ORIGINAL ARTICLE



Impact of the modernized technology on the quality of water supplied to the extended distribution system of the city of Poznań

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Abstract

The paper presents the results of a long-term study covering the development, implementation and operation of the second stage of water treatment (i.e. ozonation and subsequent granular active carbon (GAC) filtration) in the "Mosina" water treatment station supplying drinking water to the city of Poznań. The basis for the modernisation of the system was the high reactivity of the natural organic matter (NOM) present in the treated water with the disinfectant (in this case chlorine dioxide) resulting in an increased demand for ClO₂ and reduced microbiological stability of the water. During the study it was shown that simple carboxylic acids are generated during ozonation and their presence can be an indicator of the microbiological stability of the treated water. However, these compounds are effectively removed from water during filtration through biologically active GAC filters. It was also shown that the best and cheapest parameter allowing to control water quality at individual stages of its treatment is UV absorbance, which shows reactive components of NOM removal efficiency in the technological sequence. The effectiveness of the modernisation of the technological system was evaluated on the basis of the disinfectant demand as well as on the basis of selected carboxylic acids concentration in the intake points on the water supply network fed with water from the WTS "Mosina". At the last stage of the study, it was observed that the concentration of carboxylic acids in the distribution network was significantly reduced and stabilised, and a low dose of chlorine dioxide did not cause their re-formation. As a result of the modernisation, a new balance was achieved between the disinfectants used and the NOM compounds present in the treated water. Thus, the results confirmed that properly conducted pilot studies are a required element in planning of modernisation changes for water supply facilities.

Keywords Water treatment · Water stability · Granular active carbon · Disinfection

Introduction

Water is an essential element for every living organism proper functioning and plays an important role in health prevention. The quality of water for human consumption has definitely been improved in recent decades. Water producers have placed great emphasis on reducing the need for water disinfectants usage. This has translated into improved organoleptic parameters of water as assessed by consumers. However, there are still undesirable compounds that water utilities have been struggling with for years, such as excess

Joanna Świetlik askas@amu.edu.pl concentrations of iron and manganese compounds (Nowacka et al. 2014a, 2014b), natural organic matter (NOM) (Świetlik et al. 2004; Raczyk-Stanisławiak et al. 2007) that can generate biodegradable by-products in reactions with oxidants (Raczyk-Stanisławiak et al. 2005; Świetlik and Sikorska 2004; Ranieri and Świetlik 2010) as well as anthropogenic organic water admixtures (including pharmaceuticals, personal care products and endocrine disruptors) (Lara et al. 2005; Zearley and Summers 2012).

Water safety plans developed by water producers based on EU Directive guidelines (2019) identify risks and hazards along the "from intake to tap" route. In retrospect, most iron and manganese removal problems have been solved by modernisation of first stage of treatment processes, i.e. water aeration, coagulation or rapid filtration (Nowacka et al. 2014a, 2014b; Zimoch 2009). However, final tap water quality depends on the efficiency of all technological processes in treatment train. Recently, attention in water technology has

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focused on the elimination of natural organic matter (NOM), with particular emphasis on physicochemical parameters that form the basis for controlling ozonation line, filtration through activated carbon beds, and disinfection processes. As shown in the literature (Świetlik et al. 2004; Raczyk-Stanisławiak et al. 2007), indicators of the presence of NOM ozonation by-products are organic acids and aldehydes - low molecular weight organic compounds with high biodegradability. Their presence in the water supply network is extremely unfavourable due to the possibility of secondary growth of microorganisms present in the flowing water and forming biofilms on the inner walls of the distribution pipes, especially with coexisting disappearance of the remaining disinfectant (Kołwzan 2011; Wolska and Mołczan 2015; Zimoch and Bartkiewicz 2018; Zimoch and Paciej 2020; Jing et al. 2021; Lin et al. 2017; Liu et al. 2016). The presence of elevated concentrations of such compounds was recorded in treated waters after the introduction of chlorine dioxide disinfection into the process line, which was associated with high reactivity of NMO with the oxidant used (Raczyk-Stanisławiak et al. 2005). Consequently, in order to reduce the concentration of biodegradable disinfection byproducts, it became important to reduce the content of dissolved NMO in water by optimizing the technologies used by introducing a second treatment stage.

The aim of the presented study was to introduce and optimise a second stage of water treatment based on ozonation combined with filtration through biologically active carbon filters and to select simple chemical parameters to evaluate the performance of the introduced new unit processes. The need to apply additional technological processes resulted from the high concentration of highly reactive organic compounds noted in the water feeding the treatment plant, which resulted in an increased concentration of biodegradable organic compounds in the water treated in the single-stage process line. A particular intensification of this phenomenon was observed after the introduction of ClO₂ as a final disinfectant. The processes included in the second stage of water treatment were optimised after their start-up and during the first 5 years of operation in order to obtain treated water characterised by high microbiological stability during transmission through the distribution network. The paper presents the results of a long-term study covering the development, implementation and operation of the second stage of water treatment in the "Mosina" water treatment station supplying drinking water to the city of Poznań.

