



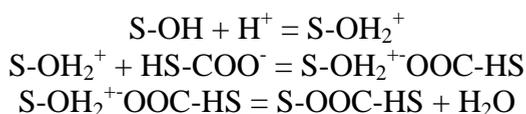
# **Ultrasound Enhanced Sorption of Humic Acids from Water**

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## **1. Introduction**

The contamination of water with organic compounds may either result directly from human activity (an anthropogenic contamination) or have its origin in processes occurring in the natural environment. A wide group of organic compounds of natural origin is referred to as the natural organic matter (NOM). This group includes humic substances (HS) that form as a result of the humification reaction [6]. It is assumed that these are compounds of a complex structure combining aromatic and aliphatic structures, as well as various functional groups (such as carboxyl, hydroxyl, phenolic, alcohol and methoxyl groups). The acid character of HS is determined by -COOH groups. It is these functional groups that give HS the high capability to form complexes with metals (e.g. Fe, Mn, Cu) present in the water. In addition, it is characteristic of humic compounds to include and absorb other organic and inorganic pollutants, e.g. pesticides [4, 5, 13]. HS present in water impart a colouring from yellow to brown to the water, and cause an impairment in its taste and smell characteristics. In chemical analysis, they reveal themselves in increased values of oxygen consumption and total organic carbon (TOC) content. Also the insufficient degree of humus substance removal in the water treatment process proves to be an issue, as this creates a potential for the occurrence of secondary contaminations, which are oxidation/disinfection by-products (OBP/DBP) [16]. In Poland, the limiting values of the above-mentioned indicators in water intended for human consumption are regulated by the Regulation of the Minister of Health of 20 April,

2010. The concentration of humic substances is not controlled directly, but only indirectly via their colour, oxygen consumption and TOC (which are determined for a water production of above 10 000 m<sup>3</sup>/day). To comply with these requirements, it is necessary to employ various processes in the water treatment technology, such as coagulation, oxidation or activated carbon sorption. Upgrading technological systems consists mainly in implementing the ozonization and activated carbon (AC) sorption processes, whereby both organic and inorganic contaminants are removed. An example of using AC for removing inorganic contaminants in the form of Cr (VI) ions from water are the positive findings reported in study [8, 9]. Removing of HS in the AC sorption process, on the other hand, not always brings about a satisfactory result. This is mainly due to the large sizes of HS molecules that clog up the micropores of the adsorbent [3, 4, 13]. Depending on the solution pH, HS exhibit varying susceptibility to sorption. The sorption capacity of carbon in solutions with pH in the range from 4 to 7 amounted to 90 mg/gC, while at pH > 8 it decreased to 20 mg/g carbon [3]. A hypothetical model of HS adsorption on the adsorbent was discussed in the study [15]. The acidic environment is the location of exchange of ligand between protons in the OH<sub>2</sub><sup>+</sup> group from sorbent and carboxyl groups from humic substance.



An essential role of pH in the sorption process was found for sorbent Norit SA Super. It was demonstrated that changes in electrokinetic potential of the sorbent from positive to negative one cause a reduces effectiveness of HS sorption in the alkaline environment [2].

Ozonization of water containing high-molecular HS results in their partial oxidation and formation of intermediate forms which, as has already been mentioned, are classified as mutagenic or carcinogenic compounds [13,16]. The literature provides the description of modifications of classic processes, aiming to increasing the efficiency of removal of undesirable water admixtures. So called advanced oxidation processes (AOP) utilize intensifying physical factors (such as UV radiation, ultrasounds (US)) and chemical factors (TiO<sub>2</sub>, Fenton's reagent) [1, 10].

