

Practical Paper

Pilot scale experiments on surface water treatment sequence including ozonation and adsorption processes

Wojciech Balcerzak and Stanislaw M. Rybicki

ABSTRACT

The paper presents results of the experimental studies on combined ozonation and activated carbon adsorption processes at the Water Treatment Plant (WTP) at Cracow (Poland). The study focused on the selection of an appropriate location of an ozonation process within the treatment scheme and on the choice of activated carbon grade for adsorption. Analysis of process efficiency in the proposed technological configuration was performed based on some specific physico-chemical parameters, monitored in the effluents from the unit processes. It was found that introduction of ozonation resulted in better reduction of parameters describing organic contaminants. The authors proposed the process sequence: ozonation – sand filtration – GAC adsorption, based on previous laboratory results. The selected activated carbon demonstrated a better reduction of organic contaminants, expressed as: permanganate COD, dissolved organic carbon (DOC), UV absorbance and SUVA₂₅₄.

Key words | GAC adsorption, ozonation, pilot plant experiments, water quality

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INTRODUCTION

Deterioration of surface water quality and implementation of more stringent water quality standards in EU countries forced water treatment plants to upgrade and modernize their technologies. This may be achieved by upgrading the existing treatment processes and/or by implementation of new and advanced technologies (Kawamura 2000; Kowal & Swiderska-Bróz 2005). Selection of treatment methods and prospective modifications should follow a pilot scale study to evaluate the feasibility and economics of this approach and establish design parameters (Vahala *et al.* 1999; Balcerzak & Zymon 2004). Large-scale pilot plants seem to be more applicable with respect to practical implementation of results in full scale (Hagmeyer *et al.* 2002); however, economic factors are leading to small-scale pilot plants, like those presented in this paper, being built and operated.

A typical modification of the treatment process, used for upgrading taste and odour control and organics removal, includes the ozonation process. Preliminary ozonation (placed at the head of the plant) improves water taste and

odour while final ozonation (placed at the end of the plant) is used for water disinfection; intermediate ozonation is usually employed to remove or oxidize organic compounds. Another method that is widely used for removal of organic micropollutants is ozonation coupled with carbon adsorption (GAC).

The Rudawa water treatment plant (WTP), Cracow, Poland, withdraws raw water from surface water intake. The catchment upstream of the intake is densely populated with significant discharge of treated municipal wastewater. Due to raw water characteristics the plant performs the following treatment processes: coagulation, sedimentation, sand filtration, GAC adsorption and chlorine dioxide disinfection. Since the water treatment technology includes GAC adsorption, an intermediate ozonation was introduced to improve the removal of organic compounds. Most of the time intermediate ozonation is conducted as follows: sand filtration – intermediate ozonation – GAC adsorption, though another process configuration is also possible:

intermediate ozonation – sand filtration – GAC adsorption (Ribas *et al.* 1997; Pryor *et al.* 1999; Gray 2010).

Application of the second option utilizes some of the facilities already existing at the plant and requires only minor modifications within the Rudawa WTP infrastructure; this way investment costs could be substantially lowered. Introduction of a new process, selection of its location and analysis of its operation, together with other processes, all required preliminary pilot-scale experimental studies (Kawamura 2000; Nawrocki & Biłozor 2000). These studies were divided into two phases.

During phase I, the ozonation process within the Rudawa WTP flow scheme was discussed as well as its location and selection of proper process configuration.

In phase II the optimal activated carbon was selected for carbon adsorption process previously proposed in phase I. Basic process parameters with respect to filtration velocity (in both sand and GAC filters) were the same as in a full-scale treatment train of the plant (i.e. 6.5 and 8.2 m/h respectively). Sand filtration filling (ordinary quartz sand) was adopted from a full-scale plant while different GAC types were used in the experiment.

