



The Possibility of Using UV Absorbance Measurements to Interpret the Results of Organic Matter Removal in the Biofiltration Process

*Dorota Holc, Alina Pruss, Małgorzata Komorowska-Kaufman
Poznan University of Technology*

1. Introduction

Organic substances present in all natural waters are most often referred to as natural organic matter (NOM). NOM is a heterogeneous mixture of compounds, still largely unexplored from a chemical point of view. Due to its heterogeneity, it is not possible to characterise NOM according to individual components. The standard water quality indicators, such as chemical oxygen demand (COD), dissolved organic carbon (DOC), UV_{254} , pH and other do not offer information on the nature of NOM, such as molar mass or hydrophobicity (Matilainen et al. 2010, Gibert et al. 2013). This complex mixture is often characterised according to chemical groups with similar properties which are identified on the basis of concentration and fractionation data (Huber et al. 2011, Pruss 2015). The methods, however, require considerable effort, as well as pre-treatment of samples which may affect the form of the compounds. In the pursuit of NOM characterisation, analytical techniques which require minimum preparation of samples are gaining popularity, including the high-performance size exclusion chromatography (HPSEC) and the fluorescence excitation-emission matrix (F-EEM) spectroscopy (Baghouth 2011) which allow for the determination of the molecular mass distribution and the hydrophilic or hydrophobic nature of the organic compounds (Matilainen et al. 2010, Huber et al. 2011).

Removal of organic micropollutants from water requires the use of advanced methods of water treatment, including sorption and biological processes which take place in biological activated carbon filters (BAF) (Pruss 2009, Holc et al. 2016a, b, Pruss et al. 2018, Mađrecka et al. 2018). The activity of BAF is based on the combination of two processes: biodegradation and adsorption. In the initial stage of BAF operation, the predominant process is sorption. When an adequate amount of pollutants is absorbed and biological film develops, biodegradation becomes predominant. Activated carbon is an adsorbent with a very high porosity and specific surface area (600-1000 m²/g). During the operation of the filter bed, the bacteria naturally occurring in water begin to settle on the porous surface of the grain. They are mainly heterotrophic bacteria for which the environmental conditions in the bed are suitable. After about 2-3 months, biofilm forms on the grain surface (Simpson 2008, Mađrecka et al. 2018).

The degradation of pollutants due to the activity of microorganisms is a very effective process. Microorganisms are useful in the biodegradation of substances which are difficult to eliminate using traditional methods (Simpson 2008, Olesiak & Stępnik 2014, Holc et al. 2016b). Thanks to high efficiency of dissolved organic matter removal by biological activated carbon filters, the demand for disinfectants from the treated water is much lower (Kołaski et al. 2017). In the case of such water, there is a lower probability of the development of undesirable by-products and of secondary bacterial load growth in the water supply network that could cause degradation of water quality supplied to the consumers (Wolska 2014, Gibert et al. 2015, Szuster-Janiaczyk 2016, Włodyka-Bergier et al. 2016).

An indirect method for determining biological activity in BAF is the Eberhardt, Madsen and Sontheimer (EMS) test. It is based on the determination of the coefficient S , which is calculated as the quotient $\Delta[\text{COD}]$ by $\Delta[\text{O}_2]$, where $\Delta[\text{COD}]$ denotes the reduction of the chemical oxygen demand of water and $\Delta[\text{O}_2]$ is the loss of dissolved oxygen in water. The test is helpful in determining the relationship between the adsorption and the biodegradation process on the BAF bed, assuming that organic compounds are removed both by way of sorption and biodegradation, and oxygen is consumed by aerobic microorganisms to oxidize carbon. If $S = 1$, both adsorption and biodegradation proceed with the

same intensity in the filter bed. If $S > 1$, adsorption predominates, and if $S < 1$, biodegradation is predominant. When S and $\Delta[\text{COD}]$ equal 0, the sorption and biodegradation processes are stopped. If $\Delta[\text{COD}] > 0$ and $\Delta[\text{O}_2] = 0$, sorption is present and biodegradation does not occur. In turn, when both $\Delta[\text{COD}]$ and $\Delta[\text{O}_2]$ are equal 0, neither of the processes takes place (Wolborska et al. 2003, Papciak et al. 2016, Mądrecka et al. 2018).