The application of US energy in a water medium brings about various phenomena of a physicochemical nature. The intensity of those phenomena, as well as their resultant effects, is particularly high at the phase boundary. Strong surface phenomena covering the neighbourhood of so called cavitation bubbles result in, occurring locally, very high increases in pressure and temperature (of approx. 500 atm. and 5000 K, respectively). A consequence of the cavitation processes is the emission of OH<sup>•</sup> hydroxyl radicals of a high oxidation potential (2.8 V), which intensifies the oxidation processes in the medium being sonicated. Localized pressure changes in the medium lead also to the formation of considerable impact forces and so called microflows of very high velocities (500 m/s). Due to the very diverse physicochemical composition of the medium and the required very long sonication duration, it is considered to use US in coupled processes, e.g. with an oxidizer (ozone, O<sub>3</sub>; hydrogen dioxide, H<sub>2</sub>O<sub>2</sub>) or ultraviolet radiation, with Fenton's reagent. In the process of removing humic acids (HA), as a result of the US/H<sub>2</sub>O<sub>2</sub> (US – 20 kHz, 50 W; H<sub>2</sub>O<sub>2</sub> – 200 mg/l), a complete degradation of HA, measured as UV<sub>254</sub>, was observed after 60 minutes of sonication, with a simultaneous reduction of the TOC index by half [1, 12, 14]. The authors suggest that the utilization of these effects in the practice of water treatment technology might provide an alternative to the conventional processes of coagulation and flocculation. In a combined US/O<sub>3</sub> process, the efficiency of degradation of a synthetic aromatic compound, which was aniline (100 mg/l), was tested. Ozoning (up to 12 mgO<sub>3</sub>/min.) aided with ultrasounds (20 kHz, 400 W) was employed in the experiment. A reduction in the aniline concentration by 6% (US), 44% (O<sub>3</sub>) and 82% (US/O<sub>3</sub>) was found. The efficiency, as measured with the TOC index, amounted to, respectively, 1%, 9% and 21% (after 5 minutes of the process) and 51% (after 30 minutes of the process). The differences in efficiencies, as measured by the change in aniline concentration and TOC concentration, were explained by the formation of intermediate products in the process, whose concentrations were determined additionally [14]. In the natural organic matter (NOM) removal tests with the use of US, the process efficiency was determined, as dependent on the HA concentration (5; 10; 15 mg/l), and the sonication duration and intensity (20 kHz, 8–57 W, 1–20 min.). The process efficiency was measured based on the variations in the UV<sub>254</sub> absorbance and TOC. It proved advantageous to use the long-

est of the durations tested, that is 20 minutes, with a field intensity of  $42 \text{ W/cm}^2$ . The reduction in TOC for the concentrations tested was 24.5–34.9%. In the  $\text{UV}_{254}$  absorbance results, a slight increase in values was observed. By quoting other researchers, the authors name several factors, whose increase correlates with the increase in  $\text{UV}_{254}$  absorbance, including the aromatic ring condensation, the total carbon content and the solution pH. An increase in the intensity of the ultrasound field caused a reduction in pH of HS solutions [12]. Other studies on HS removal by the US method showed a lower process efficiency of 9.5% and 5% (after 300 min.), as measured by the  $\text{UV}_{254}$  index and colour, respectively. In those conditions, also the TOC index decreased slightly (from 22.94 to 22.04 mg C/l) [11].

The purpose of the investigation carried out was to assess the possibility of using ultrasonic energy for intensifying the process of humic acid sorption from water solutions. The classic sorption process has a reduced

efficiency resulting from the clogging of sorbent pores by large HA molecules. The ultrasonic modification of HA in solutions to be subjected to sorption is aimed not only at reducing the HA concentration through the sonochemical oxidation reactions. The sonication of HA may also result in their mechanical decomposition. The smaller-size particles formed as a result of this modification can be more easily transferred and sorbed in the pores of the activated carbon tested. This was confirmed by the preliminary tests shown in study [7], whereby by using ultrasounds of an intensity of  $40 \text{ W/cm}^2$  in HA sorption, an increase in effects, as defined by the reduction of solution absorbance, was noted by 15–20%. However, the efficiency of sorption, as modified with ultrasounds, was not tested based on the DOC index.

## 2. Methods

The tests were conducted on model water prepared from a commercial HA preparation supplied by Fluka. The set concentration of the solution was  $20 \text{ mg HA/dm}^3$ . A sample weight of a mass of 20 mg HA was dissolved in deionized water (*Millipore* Milli-Q water purification system, TOC = 4 ppb) and then the obtained solution was filtered through the coarse filter to quickly separate the solution from the preparation

fraction that had not dissolved. The prepared HA solution had a slightly alkaline reaction (pH ~ 7.3).