Study object: Poznań water supply system (PWSS)

Aquanet is the largest water supply company in Greater Poland Region. It supplies water on a daily basis to 800,000 inhabitants of Poznań and the surrounding area. Water is produced at three key water treatment stations: WTS "Mosina", WTS "Wiśniowa" and WTS "Gruszczyn". These stations are connected to the Poznań Water Supply System (PWSS), which is 50% supplied with water produced at WTS "Mosina" (150,000 m³/d), 39% with infiltration water treated at WTS "Wiśniowa" in Poznań (80,000 m³/d) and 11% with underground water from WTS "Gruszczyn" (Fig. 1).

Raw waters feeding the WTS "Mosina" are a mixture of groundwater and infiltration water. The water treatment plant in Mosina is located approximately 20 km from Poznań. Two transit trunk mains located on the east and west side of the city with a diameter of 1000 mm feed the distribution network of the Poznań agglomeration. On a hill in Pożegowo in the Wielkopolski National Park there are retention tanks with a total capacity of 50,000 m³ volume, which provide supply to the inhabitants of Poznań in case of a station failure for about 12–16 h. The tanks are filled with pumped water from the WTS "Mosina". In Poznań, on the Morasko hill, there are further tanks with a total capacity of 30,000 m³ (Fig. 1).

The total length of the water supply network in the Poznań agglomeration is 1 744.13 km. Cast iron and PVC/PE are the basic pipe materials. The main transit mains with a diameter of DN 1000 mm are made of cast iron. There are still parts of the water supply system made of asbestos-cement pipes, which are successively replaced. The age of almost half of the pipes in the PWSS is between 10 and 40 years, and 15% of the network was made more than 40 years ago.

Research method

This paper presents the results of a long-term study aimed at improving water quality in the distribution network of the city of Poznań in terms of parameters related to the presence of dissolved organic compounds in water and optimisation of disinfectant doses. The goal was to be achieved by introducing the second stage of water treatment based on ozonisation and filtration through biologically active carbon beds. The expansion of the technological system began with pilot tests, on a semi-technical scale, which were carried out in two stages. The first stage was aimed at determining the optimal dose of ozone, the contact time of water with ozone and the selection of suitable activated carbon (GAC). In the second stage, on the basis of preliminary assumptions, technological guidelines were developed, which formed the basis for the construction design. Modernisation of the system also included increasing the capacity of the "Mosina" WTS from 100,000 to 150,000 m³/d. Modernisation works were carried out in 2010-2015 and the commissioning of the second stage of water treatment took place on 05th Jan 2015. On 17th Jan 2015 the water in the entire PWSS system was changed.

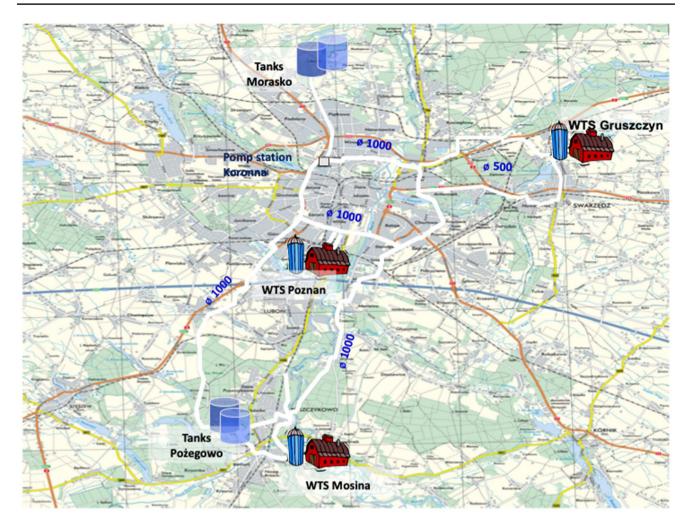


Fig. 1 Scheme of the Poznań water supply system with marked locations of intakes, stations and storage tanks

During the first two months after commissioning of ozonation and filtration through carbon filters, chemisorption dominated the system, which was replaced by biological processes once the sorption capacity of the deposits was saturated. In 2019, after more than 4 years of continuous operation, the beds of 6 filters were regenerated. In 2020, the process was carried out for another 6 filters.

Throughout the study period, the water feeding the "Mosina" WTS, water at individual stages of the treatment process and treated water was monitored for parameters characterising natural organic matter (NOM), such as TOC $[mgC/dm^3]$, UV absorbance (254 nm) [1/m], oxidisability $[mgO_2/dm^3]$, pH, dissolved oxygen $[mg O_2/dm^3]$, colour $[mg Pt/dm^3]$ and turbidity [NTU]. These indicators were determined in the water and wastewater testing laboratory according to the applicable standards. Low molecular organic acids such as oxalic acid, formic acid and acetic acid $[mg/dm^3]$ were taken as an indicator of biological stability of water in the PWSS network. The concentration of carboxylic acids in the samples was determined according to the methodology

described in (Świetlik et al. 2004; Raczyk-Stanisławiak et al. 2005).

