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EFFICIENCY OF OZONATION FOLLOWED BY FILTRATION THROUGH A BIOLOGICALLY ACTIVE ADSORPTION BED AT REMOVING BIOGENIC ORGANIC SUBSTANCES FROM SURFACE WATER

Water entering the plant varies significantly in the content of total organic carbon and its fractions. The treatment train includes coagulation, sedimentation, rapid sand filtration, ozonation, biofiltration, disinfection and alkalization. The study aimed at assessing the applicability of ozonation, followed by biological filtration, to remove organic substances from surface water. Upon coagulation, sand filtration, ozonation, adsorption onto a biological activated carbon filter (BAF), and disinfection with chlorine and chlorine dioxide, water samples differed considerably in organic matter content before ozonation, as well as before and after biofiltration. The ozonation process brought about a reduction in total organic carbon and dissolved organic carbon concentrations, which was concomitant with a significant increase in the concentrations of biodegradable dissolved organic carbon fractions and in assimilable organic carbon. This may be attributed to the transformation of non-biodegradable substances to lower molecular weight compounds that are easier to assimilate by the microorganisms normally colonizing an adsorption bed. Even though the substances that originated from the ozonation process were effectively removed during biofiltration, the extent of removal was still insufficiently high to provide desired biological stability of the water. A benefit of biofiltration was efficient removal of refractory substances as a result of adsorption. The efficiency of the ozonation and biofiltration processes at removing organic substances increased in proportion with the increase in their concentrations in the water being treated.

1. INTRODUCTION

Microbial regrowth during water transport in distribution systems (and this includes pathogens) is one of the detrimental effects observed when water entering the water-pipe network is lacking in biological stability [1–3]. To prevent regrowth, it is necessary to provide effective removal of such biogenic substances supporting growth

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of heterotrophic microorganisms. Biogens contain not only inorganic substrates, i.e. phosphates and inorganic nitrogen (N_{inorg}=NH_4^+ + NO_2^-), but also biodegradable fractions of organic substances, i.e. biodegradable dissolved organic carbon (BDOC) and assimilable organic carbon (AOC). The limit concentrations for nutrients in biologically stable water have not been clearly defined; they depend on the microorganisms present in water being treated and on the disinfectants applied. The limit concentrations of biogens for water disinfected with chlorine compounds are: 0.01 g P/m^3 (0.03 g PO_4^{3-}/m^3), 0.2 g N_{inorg}/m^3, 0.2 g C/m^3 for BDOC and 0.05 g C/m^3 for AOC [4, 5].

To reduce the organic nutrient content in water being treated to the limit values, it is necessary to extend the treatment train by inclusion of such unit processes that will enable effective removal of low-molecular-weight organic substances. Effective removal of biodegradable organic fractions (generally from surface water) is possible with a treatment train involving biologically active filtration (BAF, referred to as biofiltration) through a granular carbon bed [5–9]. Biofiltration is preceded by ozonation, where non-biodegradable organic substances are rendered biodegradable [10, 11], thus providing nutrient supply for the microorganisms that colonize the BAF bed. The extent of organic compound ozonation and the extent of high-molecular-weight organic matter degradation to forms assimilable by microorganisms growing on the BAF bed are influenced by the rate of the organic substance's reaction to ozone and by the ozone dose applied [12]. Biofiltration also enables effective removal of toxins during periods of algal blooms [13].

The efficiency of BDOC and AOC removal via biofiltration depends on a variety of factors, specifically on the structure, type and concentration of organic matter present in water, on water temperature [14], as well as on the activity of the microorganisms for biochemical oxidation of the organic biogens that are to be removed [15].

The aim of this work was to assess the efficiency of biofiltration, with ozonation as a prior step, at removing organic nutrients from surface water.