For the HA sorption, ROW 08 Supra granulated activated carbon was chosen, show detailed specification is provide in study [9]. The structure of the ROW 08 Supra carbon is characterized by similar contents of micro-, meso- and macro-pores. The HA solution (0.125 dm<sup>3</sup>) was metered to the flasks with a fixed activated carbon dose (0.5 g), after which all the samples were subjected to 2 hours' shaking – variant W1 (2 h). After this time, part of the samples were filtered through the coarse filter and then analyzed. The other samples remained in static contact with the activated carbon for another 2h – variant W2 (2 h+2 h) or another 22 h – variant W3 (2 h+22 h). Afterwards, the procedure as above was followed to separate the activated carbon; the samples were then filtered and analysed. In the sono-sorption process, the sorption was preceded by the sonication of the HA solution. Ultrasounds were generated with a VCX 750 high-power Sonics&Materials disintegrator (20 kHz, 750 W) using the parameters determined in the preliminary tests: sonication duration – 1 and 5 minutes (US 1 and US 5), and vibration amplitude (A) – 23, 57, 86 and 114  $\mu\text{m}$ . Ultrasonic energy was introduced to the medium tested through a 13 mm diameter probe. The ultrasonic field intensity, as calculated based on the quantity of energy input to the system for the range of amplitude values used, was 8–74 W/cm<sup>2</sup>. For the assessment of the effects of the processes examined, the organic contamination indexes, DOC, UV<sub>254</sub> absorbance and oxygen consumption, were determined. It was decided that the samples would be filtered through a syringe filter of a pore diameter of 0.45  $\mu\text{m}$ , and the dissolved organic carbon (DOC) fraction would be determined according to standard PN-EN ISO 7887:2002. The determination was made using a Multi N/C 2000 Analytic Jena analyzer. Humus substances present in water strongly absorb UV radiation, which is highly correlated with the colour and contents of organic compounds. The determination of the absorbance is therefore used for indirect assaying the contents of organic compounds and assessing their removal. Direct spectrophotometric measurements were made on the samples in 1 cm-long cuvettes at a wavelength of  $\lambda = 254 \text{ nm}$ , according to standard PN-84/C-04572. The measurements were made on a Helios  $\alpha$  apparatus. Variations in the contents of HA, as expressed by the oxygen consumption of the samples, were measured by the perman-

ganate index determination method in accordance with standard PN-EN ISO 8467:2001.

The efficiency of the process (E) of HA removal from the solutions, as obtained in the processes of sorption (s) and sono-sorption (s-s), was determined from the relationship:

$$E_{s, s-s} = \frac{X_0 - X_k}{X_0} \cdot 100, \% \quad (1)$$

where:

$X_0$  – initial value,

$X_k$  – final value.

The intensity of aiding the sorption process with ultrasounds is given as the percentage efficiency increment ( $\Delta E$ ) of the process of sono-sorption relative to sorption, according to the relationship:

$$\Delta E = E_{s-s} - E_s, \% \quad (2)$$

The Kruskal-Wallis statistics was used to compare the changes of DOC and absorption  $UV_{254}$  of the HS solution depending on sorption conditions described as Variant 1, 2 and 3. The difference was significant for the  $p$  value  $<0,05$ .

In order to evaluate the effects of the amplitude of vibrations on sorption, the author analysed correlation coefficient (R). The correlation was evaluated for  $DOC = f(A)$  and  $UV_{254} = f(A)$  absorbance.