Quality of raw water supplied to WTS "Mosina"

Water supplied WTS "Mosina" is obtained from several places in the Krajkowo-Sowinki intake in this area the Warsaw-Berlin Proglacial Stream Valley intersected with the Greater Poland Fossil Valley. Two Quaternary aquifer structures, separated by clays, overlapped in the Warta River valley. The intake has been in operation for over 40 years and supplies water to the inhabitants of the Poznań agglomeration and neighbouring communes on a daily basis. At present, 60% of the untreated water is obtained from the artificially constructed Krajkowo Island and 40% from wells of the Super-Lagoon Terrace, the aquifer of which is part of the Main Groundwater Reservoir in Poland. The current water permit for groundwater abstraction is: $Qh = 6375 \text{ m}^3/h$,

 $Qd = 153,000 \text{ m}^3/\text{d}$ and $Qy = 55,845,000 \text{ m}^3/\text{year}$ and for the abstraction of infiltration surface water by means of a radial well in Krajkowo in the amount of: $Qh = 834 \text{ m}^3/\text{h}$, $Qd = 20,000 \text{ m}^3/\text{d}$ and $Qy = 7,300,000 \text{ m}^3/\text{year}$. Whereas, surface water intake from the Warta River to supply the infiltration intake is $Qh = 750 \text{ m}^3/\text{h}$, $Qd = 15,000 \text{ m}^3/\text{d}$, $Qr = 6,500,000 \text{ m}^3/\text{year}$. The intake facilities from which infiltration water is pumped include wells from the shoreline drilled in the Warta River dyke, wells located near infiltration ponds and a radial well whose drains are under the Warta River bottom. In the groundwater changes in water quality occur not only due to anthropogenic pollution but also as a consequence of environmental changes (Table 1).

In the 1980s, water abstraction was much more intense than it is nowadays. In addition, there was a great drought in 1989–1992. The Greater Poland region was hit by floods in 1997–2011. The climatic changes contributed to the formation of a depression funnel and later to its gradual flooding. As a consequence, an aeration zone was formed during which sulphides and organic substances were oxidised and subsequently manganese, iron and sulphate compounds were washed out.

Water obtained from different parts of the intake is mixed in order to average its quality by means of a static mixer installed at the station, directly on the inflow pipeline. Over the many years of research, the quality of raw water feeding the WTS "Mosina" was characterised by relatively high stability (Table 2). Parameters such as pH, conductivity or hardness fluctuated within the value ranges which did not influence the water treatment technology. However, abovenormative concentrations of substances typical for groundwater, including iron compounds (0.094–19.1 mg Fe/dm³)

Table 1 Changes in raw waterquality during the periods2012–2014 and 2015–2020

and manganese compounds $(0.066-1.5 \text{ mgMn/dm}^3)$ were recorded in the raw water. A slightly different trends were observed for the parameters related to the presence of natural organic matter in raw water. The mean content of organic compounds defined as TOC ranged from 3.3 to 6.6 mgC/ dm³, oxidisability ranged from 2.8 to 4.1 mgC/dm³, while UV absorbance (254 nm) ranged from 2.8 to 24 1/m. Comparing the analysed periods one can clearly state that the concentration of organic matter in the raw water increased (Table 2). Currently, in the feeding water, the presence of NOM with a less complex molecular structure is observed, which is associated with its higher reactivity with oxidants. This change in NOM characteristics may result in an increased demand for oxidising agents, including O_3 , and a higher potential for the formation of biodegradable compounds, whose presence is undesirable in the distribution network. Consequently, it was necessary to optimise the processes included in second stage of water treatment aimed at maintaining the microbiological stability of the water in the network.

Quality of treated water at WTS "Mosina"

The WTS "Mosina" is the largest facility, producing water for the PWSS built in the 1960s. In this time at the station it has been removed mainly iron and manganese compounds from water. The technological line included the first stage of treatment: open aeration, rapid filtration through quartz bed and final disinfection with chlorine water obtained from chlorine gas. In 2000, a chlorination plant was set up using chlorine dioxide for disinfection. Despite many attempts, it

Parameter	Raw water between 2012 and 2014				Raw water between 2015 and 2020			
	Number of analy- ses	Min	Max	Average	Number of analy- ses	Min	Max	Average
рН	127	7.1	7.7	7.36	261	6.9	7.6	7.3
Alkalinity mmol/dm ³	123	3.02	5.6	4.48	55	3.9	5.4	4.51
Total iron mg Fe/dm ³	154	1.2	7.2	3.1	261	0.094	19.1	2.39
Manganese mg Mn/dm ³	127	0.26	1.2	0.66	243	0.066	1.5	0.63
Sulphates mg SO ₄ /dm ³	515	53	330	162.8	461	73	1000	143.65
Total hardness mg CaCO ₃ /dm ³	124	290	520	372.35	164	220	470	349.91
Temperature st °C	507	6.8	13	9.67	260	6.6	14	10.37
Conductivity µS/cm	127	684	1080	814.8	261	601	977	773.13
Colour mg Pt/dm ³	138	5	65	19.71	261	2.5	40	12.7
Turbidity NTU	154	3.3	40	13.56	261	0.38	160	13.55
Oxidability mg O ₂ /dm ³	138	2	4.3	3.11	12	2.8	4.1	3.35
TOC mg C/dm ³	152	3.3	5.8	4.37	266	3.3	6.6	4.7
UV absorbance (254 nm) 1/m	112	7.8	20	12.68	266	5.8	24	12.55
Ammonium ion mg NH ₄ /dm ³	151	0.015	0.51	0.32	261	0.095	0.72	0.30

