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Potential Ozone Applications for Water/Wastewater Treatment

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Abstract: Several applications of ozonation were examined in this study for:

i. the treatment of stabilized high strength municipal landfill leachates,
ii. the reclamation potential and toxicity reduction of municipal secondary effluents, and
iii. the removal potential of phytoplanktons from surface waters.

The major parameters examined were the applied ozone dosage and the respective contact time. The application of single ozonation on leachates resulted in the efficient removal of color and organic loading, due to the respective oxidation, induced by ozonation. In addition, ozonation was found to be effective for the removal of the residual organic content of secondary municipal effluents. However, acute toxic effects after ozonation were observed on *V. fischeri* and were related to ozone concentration and contact time. Furthermore, the surface water used for drinking water production, was subjected to ozonation treatment for the removal of harmful cyanobacteria. Ozonation resulted in the reduction of the number of

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cyanobacteria species and in the breakage of the chain-type species to cells with a lower number of atoms.

Keywords: Ozonation, phytoplankton removal, wastewater treatment, reclamation, toxicity reduction

INTRODUCTION

Ozone is a highly oxidative agent, reacting directly or via a hydroxyl radical mechanism with organic and inorganic compounds. It has been found that ozone may increase the biodegradability of organic pollutants (including natural organic matter) and induce the efficient inactivation of a wide range of microorganisms (1). Therefore, the ozonation process may be applied as an effective disinfection technique, as well as an efficient treatment method for upgrading wastewater or drinking water quality.

Several ozone applications have been reported for the treatment of both wastewater and water, according to their characteristics and the required effluent quality. Landfill leachates are considered heavily polluted wastewaters with complex composition, while their characteristics are site specific (2). Due to the specificity and complexity of landfill leachates many treatment techniques have been investigated. In particular, treatment of old (stabilized) leachates by coagulation and ozonation are recommended among other methods (3). Coagulation followed by flocculation is considered a rather simple technique; however, only moderate removals of COD have been reported, while excess sludge volume may be produced during the process (2, 4). On the other hand, ozonation may result in the transformation of initially contained recalcitrant compounds into biodegradable products, or even to CO_2. However, as a single process, oxidation with ozone may not be economically favorable, mainly due to the applied high ozone doses (5). Therefore, ozonation is part of a multistage treatment process. In this study, ozonation was applied to old leachates using rather low ozone doses in a bubble column reactor.

The treatment of municipal secondary effluents by ozonation results in both effective disinfection of effluents and removal of residual organic loading (6, 7). Nevertheless, due to the complex nature of the wastewaters, organic substances are not completely degraded by ozone, resulting in the formation of several by-products, such as aldehydes, carboxylic constituents, and brominated organics (1). In order to estimate the overall environmental impact of ozonated wastewaters, few studies have been conducted, incorporating bioassays along with physicochemical and microbiological determinations (7). Moreover, the results from these studies are rather contradictory and inconclusive; i.e. Takanashi et al. (8) found that ozone treatment was effective for the removal of wastewater mutagen precursors, whereas other researchers (9, 10) did not observe any significant change in the toxic response of ozonated secondary effluents on crustaceans and fish.

In surface waters, the presence of phytoplankton contributes significantly to the augmentation of organic matter, whereas it is associated also with odor and taste problems of potable water (11, 12). Cyanobacteria are common members of the freshwater phytoplankton communities in surface waters and are of major concern when surface water is used as drinking water source (13). Moreover, the European Water Framework Directive 2000 (2000/60/EC) characterizes the cyanobacteria as high-priority water pollutants and potential key hazardous pollutants. Therefore, the elimination of cyanobacteria and their toxins (produced by algae) by water treatment systems is of major concern. Coagulation/flocculation and/or filtration has been shown ineffective in removing cyanobacteria and their toxins, since the removal rates are moderate (14). Moreover, if the load of cyanobacteria cells entering a treatment plant becomes very large, i.e. $10^5 - 10^6$ cells per millilitre, these processes become less effective (15). Activated carbon filters can be very effective; however, high activated carbon doses are required frequently. Therefore these filters are used as the last step prior to disinfection (Falconer, 2004). Membrane filtration is mentioned as a promising technology to obtain high removal efficiencies, (16) yet membrane processes are associated with certain operational problems. Furthermore, ozonation is regularly used as a pre-oxidation step of organic matter prior to the coagulation process (followed by filtration) and/or as a final purification/disinfection step, during the treatment of surface waters for the production of drinking water (1). The use of chemical oxidation by ozone could effectively deal with these problems by damaging the phytoplankton organisms and helping in their efficient removal. In general, the application of ozone and its corresponding efficiency for the reduction of pollutants content is associated with the particular experimental conditions, i.e. to reaction time and ozone dosage.