2. SCOPE OF THE STUDY AND METHODS

The efficiency of biofiltration at removing organic nutrients from surface water with ozonation as a prior step was tested in a water treatment plant, where surface water was treated by volume coagulation, sedimentation, rapid sand filtration, ozonation, biofiltration, disinfection and alkalization. Ozonation was conducted with various ozone doses (obtained from tonnage oxygen), which in the period of investigations ranged between 0.51 and 4.60 g O_3/m^3 (0.183–0.726 g O_3/g C). The time of water contact with ozone varied from 48.0 min to 82.3 min. Biofiltration was conducted with a WG Gryfskand active carbon bed colonized by microorganisms.

The water treatment plant operates 12 filter beds, 1.5 m deep. During our studies, filtration rate ranged from 2.1 to 3.7 m/h, whereas the time of contact between water

and BAF bed varied from 27.1 min. to 46.5 min. Samples were collected from water mains prior to ozonation, as well as before and after biofiltration.

The study was conducted for 23 months; water samples for analyses were collected at monthly intervals. All samples were analyzed for total organic carbon (TOC), dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), as well as UV absorbance (UV_{254}), temperature and pH were measured. Non-biodegradable dissolved organic carbon (NBDOC) was determined from the difference between DOC and BDOC. Eleven water samples were also analyzed for assimilable organic carbon (AOC). The limit concentrations adopted for biologically stable disinfected water amounted to 200 mg C/m^3 and 50 mg C/m^3 for BDOC and AOC, respectively [4, 5]. Sampling and water quality analyses were performed in compliance with relevant Polish standards; only BDOC and AOC were determined according to the procedures recommended in Standard Methods.

3. RESULTS AND DISCUSSION

Before ozonation, the surface water being treated was characterized by a highly variable content of organic substances (Table 1), where the dissolved fraction was dominant, ranging from 72.4% to 100.0% of total organic carbon, with the exception of one sample, where the dissolved fraction was 47.1% of TOC.

Table 1

Water quality parameters measured before ozonation as well as before and after biofiltration

Parameter	Ranges of water quality parameters			Efficiency of (removed during)	
	Before ozonation	Before biofiltration	After biofiltration	Ozonation [% (g/m^3)]	Biofiltration [% (g/m^3)]
Temperature, °C	0.6–21.6	0.4–21.7	0.5–21.7	–	–
pH	6.8–7.8	6.8–7.8	6.7–7.6	–	–
TOC, g C/m^3	1.62–6.91	1.24–6.71	0.80–4.32	2.6–31.2 (0.10–1.95)	9.2–54.5 (0.39–2.58)
DOC, g C/m^3	1.45–5.88	1.15–5.70	0.75–3.82	2.1–30.8 (0.08–1.45)	9.0–55.5 (0.32–2.49)
BDOC, mg C/m^3	111–442	230–770	98–345	4.7–181.1[a] (0.014–0.370)	30.4–84.4 (0.07–0.529)
AOC, mg C/m^3	20–180	70–280	20–100	33.3–350.0[a] (0.023–0.100)	50.0–77.3 (0.040–0.180)
NBDOC, g C/m^3	1.27–5.48	0.82–4.93	0.62–3.70	9.5–49.2 (0.320–1.650)	3.2–54.3 (0.060–2.065)
UV_{254}, m^{-1}	4.06–15.62	2.74–9.44	1.16–6.68	1.3–60.1 (0.08–8.18)	6.7–72.4 (0.34–4.90)

[a]Increase of concentration.

UV absorbance was also found to vary within a wide range of values (from 4.06 to 15.62 m^{-1}), which suggests that the content of aromatic organic substances reacting with ozone differed from one water sample to another.

The proportion of BDOC to DOC varied from 4.6% to 13.2%. In spite this, only 29.2% of the surface water samples showed BDOC concentrations lower than those admissible for biologically stable water, and only 5 out of 11 samples contained less than 50 mg C/m^3 of AOC, which accounted for 16.7–50.7% of BDOC and 1.4–3.4% of DOC.

The ozonation process brought about a reduction in total organic carbon (ΔTOC = 0.10–1.95 g C/m^3) which was concomitant with a rise (from 87.5% to 91.7%) in the proportion of water samples with TOC values lower than those admissible for drinking water. As expected, BDOC and AOC followed a reverse pattern (Fig. 1); after ozonation, their concentrations in the water samples increased, on average by 66.4% and 107.2%, respectively.