METHODS

Pilot plant description

Phase I – process configuration selection

A continuous experimental study was conducted over 48 summer days. The schematic layout of the pilot plant (phase I) is presented in Figure 1. The pilot plant was

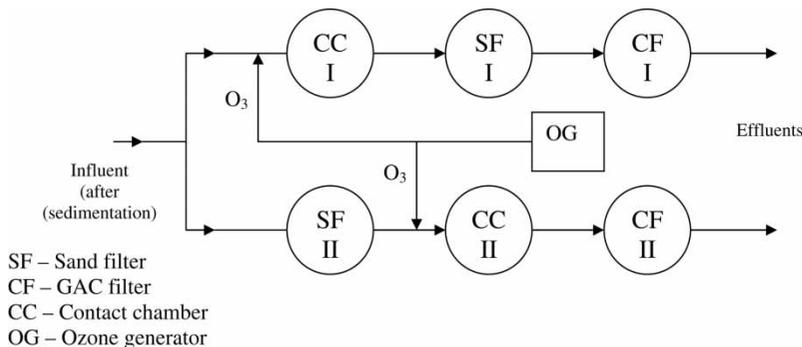


Figure 1 | Pilot plant layout (phase I).

supplied with water from the Rudawa WTP after coagulation and clarification processes. Water was fed into two separate treatment units:

Unit I: ozonation (intermediate) – sand filtration – GAC adsorption

Unit II: sand filtration – ozonation (intermediate) – GAC adsorption

Basic operational parameters of the pilot plant:

Total capacity: $0.3 \text{ m}^3 \text{ h}^{-1}$ (two parallel units of $0.15 \text{ m}^3 \text{ h}^{-1}$ each)

Filtration velocity: $6.5 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$

Sand filters backwashing frequency: twice a day

Carbon filters backwashing frequency: every other day

Average ozone contact time: 12 min

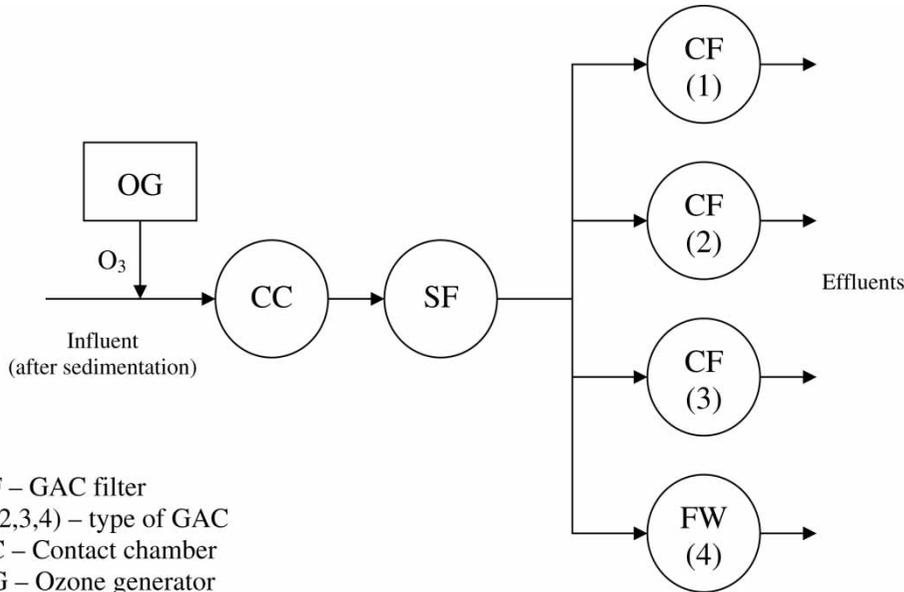
Ozone doses: $0.2\text{--}2.1 \text{ g O}_3 \text{ m}^{-3}$

To avoid adverse impact of suspended matter which may be stored on the GAC grains, the GAC filters at the pilot plant were backwashed relatively frequently. This procedure was performed until 0 NTU turbidity was measured in wastewater; the same mode of operation was applied for phase II.

Phase II – activated carbon selection

A continuous experimental study was conducted over 70 days in the fall. The schematic layout of the pilot plant (phase II) is presented in Figure 2. The pilot plant was supplied with water from the Rudawa WTP, as during phase I.