UV absorption is a popular and relatively simple indicator used to determine the content of organic pollutants in water. The functional groups of organic compounds which absorb UV and VIS radiation are chromophores. Most chromophore groups are found in humic acid particles. Water which contains organic compounds with chromophores demonstrates absorbance within the range of 200 to 350 nm. To track UV absorption changes, the 254 nm wavelength was considered most suitable and is widely used in drinking water analysis. Based on absorbance, it is possible to determine the total dissolved organic carbon fraction and organic compounds with a high content of aromatic rings which are precursors of disinfection or oxidation by-products. Its value is often interpreted as an indicator of the degree of aromatic rings activation which serves as the basis for predicting the reactivity of aromatic components during chlorination (Mołczan et al. 2006, Nowacka et al. 2012, Szerzyna et al. 2017). The different wavelengths are believed to identify different chromophores: absorbance at 220 nm is associated with both the carboxylic and aromatic chromophores, whereas absorbance at 254 nm is typical for aromatic groups with varying degrees of activation (Korshin et al. 2009). The correlation of the UV absorbance in the range 251-256 nm to values in the range 202-205 nm is used as an indicator of the relative proportion of aromatic to aliphatic groups present in NOM. UV_{254} has been identified as a potential surrogate measure for DOC despite its tendency to represent only the aromatic character. The absorbance at 436 nm represents functional groups contributing to the color of water, from yellow to brown. Ratios between two different wavelengths, such as 254 nm/204 nm, 254 nm/436 nm or 250 nm/365 nm have also been reported to aid NOM characterization (Hur et al. 2006, Valencia et al. 2012). For example, the ratio of 253 nm/203 nm correlates with the formation of disinfection by-products (DBP_S). The value of the 254 nm/436 nm correlation is higher, when the functional groups causing color of water are removed from the water (Kim & Yu 2007, Valencia et al. 2012).

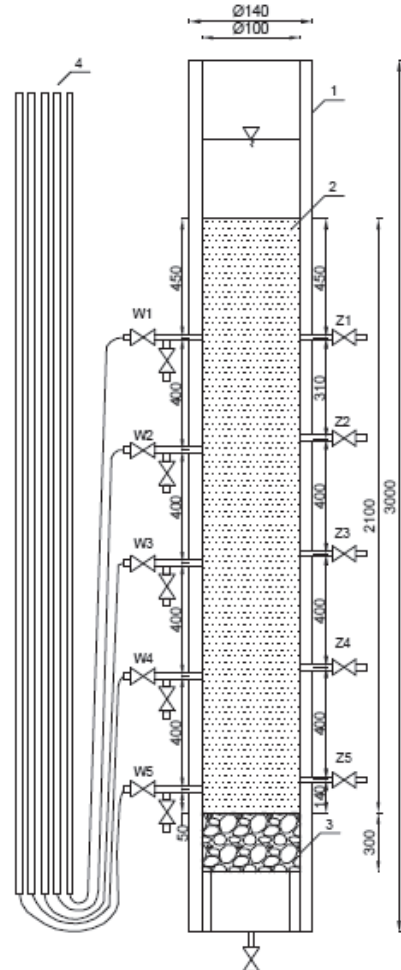
This article, present the results of research on the use of different wavelengths UV absorbance and their ratios to interpret the transformations of organic compounds in biologically active filters. The analysis of these results is a supplement to the information published in 2016 (Holc et al. 2016a, b).

2. Methods

The technological investigation was conducted on a pilot scale. The experimental stand consisted of two filtration columns with the diameter of 100 mm and the height of 300 cm (Fig. 1). The columns were filled with WG-12 granulated activated carbon with parameters: iodine number 1100 mg/g, methylene blue adsorption 30 g/100 g, total surface area B.E.T 1100 m²/g, particle size 0.75-1.5 mm. Stable temperature was maintained across the entire filter bed height thanks to a water jacket – a pipe with the inner diameter of 140 mm filled with water. The water flowing through the pipe had a temperature equal to the filtered water temperature. In order to prevent the growth of algae, the filters were covered with black geotextile. The water supplied to the filters was dechlorinated tap water. The filtration rate was 2.5 m/h and the contact time was 50 minutes, respectively. Across the entire filter height, stub pipes were located for the sampling of water and the filter bed. Samples were taken at the beginning of filters exploitation in April 2015. The system is still operated.