The objective of this study was the investigation of the ozonation process as a potential method for the treatment of surface waters and wastewaters (landfill leachates and secondary effluents). In particular, the aims of this work included the study of the efficiency of ozonation on

i. the removal of certain pollutants from landfill leachates,
ii. the inactivation of microorganisms, existing in secondary effluents (i.e. for disinfection),
iii. the toxic properties of secondary effluents before and after ozonation, and the removal of phytoplankton from surface waters.

The aforementioned will be exemplified through the presentation of selected results from our current research.

MATERIALS AND METHODS

The samples that were studied in this work included sanitary landfill leachates, secondary municipal effluents, and surface water. Leachates were collected

from the stabilization (accumulation) pond of a municipal landfill site of Thessaloniki (N. Greece) in plastic carboys. Samples were transported to the laboratory, stored at 4°C and analyzed within 2 d, according to the standard methods of chemical analysis (17), for the determination of the following parameters: pH, BOD_5, COD, color and UV absorbance at 254 nm. The pH value of the samples was about 8, with a rather high non-biodegradable organic content (BOD_5= 840 mg/L; COD= 5050 mg/L), corresponding to a BOD_5/COD ratio of 0.17; the collected samples could be classified as stabilized or "old" leachates.

Secondary municipal wastewaters were collected from the small sewage treatment plant of Chortiati village, Thessaloniki, located in Northern Greece. Samples were collected in plastic containers from the outlet channel prior to chlorination and transferred to the laboratory for further analysis and treatment. Secondary wastewater and treated samples were subjected to analysis, including pH, absorbance at wavelength 254 nm, chemical oxygen demand (COD), nitrite-nitrogen (NO_2/N) and residual ozone in liquid phase, according to standard methods (17). These samples were also examined for microbiological content including total coliforms, faecal coliforms, and *E. coli*, after being kept at 4°C for 14 hours, using the method of the Most Probable Number (17). The toxic effects of the raw and treated effluents were estimated using the marine bacteria *Vibrio fischeri* (Microtox test) that were in freeze-dried form and activated prior to use by a reconstitution solution. The bacterium *V. fischeri* was chosen as the test organism because of its wide use, and its simplicity and rapid response to toxic samples. The Microtox test was based on the measurement of bioluminescence inhibition of the bacteria within a short exposure time (15 min) on the samples (90% sample concentration). The light emission of test organisms, obtained by their direct contact with the samples, was measured using the Microtox 500 Analyzer (SDI).

Surface waters were collected from Polyphytos Lake, located in Northern Greece, in plastic containers. The samples prior to and after treatment were subjected to physicochemical analysis, including turbidity and absorbance at 254 nm. In addition, the species of phytoplankton were identified using the microscopes ZEISS ID03 and NIKON TE 200-S, and the taxonomic study by Nuygaard (18). The samples were preserved with Lugol and formalin, and were left from 6 to 24 hours to settle in the specific settling chambers of the inverted microscope.