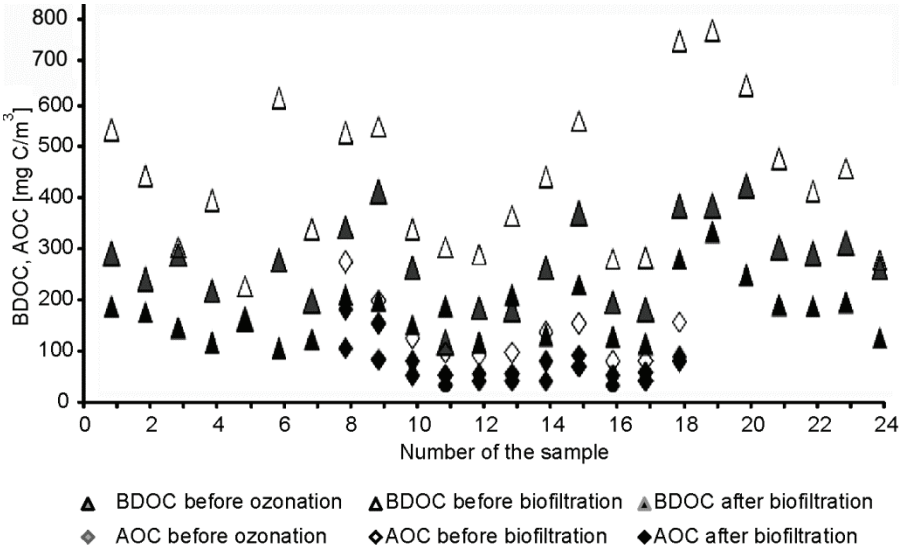

Fig. 1. BDOC and AOC concentrations in surface water before ozonation, before and after biofiltration

In all samples examined, the transformation of high-molecular-weight substances into simpler and biodegradable forms, which occurred during ozonation, not only caused the concentrations of BDOC and AOC to reach levels exceeding the limit values for biologically stable water, but also improved the proportions of BDOC and AOC to DOC (Fig. 2).

In the course of the ozonation process, non-biodegradable dissolved organic substances (NBDOC) were rendered biodegradable, and some of the NBDOC fractions were completely oxidized. There is also some evidence to suggest that certain amounts

of BDOC and AOC might were subject to mineralization. The quantity of oxidized dissolved organic matter varied between 0.08 and 1.45 g C/m^3. The oxidation of aromatic organic compounds and their transformation to lower molecular-weight forms concurred with reduction in the UV_{254} value varying from 0.08 m^{-1} to 6.18 m^{-1} (60.1%).

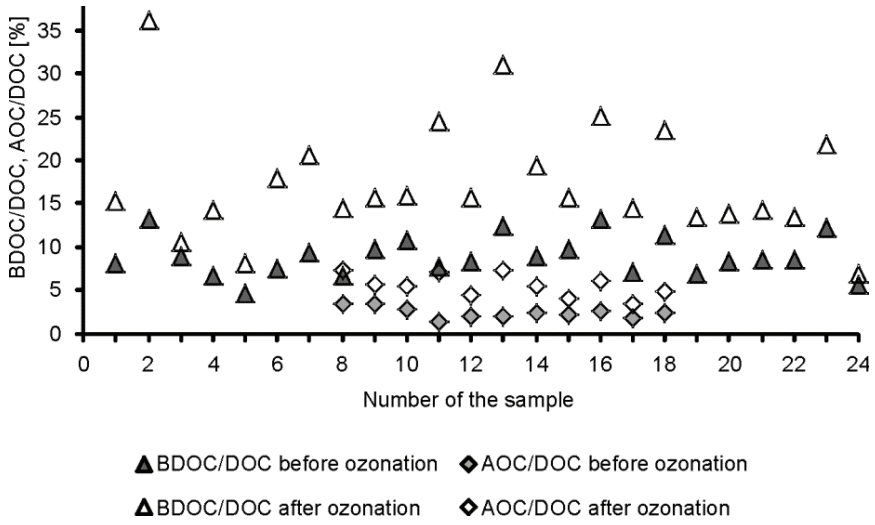

Fig. 2. Proportions of BDOC and AOC to DOC in surface water before and after ozonation