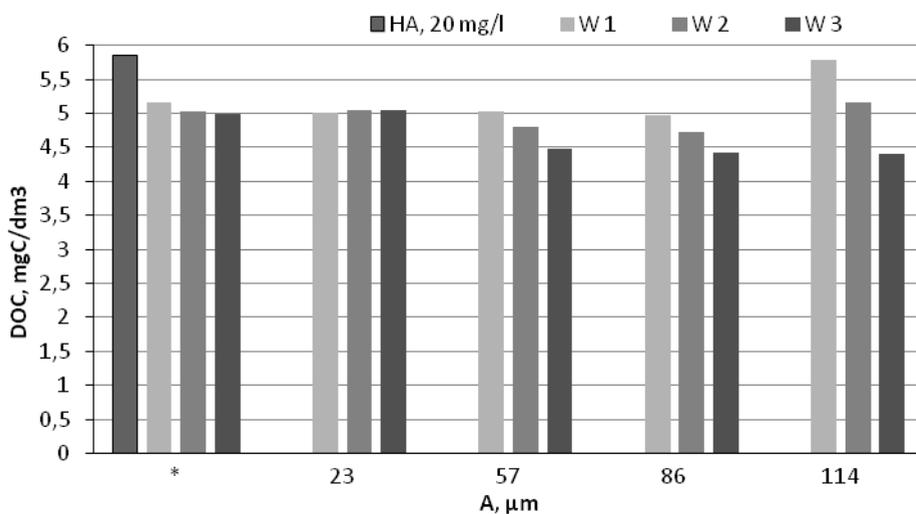
### 3. Results and discussion

The application of US as an aiding factor in the HA sorption process resulted in varying changes in the efficiency of this process, depending on the sorption parameters (static contact duration) and US parameters (sonication time and the vibration amplitude).

A reduced pH was observed in HS solutions which were exposed to ultrasound field with the intensity adopted for the study. This effect was intensifying with the amplitude of vibrations and sonication time, from pH = 7.3 to pH = 6.7 (US1) and to pH = 6.6 (US5). Therefore, the process of sono-sorption was used for the solution with slightly acidic solution.

### 3.1. Process efficiency as measured with the DOC

The efficiency of HA sorption on the activated carbon tested was  $E(\text{DOC}) = 10\text{--}30\%$ , depending on the initial DOC value and the duration of contact between the solution and the activated carbon. The sono-sorption process, with the shorter sonication duration (US 1) for variant (2 h) had an efficiency of  $E(\text{DOC}) = 13\text{--}16\%$  (23–86  $\mu\text{m}$ ) (Figure 1). The obtained  $\Delta E(\text{DOC})$  efficiency increment over the sorption was at a level of 3%. The amplitude increase up to the maximum value of 114  $\mu\text{m}$  impaired this effect.



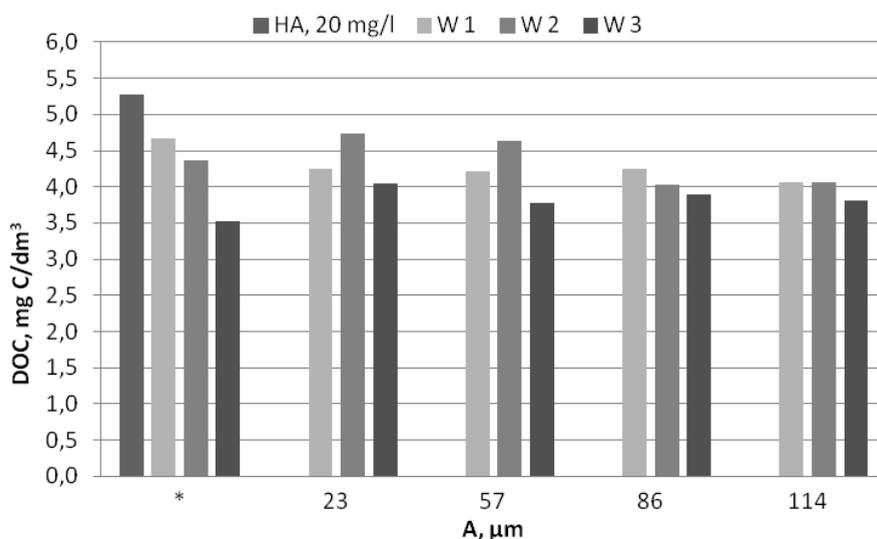
**Fig. 1.** DOC results for HA solutions in the examined processes as a function of vibration amplitude, (US 1); \* – reference sample

**Rys.1.** Wyniki RWO dla roztworów KH w badanych procesach w zależności od amplitudy drgań, (UD 1); \* – próbka odniesienia

A similar relationship was observed in variant (2 h + 2 h). The efficiency of DOC removal was  $E = 15\%$  for samples sonicated at the lowest amplitude of 23  $\mu\text{m}$  and increased to  $E(\text{DOC}) = 20\%$  at amplitudes of 57 and 86  $\mu\text{m}$ . For the maximum amplitude of 114  $\mu\text{m}$ , the sono-sorption efficiency was the lowest, being  $E(\text{DOC}) = 13\%$ . A sono-sorption efficiency increase of  $\Delta E(\text{DOC}) = 4\text{--}5\%$  was only noted for samples sonicated at amplitudes of 57  $\mu\text{m}$  and 86  $\mu\text{m}$ .

