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# Influence of a high-intensity ultrasonic field on the removal of natural organic compounds from water

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**ABSTRACT**

Organic compounds, which are considered water pollutants, have the ability to react with chlorine or other oxidants leading to the formation of products which pose a significant threat to human health. Humic substances play an important role in the formation of disinfection by-products. Therefore, the removal of organic compounds in the process of water treatment is of great importance. The application of ultrasound initiates a number of physicochemical processes in water which can be used in water treatment technologies, e.g. coagulation or adsorption. These methods, as well as the ion-exchange process, are applied in order to remove organic contaminants. With reference to the theoretical fundamentals of ultrasound, some sonochemical processes can result in a decrease in the content of color organic compounds in water. Increasing the intensity of ultrasonic field enhances the occurrence of sonochemical processes including the destruction of high-molecular organic compounds or the oxidation reactions with radicals. The effect of the ultrasonic field is investigated as a method of water treatment by removal of color contaminants from water. Water samples were subjected to an ultrasonic field generated by the UP-400S ultrasound generator with a frequency of 24 kHz and useful power of 300 W. The samples were exposed to sonification for the time periods of 1 and 5 min; the range of the applied amplitude vibration was 18–90 $\mu$m, and the ultrasonic field intensity was in the range 21–105 W/cm$^2$. The applied parameters allowed for the observation of changes in the content of organic compounds in water. The effect of the ultrasonic field was investigated for surface water. The water analysis included TOC, oxygen consumption and color. The efficiency of the investigated process (30–40%) was achieved for the highest value of the applied amplitude.

***Keywords***: Ultrasounds; Sonochemical processes; Water treatment; Organic contaminants

## 1. Introduction

The type and sequence of processes in the contemporary water treatment systems are often selected in order to optimize the removal of natural organic matter (NOM). The reason for optimizing conventional water treatment process for NOM removal is to reduce the formation of disinfection by-products (DBPs) during disinfection processes. In this context, the removal of organic compounds from water is considered an important technological problem.

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According to the theoretical fundamentals of ultrasound, a number of sonochemical processes which are initiated in water can lead to the degradation of many organic compounds. The main reason for th is the concentration of oxidizing particles present in the form of hydroxyl radicals. Significantly high temperature and pressure (i.e. 5000 K and 500 atm.) which are observed locally in the solution subjected to sonification result in a temporary state of "supercritical water". These processes occur at high intensity of the ultrasonic field which is required for ultrasonic cavitation [1–3]. There are two mechanisms of the removal of organic compounds: (a) chemical degradation through the oxidation by hydroxyl radicals in the cavitation bubbles and (b) mechanical fragmentation.

Till now, the researchers have investigated the effect of sonochemical degradation of the selected contaminants including chlorinated hydrocarbons, pesticides, phenols and esters. The results were reported for the model solutions of the selected compounds. These compounds subjected to ultrasound were transformed into short-chain organic acids, carbon dioxide and inorganic ions as the final products [4–7]. The efficiency of ultrasound is investigated in terms of the removal of organic contaminants from natural water during water treatment [8–13]. Due to the presence of humic acids as the predominant organic constituents in surface and ground water, the investigations are usually conducted in the model solutions of humic acids (HA) with the concentration range of 5–50 mg/l [14]. The obtained results confirm the increase in the efficiency of TOC removal from the model solutions by approximately 30%. The efficiency can increase at higher ultrasound intensity and longer exposure time. The best results (i.e. 35% reduction in humic acids measured as the TOC) were obtained at the maximum intensity of 42 W/cm$^2$ and an exposure time of 20 min [15]. According to many investigations the increase in the process efficiency is achieved by combining ultrasound and $H_2O_2$ [16,17].

