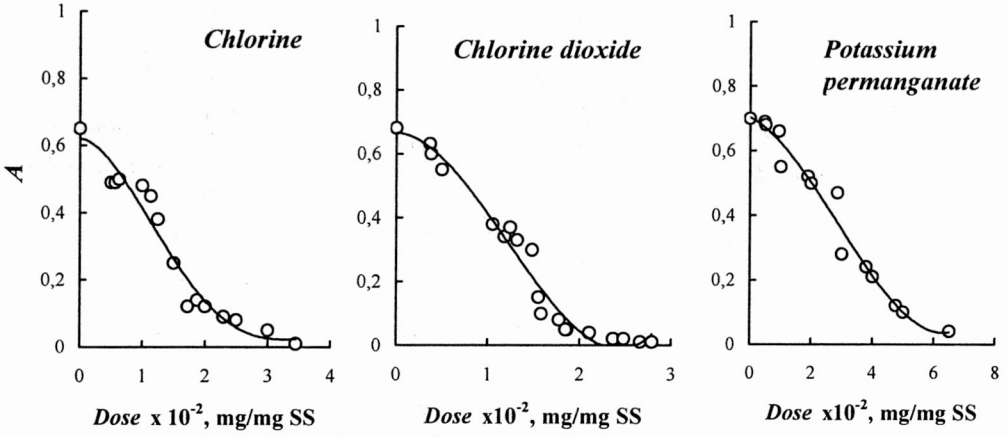

Fig. 2. Effect of pre-oxidation with chlorine, chlorine dioxide and potassium permanganate on flotation rate of flocculated algae

The pre-oxidation applied before coagulant introduction eliminated or diminished sludge autoflotation, especially in the presence of such oxidants as chlorine, chlorine

dioxide and potassium permanganate. It was found that for each of these oxidants there was a certain dose beyond which autoflotation ceased (figure 2). The investigation revealed that the smallest dose confining the autoflotation of algal agglomerates was that of chlorine dioxide. The dose of 1.8×10^{-2} mg Cl_2/mg SS corresponded to a flotation rate of $A = 0.01$. Chlorine and potassium permanganate in the respective doses of 2.3×10^{-2} mg/mg SS and 4.6×10^{-2} mg/mg SS were required for the same flotation rate.

Quite different results were obtained when hydrogen peroxide, ozone and gamma irradiation were used during the pre-oxidation step of treatment (figure 3). As small dose as 1.0×10^{-2} mg H_2O_2/mg SS resulted in easy floating of agglomerates at the top of the water column. A similar result was observed when ozone was used. Although small doses (1×10^{-2} mg O_3/mg SS) improved the efficiency of agglomerates' separation (autoflotation rate A was of 0.5), higher doses intensified flotation. Gamma irradiation of water sample prior to coagulation produced interesting results. Autoflotation ceased at the irradiation dose approaching 2 kGy. Prolonged exposure of raw water to irradiation was responsible for a better absorption of gamma rays and increase in the flotation rate. The value of A reached 0.9 at the irradiation dose of 4 kGy.

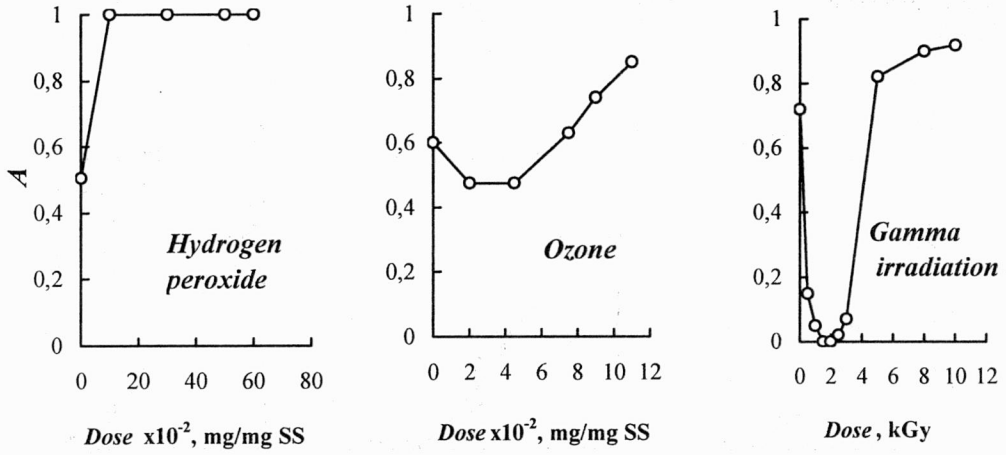

Fig. 3. Effect of pre-oxidation with hydrogen peroxide, ozone and gamma irradiation on flotation rate of flocculated algae