Ozonation experiments were performed in a laboratory semi-batch column reactor, consisted of a 200 cm long cylindrical tube with a 4 cm internal diameter. A Schott ceramic porous diffuser (porosity 4, 10–16 μm) was placed in the bottom of the reactor for ozone introduction. Compressed and dried atmospheric air, at a flowrate of 3-4 L/min, was used for the production of ozone by an ozone generator (Model TOGC2A, Ozonia). All experiments were performed at room temperature using 1 L sample, for various reaction contact times between 2 and 240 min. The applied ozone dosages varied from about 2 to 8.3 mg O_3/L. In all cases, the applied ozone doses

refer to the ozone concentrations in the gas phase. At the end of the desired reaction time, samples were withdrawn from the reactor and were further analysed for the determination of physical, chemical and biological properties and for the estimation of process efficiency.

RESULTS AND DISCUSSION

Ozonation of Landfill Leachates

The raw leachate undergoes anaerobic treatment during its percolation through the bulk volume of landfilled solid wastes, whereas additional stabilization may take place in the artificial pond itself, which is acting as a facultative stabilization pond and results to the production of a relatively stabilized leachate, characterized by high content of refractory organics and alkaline pH values (19). These substances have been observed after biological treatment of landfill leachates, resulting in COD values of about 1000 mg/L (20). In order to examine the treatment of stabilized leachates, an artificial sample with a stable desired composition was prepared, by diluting the leachate samples with tap water using a ratio leachate:water = 1:5. Ozonation of the diluted sample carried out in the bench scale reactor system under an applied ozone dosage of 2.0 g O_3/h, corresponding to about 8.3 mg O_3/L, and a contact time ranging from 15 to 240 min. The effect of reaction time on the removal of certain physicochemical characteristics (color, absorbance at 254 nm, and COD) is depicted in Fig. 1.

As shown in Fig. 1, significant decolorization was observed during ozonation, resulting in more than 95% reduction of color after 120 min of contact time. Similar results have been presented by other investigators in

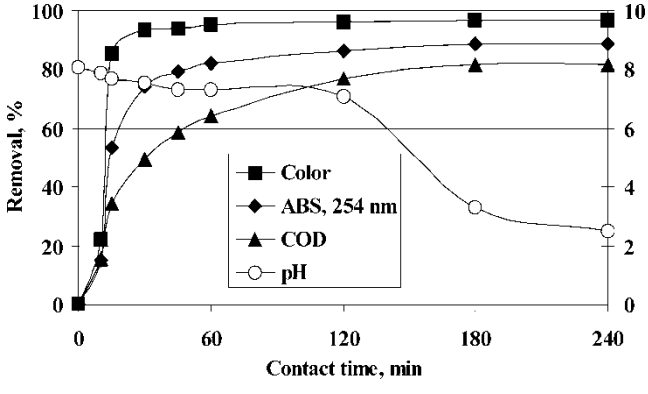

Figure 1. Reduction of color, UV absorbance at 254 nm and COD content, as a function of contact time, during the ozonation experiments of landfill leachates (initial values: color = 2310 units; UV_{254nm} = 6.76; COD = 1010 mg/L).

recent studies (2). During the current study, the initial dark brown color of the leachate sample, attributed to the presence of humic substances, became light yellow by the oxidation ozone reaction. In addition, the decolorization rate was remarkably high during the initial stages of the ozonation reactions. In the initial 30 min of ozonation the observed color removal was more than 90%. After prolonged reaction time the removal of color reached up to 97%. Similarly to the decolorization reactions, the reduction of UV absorbance took place by a high rate during the initial stages of ozone treatment, which however decreased after prolonged reaction times, leading to an equilibrium stage. The reduction of absorbance after 30 min of reaction time was 74%. Furthermore, as shown in Fig. 1, the COD removal rate followed a similar pattern to the corresponding profile of absorbance reduction; however, a lower COD removal capacity was observed than the color and UV absorbance reduction capacity. During the initial reaction stage (up to 30 min), COD values were decreased substantially (down to 500 mg/L), while after extended reaction times (3 h), COD values reached the value 185 mg/L, corresponding to an overall removal rate of 81%.