The experimental pilot unit comprised the following processes: ozonation – sand filtration – carbon adsorption (activated carbon filters have been characterized in Table 1).



CF – GAC filter
(1,2,3,4) – type of GAC
CC – Contact chamber
OG – Ozone generator

Figure 2 | Pilot plant layout (phase II).

Table 1 | Activated carbon characteristics, as specified by the manufacturers

Column number	(1)	(2)	(3)	(4)
Raw material	Coal	Coal	Coal	Coal
Grade (mm)	0.6–2.36	0.6–2.4	0.6–2.36	0.6–2.36
Specific surface BET ($\text{m}^2 \text{g}^{-1}$)	1,000	1,100	1,100	1,000
Iodine number (min) (mg g^{-1})	950–1,050	1,050	1,050	950
Methylene number	24	20	28	26–28
Bulk density after washing and drying (kg m^{-3})	460	No data	410	460
Ash content (max) (%)	6	8	No data	No data

Basic operational parameters of the pilot plant:

Plant capacity: $0.58 \text{ m}^3 \text{ h}^{-1}$
 Sand filter velocity: 8.2 m h^{-1}
 Sand filters backwashing frequency: twice a day
 Carbon filters velocity: 5.7 m h^{-1}
 Carbon filters backwashing frequency: every other day
 Average ozone contact time: 12 min.
 Ozone doses: $1.0 \text{ g O}_3 \text{ m}^{-3}$

Measurements

Water samples were taken once a day at sampling points located downstream of each unit process. The exact location of the sampling points in phases I and II were:

Phase I: raw water (collection well), downstream from the clarifier;

- *Unit I (ozonation ahead of sand filtration)*: downstream from the contact chamber I (CC I), downstream from the sand filter I (SF I), downstream from the carbon filter I (CF I);
- *Unit II (ozonation after sand filtration)*: downstream from the sand filter II (SF II), downstream from the contact chamber II (CC II), downstream from the carbon filter II (CF II).

The existing treatment train of the Rudawa WTP was used as a basis for a comparative study; the water samples for physico-chemical analysis were taken downstream from the sand (SF) and carbon filters (CF) respectively.

Phase II: raw water, downstream from the clarifier, downstream from the contact chamber I (CC I), downstream from the sand filter I (SF I), downstream from the carbon filter (1) (CF 1), downstream from the carbon filter (2) (CF 2), downstream from the carbon filter (3) (CF 3), downstream from the carbon filter (4) (CF 4).

Process performance was monitored using the following parameters:

pH: measured with a pH electrode

Turbidity: nephelometric method

Colour: spectrometric method

Permanganate COD: titration method (permanganate COD has been tested as by now it is commonly used as a simplified measurement of organic matter content in water)

UV absorbance: spectrophotometer UNICAM at 254 nm

Dissolved organic carbon (DOC): OWO SKALAR analyser

Samples before analysing were treated in a centrifuge; inorganic carbon was removed using phosphoric acid (acidification) and aeration with synthetic air. Since DOC measurements were not performed immediately, the samples were stabilized with phosphoric acid.

Bromates: ion chromatography

Aldehydes: high performance liquid chromatography (HPLC)

Specific UV absorbance at 254 nm ($SUVA_{254}$) has been calculated dividing the UV absorbance value of the sample by the DOC value of the sample; normalization to the light path of 1 m is achieved by multiplying by 100 cm m^{-1} (Edzwald & van Benschoten 1990; Edzwald & Tobiason 1999) as specified in the formula:

$$SUVA_{254} = \frac{\text{Abs UV}}{\text{DOC}} [\text{L} * \text{mg C}^{-1} * \text{m}^{-1}]$$

where $SUVA_{254}$, specific absorbance; Abs UV, m^{-1} , UV absorbance at 254 nm, normalized to light path of 1 m; DOC, g C m^{-3} , dissolved organic carbon concentration.