Both separation processes, i.e. settling and flotation, were more efficient after pre-oxidation. Based on the hydrobiological investigation we could state that algae were removed more efficiently when pre-oxidation was applied. Pre-chlorination by chlorine, chlorine dioxide and potassium permanganate improved algal removal during coagulation up to 94%, 99.7% and 91%, respectively. The application of hydrogen

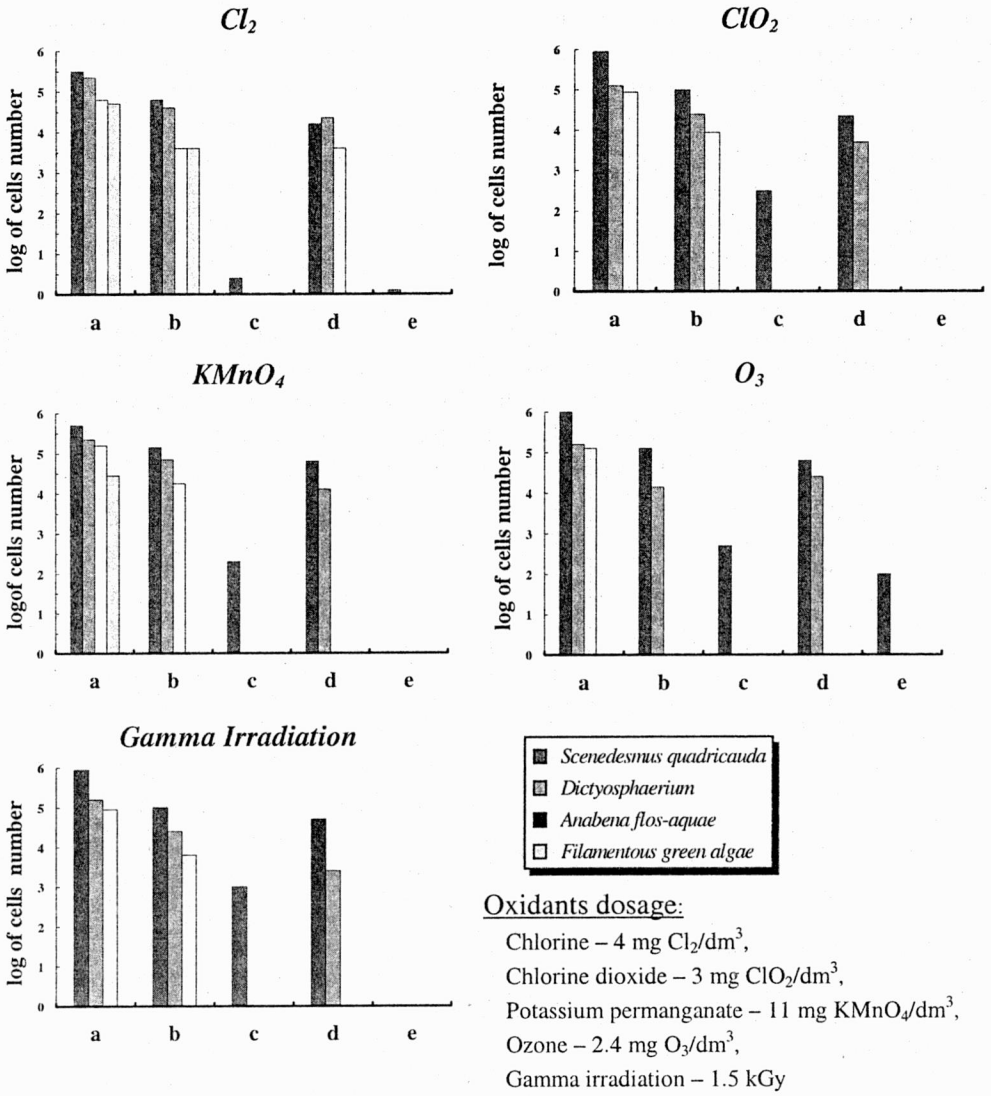

Fig. 4. The number of algae in water after certain purification stages:
raw water (a); water after coagulation/flocculation (b); water after coagulation/flocculation/filtration (c);
water after pre-oxidation/coagulation/flocculation (d);
water after pre-oxidation/coagulation/flocculation/filtration (e)