The reduction of color could be attributed to the direct attack of ozone on carbon double bonds in the chromophoric groups, resulting to the formation of "bleached" products, such as aliphatic acids, ketones and aldehydes; these reactions are taking place at a high rate and are almost completed during the initial reaction stages (1). Similarly to the decolorization reactions, the reduction of UV absorbance took place by a high rate during the initial stages of ozone treatment, which however ceased at prolonged reaction times reaching an equilibrium. The UV absorbance values can be considered as an indication of organic compounds containing unsaturated carbon bonds, such as aromatic compounds contained in wastewaters in the form of humic-like substances (21). These compounds are generally recalcitrant for biodegradation, and a decrease of absorbance results in an increase of biodegradability potential of the sample. The reduction of UV absorbance could be attributed to the reaction of ozone with the unsaturated bonds and the aromatic rings, leading to the splitting of bonds and the dissociation of the rings according to the Criegee mechanism (1). The chemical oxidation is accomplished by two mechanisms, a molecular ozone reaction (direct oxidation) and a hydroxyl radical reaction mechanism (indirect oxidation). In general, the first mechanism is dominating during acidic conditions, while the latter is the main mechanism under alkaline conditions (1). The pH values of ozonated samples were measured and it was found that pH decreased from 8 to about 2.5 at prolonged ozonation time. Therefore, the initial sharp removal of color could be attributed to both direct and indirect oxidation mechanisms, while after prolonged oxidation times direct oxidation was dominant. As shown also in Fig. 1, the initial reduction of measured parameters was observed for pH values of the treated leachate around 8, confirming the presence of both direct and indirect oxidation. However, measurements of alkalinity (about 1060 mg/L) revealed that the most

dominant mechanism at this stage was that of direct oxidation due to the presence of carbonate ions, which act as scavengers of OH^- radicals (1). Further treatment resulted in lower rates of pollutants removal and in a rapid decrease of pH value (direct oxidation was the main mechanism). After 240 min of reaction, color removal exceeded 80%, indicating the presence of residual non-chromophoric compounds containing aromatic rings or unsaturated bonds that could not be further oxidized by ozone. In addition, the observed COD removal capacities may be related to the initial composition of stabilized leachates; these leachates are usually characterized by a considerable fraction of organic substances with high molecular weight and recalcitrant characteristics that are usually removed by ozone treatment (22). At short reaction times, ozone oxidation of easily degradable organics took place; at extended times, the reaction rate was decreased, due to the lower activity of by-products formed during the initial stages, such as aldehydes and ketones, as well as due to the presence of recalcitrant compounds.

Ozonation of Secondary Effluents

The application of ozonation for the production of high quality reclaimed wastewaters was also examined as an alternative disinfection method to chlorination. Ozonation is considered as an efficient method for the disinfection of wastewaters; however, it should be noted that, contrary to chlorination, ozonation has no residual effect. Special emphasis was given to the investigation of the toxic properties of the samples by the application of bioassays, and their modification due to ozone activity. The applied ozone concentrations in the feed gas were 5.0, 7.0, and 8.2 mg/L, whereas the corresponding reaction time was varied between 5 and 40 min. The initial values of the measured physicochemical parameters were 70 mg/L COD, 0.4 cm^{-1} UV absorbance, pH 7.7, 1.1 mg/L NO_3/N, 0.1 mg/L NO_2/N, and 2.0 mg/L PO_4/P. Most of the physicochemical parameters values decreased during the ozone disinfection process with the reaction time. However, the dose of the ozone proved to be the most significant parameter of the process. COD removal as a function of ozone doses and reaction time is shown in Fig. 2. As shown in this figure, COD removal reached up to 90% at prolonged periods and at the highest ozone dosage. However, at short reaction times and low ozone doses, low COD removals were obtained, lower than 60%. Comparable COD removal values have also been reported in the literature, but in most cases the organic matter reduction did not exceed 50% (7).