The filtration columns differed with regard to the method of the filter bed activation (Holc et al. 2016a) and the microorganisms found there (Holc et al. 2016b). In the first filtration column (F1), the microorganisms residing in the filter bed came from the water passing through the filter i.e. from the network water. The filter bed of the other filtration column (F2) was inoculated with the wastewater from the backwashing of carbon filters operated in a selected water treatment plant. Detailed information about this water treatment plant technology and technical BAF exploitation are presented in other publication (Kołaski et al. 2017, 2018).

The samples of water for analysis were collected on the supply line from the filtration columns and from the filter bed cross-section, at the depth of 45 cm, 85 cm, 125 cm, 165 cm and 205 cm. BAF were backwashed with a one-day shift according to a predetermined schedule. A detailed method of BAF backwashing was presented in another publication (Komorowska-Kaufman et al. 2018).



1 – filtration column, 2 – WG-12 activated carbon filter bed, 3 – gravel support layer, 4 – piezometers W1-W5 – water sampling points, Z1-Z5 – filter bed sampling points

Fig. 1. The experimental station consisting of two identical filtration columns
Rys. 1. Model badawczy złożony z dwóch identycznych kolumn filtracyjnych

The effectiveness of organic substances elimination from water was assessed using the following parameters: chemical oxygen demand (COD KMnO_4), dissolved oxygen (DO) concentration, total organic carbon (TOC), pH, alkalinity and UV absorbance for the following wavelengths: 204 nm, 254 nm, 365 nm and 436 nm.

Absorbance measurements were made using a Merck Spectroquant Pharo 300 spectrophotometer. Water samples before the measurement were not filtered.

3. Results and discussion

The analysis of the EMS value shows that biodegradation processes took place ($\text{EMS} < 1$) from the twenty third day of Filter 1 operation and essentially throughout the entire period of Filter 2 operation. The reduction of COD (KMnO_4), TOC and UV_{254} absorbance proceeded with a very high efficiency in both analysed filters, although higher effectiveness in terms of the change in COD (KMnO_4) (by 74% on average), TOC (by 80% on average) and UV_{254} absorbance (by 81% on average) was observed in the case of Filter 2 inoculated with filter backwashings. Detailed results were presented in the publications of 2016 (Holc et al. 2016a, b).

The research results presented herein are complementary to the ones already published and pertain to the possibility of using the measurements of UV absorbance at the wavelengths of 204 nm, 254 nm, 365 nm and 436 nm, respectively, for the purpose of interpretation of the transformations of organic compounds in biological activated carbon filter beds.

The quality of water at entry to the physical filter model is presented in Table 1.

Figure 2 show the changes in the UV_{254} absorbance value in water across the F1 and F2 filter beds. The UV_{254} absorbance value at entry differed significantly and ranged from 0.001 cm^{-1} to 0.0194 cm^{-1} . The average value of UV_{254} absorbance in water supplied to the filter was 0.0051 cm^{-1} . As a result of the filtration of water through the biologically active filter bed, the absorbance value went down even to 0.0000 cm^{-1} , which is an evidence of very high effectiveness of organic pollutants removal. The difference in the UV_{254} absorbance value in water occurring

between the inflow and the outflow is the smallest at day 23 of filter operation. On this day, based on the EMS value, for the first time the biodegradation processes prevailed in the filter bed. Since then, the change of absorbance value UV_{254} , in inflow and outflow, is systematically increasing. This indicates that organic compounds containing an aromatic ring in their molecule are removed in the biodegradation process.

Table 1. Quality parameters and concentrations found in the water supplied to BAF columns

Tabela 1. Parametry jakościowe i stężenia w wodzie dopływającej do kolumn BAF

Parameter	Unit	Range	Average value	Standard deviation
Temperature	°C	16.2-21.8	18.5	1.5
pH	–	7.23-7.35	7.3	0.05
DO	mg O ₂ /dm ³	6.85-8.90	8.2	0.6
Alkalinity	mg CaCO ₃ /dm ³	147-230	169	24
COD (KMnO ₄)	mg O ₂ /dm ³	2.65-4.88	3.6	0.7
TOC	mg C/dm ³	4.4-5.5	4.8	0.6
UV ₂₅₄	cm ⁻¹	0.001-0.0194	0.0067	0.0051

The different values of the UV_{254} absorbance within the filtration bed reflect the varying effectiveness of the elimination of organic compounds determined on the basis of UV_{254} absorbance in both filters. Most likely, the differences can be attributed to the methods of the filter bed activation and different microorganisms found in the two beds which played a role in the biodegradation process (Holc et al. 2016a, b).