peroxide or ozone resulted in 92% algal removal. Over 95% of algae were removed from water being purified at such dose of gamma irradiation that ceased agglomerate flotation. Almost complete algal removal from water occurred after pre-oxida-

tion/coagulation/filtration. High efficiency of these purification steps is supported by the values in table 2. The efficiency of algal removal ranged from 4 log to almost 6 log (99.99%–99.9999%). Figure 4 shows the number of organisms in the raw water and in samples taken from the clarified zone after pre-oxidation/coagulation/flocculation/filtration. Some results are shown additionally for coagulation/flocculation only and also for coagulation/flocculation/ filtration. Green algae, *Scenedesmus quadricauda* (dimensions of about 4 μm × 9 μm), a common species which can be found in several types of surface waters, proved to be most resistant to this purification process.

It was observed that pre-oxidation comprised in the water treatment train influenced the quality of purified water. The effect of pre-oxidation on the quality of purified water was revealed by the changes in its chlorine demand (Cl.D.). A distinct decrease in Cl.D. of water being pre-oxidized by chlorine, chlorine dioxide and potassium permanganate was compared to the Cl.D. of water undergoing coagulation/flocculation only. The ratio of chlorine demand of water after the coagulation preceded by oxidation (Cl.D.) to chlorine demand of the sample after coagulation only ($Cl.D.^0$) is shown in table 3.

Table 3

Effect of pre-oxidation on chlorine demand (Cl.D.) of the water treated

Oxidant	Oxidant dosage, mg/mg SS	$Cl.D./Cl.D.^0$
Chlorine	0	1.0
	2.0×10^{-2}	0.55
	3.5×10^{-2}	0.34
Chlorine dioxide	0	1.0
	5.5×10^{-2}	0.48
	7.5×10^{-2}	0.31
Potassium permanganate	0	1.0
	1.5×10^{-2}	0.68
	2.5×10^{-2}	0.35
Hydrogen peroxide	0	1.0
	20.0×10^{-2}	1.75
	40.0×10^{-2}	2.25
Ozone	0	1.0
	1.0×10^{-2}	0.62
	5.0×10^{-2}	0.40
Gamma irradiation (kGy)	0	1.0
	3	0.75
	6	1.75

Chlorine dioxide was responsible for the most pronounced decrease in Cl.D., while hydrogen peroxide – for the increase in Cl.D. Gamma irradiation at the dose of

1.5 kGy caused a Cl.D. decrease, and after applying 5.0 kGy, the Cl.D. increased. The Cl.D. increase is disadvantageous to final disinfection. Chlorine may have been consumed during the reaction with hydrogen peroxide remaining in the water or with the products of water radiolysis that also occurs with H_2O_2. This reaction is as follows:

$$HOCl + H_2O_2 \rightarrow O_2 + HCl + H_2O\,. \tag{4}$$

In this case, hydrogen peroxide is a dechlorinating agent.

The improvement of coagulation/flocculation efficiency was probably induced by the algal susceptibility to agglomeration after pre-oxidation. The pre-oxidant overdosage caused cell disrupting which deteriorated the quality of the water being treated. The production of THMs (regarded as potentially cancerogenous) takes place during pre-chlorination of algal-laden water [15], [16]. Chlorine cannot be recommended as the pre-oxidant despite its advantageous effect on the coagulation.

5. CONCLUSIONS

1. Autoflotation of algal agglomerates during clarification ceased after coagulation/flocculation preceded by pre-oxidation of algal-laden water with chlorine, chlorine dioxide and potassium permanganate. Autoflotation rate was reduced in a certain dosage range of ozone and gamma irradiation. Intensification of flotation was observed in the samples treated with hydrogen peroxide.

2. All oxidizing agents being tested improved the susceptibility of algal cells to coagulation, hence their removal from water.

3. Hydrogen peroxide (in the whole dosage range) as well as gamma irradiation (at the doses over 2 kGy) caused an increase in the Cl.D. value during final disinfection as a result of formation of compounds of a lower oxidizing potential.