In variant 3 (2 h + 22 h), the sono-sorption efficiency, depending on the vibration amplitude, was: 15% (23  $\mu\text{m}$ ), 25% (57  $\mu\text{m}$  and 86  $\mu\text{m}$ ), 26% (114  $\mu\text{m}$ ). As a result of applying the lowest-amplitude ultrasounds, no improvement in HA was obtained (no efficiency increment,  $\Delta E$ ). The analyzed values indicate, however, that prolonging the static contact between HA and activated carbon favours the improvement of sorption effects in HA solutions sonicated at high amplitudes. The achieved increment in process efficiency was 9–10% (57, 86, 114  $\mu\text{m}$ ).

With a longer sonication duration (US 5), the efficiency of sono-sorption (2 h) was higher than for US 1, amounting to approx. 20% (Figure 2).



**Fig. 2.** DOC results for HA solutions in the examined processes as a function of vibration amplitude, (US 5);\* – reference sample

**Rys. 2.** Wyniki RWO dla roztworów KH w badanych procesach w zależności od amplitudy drgań, (UD 5); \* – próbka odniesienia

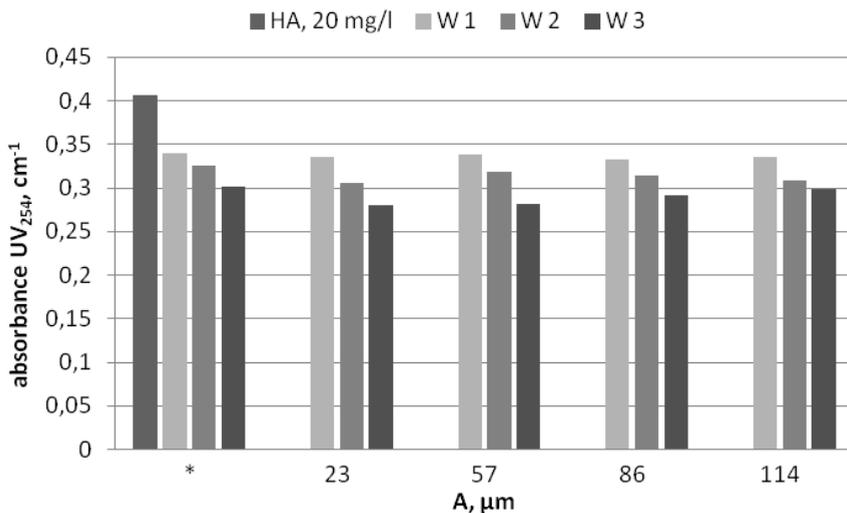
The most favourable ultrasonic effect, an efficiency increment of  $\Delta E = 12\%$ , was noted for samples sonicated at the maximum amplitude, 114  $\mu\text{m}$ . For the remaining amplitude values, this was approx. 8%.

In the next variant (2 h + 2 h), the DOC results after the sono-sorption process showed a 6% efficiency increment also in samples sonicated at higher vibration amplitudes, 86  $\mu\text{m}$  and 114  $\mu\text{m}$ . In the remaining samples, at the lowest ultrasound intensities (for amplitudes of 23  $\mu\text{m}$

and 57  $\mu\text{m}$ ), no efficiency increment in HA sorption was noted. So, elongating the static contact between the HA and the activated carbon in variant (2 h + 22 h) did not have any favourable influence on the sono-sorption effects. Similarly as for the system with the shortest sonication duration (US 1), sono-sorption had the least favourable effect in samples sonicated at the lowest vibration amplitude, 23  $\mu\text{m}$ .