Irrespective of the initial DOC concentration, ozone dose, time of ozone contact with water, water temperature and pH, all the samples examined showed almost complete utilization of the chemical oxidizer (99.2% on average). Analysis of the results disclosed no clear relation of the ozone dose with the concentrations of DOC and its components, which indicates that organic substances present in water react differently with ozone. It was found, however, that the concentrations of TOC and its fractions before ozonation had an influence on the degree of reduction in the TOC and DOC content, as well as on the increase in the content of BDOC and AOC, measured after ozonation (Table 2).

Table 2

Concentrations of organic substances before ozonation and biofiltration and its changes during ozonation and biofiltration

Ozonation	*R*	Biofiltration	*R*
$\Delta DOC = 0.112DOC_0$	0.54	$\Delta DOC = 0.323DOC_0 - 0.152$	0.73
$\Delta BDOC = -0.366BDOC_0 - 74.09$	0.57	$\Delta BDOC = 0.703BDOC_0 - 41.38$	0.93
$\Delta AOC = -0.295AOC_0 - 34.69$	0.72	$\Delta AOC = 0.645AOC_0 - 2.672$	0.98
$\Delta NBDOC = 0.101NBDOC_0 + 0.217$	0.50	$\Delta NBDOC = 0.284NBDOC_0 + 0.191$	0.72

The degree of reduction in DOC and its fractions achieved during biofiltration was found to increase with the increase in the concentrations of these substances in the water after ozonation (Table 2). The TOC removal, which ranged between 0.39 and 2.58 g C/m^3, were high enough to cause the TOC concentrations to fall and reach levels lower than 5 g C/m^3 in all of the filtrate samples (Table 1). Biofiltration provided efficient removal primarily of those dissolved organic matter fractions (Fig. 3) whose proportion in the DOC removed averaged 89.6%.

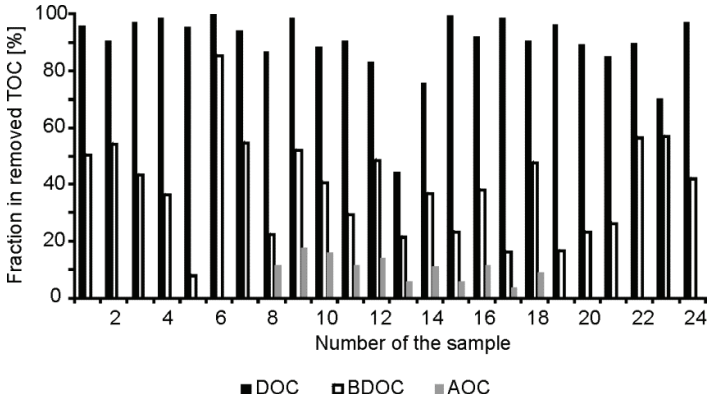

Fig. 3. Proportions of organic matter fractions in TOC removed by biofiltration

DOC removal, which varied from 0.32 g C/m^3 to 2.49 g C/m^3 (9.1 to 55.5%, 27.1% on average) comprises the sum of the AOC removed and the dissolved organic compounds adsorbed. The removal efficiency for the biodegradable fraction and that for the refractory organic substances varied from one sample to another, ranging from 30.4 to 84.4% (59.8% on average) and from 3.2% to 54.3% (20.1% on average), respectively (Fig. 4).