The total organic carbon (TOC) is used as an indicator of the content of organic compounds. According to the Polish regulations on drinking water from 2007, the permissible value of the TOC is 5.0 mg C/l [18]. Determination of the TOC is required in larger water treatment stations (above 10,000 m$^3$/d). Smaller water treatment stations use indirect measurements of the water organic contaminations, i.e. color (15 mg/l Pt), oxygen consumption (up to 5.0 mg $O_2$/l) and $UV_{254}$ absorbance. The measurement of $UV_{254}$ does not only reflect the content of organic compounds or active forms (also nitrates and bromides show the ability to be absorbed). However, for natural water with rather stable content, the correlation between the TOC and $UV_{254}$ is higher than between the TOC and oxygen consumption or color. More and more researchers tend to use both measurements, i.e. the TOC and $UV_{254}$ in their investigations. With the reference to the specific ultraviolet absorbance, the $SUVA_{254}$ ($UV_{254}$/DOC), selected properties of organic compounds can be determined. Also, the efficiency of the DOC removal during coagulation can be predicted. This indicator determines the level of the DOC reactivity as it correlates with the formation of oxidation by-products/disinfection by-products (OBP/DBP) [19].

This article presents the effect of the ultrasonic field on the removal of organic compounds from water. The changes in water organic contamination were determined by the TOC and $UV_{254}$ absorbance.

## 2. Materials and methods

Water from a selected river was sampled and used for the experiments. With the reference to the water analysis, the indicators of organic contamination, i.e. the values of the TOC and the $UV_{254}$ absorbance were increased (Table 1). During the investigations (from March to May), an insignificant variability in the water quality indicators was observed. In view of the specific ultraviolet absorbance, the $SUVA_{254}$ above 4 m$^2$/gC (in the range of 4.5–5.4 m$^2$/gC) the reactivity of compounds defined as the DOC is considerably high which also allows for achieving high efficiency of the removal during coagulation [19].

Water samples were sonificated using a Hielscher UP400S high-power ultrasonic generator with a fixed frequency of 24 kHz and a maximum effective power of 300 W. The effect of the exposure time and the vibration amplitude (in the range 18–90 $\mu$m) on the ultrasonic field intensity was investigated. The maximum ultrasound intensity at the amplitude of 90 $\mu$m was 105 W/cm$^2$. The 500-ml volume water samples were subjected to sonification for the time periods of 1 and 5 min.

The $UV_{254}$ indicator was determined based on the measurement of absorption at a wavelength of $\lambda = 254$ nm

Table 1
Physicochemical analysis of the water

| Indicator | Unit | Natural water |
|---|---|---|
| Temperature | °C | 12.4–15.6 |
| pH | — | 6.58–6.87 |
| Alkalinity | mval/l | 0.55–0.60 |
| Color | mg/l(Pt) | 23–35 |
| Turbidity | NTU | 12.66–18.40 |
| Oxygen consumption | mg$O_2$/l | 5.6–6.5 |
| Total iron | mg/l | 1.20–1.35 |
| Total hardness | mval/l | 0.85–1.52 |
| Absorbance, $UV_{254}$ | 1/cm | 0.21–0.33 |
| TOC | mgC/l | 5.23–7.1 |
| DOC | mgC/l | 4.7–6.6 |

(with a cuvette optical path length of 1 cm) by the Hach DR/4000U spectrophotometer apparatus. The TOC and DOC were determined by the Ströhlein Instruments Coulomat 702/Li analyzer. The $SUVA_{254}$ indicator was calculated as the $UV_{254}$/DOC. Other water quality indicators, i.e. temperature, pH, alkalinity, color, turbidity, oxygen consumption, total iron and total hardness, were determined by standard methods for water analysis.

### 3. Results and discussion

With reference to the preliminary analysis of the investigated water, the linear regression relationships for selected indicators, i.e. color, oxygen consumption, the $UV_{254}$ absorbance and TOC, were determined. The correlation coefficients were calculated for TOC and color, TOC and the oxygen consumption, and TOC and $UV_{254}$ absorbance. The highest correlation ($r$ =0.94) was determined for TOC and $UV_{254}$ (Fig. 1).