### 3.2. Process efficiency as measured with UV<sub>254</sub>

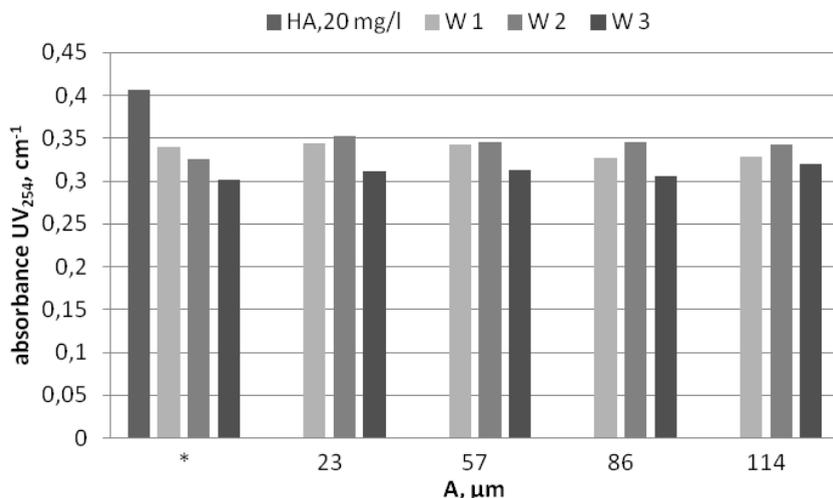
The analysis results show that the sorption efficiency, as measured with UV<sub>254</sub>, was as follows:  $E_{2\text{h}} = 18\%$ ,  $E_{2\text{h}+2\text{h}} = 21\%$ ,  $E_{2\text{h}+22\text{h}} = 27\%$  (Figure 3). So, extending the static contact duration by another 2 or 22 hours only negligibly influenced the outcomes of the sorption, as determined by absorbance. Upon a short exposure of the solutions (US 1) to the magnetic field, the UV<sub>254</sub> absorbance decreased, particularly with a longer sorption duration. The efficiency of sorption aided with ultrasounds slightly differed, however, from the values obtained for the classic sorption process.



**Fig. 3.** UV<sub>254</sub> absorbance results for HA solutions in the examined processes as a function of vibration amplitude, (US 1) \* – reference sample

**Rys. 3.** Wyniki absorbancji UV<sub>254</sub> dla roztworów KH w badanych procesach w zależności od amplitudy drgań, (UD 1) \* – próbka odniesienia

The elongation of the sonication duration (US 5) of the HA solution resulted in an increase in  $UV_{254}$  absorbance after the sono-sorption process (Figure 4).



**Fig. 4.**  $UV_{254}$  absorbance results for HA solutions in the examined processes as a function of vibration amplitude, (US 5) \* – reference sample

**Rys. 4.** Wyniki absorbancji  $UV_{254}$  dla roztworów KH w badanych procesach w zależności od amplitudy drgań, (UD 5) \* – próbka odniesienia

As has been mentioned in the Introduction, and is also noted in studies by other authors, the increase in  $UV_{254}$  absorbance in sonicated solutions can be influenced not only by changes in HA concentrations, but also indirectly by transformation that these compounds undergo due to sonication.

This might be caused by the increase in the degree of condensation of aromatic rings, the total C content, the molecular weight, or the ratio of the C in aromatic rings to the C in aliphatic rings, and the solution pH. In some instances, differences in efficiency between sono-sorption and sorption, as expressed by  $\Delta E(UV)$ , indicate a slight end result of ultrasonic HA sorption aiding for the adopted experimental conditions. However, the noted  $UV_{254}$  increase/decrease after sonication, as considered in parallel with the DOC analysis results, should be regarded primarily as the confirmation of the transformations that HA undergo as the US field acts.

### 3.3. Process efficiency as measured with the chemical oxygen demand

The chemical oxygen demand of the HA solutions subjected to the sonication process decreased compared to the control sample, with the lowest value being noted for the shortest static contact duration of 2 h (W 1). The process efficiency was in this case over 20%, and extending the duration of HA and AC contact did not influence advantageously. The sono-sorption efficiency increment ( $\Delta E$ ) for Variant (US 1; 2 h + 22 h), as measured with the chemical oxygen demand, was: 4% (114  $\mu\text{m}$ ), 9% (23  $\mu\text{m}$  i 86  $\mu\text{m}$ ) and 17% (57  $\mu\text{m}$ ). The sono-sorption effect with a longer static contact duration were, however, less advantageous compared to the 2 h sorption (Table 1).

The elongation of the sample sonication duration (US 5) did not improve the sorption effects (Table 2). The results found, as determined by the change in chemical oxygen demand, justify therefore the assessment of the efficiency of the processes examined based on the changes in the DOC index.