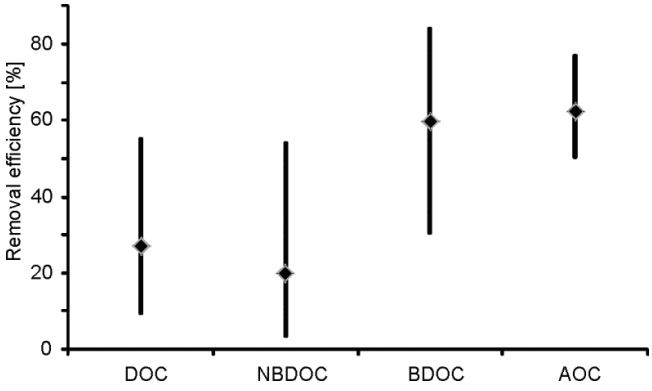

Fig. 4. Removal efficiency and average removal efficiency of organic matter fractions during biofiltration

Nevertheless, owing to the higher NBDOC than BDOC content of the water after ozonation, the reduction in the DOC content of most water samples depended largely on the adsorption of NBDOC (Δ = 65–2065 mg C/m^3), as can be inferred from the proportion of BDOC in DOC removed (Fig. 5).

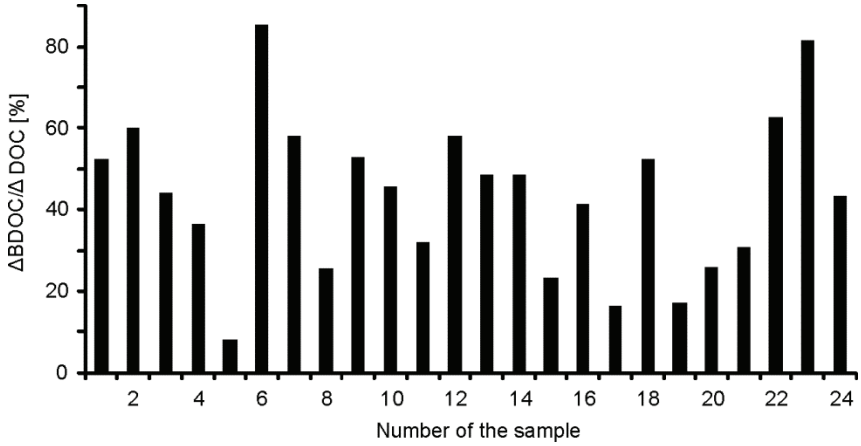

Fig. 5. Proportion of BDOC in DOC removed by biofiltration

A comparison of the UV_{254} reduction obtained in the two processes (Fig. 6) also points to important contribution of biofiltration to the removal of dissolved compounds absorbing UV radiation.

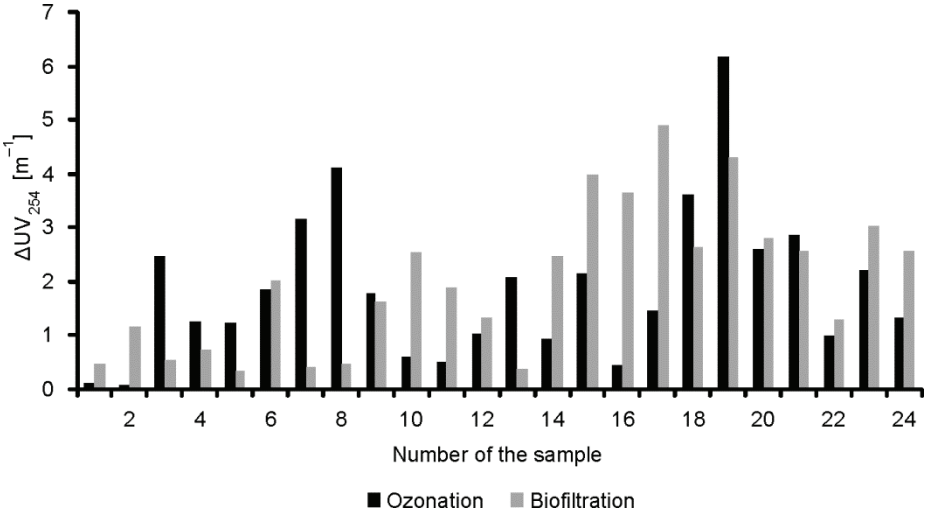

Fig. 6. Extent of reduction in UV_{254} values during ozonation and biofiltration

The quantity of BDOC removed ($\Delta BDOC_{BAF}$) varied from 70 to 529 mg C/m^3 and increased with the increase in BDOC concentration in the course of the ozonation process ($\Delta BDOC_{O3}$) (Fig. 7).