Table 2	Changes in treated	water quality	during the	periods 2012-	-2014 and 2015–2020

Parameter	Treated water in the years 2012–2014 (before switching on the second treatment stage)				Treated water in 2015–2020 (after modernisa- tion)			
	Number of analyses	Min	Max	Average	Number of analyses	Min	Max	Average
рН	303	7.1	7.7	7.4	888	7	730	8.21
Alkalinity mmol/dm ³	103	3.9	5.6	4.44	264	3.8	5.4	4.46
Total iron mg Fe/dm ³	518	0	0.23	0.019	612	0	0.13	0.012
Manganese mg Mn/dm ³	378	0	0.06	0.0058	594	0	0.077	0.005
Sulphates mg SO4/dm ³	67	74	230	145.76	612	0	230	141.45
Total hardness mg CaCO ₃ /dm ³	63	290	460	353.89	174	220	470	348.6
Temperature °C	293	8.1	15.1	11.93	659	7	17	11.42
Conductivity µS/cm	299	613	939	788.98	604	599	954	774.99
Colour mg Pt/dm ³	516	0	10	3.45	1046	0	7.5	1.24
Turbidity NTU	527	0.7	1.7	1.1	1046	0	4	0.27
Oxidisability mg O ₂ /dm ³	64	0.89	3.4	2.06	166	0.06	3.5	1.55
TOC mg C/dm ³	114	3.2	5.3	3.97	603	1.7	5.5	3.5
UV absorbance (254 nm) 1/m	214	6	15	9.64	457	2.9	14	5.84
Ammonium ion mg NH ₄ /dm ³	68	0	0.019	0.0018	49	0	0.5	0.014
Total THM µg/dm ³	111	0	22	2.74	268	0	17	0.22
Tetrachloromethane $\mu g/dm^3$	110	0	0	0	110	0	0	0
Total chlorites and chlorates mg/dm ³	110	0	0.99	0.32	99	0	0.98	0.32
Chlorites mg/dm ³	72	0	0.49	0.18	1	0.14	0.14	0.14
Chlorates mg/dm ³	66	0	0.28	0.087	1	0.085	0.085	0.085
Dissolved oxygen mg O_2/dm^3	190	4.9	13	8.75	264	1.8	20	10.31

was not possible to switch to using only the new reagent due to the growth of psychrophilic bacteria in the water supply systems (Lasocka-Gomuła et al. 2007). Consequently, until the facility upgrade was completed (2015), the water was disinfected continuously with a mixture of two disinfectants: chlorine and chlorine dioxide, in a ratio of 60-40%. A fixed dose of chlorine dioxide (the average ClO₂ dose was 1.12 mg/dm³; Fig. 8) was used and chlorine gas was the variable agent. Scientific studies and operational experience have shown that dosing the water only with chlorine dioxide results in unfavourable processes in the disinfected water. These include reactions with organic compounds present in the water, which proceed until one of the substrates is depleted, and the rapid decomposition of ClO₂ into normal chlorites and chlorates (Świetlik et al. 2004; Ranieri and Świetlik 2010). However, the mixing of disinfectants with seasonal capacity changes was not entirely effective and created many problems in maintaining water quality in the system in terms of colour, iron and manganese concentration and turbidity. Customers complained about the smell and taste of the water (Lasocka-Gomuła 2007).

The chemical disinfection methods are used in order to ensure effective removal of microorganisms, but the disinfected water must be properly prepared so that the concentration of disinfectant and by-products does not exceed acceptable values (Raczyk-Stanisławiak et al. 2005). Problems with maintaining the microbiological stability of water in the network were compounded by operational difficulties during filter flushing and filter bed replacement. The key to solving these issues, at the turn of the century, was detailed raw waters testing subjected to treatment processes, which allowed the seasonality of changes in the composition of intake waters to be analysed in detail. New laboratory techniques also made it possible to characterise and assess the reactivity of organic matter present in the treated water (Świetlik et al. 2004; Świetlik and Sikorska 2004).

Due to the recorded elevated concentrations of parameters describing NOM and the consequent increased disinfectants demand of treated water, after nearly 50 years, the WTS "Mosina" was modernised and extended by adding a second stage of treatment, i.e. ozonation and filtration through a carbon bed. The modernisation period was carried out between 2010 and 2015. Throughout this time the station was producing water for the PWSS, which posed the major operational challenge. In the first stage, a new aeration hall equipped with aeration cascades including first and second stage reaction chambers was commissioned. The aerated and degassed water was averaged by means of a static mixer at an earlier stage. The upgrade carried out made it possible to dose dusty activated carbon into the second-stage reaction chambers

in the event of, for example, a periodic deterioration in the quality of the intake water. Throughout 2014, a pulverized activated carbon (PAC) plant was in operation to reduce the dose and change the ratio of chlorine to chlorine dioxide in the disinfection mixture from 20 to 80% while maintaining the bacteriological stability of the water supply. The average dose of chlorine dioxide was 0.54 mg/dm^3 (Fig. 8). The applied PAC was retained in the rapid filter beds, which after modernization were backfilled with anthracite-quartz bed.