**Table 1.** Chemical oxygen demand results in the examined processes, (US 1)

**Tabela 1.** Wyniki utlenialności w badanych procesach, (UD 1)

Sorption Variant	Chemical oxygen demand ( $\text{Ox}_0 = 9.2 \text{ mgO}_2/\text{l}$ )				
	Sorption	Sono-sorption			
		23 $\mu\text{m}$	57 $\mu\text{m}$	86 $\mu\text{m}$	114 $\mu\text{m}$
W1 (2 h)	7.2	9.2	8.8	9.2	9.6
W2 (2 h+2h)	8.8	8.8	9.2	9.2	9.2
W3 (2 h+22 h)	9.1	8.3	7.5	8.3	8.7

**Table 2.** Chemical oxygen demand results in the examined processes, (US 5)

**Tabela 2.** Wyniki utlenialności w badanych procesach, (UD 5)

Sorption Variant	Chemical oxygen demand ( $\text{Ox}_0 = 9.1 \text{ mgO}_2/\text{l}$ )				
	Sorption	Sono-sorption			
		23 $\mu\text{m}$	57 $\mu\text{m}$	86 $\mu\text{m}$	114 $\mu\text{m}$
W1 (2 h)	7.2	9.9	9.5	8.3	9.1
W2 (2 h+2 h)	8.9	9.5	9.5	10.7	10.3
W3 (2 h+22 h)	9.1	9.1	8.7	9.1	9.5

### 3.4. Statistical analysis

The statistically significant results of the Kruskal-Wallis test was obtained only for the arrangement W1 and W3 ( $p = 0.001$ ) for changes in  $UV_{254}$  absorbance (US1). For other arrangements, the results were less significant ( $p = 0.003$ ) or it was impossible to reject the null hypothesis. Therefore, it can be expected that DOC and  $UV_{254}$  absorbance show the same distribution vs. amplitude, regardless of the sorption arrangement.

Analysis of the obtained effects of using ultrasounds in the sorption process by means of correlation confirmed significant relationship in W3 arrangement between DOC and the amplitude at US1 ( $R = -0.90$ ,  $R^2 = 0.81$ ). The results which describe the decreasing correlation of absorbance with the increase in amplitude were less statistically dependent ( $R = -0.80$ ) and exhibited low coefficient of determination ( $R^2 = 0.64$ ).

The basic statistical analysis of the results obtained in the study suggests the necessity of correction and points to the direction of further experiments. The most favourable values presented in the Discussion relate to the effect of removing DOC ( $\Delta E = 10\%$ , W3, US1 A = 114  $\mu\text{m}$ ). The high correlation of quantitative changes in the DOC index with amplitude points to further investigations of the process at higher intensities of the ultrasound field. The purposefulness of using longer sonication of the solutions necessitates additional tests in order to confirm the statistical significance of the obtained results.

## 4. Conclusions

The study demonstrated that using the ultrasound energy for modification of HA solutions might increase the effectiveness of sorption on the activated carbon used.

The degree of HA removal was measured by several organic contamination indexes, namely: DOC,  $UV_{254}$  absorbance, and oxygen consumption. The DOC results are regarded as an accurate organic carbon content measurement which is not affected by the transformations of the organic matter (the aromatic ring C/aliphatic C), nor by the colour or turbidity of the sample. The reported (DOC) results enable one to state that the ultrasonic modification of HA may have, under specific process conditions, a favourable effect on the HA sorption. It is assumed that a cycle of phenomena of a chemical (oxidation) and a mechanical (disin-

tegration) natures occurs as a result of US action on HA. The favourable effect (~10%) achieved for sono-sorption (1 min. US) in the extended static contact duration variant, 2 h + 22 h (W3), indicates the mechanical decomposition of HA as they are sonicated. The occurred intermediate forms of smaller spatial-sizes were able to migrate more freely and undergo sorption. The achieved higher efficiency in removal of HA, measured as DOC, might indicate that part of the meso- and micro-pores has become available for the forms formed as a result of ultrasonic modification. Furthermore, this arrangement of sono-sorption showed a reduced concentration of HA (as DOC) caused by reduced oxidability.

The use of a longer sample exposure time (US 5) resulted in an increase in efficiency up to 12% for sono-sorption conducted according to variant W1 (2 h), that is in a shorter sorption duration. This might suggest that also sonochemical processes occur during US field action. As a result of advanced oxidation sonochemical processes, intensified by the increased ultrasound intensity and the reaction time identical to the sonication duration, the HA concentration in the solution directed to activated carbon adsorption has decreased.