In the analysis of the results, attention was paid to the interdependencies of the absorbance ratios measured at different wavelengths. Such a correlation offers indirect information about organic substances contained in the analysed water and the transformations they undergo. The evaluated ratios included UV_{254}/UV_{204} , UV_{254}/UV_{436} and UV_{254}/UV_{365} and the results are presented in Figures 3-5.

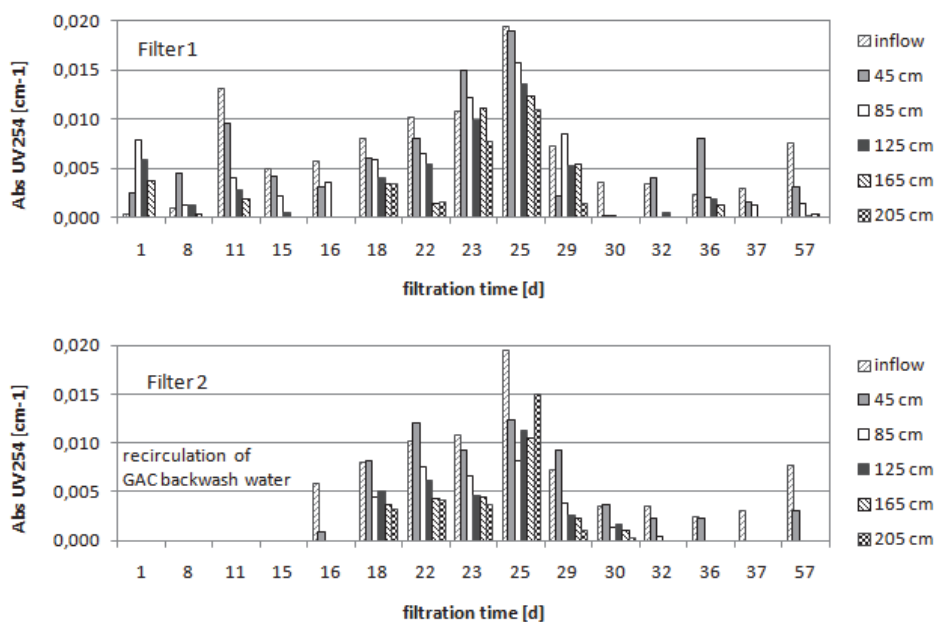


Fig. 2. Changes in the UV_{254} absorbance ratio in filter F1 and F2

Rys. 2. Zmiany wartości absorbancji UV_{254} w filtrze F1 i F2

The values of UV_{254}/UV_{204} and UV_{254}/UV_{436} ratios in both F1 and F2 filter showed minor changes in the initial period of the system operation. From the 30th day of continuous operation, a clear drop in the values of the abovementioned absorbance ratios was observed. The values recorded at the time were very low which evidences high effectiveness of aromatic organic compounds removal by way of biodegradation and that water potential for the formation of disinfection by-products is very low. Analyzing the obtained values in the vertical cross-section of filters, from the 30th day, it should be noted that for the correlation UV_{254}/UV_{204} the highest values were obtained in samples taken from the upper filter layers that indicate the most intense development of microorganisms capable of biodegradation in that part of the filter. This phenomenon is known and often described in many literature items (Simpson 2008, Pruss et al. 2009).