The TOC and UV absorbance as the indicators of organic contamination in natural water with a stable content are more useful than the oxygen consumption or color which only allow for rough estimation of organic contamination. The effect of the ultrasonic field on the removal of organic compounds from the investigated water was evaluated based on the changes in the TOC and $UV_{254}$ absorbance. The results obtained for variable ultrasound intensity in function of the amplitude vibration are presented in Fig. 2.

The application of ultrasound resulted in a decrease of organic water contamination (TOC) from 6.3 and 6.8 mgC/l to a level below 4 mgC/l (for the exposure time of 5 min). The increase in the amplitude vibration had a positive effect on the investigated process. The most beneficial effects were observed with the increase in the amplitude up to 54 $\mu$m (60 W/cm$^2$). With the reference to the plotted curves, further increasing the ultrasonic field intensity does not significantly influence the final effect. Longer exposure time (i.e. 5 min) enhanced the efficiency of the process and resulted in lower values of the TOC. The reduction in the TOC below the permissible value of 5 mgC/l was achieved after the exposure time of 1 minute at the amplitude of 54 $\mu$m. The observed influence of ultrasound on the removal of organic compounds from water based on the $UV_{254}$ absorbance confirms the efficiency of the investigated process. Increasing the intensity of ultrasound field in the applied range of amplitude values enhances the final result. The differences between diagrams can result from the discrepancies in the type of compounds determined by the TOC and $UV_{254}$. The investigated relationships are approximated by the linear regression equations (Fig. 3). The correlation coefficients for the TOC and $UV_{254}$ are similar (TOC, $r$ =–-0.95; $UV_{254}$, $r$ = –0.98).

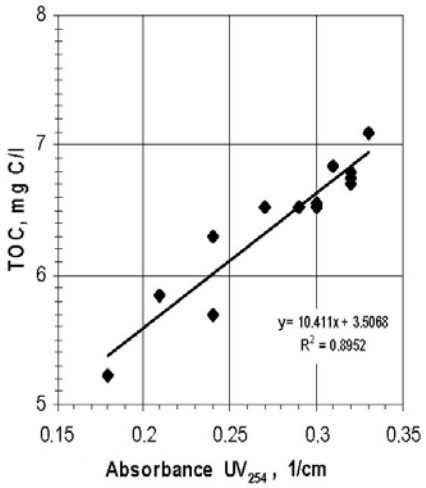


Fig. 1. Relationship between the TOC and absorbance $UV_{254}$ for the investigated water.

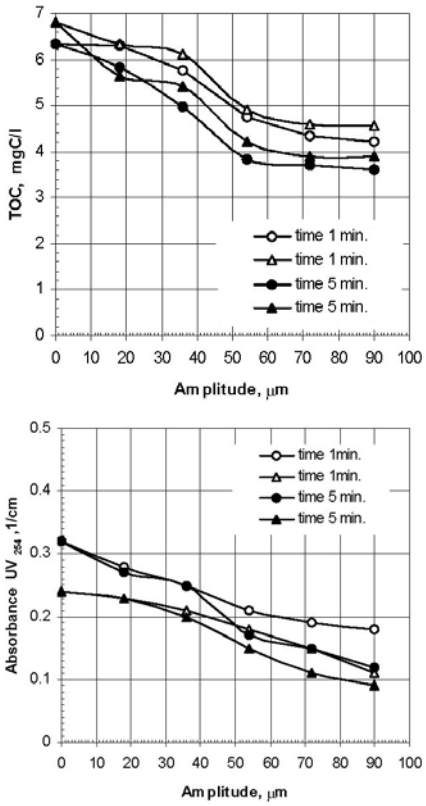


Fig. 2. Effect of the applied range of amplitude on the TOC and $UV_{254}$ values.