The introduction of an additional water treatment stage eliminated the high molecular fractions of organic matter (reduction of UV absorbance and TOC concentration, Table 2) having the greatest impact on the final chlorine dioxide dose (an average 1.12 mg/dm³; Fig. 8). In the final stage of the modernisation, disinfection with chlorine gas was replaced by a sodium hypochlorite plant using a more environmentally friendly electrolyser. The pure water pumping station was equipped with four sodium hypochlorite dosing points on the four outgoing discharge pipelines. This means that the water directed to the PWSS is disinfected, as required, with different doses on each of the mains (western and eastern). After completion of the technological startup and commissioning of the entire technological line, customers noticed an improvement in the quality of drinking

Table 3Number ofsubstantiated consumer'scomplaints - PWSS togetherwith municipalities	Period	Number of complaints		
	2010	88		
	2011	65		
	2012	106		
	2013	126		
	2014	148		
	Jan–Jun 2015	140		
	July-Dec 2015	54		
	2016	25		
	2017	26		
	2018	14		
	2019	18		

water based on an evaluation of its smell, colour and taste (Table 3).

The process of ozonation and filtration through a bed of granular activated carbon (GAC)

It was observed that during ozonation of water, the concentration of biodegradable organic carbon is increased, which provides the nutrients for, among other, the growth of psychrophilic bacteria. On the basis of measurements of the total number of microorganisms before and after ozonation, it was found that significant numbers of these bacteria are already observed in water after ozonation entering the carbon filters (Table 4).

Prior to the modernisation, the two step pilot studies were carried out. In the first stage of the study the influence of the ozonation process on the molecular weight distribution of organic matter present in the water from WTS "Mosina" in different process variants-various contact time and different ozone doses of 1.0; 2.0; 3.0; and 4.0 mg O₃/dm³ in each scenario were analysed in details. The study also included the isolation and fractionation of natural organic matter (NOM) and the full characterisation of its different fractions in terms of reactivity with ozone and chlorine dioxide, together with the determination of the by-product formation potential and the possibility its removal during biofiltration (Świetlik et al. 2004; Świetlik and Sikorska 2004). On the basis of the results obtained for water treated at WTS "Mosina", it was shown that with increasing doses of ozone, there is a decrease in the absorbance observed for almost the entire range of molecular weights of the organic compounds analysed, indicating the high reactivity of NOM components and their relatively easy degradation under the influence of oxidants. The fractions with the highest molecular weights, identified by complex structural composition, were characterised by the highest ozone demand and the presence of numerous double bonds. As a consequence of the ozone oxidation processes, macromolecular components of NOM

Table 4 Comparison of microorganisms in water before and after ozonation with a dose of 1.5 mg/dm^3 .

Date	Total microorganism count at 22 °C [cfu/1 cm ³] before ozonation	Total microorganism count at 22 °C [cfu/1 cm ³] after ozona- tion			
20.05.2020	65	1500			
13.06.2020	3	300			
26.06.2020	17	1500			
19.07.2020	26	5000			
29.07.2020	3	2000			
08.08.2020	1	1600			

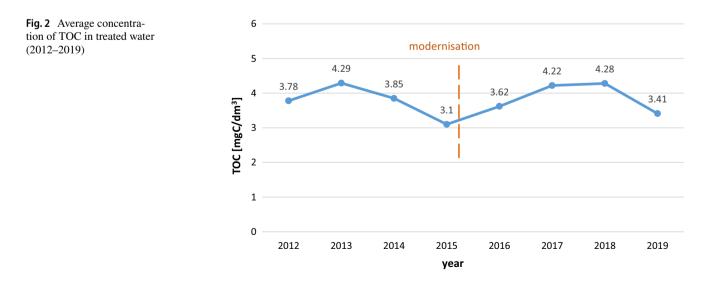
Determinations at 22 ± 2 °C after 68 ± 4 h [cfu/1 cm³]

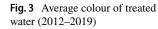
are broken down into smaller fragments with higher bioavailability (biodegradable organic carbon, i.e. assimilable carbon), including in particular readily biodegradable carboxylic acids and aldehydes. This trend was particularly observed for the water samples abstracted from the Lagoon Terrace. On the basis of literature reports, it is assumed that only 37% of the assimilable organic carbon formed after water ozonation can be identified, and the largest share in this group of compounds belongs to carboxylic acids -26%. Other compounds include aldoketoacids -7% and aldehydes at 4% (Raczyk-Stanisławiak et al. 2007). These proportions may undergo some seasonal variation and also vary for individual waters due to differences in NOM structure. However, unidentified compounds are still the largest group of compounds classified as assimilable/biodegradable organic carbon. The studies carried out to develop and fully optimise the ozonation process, performed during the second stage of the pilot study, resulted in the determination of an optimal ozone dose, which is currently maintained at 1.0-1.5 mg/ dm³, while the water retention time in the reaction and degassing chamber is 20 min.