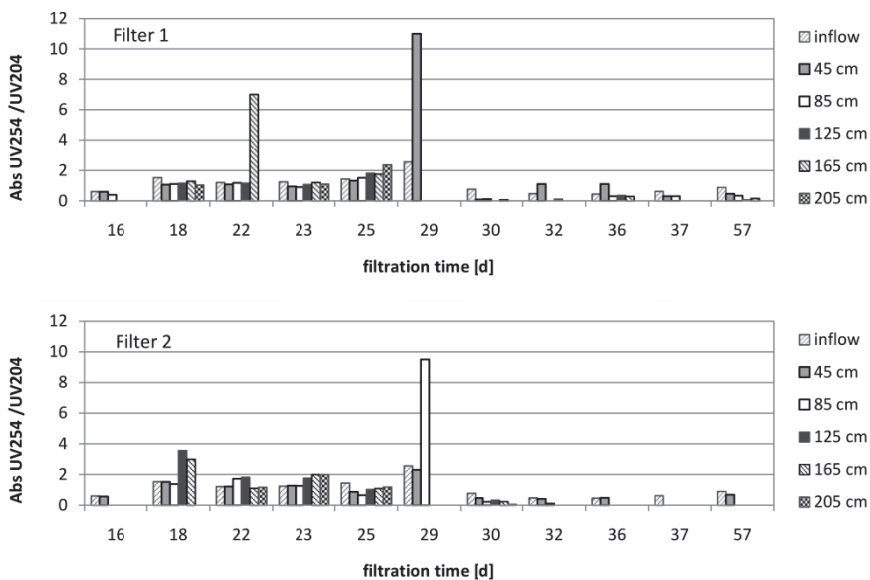


Fig. 3. Changes in the UV_{254}/UV_{204} absorbance ratio in filter F1 and F2
Rys. 3. Zmiany wartości absorbancji UV_{254}/UV_{204} w filtrze F1 i F2

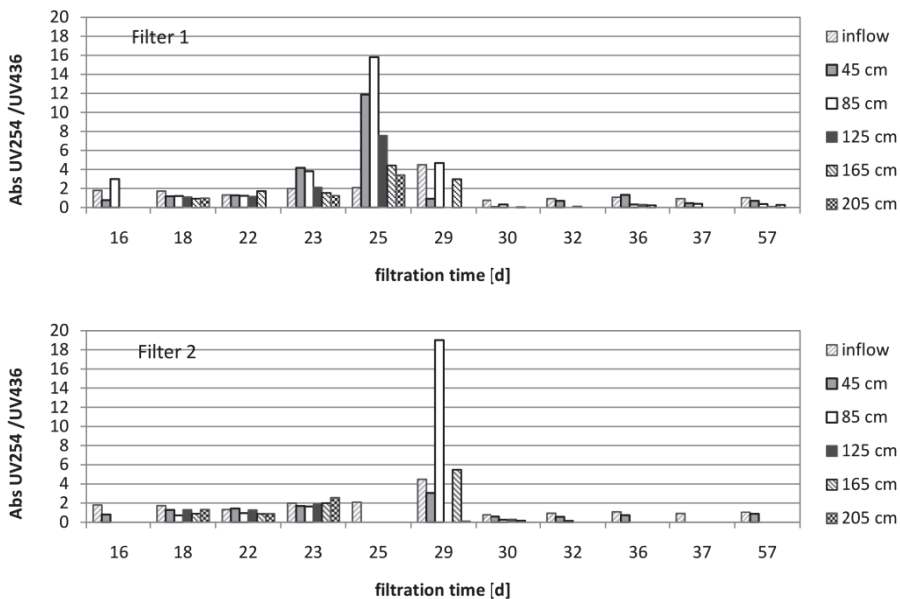


Fig. 4. Changes in the UV_{254}/UV_{436} absorbance ratio in filter F1 and F2
Rys. 4. Zmiany wartości absorbancji UV_{254}/UV_{436} w filtrze F1 i F2