REFERENCES

[1] TENNEY M.W., ECHELBERGER W.F., SCHUESSLER R.G., PAVONI J.L., *Algal Flocculation with Synthetic Organic Polyelectrolytes*, Appl. Microbiol., 1969, 18(6), 965–971.

[2] MCGARRY M.G., *Algal Flocculation With Aluminum Sulfate and Polyelectrolytes*, Jour. WPCF, 1970, 42, R191–R201.

[3] TILTON R.C., MURPHY J., DIXON J.K., *The Flocculation of Algae with Synthetic Polymeric Flocculants*, Wat. Res., 1972, 6, 155–164.

[4] SPEEDY R.R., FISHER N.B., MCDONALD D.B., *Algal Removal in Unit Processes*, Jour. AWWA, 1969, 61(6), 289–292.

[5] STEYNBERG M.C., PIETERSE A.J.H., GELDENHUYS J.C., *Improved Coagulation and Filtration of Algae as a Result of Morphological and Behavioural Changes Due to Pre-oxidation*, J. Water SRT – Aqua, 1996, 45(6), 292–298.

[6] VUUREN VAN L.R.J., DUUREN VAN F.A., *Removal of Algae from Waste-Water Maturation Pond Effluent*, Jour. WPCF, 1965, 37, 1256–1262.

[7] BERNHARDT H., CLASEN J., *Flocculation of Micro-organisms*, J. Water SRT – Aqua, 1991, 40(2), 76–87.
[8] SUKENIK A., TELTCH B., WACHS W., SHELEF G., NIR I., LEVANON D., *Effect of Oxidants on Microalgal Flocculation*, Wat. Res., 1987, 21(5), 533–539.
[9] SHULER R.L., AFENS W.A., *Effect of Light Intensity and Thickness of Culture Solutions on Oxygen Production by Algae*, Appl. Microbiol., 1970, 19, 76–86.
[10] STUMM W., MORGAN J.J., *Aquatic Chemistry. Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley and Sons Inc., New York, 1996.
[11] GLOYNA E.F., *Waste Stabilization Pond Design*, WHO Course, Vol. 4, *Waste Treatment Plant Design and Operational Control*, Austin, 1967.
[12] TUROBOYSKI L., *Hydrobiologia techniczna*, PWN, Warszawa, 1979.
[13] SANDBANK E., VUUREN VAN L.J., *Microalgal Harvesting by in situ Autoflotation*, Wat. Sci. Tech., 1987, 19(12) 385–387.
[14] ZADIN W.J., *Metody badań hydrobiologicznych*, PWN, Warszawa, 1966.
[15] HOEHN R.C., BARNES D.B., THOMPSON B.C., RANDALL C.W., GRIZZARD T.J., SHAFFER P.T.B., *Algae as Sources of Trihalomethane Precursors*, Jour. AWWA, 1980, 72(6), 344–350.
[16] OLIVER B.G., SHINDLER D.B., *Trihalomethanes from the Chlorination of Aquatic Algae*, Environ. Sci. Technol., 1980, 14(12), 1502–1505.

WPŁYW WSTĘPNEGO UTLENIANIA NA AUTOFLOTACJĘ GLONÓW PODDANYCH FLOKULACJI

Tlen powstający w wyniku fotosyntetycznej aktywności glonów może zmniejszać skuteczność ich usuwania metodą konwencjonalnej sedymentacji pokoagulacyjnych aglomeratów glonowych. Przeprowadzono badania laboratoryjne, aby sprawdzić skuteczność wstępnego utleniania wody podczas usuwania z niej glonów w procesie konwencjonalnej koagulacji/flokulacji. Autoflotacja glonów zmniejszyła się po zastosowaniu chloru, dwutlenku chloru i nadmanganianu potasu przed koagulacją spowodowaną przez siarczan glinu. Autoflotacja została częściowo ograniczona po zastosowaniu ozonu i promieniowania gamma. Zapotrzebowanie chloru, wykorzystane w badaniach jako miernik zawartości związków organicznych w wodzie oczyszczonej, zwiększyło się po zastosowaniu nadtlenku wodoru i promieniowania gamma w wyniku reakcji kwasu podchlorawego z nadtlenkiem wodoru.