Assessment of the efficiency of carbon filters in terms of parameters describing natural organic matter

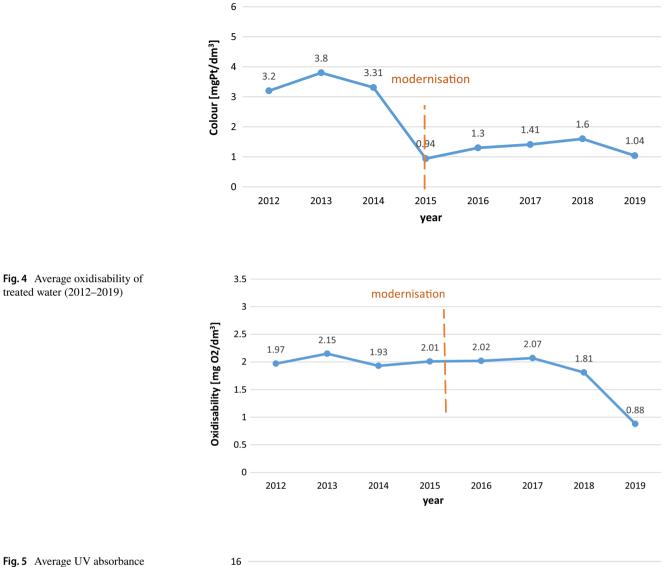
Filtration through biologically active carbon filters is the final water treatment process. The purpose of the process is to efficiently remove the generated biodegradable compounds from the water, primarily the precursors of the final disinfection by-products. WTS "Mosina" operates 24 filter chambers filled with granulated activated carbon. These filters started working as biological beds once their sorption capacity was exhausted (after about 3 months of operation). Organic compounds, as a source of carbon, can be directly assimilated by the inhabiting microorganisms or can be broken down by biochemical processes into smaller fragments available as the energy source for bacteria. Removal of this part of the NOM is crucial due to its reactivity with the chlorine dioxide used for disinfection (Raczyk-Stanisławiak et al. 2005, 2007; Biłozor et al. 2003). This is because the reaction of organic compounds with ClO₂ leads to an increased demand for disinfectant in the water, and as a result of the reactions taking place, fine biodegradable compounds may be generated again in the water pumped into the network. During the pilot study (see chapter Research Method), a number of tests were carried out to select the appropriate activated carbon and contact time between ozonated water and GAC. The results of the experiments showed that the contact time necessary to achieve the desired filter efficiency is about 15-20 min. Currently, in all working filters with biologically active carbon at the WTS "Mosina" the contact time is at least 15 min. The effectiveness of the ozonation process combined with biofiltration is controlled by water quality parameters describing organic matter, such as total organic carbon (TOC), colour, UV absorbance at 254 nm and oxidisability. For comparison purposes, Figs. 2, 3, 4 and 5 show graphs of the average values of these parameters determined for treated water from 2012 to 2019. In 2014, powdered carbon was dosed into the water. Since January 2015, the entire process line, which included ozonation and filtration through carbon beds, has been commissioned. On the other hand, the regeneration of the carbon deposits of the 6 filter chambers started in 2019.

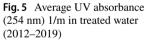
The obtained results unequivocally confirmed the results of pilot studies in a semi-technical scale preceding the modernisation of the WTS "Mosina" (Biłozor et al. 2003; Raczyk-Stanisławiak et al. 2007) - the introduction of ozonation and filtration by activated carbon to the system resulted in a sharp decrease in all parameters, whose value gradually increased in subsequent years. The visibly reduced values

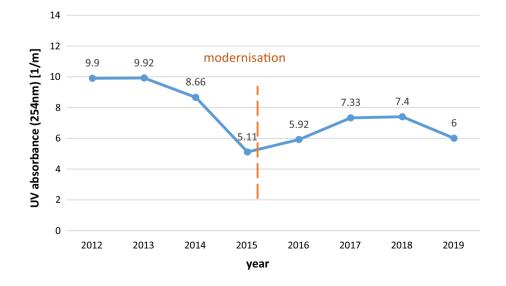




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of the parameters describing NOM in 2015 were related to the chemisorption process dominating in the carbon beds (Fig. 2). Once activated carbon achieved the sorption capacity saturation the development of its biological activity was observed and a gradual increase in the concentration of TOC and oxidisability was noticeable in the water after the filters, while maintaining a reduction in colour and UV absorbance as well (Figs. 2,3,45). This indicates the efficient breakdown and removal of NOM macromolecular structures during ozonation and biofiltration, thus reducing the concentration of the most reactive NOM fractions. Figure 6 shows the changes in UV absorbance levels between May and November 2019. During this time the capacity of the station, due to the summer period, increased. The operation of more wells significantly affects the variable quality of raw water in terms of organic matter. The presented results illustrate that the applied ozone dose causes a reduction and stabilisation of the compounds responsible for the UV absorption of water. A further reduction in organic matter content of around 15-20% was noticed by carbon filters. During the mentioned period of increased water production, the concentration of biologically degradable compounds increased, both after ozonation and after carbon filters.