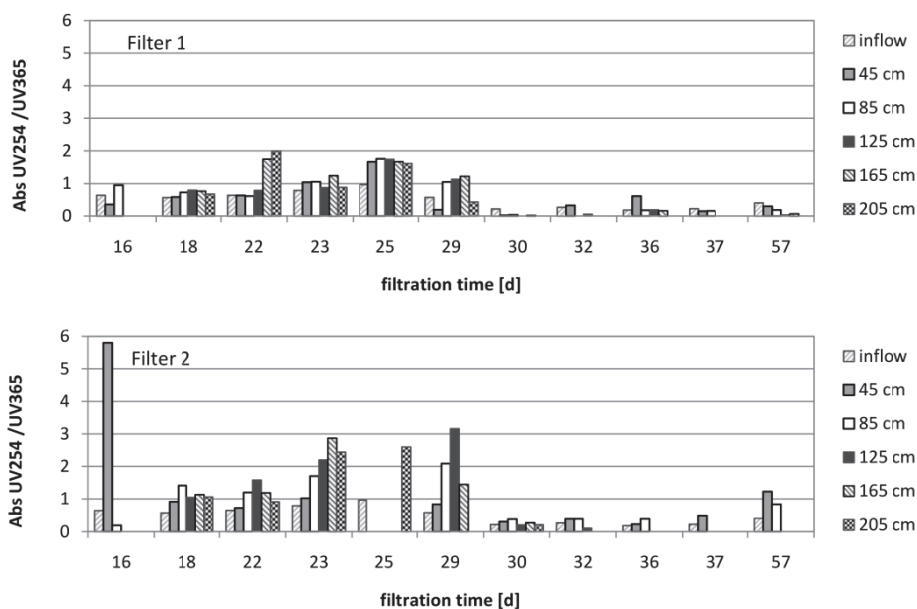


Fig. 5. Changes in the UV_{254}/UV_{365} absorbance ratio in filter F1 and F2
Rys. 5. Zmiany wartości absorbancji UV_{254}/UV_{365} w filtrze F1 i F2

The UV_{254}/UV_{365} relationship allows for the tracking of changes in the size of particles of the dissolved organic matter. Throughout the entire period under review, the value of UV_{254}/UV_{365} ratio remained low in both analysed filters. As of the 30th day of operation a clear decrease in its value was observed. Low values of the UV_{254}/UV_{365} ratio are often recorded in the presence of aromatic functional groups (Yan et al. 2012).

4. Conclusion

The filtration of water using biological activated carbon filters is a process which ensures effective removal of organic substances from water. Due to the significant role of microorganisms found in biological activated carbon filters in the elimination of biodegradable organic matter, the proper operation of the filters is very important.

The use of UV radiation may greatly improve the monitoring of the filter performance. The investigations have proven that it is possible to use the measurements of UV absorbance at the wavelengths of 204 nm, 254 nm, 365 nm and 436 nm, respectively, for the interpretation

of the transformations of organic compounds in biological activated carbon filters. It is worth emphasising that absorbance measurements are quick and can significantly facilitate the work of water technology engineers in charge of the treatment processes, especially in that Water Treatment Plants which use biological activated carbon filters and are equipped with UV absorbance analyzers operating in an online mode.

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Możliwość wykorzystania pomiarów absorbancji UV do interpretacji wyników usuwania materii organicznej w procesie biofiltracji

Streszczenie

Naturalna materia organiczna (NOM), czyli substancje organiczne występujące w wodach naturalnych, to heterogeniczna mieszanina związków, wciąż nieodkryta z chemicznego punktu widzenia. Standardowe wskaźniki jakości wody, takie jak chemiczne zapotrzebowanie na tlen (ChZT), rozpuszczony węgiel organiczny, absorbancja UV₂₅₄, pH i inne, nie dostarczają wystarczających informacji o charakterze NOM, takich jak masa molowa, czy hydrofobowość. Do scharakteryzowania NOM coraz bardziej przydatna okazuje się absorbancja UV dla różnych długości fal.

Absorpcja UV jest popularnym i względnie prostym wskaźnikiem określającym zawartość zanieczyszczeń organicznych w wodzie. Grupy funkcyjne związków organicznych pochłaniających promieniowanie UV i VIS to chromofory. Uważa się, że różne chromofory są identyfikowane przez różne długości fal. Absorbancja UV przy długości 220 nm jest związana zarówno z chromoforami karboksylowymi jak i aromatycznymi, podczas gdy absorpcja UV przy długości 254 nm jest typowa dla grup aromatycznych o różnych stopniach aktywności. Na podstawie wartości absorbancji można określić całkowitą zawar-

tość rozpuszczonego węgla organicznego i związków organicznych o wysokiej zawartości pierścieni aromatycznych, które uważa się za prekursory ubocznych produktów dezynfekcji lub utleniania. Zauważono także, że zależności występujące między dwoma różnymi długościami fal, jak na przykład: 254 nm/204 nm, 254 nm/436 nm, czy 250 nm/365 nm, pomagają w charakteryzowaniu NOM.

W artykule przedstawiono wyniki badań nad wykorzystaniem absorbancji UV o różnych długościach fal do interpretacji przekształceń związków organicznych w biologicznie aktywnych filtrach węglowych (BAF). Analiza tych wyników stanowi uzupełnienie informacji opublikowanych w 2016 roku (Holc i in. 2016a, b).