The $SUVA_{254}$ value has been recommended for description of organic contamination in raw water also for initial choice of proper treatment process. Table 2 briefly describes the application of this parameter.

Table 2 | Application of a $SUVA_{254}$ parameter for treatment process choice

$SUVA_{254}$ ($\text{m}^2 \text{ g C}^{-1}$)	Organic contamination in water	Process recommendation
>4	High hydrophobic and aromatic fractions of DOC	Coagulation recommended
<3	Hydrophilic and low-weight substances	Sorption more efficient than coagulation
<2	–	In raw water – no need for coagulation In treated water – no need for the DOC removal

Based on Edzwald & van Benschoten (1990); White *et al.* (1997); Edzwald & Tobiason (1999); Karanfil *et al.* (2002); Molczan *et al.* (2006).

Raw water characteristic

Raw water characteristic was determined based on selected physico-chemical parameters measured during the pilot plant operation. The analysis was conducted based on the average, maximum and minimum values obtained during both phases of the study (Table 3).

Raw water had a stable characteristic in terms of colour, pH and turbidity; values for permanganate COD, UV absorbance, DOC and $SUVA_{254}$ varied due to a fluctuation of organic compound concentrations in raw water. Average values and the range of $SUVA_{254}$ in raw water and water after consecutive processes is presented in Figure 3 (results concerning treated water will be discussed later).

Raw water characteristics during both tests showed that it required coagulation followed by sorption for most of the operation time to remove organic matter.

RESULTS AND DISCUSSION

Ozonation efficiency (phase I)

Turbidity

Effluent turbidity did not exceed 0.5 NTU and its average values were approximately 0.13 NTU. An increase of turbidity at the point of ozone dosing (contact chamber) was

Table 3 | Raw water characteristic during experimental studies

Parameter	Values	Phase I	Phase II
pH	Max	8.3	8.4
	Average	8.0	8.0
	Min	7.7	7.7
	Standard deviation	0.1	0.1
Turbidity (NTU)	Max	6.09	13.00
	Average	3.57	2.91
	Min	2.30	2.00
	Standard deviation	1.07	1.58
Color (g Pt m ⁻³)	Max	14.0	16.0
	Average	11.5	11.3
	Min	8.0	8.0
	Standard deviation	1.5	1.5
Permanganate COD (g O ₂ dm ⁻³)	Max	4.3	4.4
	Average	2.5	2.0
	Min	1.0	1.2
	Standard deviation	0.6	0.6
UV absorbance (cm ⁻¹)	Max	7.70	13.32
	Average	4.75	6.16
	Min	3.54	4.10
	Standard deviation	1.10	1.87
Dissolved organic carbon (g C m ⁻³)	Max	3.50	3.01
	Average	2.59	1.91
	Min	1.70	0.90
	Standard deviation	0.42	0.43
SUVA ₂₅₄ (m ⁻¹ g C ⁻¹ m ⁻¹)	Max	3.19	6.23
	Average	1.87	3.35
	Min	1.14	1.87
	Standard deviation	0.48	1.07

observed; it was much higher for Unit I (ozonation ahead of the sand filter) than for Unit II.

Colour

Introduction of the ozonation process (in both units) enhanced colour removal by 20–25%, compared with a system without ozonation. Colour in water treated with ozonation ranged from 1–4 g Pt m⁻³. Similar effects were achieved in both experimental units; no specific impact of an ozone dose on colour removal efficiency was observed.

Permanganate COD

Similar permanganate COD removal was obtained in all technological systems. In most cases, the systems that employed the ozonation process showed slightly better effects, especially at ozone dosages above 1.5 g O₃ m⁻³. Permanganate COD concentrations in water treated with ozonation ranged from 0.5 to 1.8 g O₃ m⁻³.