The observed increase in the effectiveness of HA removal (as DOC) might be also connected with reduced pH in the solutions after sonication. The process of sorption occurs more effectively in the acidic environment due to high electrostatic affinity of activated carbon and humic acids.

Changes in  $UV_{254}$ , absorbance as an indicator that provides information about HA content were not well correlated with the amplitude of vibrations. The effects obtained in this measurement were lower and variable.

Sonochemical oxidation (free-radical) of HA, mechanical fragmentation of HA to small and better sorbed forms in sorbent pores and reduction in pH in the environment are possible causes of the effect of DOC reduction in the samples modified with ultrasounds. The contribution of the sources listed in the observed increase in sorption effectiveness remains indefinable.

The analysis of the effects of the investigated processes, as determined with different indexes, confirms that the quantitative determination of DOC best reflects the achieved final result. The obtained effects, depending on the sonication duration and the amplitude, indicate the need

for increasing the ultrasonic field intensity and determining the influence of US on the sorption conducted at a varying pH of the HA solutions.

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## Ultradźwiękowe wspomaganie sorpcji kwasów humusowych z wody

### Streszczenie

Procesy usuwania związków organicznych, w tym substancji humusowych (SH), oraz ich intensyfikacja zajmuje ważne miejsce w technologii wody. Prowadzone są badania nad możliwością podniesienia skuteczności usuwania SH w konwencjonalnych procesach

jej uzdatniania jak: koagulacja, sorpcja czy utlenianie. Badania te dotyczą m.in. tzw. procesów pogłębianego utleniania (AOP), w których stosowane są kombinacje czynników fizycznych (promieniowanie UV, ultradźwięki) lub chemicznych (reakcja Fentona) z klasycznym procesem. Do usuwania naturalnej materii organicznej lub intensyfikacji tego procesu, mogą być stosowane ultradźwięki (UD) Uważa się, że UD powodują sonochemiczne utlenianie związków humusowych w pęcherzykach kawitacyjnych, jak również fizyczną dekompozycję lub agregację fragmentów SH. Ze względu na niską skuteczność sonochemicznego utleniania związków o strukturach aromatycznych, badano również metody łączące UD z UV czy O<sub>3</sub>.

Celem przedstawionych badań była ocena możliwości zastosowania energii ultradźwiękowej do intensyfikacji procesu sorpcji kwasów humusowych (KH). Ultradźwięki generowano przy użyciu dezintegratora VCX 750 Sonics&Materials (20 kHz, 750 W), stosując czas sonifikacji 1 i 5 minut (UD 1, UD 5) oraz amplitudę drgań 23–114 μm. Proces sorpcji KH z roztworu (20 mg/dm<sup>3</sup>) prowadzono na granulowanym węglu aktywnym ROW 08 Supra. Próbkę poddawano sorpcji lub sono-sorpcji, przesączono a następnie poddawano

analizie (RWO, absorbancja  $UV_{254}$ , utlenialność). Skuteczność sorpcji KH wyrażona jako RWO wynosiła 18–27% w zależności od długości czasu kontaktu z węglem. Sonifikacja roztworów powodowała wzrost skuteczności procesu sono-sorpcji względem klasycznej sorpcji, który wynosił dla RWO 10% (UD 1, 114  $\mu\text{m}$ ). Wydłużenie czasu sonifikacji do 5 minut zwiększało efekt do 12% (UD 5, 114  $\mu\text{m}$ ). Uzyskano także nieznaczne obniżenie absorbancji UV, jednak efekty te nie odpowiadały najkorzystniejszym wynikom ultradźwiękowego wspomaganie sorpcji wyrażonym RWO. Przyjmując jako najbardziej miarodajny do ilościowego oznaczenia badanych związków wskaźnik RWO, potwierdzono korzystne działanie ultradźwięków przy krótkim czasie ekspozycji (1 min.) i wyższym natężeniu określonym amplitudą drgań w zakresie 57–114  $\mu\text{m}$ . Sonochemiczne utlenianie KH przed procesem sorpcji potwierdzało obniżenie utlenialności roztworu po sono-sorpcji względem procesu sorpcji (W3). Wzrost skuteczności do 17%, dał jednak rezultat mniej korzystny niż sorpcja KH w krótszym czasie kontaktu z węglem (W1).