Practical aspects of carbon filter operation

During the pilot studies conducted under semi-technical conditions (see Research Method section), technological guidelines were defined for the modernisation of the WTS "Mosina". However, each station must develop its own optimum technological conditions for technical scale in the first years of operation. The WTS "Mosina" station gained its own experience, which in later operation formed the basis for optimising the water treatment process by granular activated carbon. The purpose of the carbon bed usage is biologically elimination of organic compounds at a level of approximately 20%. At WTS "Mosina", it has been observed that the time of stable operation of the deposits influences the decrease in organic matter content responsible primarily for the disinfectants demand (Fig. 7).

Carbon beds tested under technical conditions, have been in operation at the WTS "Mosina" continuously since January 2015. In 2020, the disinfectant demand after the second water treatment stage continued to be kept constant, allowing to use a stable dose of disinfectants (chlorine dioxide and sodium hypochlorite). In 2019, six of the 24 operating filter chambers were regenerated, and a year later the process was carried out on a further six filters. It is planned to regenerate carbon from six more filter chambers, which means that each filter will be regenerated every four years. It is a solution that ensures a stable reduction in the concentration of natural organic matter in treated water at a constant level of 20%.

An investment to relocate the chlorine dioxide dosing point from the suction pipeline to the sub-filter chambers was completed in January 2020. After the upgrade, the water residing in the sub-filter chambers was unprotected. Water treated after the biosorption process in the carbon bed contains large quantities of psychrophilic bacteria, which does not guarantee that water quality will be maintained at a high level. After only one year of operation, the first performance tests were conducted, focusing on the dosing of sodium hypochlorite to the subfilter chambers using portable disinfection sets. The obtained results indicated that each chamber with retained water should be equipped with a disinfectant dispenser, in order to limit the multiplication of microorganisms in the treated water. The introduction of investment-level changes to individual processes affects the

Fig. 6 UV absorbance at 254 nm of the tested samples in water before ozonation, after ozonation, after carbon filter No. 13 and after carbon filter No. 16 (operating 54 months) during the study period from May to November in 2019

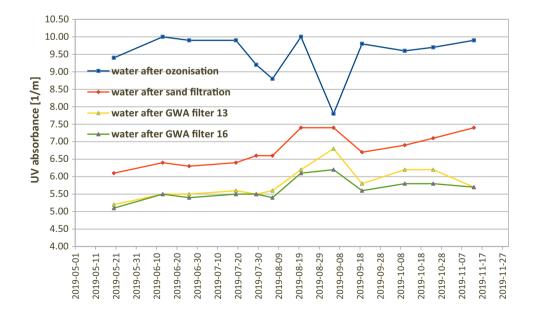
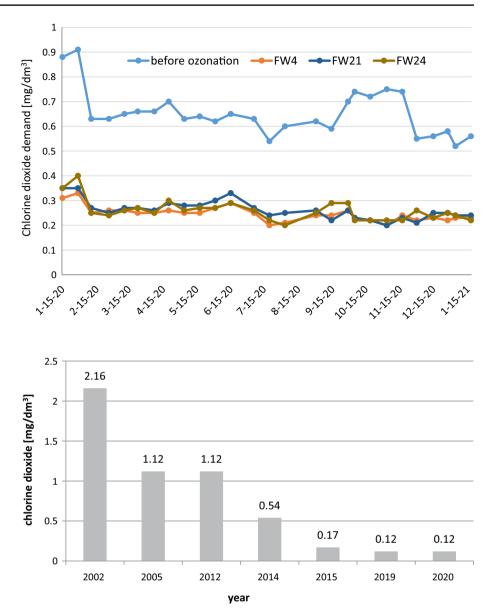
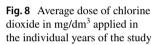


Fig. 7 Changes in chlorine dioxide demand in water before ozonation and after selected GAC filters (FW) in 2020 during the stabilisation phase (ClO₂ concentration in water after 30 min of contact time)





water disinfectants demand. The figure below shows which technologies correlate with the chlorine dioxide dose applied at the WTS "Mosina". The introduction of chlorine dioxide alone, without lowering the content of NOM compounds, have not resulted in achieving water quality (Fig. 8) that would be acceptable to consumers. The dose of chlorine dioxide that eliminated the effect of secondary growth of psychrophilic bacteria on the water supply was very high. The upgrade of the post-filters in 2005 had the first effect of reducing disinfectants demand due to the elimination of iron and manganese compounds. A new aeration plant was commissioned in 2012, which had no effect on the disinfectant dose used. Another reduction occurred in 2014 when powdered activated carbon (PAC) was dosed into the water. The modernisation was completed in 2015. Today, no PAC is dosed into the water. Filtration through the activated carbon bed has achieved stabilisation, which is reflected in the amount of chlorine dioxide applied to the treated water.