The efficiency of the investigated process is also confirmed by the reduction in the $SUVA_{254}$ indicator (Table 2). The final results of the $SUVA_{254}$ for water exposed to ultrasound for 5 min were 3.1 and 3.7 m$^2$/gC (i.e. below 4 m$^2$/gC), respectively. This can indicate that the quantity of hydrophobic, aromatic and high-molecular fractions of the DOC is lower than in raw water. Also, it

Table 2
Effect of amplitude on the $SUVA_{254}$ indicator (exposure time, $t$ = 5 min)

| Initial value | | | | Amplitude ($\mu$m) | | | | |
|---|---|---|---|---|---|---|---|---|
| TOC | DOC | $UV_{254}$ | $SUVA_{254}$ | 18 | 36 | 54 | 72 | 90 |
| 6.3 | 5.7 | 0.24 | 4.2 | 4.3 | 4.1 | 4.1 | 3.7 | 3.1 |
| 6.8 | 5.9 | 0.32 | 5.4 | 5.2 | 4.7 | 4.4 | 4.3 | 3.7 |

Table 3
Efficiency of the TOC reduction for the investigated water in relation to the ultrasonic field parameters (%)

| TOC initial value | Exposure time (min) | Amplitude ($\mu$m) | | | | |
|---|---|---|---|---|---|---|
| | | 18 | 36 | 54 | 72 | 90 |
| 6.3 | 1 | 0.5 | 8.5 | 24.8 | 31.5 | 33.5 |
| | 5 | 7.6 | 21.4 | 39.6 | 41.5 | 43.0 |
| 6.8 | 1 | 6.6 | 10.3 | 27.8 | 32.4 | 33.1 |
| | 5 | 17.1 | 20.1 | 38.2 | 42.6 | 42.6 |

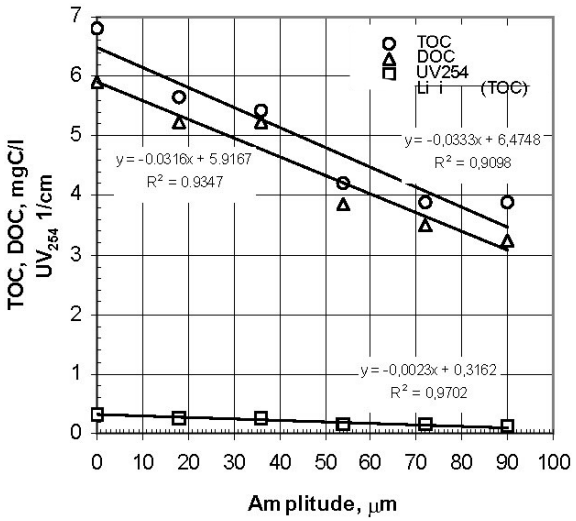


Fig. 3. Effect of the applied range of amplitude on the TOC, DOC and $UV_{254}$ for the investigated water (exposure time, $t$ = 5 min)

can indicate the reduction in reactivity of other constituents remaining in water, and in consequence the reduction in the potential of the DBP formation. Apart from the mechanical mechanism for removal of organic compounds (i.e. radical oxidation), the obtained results confirm the occurrence of physical degradation (i.e. fragmentation) which leads to the formation of compounds of a smaller molecular weight. In view to the results of the process efficiency (Tabl3 3), the highest efficiency above 40% was achieved at the maximum amplitude of 90 $\mu$m (the highest applied value). The similar result was observed for the reduction of the DOC in water. The slightly lower result was already achieved at an amplitude of 54 $\mu$m. According to the $SUVA_{254}$ values, this result is comparable to the predicted efficiency of removal of organic compounds from water during coagulation.

## 4. Conclusions

- Effect of the ultrasonic field on the content of organic compounds in water expressed in the TOC and $UV_{254}$ was confirmed.
- Increasing the values of amplitude and extending the exposure time resulted in improvement of efficiency, which was above 40% (at 90 $\mu$m for 5 min) for the investigated water.
- Similar correlation coefficients determined to describe the relationship between the vibration amplitude and the TOC and $UV_{254}$ allow for application of these indicators in other investigations.
- Reduction in values of the $SUVA_{254}$ (below 4 $m^2/gC$) obtained for the investigated water shows that the application of ultrasound results in a decrease of hydrophobic, aromatic and high-molecular fractions of DOC. In consequence, the potential of the formation of DBPs also decreased.

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