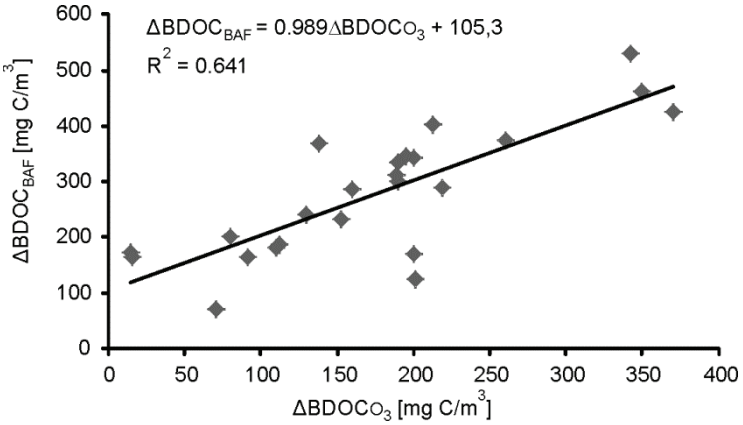

Fig. 7. Effect of the increase in BDOC concentration during ozonation on the reduction in BDOC concentration during biofiltration

Reduction in AOC (11 samples) ranged between 40 mg C/m^3 and 180 mg C/m^3, which accounted for 50.0–77.3% (62.2% on average) of the AOC concentration measured in the samples before biofiltration. However, there were three samples with the reduction in BDOC and two samples with the reduction in AOC lower than the increase in the two parameters measured upon ozonation. Analysis of the results obtained failed to reveal a clear relationship between the quantity of BDOC removed and the time of water retention in the BAF bed or water temperature. The lack of the temperature effect implies that the BDOC components in particular water samples differ in their sensitivity to biochemical mineralization. The lack of measurable time of water retention in the BAF bed might be attributed to the long period (ranging from 27.1 to 46.5 min and thus significantly exceeding 20 min) when the efficiency of biodegradation increased only slightly [16].

Table 3

Proportion of water samples with biogen content lower than the limit content for biologically stable water

Parameter	Participation of biostable water samples [%]		
	Before ozonation	Before biofiltration	After biofiltration
BDOC	29.2	0	75
AOC	45.5	0	63.6

The biofiltration process produced only partial removal of biodegradable organic substances. However, the reduction in BDOC and AOC (87.5% and 81.8% of the filtrate samples, respectively) was sufficiently high to reduce their concentrations to levels lower than those before ozonation (Fig. 1). Another major benefit derived from biofiltration is the rise in the proportion of biologically stable samples (Table 3).

Effective removal of refractory compounds not only decreases the demand for disinfectants, but also reduces the number of disinfection by-product precursors, and, consequently, the supply of potential nutrients for heterotrophic regrowth.

4. CONCLUSIONS

The ozonation process provided not only transformation of high-molecular-weight substances to biodegradable lower molecular-weight compounds, but also mineralization of some refractory fractions of total organic carbon.

Filtration through a granular, biologically active adsorption bed with ozonation as a prior step reduced the concentrations of both biodegradable and non-biodegradable organic substances and increased the number of water samples where the concentrations of BDOC and AOC met the requirements for biologically stable water.

The efficiency of BDOC removal by biofiltration generally increased with the efficiency of the ozonation process at degrading non-biodegradable dissolved organic compounds to biodegradable forms.

Ozonation and biofiltration applied after volume coagulation, sedimentation and rapid sand filtration failed to provide sufficient removal of BDOC in general, and AOC in particular.

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