Badania nad efektywnością usuwania związków organicznych w procesie biofiltracji prowadzono w skali pilotowej. Stanowisko badawcze stanowiły dwie kolumny filtracyjne o średnicy 100 mm oraz wysokości 3,0 m, wypełnione granulowanym węglem aktywnym WG-12. Filtry zasilano dechlorowaną wodą wodociągową. Kolumny filtracyjne różniły się między sobą sposobem aktywacji złoża filtracyjnego. Skuteczność eliminacji substancji organicznych z wody oceniano za pomocą następujących parametrów: pH, tlen rozpuszczony, zasadowość, utlenialność, OWO, absorbancję UV dla kilku długości fal: 204 nm, 254 nm, 365 nm i 436 nm.

W trakcie prowadzonych badań zauważono, że w wyniku filtracji wody przez złożo BAF, wartość absorbancji UV_{254} obniżyła się nawet do 0 cm^{-1} , co świadczy o bardzo wysokiej efektywności usuwania zanieczyszczeń organicznych. W trakcie przeprowadzonych badań zaobserwowano także korelację między wartościami absorbancji mierzonymi dla różnych długości fal. W obu kolumnach filtracyjnych odnotowano bardzo niskie wartości stosunku absorbancji: UV_{254}/UV_{204} i UV_{254}/UV_{436} , co wskazuje na skuteczne usuwanie aromatycznych związków organicznych z wody poprzez biodegradację.

Abstract

Natural organic matter (NOM) found in natural waters, is a heterogeneous mixture of compounds, still undiscovered from a chemical point of view. Standard water quality indicators, such as chemical oxygen demand (COD), dissolved organic carbon (DOC), UV_{254} , pH and others, do not provide information about the nature of NOM, such as molar mass or hydrophobicity. UV absorbance at different wavelengths is becoming more and more useful for characterizing NOM.

UV absorption is a popular and relatively simple indicator determining the content of organic pollutants in water. The functional groups of organic compounds absorbing UV and VIS radiation are chromophores. It is believed that different chromophores are identified by different wavelengths. The UV

absorbance at 220 nm is associated with both carboxylic and aromatic chromophores, while UV absorption at 254 nm is typical of aromatic groups with different degrees of activity. From the absorbance it is possible to determine the total content of dissolved organic carbon and organic compounds with a high content of aromatic rings that are precursors of by-products of disinfection or oxidation. It was also noticed that the relationships between two different wavelengths, such as: 254 nm/204 nm, 254 nm/436 nm, or 250 nm/365 nm, can characterize NOM.

This article, presents the results of research on the use of UV absorbance at different wavelengths to interpret transformations of organic compounds in biologically active carbon filters (BAF). The analysis of these results complements the information published in 2016 (Holc et al 2016a, b).

Research on the effectiveness of organic compounds removal in the biofiltration process was carried out on a pilot scale. The test stand consisted of two filtration columns with a diameter of 100 mm and a height of 3.0 m, filled with granulated activated carbon WG-12. The filters were fed with dechlorinated tap water. The filter columns differed from each other in the manner of activation of the filter bed. The effectiveness of organic substances elimination from water was assessed using the following parameters: pH, dissolved oxygen (DO) concentration, alkalinity, chemical oxygen demand (COD KMnO_4), total organic carbon (TOC) and UV absorbance for the following wavelengths: 204 nm, 254 nm, 365 nm and 436 nm.

In the research, it was noticed that as a result of filtration of water through the BAF bed, the absorbance value of UV_{254} decreased even to 0 cm^{-1} , which indicates very high efficiency of removing organic pollutants. During the research, was observed the correlation between the absorbance value measured at different wavelengths. There were very low values of the absorbance ratio: $\text{UV}_{254}/\text{UV}_{204}$ and $\text{UV}_{254}/\text{UV}_{436}$ in both filter columns, which indicates effective removal of aromatic organic compounds from water through biodegradation.

Słowa kluczowe:

biofiltracja, filtry biologicznie aktywne, związki organiczne, badania technologiczne w skali pilotowej, absorbancja UV

Keywords:

biofiltration, biologically active filter (BAF), organic compounds, pilot scale technological investigation, UV absorbance