UV absorbance (Figure 4)

Application of the ozonation process improved the decrease of UV absorbance in both units. This value was 13 to 40% lower, compared with the system without ozonation, which confirms better operation. The optimum ozone dosage was approximately 1 g O₃ m⁻³; a further increase of the ozone dosage only slightly improved the decrease of UV absorbance. Incorporation of ozonation into the operation of both experimental units produced effluents of similar quality.

DOC

Analysis of DOC concentrations in the effluents did not reveal any particular differences in removal of this parameter in both investigated units; the average removal of DOC was 22–26%. There was no significant relationship found between ozonation and DOC decrease. The DOC concentrations in water treated with ozone varied over a broad range from 0.88 to 3.30 g C m⁻³.

SUVA₂₅₄ (Figure 5)

A significant decrease of specific absorbance SUVA₂₅₄ was observed once the ozonation process was introduced, especially when ozone dosages exceeded 1 g O₃ m⁻³.

Decreasing SUVA values as shown previously in Figure 3 proved that the chosen process sequence had been properly optimized for reduction of concentration of parameters describing organic matter presence in water. The best results have been obtained using GAC (4) filter. The average SUVA value is below 1.0 m³ g C⁻¹ m⁻¹ and the maximum observed value slightly exceeded 2.0 SUVA units, which means that there is no reason for further DOC removal. Tests on

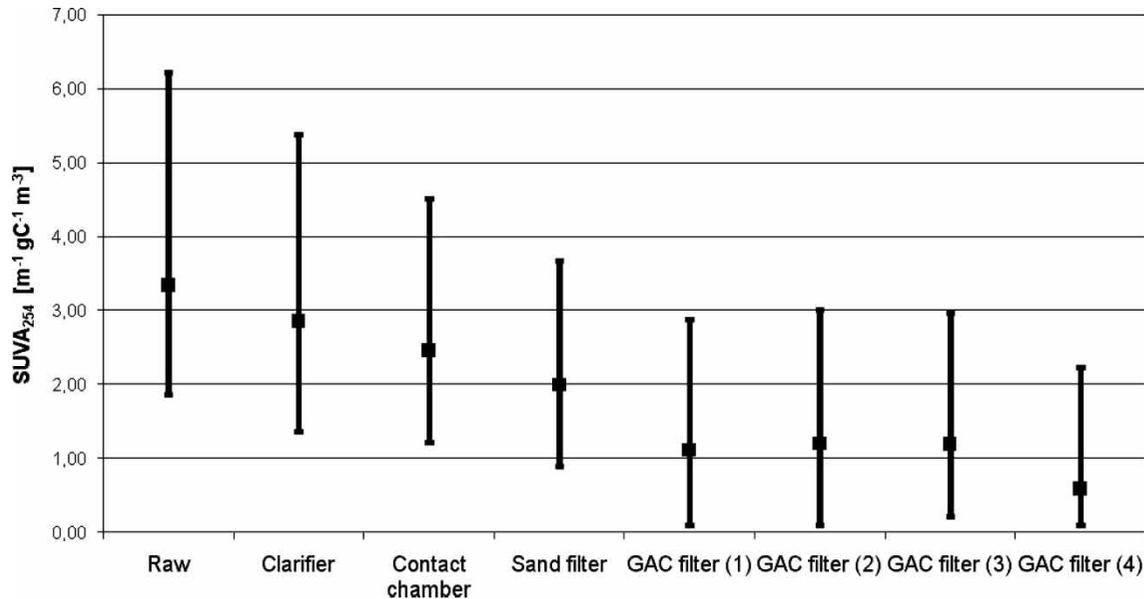


Figure 3 | Average values and the range of SUVA₂₅₄ values downstream of the different units.