On the other hand, UV absorbance was reduced only after ozonation with 8.2 mg O_3/L. Lower doses were not effective in attacking and dissociating the unsaturated bonds and aromatic rings of organic matter. The pH of samples increased slightly after ozonation and reached up to 8.6 after ozonation with 8.2 mg O_3/L and could be attributed to the formation and stripping of

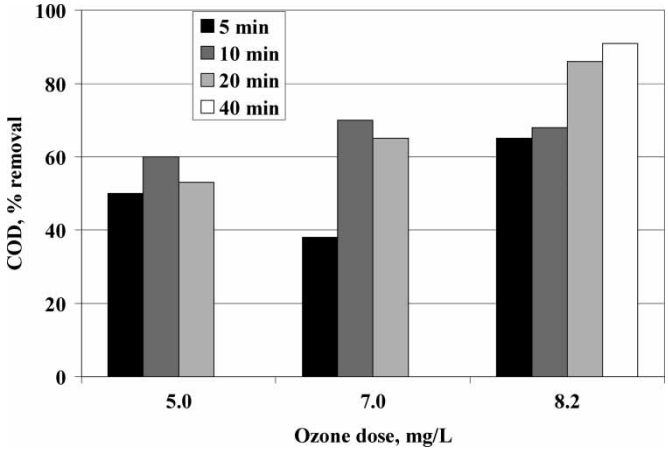

Figure 2. COD removal of ozone treated effluents as a function of ozone dosage and retention time.

carbon dioxide and volatile fatty acids content (23). Therefore, indirect oxidation, which takes place during the application of high ozone doses (alkaline pH conditions), is more effective for the degradation of organic matter (resulting from COD measurements).

Effluents nitrite-nitrogen contents were higher than the influents values at ozone concentrations below than 8.2 mg/L, resulting in negative removal capacities. The increase in nitrite-nitrogen content was attributed to the oxidation of organic and ammonia nitrogen. Secondary effluents from the activated sludge unit were characterized by high ammonia-nitrogen content, exceeding 40 mg/L. However, at the high ozone dosage, almost complete nitrite-nitrogen removal was achieved, especially at long reaction times. The removal of nitrite nitrogen was attributed to their oxidation towards nitrate-nitrogen (1). Measurement of residual ozone revealed that ozone concentrations exceeding 0.044 mg/L were detected only in experiments conducted at high ozone concentrations.

Microbiological analysis was performed on the ozone-disinfected samples for the determination of biological factors and the results are presented in Table 1, for the two different ozone dosages (5 and 7.0 mg/L respectively). According to these results, *Total Coliforms* and *Feacal Coliforms* were substantially removed after disinfection of samples, using an ozone concentration of about 7.0 mg/L. *Enterococcus sp.* were more resistant bacteria, but operation at higher contact time proved to be efficient enough, even when ozone doses were applied. At higher dose (7.0 mg/L) the removal efficiency increased to more than 95%, while certain measurements after ozonation with 8.2 mg O_3/L, showed that ozone destroyed completely *Enterococcus sp*., even during the first 2 min of reaction.

Table 1. Microbiological analysis of the secondary effluents treated at various ozone dosages and reaction times

		Ozone dose: 5.0 mg/L				Ozone dose: 7.0 mg/L		
	Secondary effluents	5 min	10 min	20 min	40 min	5 min	10 min	20 min
Total Coliforms	460000	43000	24000	24000	4600	2400	2400	2400
Faecal Coliforms	93000	24000	24000	4600	4600	2300	2300	2400
E. coli	93000	24000	24000	4600	4600	2300	2300	2400
Enterococcus sp.	460	230	230	230	460	460	460	460

These results were similar to those reported by Lazarova et al. (24), indicating that high ozone doses should be applied in order to achieve the stringent microbiological requirements, applied for wastewater reuse. However, Liberti and Notarnicola (6) showed that coagulation and sand filtration of secondary effluents, followed by disinfection at an ozone dosage of 15 mg/L, was not sufficient for the adequate removal of *total coliforms*, whereas Xu et al. (10) stressed that the ozone dosage was the key factor for the efficient performance of a wastewater ozonation process, proposing that the optimum disinfection treatment should be carried at ozone dosages between 2 and 15 mg/L, depending upon the quality of raw effluents. This study revealed that the ozone dosage was the key factor for the effective removal of the measured microbiological parameters.