Evaluation of water quality with organic acids

The introduction of the second stage of water treatment to the technology used at WTS "Mosina" resulted in an increase in the quality of the product introduced into the distribution network. The water after the two-stage treatment is characterised by a reduced NOM content, which results in a reduced disinfectant demand. It is assumed that the ozonation and biofiltration process primarily removes the reactive NOM fraction from the treated water, which in turn reduces the formation potential of biodegradable organic compounds - carboxylic acids - in the water after disinfection. In order to determine the potential for the formation of BOMs in water from WTS "Mosina", quantitative analyses of selected, indicator carboxylic acids in water at different stages of treatment and distribution have been done. The results obtained are shown in Figs. 9 and 10.

In the case of carboxylic acids, a significant increase in the concentration of these compounds in water after ozonation was observed. However, in treated and disinfected water taken at WTS "Mosina" and from the points on the PWSS, their content was much lower and stabilised (Fig. 9). This indicates effective removal of BOM precursors during biofiltration. Figure 10, in turn, shows the changes in carboxylic acid concentrations at different points in the water supply network between 2014 and 2019. Changes in the concentration of the monitored compounds clearly indicate the effectiveness of the introduced modernisation. The introduction of ozonation and filtration through activated carbon, reduced the concentration of formic acid, while increasing the concentration of acetic and oxalic acids (compounds with higher molecular weights). This is because ozonation breaks down large NOM molecules resulting in the formation of various by-products. After the stage of full reworking of the carbon filtration beds (2019 data), there was a stable reduction in the concentration of all monitored acids, indicating almost complete removal of their precursors in the second stage of water treatment. A new microbiocenosis has been established on the water supply network over a period of four years. The start-up of the second water treatment stage reduced the disinfectant dose (chlorine dioxide) used and, as shown in the graphs, changed the chemical composition of the water by depriving it of the bioavailable BOM fractions. In 2015, leaching of organic compounds that were present in the water supply network prior to the upgrade was observed. The leaching process was not observed in

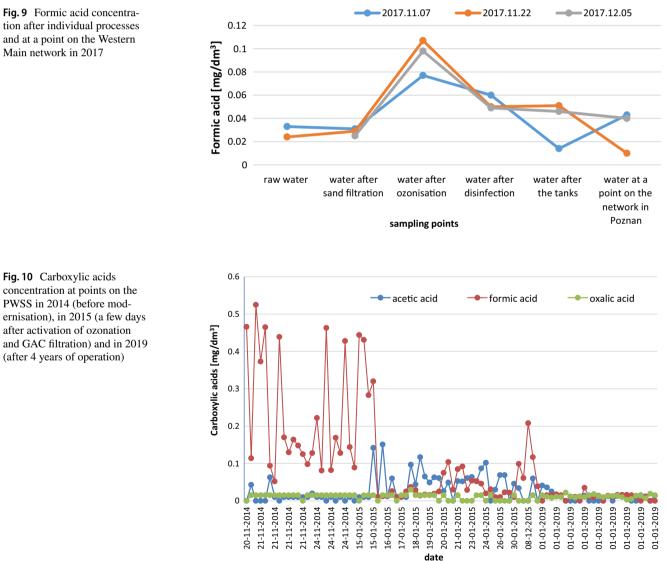


Fig. 9 Formic acid concentration after individual processes and at a point on the Western Main network in 2017

2019. Bringing about the establishment of a new equilibrium in the water residing in the water supply network is a lengthy process. A further step to inhibit the growth of bacteria in the network water will be the commissioning of two additional disinfection points at PWSS in the second quarter of 2021. One located on the eastern main and the other on the western main at the reservoirs in Pożegowo. The bacteriostatic effect of the disinfectant on microorganisms is expected. The aim is to achieve biologically stable water in the distribution network, in which the combination of physico-chemical factors (considering the role of the disinfectant) is at a level that precludes uncontrolled bacterial growth.

Conclusion

The monitoring studies, carried out on changes in the quality of raw water feeding the WTS "Mosina" and treated water leaving the station, clearly show that the modernisation of the station and introduction of the second stage of water treatment, i.e. ozonisation and filtration through biologically active carbon beds, significantly improved the quality of produced water and increased its microbiological stability. The study showed that any unitary process that reduces the possibility of a reaction between substances present in the water such as iron, manganese or NOM and the disinfectant used (in this case ClO_2), reduces the demand for disinfectant in the water and thus its final dose. In the course of the research, it was found that the most effective and cheapest parameter to control water quality at the different stages of its treatment is UV absorbance, which quickly determines the effectiveness of processes aimed at reducing the concentration of reactive NOM fractions in water, in the used technological sequence. Research has also shown that the introduction of ozonation generates the formation of biodegradable compounds. Their easy to determine indicators are small molecular carboxylic acids, which are effectively eliminated from water during filtration through biologically active carbon beds. The control of water quality in PWSS carried out after five years of operation of the second stage of treatment, conducted in selected points on the water supply network fed with water from WTS "Mosina", showed that after this period there is practically no presence of carboxylic acids in the distributed water and the applied low and stable dose of chlorine dioxide does not cause their re-formation. As a result of the modernization, a new balance was achieved between the disinfectants used and the NOM compounds present in the treated water. Thus, the results confirmed that properly conducted pilot studies are a required element in planning of modernisation changes for water supply facilities.

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