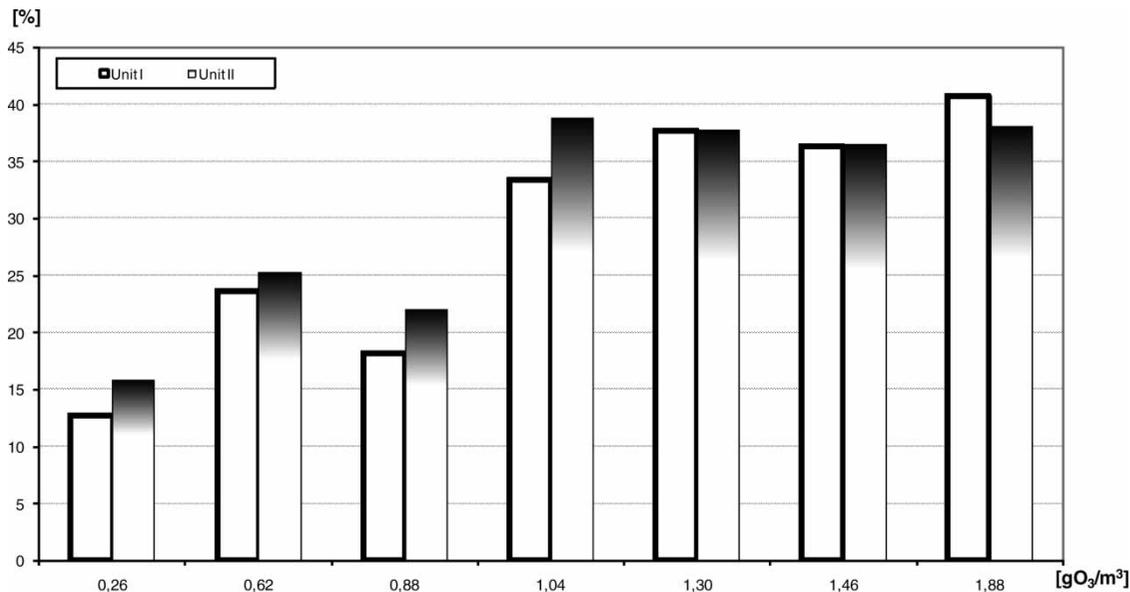


Figure 4 | Average UV absorbance reduction depending on the average ozone dosage at the Rudawa pilot plant (compared with the Rudawa WTP).

ozone dosage showed that ozone dose over 1 ppm (1 g m^{-3}) was not recommended for this process.

Aldehydes

Concentration of aldehydes was measured in all samples of this series as it is one of the major ozonation by-products.

Increase of aldehydes was observed after ozonation with a decrease after GAC filtration; however, a slight increase was observed in the effluents, compared with raw water. Average concentration in raw water was $36 \mu\text{g l}^{-1}$ for Unit I and $32 \mu\text{g l}^{-1}$ for Unit II, while maximum values were 48 and $53 \mu\text{g l}^{-1}$ respectively. The average increase after ozonation was 19.4% in Unit I and 5.9% in Unit II. This