The determination of ecotoxic effects of ozonation on aquatic species *V. fischeri* are illustrated in Fig. 3. The bacteria were exposed to samples treated by various ozone doses for 10 min contact time and the emitted bioluminescence was recorded after 5 and 15 min of exposure time. The secondary effluents indicated a negative response on *V. fischeri*, denoting the existence of rather stimulation effects. Stimulation results were observed for the ozonated samples, treated by 2.5 – 5.5 mg/L of ozone applied dose. This stimulation was attributed to the presence of nutrients or contaminants in the water samples, in non-lethal concentrations, that might affect the bioluminescence activity of *V. fischeri*, requiring a more careful examination of sample characteristics and the respective interpretation of obtained results (25). Noticeable positive effects were observed after disinfection using higher doses of ozone. Disinfection at ozone doses of 6.8 and 8.2 mg/L caused about 20% and 60% inhibition of *V. fischeri*, regardless the exposure time of bacteria on the ozonated samples.

A stimulation response is produced when a sample light level is higher than the control light output. In such a case, the light stimulation (as a result of exposure to low levels of contaminants) can also represent toxicity. The

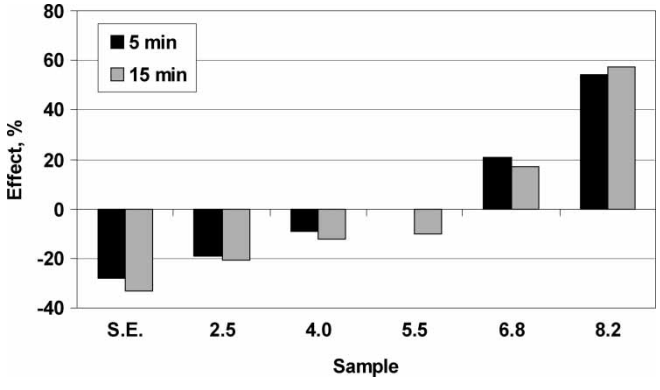

Figure 3. Toxicity of treated effluents after ozonation, at various ozone doses.

frequency of occurrence and magnitude of light stimulation in the Microtox test can be affected by several factors (26). These include the type and level of contaminants, test temperature, test procedure, sample characteristics and the age of the reagent after reconstitution. Hormesis may occur when an organism overcompensates while combating the effects of low levels of stress. Although hormesis may initially sound like a beneficial reaction, it should not be assumed that it is a phenomenon with a positive effect on the organisms. The total amount of energy available to an organism is limited by the available amount in the environment and the resources devoted by the organism for gathering additional energy. When a finite amount of available energy is spent on one task, such as survival, residual energy is no longer available to the organism to perform other tasks, such as growth or reproduction. Energy spent on a hormesis is not necessarily used in the most efficient manner. Anything that reduces an organism's efficiency will affect its ability to survive.

The toxic effects of high ozone doses could be attributed to by-products that might be formed during the reaction of ozone with the residual pollutants, presented in the reclaimed wastewaters in trace concentrations (27). It should be also stressed that although almost complete removal of the microorganisms was achieved and high removal rate of certain pollutants were observed, when using the highest ozone dose, the reclaimed water might cause significant adverse effects on aquatic life, according to the results of these bioassays.