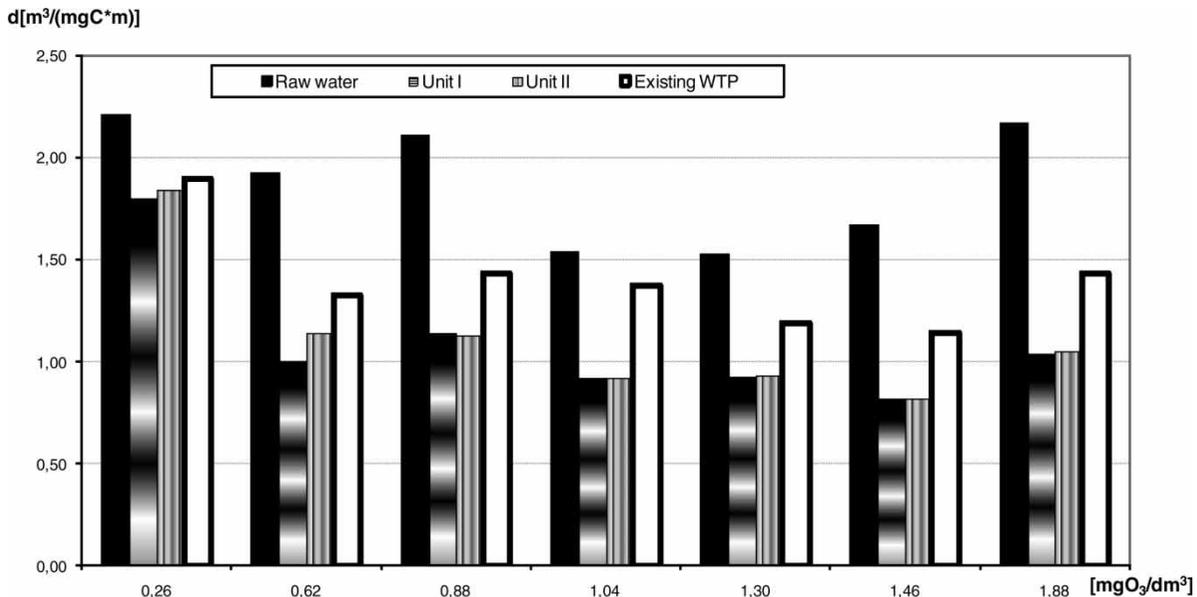


Figure 5 | Average values of $SUVA_{254}$ in the system being analysed at the average ozone dosages at the Rudawa pilot plant.

contaminant was diminished during a GAC adsorption, but an overall increase during treatment of 1.4% and 2.1% was observed for Units I and II, respectively. Final concentration had not exceeded allowed values issued by waterworks (as this parameter has no legally established maximum value).

Bromates

Bromate concentration was analysed only twice over the entire period of experimental studies. In both cases the bromine concentration was below the detection limit (2 ppb i.e. $2 \mu\text{g l}^{-1}$), at each sampling point location.

Efficiency of systems with activated carbon adsorption (phase II)

Turbidity

Turbidity in water after activated carbon adsorption ranged from 0.05 to 0.32 NTU. The lowest turbidity values (0.05–0.20 NTU) were detected after the GAC filter no 4.

Colour

Colour was maintained at a constant level and was 1 g Pt m^{-3} in the effluent from all GAC filters; higher concentrations

(2–3 g Pt m^{-3}) in the effluent were observed only a few times.

UV absorbance

UV absorbance in the GAC effluents varied over a broad range of $0.05\text{--}3.23 \text{ m}^{-1}$. During both the preliminary and the final phase of the experiment similar values of UV absorbance were observed in the effluent from GAC filters (1), (2) and (3); the average value was $1.04\text{--}1.12 \text{ m}^{-1}$. UV absorbance after the GAC filter (4) remained below 1.12 m^{-1} (average 0.36 m^{-1}). Comparing the cumulative curves of load removed *vs.* inflow load (Figure 6) it may be concluded that adsorption in the GAC filter 4 was much higher than in the other units, over almost the entire time of the operation.

DOC

DOC concentrations in the effluents varied over a broad range of $0.14\text{--}1.69 \text{ g C m}^{-3}$. Just as in the case of permanganate COD, similar values of DOC (average $0.88\text{--}1.10 \text{ g C m}^{-3}$) were observed in the preliminary phase of experiments for all the GAC filters; at the final stage, the DOC concentrations in the effluent from the GAC filters 1, 2 and 3 were $0.87\text{--}0.90 \text{ g C m}^{-3}$, while for the GAC filter 1 the average concentration was 0.55 g C m^{-3} .

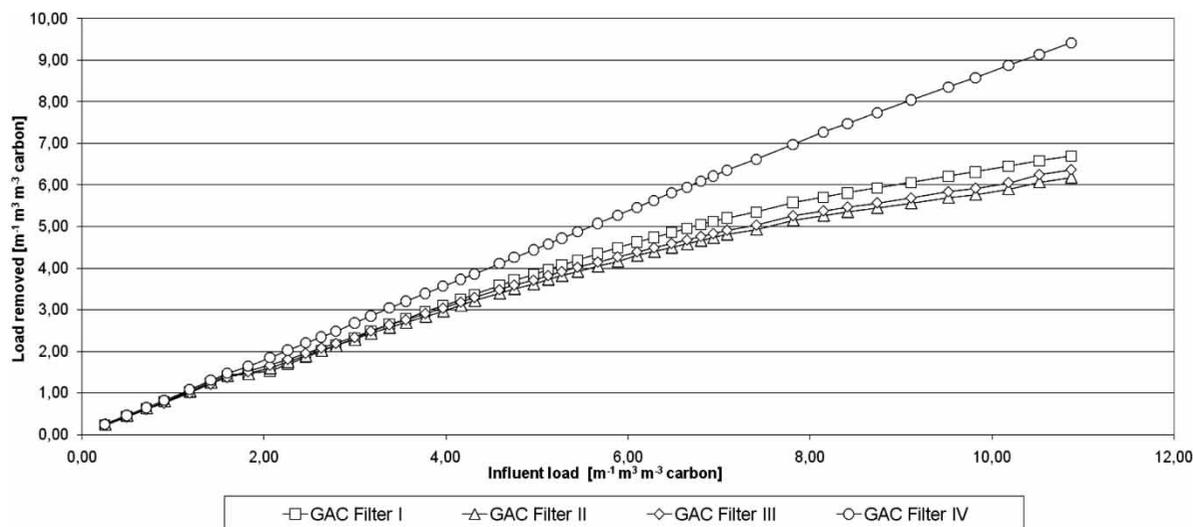


Figure 6 | Cumulative relationship of influent UV absorbance vs. absorbance removed in GAC filter.

SUVA₂₅₄ (Figure 3)

Specific absorbance SUVA₂₅₄ in the effluents varied over a broad range of 0.10–3.01 m³ g C⁻¹ m⁻¹. In the effluents from GAC filters (1), (2) and (3) similar average values of SUVA₂₅₄ were observed of 1.12–1.21 m³ g C⁻¹ m⁻¹; in the effluent from GAC filter 4 the average SUVA₂₅₄ value was 0.59 m³ g C⁻¹ m⁻¹. All results showed no need for further reduction of concentration of organics from water.

Aldehydes

Based on results obtained in phase I, aldehydes in phase II were tested only in random samples; a substantial increase of aldehydes concentration was observed after ozonation (up to 18%). However, GAC filters reduced aldehyde concentrations below their concentration in raw water; GAC filter 4 exhibited the highest process efficiency. This efficiency might be credited to this carbon structure causing an affinity to aldehydes.

CONCLUSIONS

A significant improvement in the organic compounds concentration decrease was noticed in the systems

incorporating the ozonation process. This is expressed by a better reduction of permanganate COD and UV absorbance, compared with the original technology of the Rudawa WTP (without ozonation).

A strong relationship between ozone dosage and removal efficiency of some organic compounds, expressed as UV absorbance, SUVA₂₅₄ and permanganate COD, was observed. The lowest ozone dosage (about 1 g O₃ m⁻³) that guaranteed a sufficient process efficiency should be considered as the optimum one; this way a possibility of formation of ozonation by-products may be limited.

The experimental studies confirmed the possibility of application of the treatment system comprising: ozonation – sand filtration – GAC filtration. The system showed similar process performance to the system comprising: sand filter – ozonation – GAC filtration but taking into account the current infrastructure of the water treatment plant the first system configuration was proposed as being more preferable. These tests confirmed a necessity to perform pilot plant studies prior to design procedures.

At the end of the study, substantially lower concentrations of these parameters were found in the effluent from GAC filter 4, confirming its better applicability for organics removal. Much lower values of SUVA₂₅₄ observed in the effluent from GAC filter 4 provide evidence about

better reduction of concentration of complex organic structures within this filter column.

The $SUVA_{254}$ parameter has a proven applicability in water treatment process choice. Using this parameter as a leading decision-making factor in routine operation allows overdosing both coagulation chemicals and ozone dosage to be avoided, thus it eliminates unnecessary costs of treatment and ensures minimization of treatment by-products.

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