Ozonation of Surface Waters

Surface water samples were collected from the Polyphytos Lake, near Kozani city, Northern Greece, which is used as the principal drinking water source for Thessaloniki. The presence of phytoplanktonic organisms and especially the most toxic cyanobacteria, producing the harmful cyanotoxins (28) was investigated in this work, together with the potential removal capacity after ozonation. Cyanobacteria on the upper layers of surface water reservoirs may be originating from the disposal of untreated municipal wastewaters in water aquifers and represent the main factor for the development of "algal blooms"; the evolution of cyanobacteria populations is sensitive to the composition (quality) of surface waters, and monitoring of these populations may be used as an indicator of the surface water condition (28). During preliminary investigation of Polyphytos surface water, about $2.99 \cdot 10^6$ phytoplanktonic cells/L were measured, containing about 0.5% of cyanobacteria; *Aphanizomenon sp.* was the most abundant species.

The removal of the cyanobacteria species was examined by ozone treatment of water samples. Surface water samples were collected from Polyphytos reservoir and were ozone treated using ozone dosages between 1.0 to 8.2 mg O_3/L, at contact times 1, 2.5 and 5 min. The effect of both the ozone dose and the contact time on the abundance of cyanobacteria species is illustrated in Fig. 4.

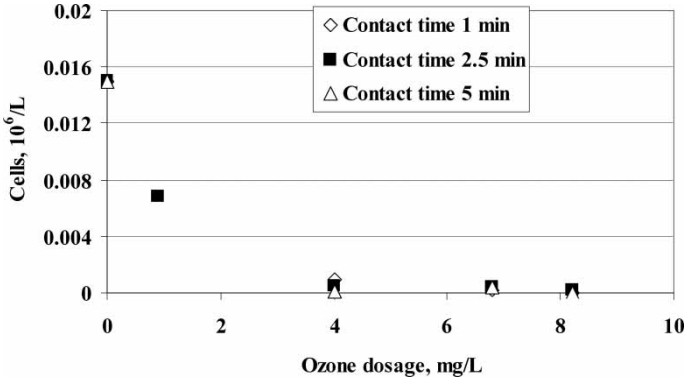

Figure 4. Effect of ozone dose and contact time on the population of cyanobacteria, in surface water samples.

As shown in Fig. 4, the ozone dose was the most significant factor for the removal of cyanobacteria. Ozone dose of 4.0 mg/L resulted in noticeable removal of cyanobacteria, even after 1 min of reaction time, whereas when using extended ozonation time, cyanobacteria were not detected at this ozone dose. Ozonation at higher doses (above 6.5 mg O_3/L) resulted in almost complete removal of cyanobacteria from the samples. Investigation of the composition of the cyanobacteria species in raw and treated water revealed that although the population of cyanobacteria decreased significantly by ozone treatment, the cells were not completely damaged (oxidized). Cells structure was altered severely i.e. ozonation of the nematode cyanobacteria with a chain structure, resulted in the breakage of the chain and in the formation of cells with a smaller number of atoms. Most published studies refer to ozonation as a pre- or post- treatment step to water clarification processes. Thus, the applied ozone doses are low, not exceeding 1 mg O_3/L. In many cases, moderate (as it was observed also in this study) or even higher removal rates have been observed; however, the cells were not damaged severely making possible the existence of cyanobacteria toxins (12, 14, 15).

CONCLUSIONS

In this study, several potential applications of ozonation for the treatment of wastewaters, as well as of surface waters were shortly examined. Ozonation of stabilized landfill leachates using 8.3 mg O_3/L resulted in a significant reduction of color after 120 min of ozonation time, while organic matter removal (in terms of COD) reached 81% after 240 min of ozonation time. The ozone dose was the major factor affecting the disinfection process of secondary effluents; the ozone dose of 8.2 mg/L resulted in complete removal of pathogenic bacteria after 5 min of ozonation time, whereas

lower doses resulted in lower removal rates. However, ozonation using the highest dose of 8.2 mg/L caused adverse effects on the bacteria *V. fischeri*, indicating that the ozonated samples showed acute toxic properties. Furthermore, ozonation proved to be an efficient technique for the removal of cyanobacteria species, which are considered as responsible for cyanotoxin releases in drinking water supplies.

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