Longina STĘPNIAK*, Ewa STAŃCZYK-MAZANEK, Magdalena KUSIAK
Czestochowa University of Technology, Institute of Environmental Engineering
Brzeźnicka 60a, 42-200 Częstochowa
* e-mail: stepniak@is.pcz.czest.pl

Ultrasounds and ozone in removal of humic substances from water

Humic substances (HS) exist in the water-soil medium. HS are a basic component of soil humus and have great importance for conditioning, stabilizing and correcting the structure of soils. They penetrate also into natural waters, in composition of which they present 60÷80% total organic matter. HS due to their sorption ability of numerous harmful organic pollutants produced by human and their ability of forming complexes with heavy metals, should be removed from water during its treatment. Also, HS are known to form trihalomethanes (THM) upon final chlorination. HS-containing water is indirectly defined by sanitary norm as non-potable.

The combination of ultrasound (24 kHz) and ozone US/O_3 for removal of HS from water was studied. Due to the application of US/O_3 process the decrease of researched parameter was observed. With the reference to the obtained results it is possible to conclude that the US/O_3 combined process was more effective in degrading HS than each process separately (synergetic effect). The most favourable reduction of the content of HA compounds was observed for higher intensities of the ultrasonic field.

Keywords: water treatment, humic substances, ultrasounds, ozone

Introduction

Humic substances (HS) exist in the water-soil medium. HS are basic component of the soil humus and has great importance for soils: their condition, stabilize and correct their structure. They penetrate also into natural waters. In their compositions HS present 60÷80% total organic matter. HS due to their sorption ability of many harmful organic pollutants produced by human and their ability of forming complexes with heavy metals, should be removed from water during its treatment. Also, HS are known to form trihalomethanes (THM) upon final chlorination. HS are ineligible in drinking water and that sanitary norm indirectly define. Mainly, HS are removed from the water with conventional coagulation. Chemical oxidation is an alternative technology that has been successfully applied for destruction of a broad spectrum of organic compounds, including HS. Intermediate oxidation is intended to degrade toxic micropollutants, remove THM precursors and increase biodegradability. Ozone is most frequently used for that. A significant problem of using ozone, despite its unquestionable advantages, is creation of the oxidation by-products. Moreover, its effect, especially on organic compounds, is characterized by high

selectivity. The reactions of ozone with organic contaminants contained in water destined for treatment are predominantly reactions with HS, since they are the main group of organic compounds. The reactions of ozone with HS at neutral values of pH cause a considerable reduction in colour and UV absorbance, with inconsiderable reduction in TOC. Therefore, ozonation does not lead to full decomposition of HS. The products which are obtained exhibit a substantial reduction in molecular weight. The obtained small molecules include mainly aldehydes (amongthem formaldehyde) and carboxylic acids. Problems also arise with ozonation of water with elevated bromide content, which is connected with the appearance of bromates. Apart from undesirable products of oxidation with ozone, with its harmful effect on human health, high costs of using ozone should also be emphasized. Limitation of the harmful effect of ozonation, combined with the enhanced effectiveness of oxidation of organic water contaminants, is ensured, to a different degree, by advanced oxidation processes (AOP). The basic mechanism in these processes is connected with intensification of generation of radicals, the particles with very high oxidation potential, OH° - 2.8 V. The reactions between hydroxyl radicals and organic compounds are controlled by mass transport of radicals to organic molecule and the process of radical creation. In order to increase the efficiency of the radical reactions, the researchers today focus mainly on the modification of AOP processes towards improved kinetics of absorption of ozone in water. The AOP processes with ozone with confirmed effectiveness of HS removal include H_2O_2/O_3, O_3/UV, O_3/US. The AOP methods (also the H_2O_2/UV, UV/US arrangements) have been recently intensively researched in terms of removal of specific organic and non-organic contaminants from water and sewage sludge [1-4]. The O_3/UV process was found to be the most effective AOP for Natural Organic Matter (NOM) reduction TOC = 31% (UV_{254} = 88%) [5]. It was confirmed that simultaneous application of sorption and oxidation process with H_2O_2 indicated on the catalitic aility of activated carbon (AC) to the H_2O_2 decomposition reaction with hydroxyl radicals generation. AC caused catalisation of colours oxidation with H_2O_2 what increased the process efficiency [6].

The investigations of ultrasound methods (US), both independent and combined, e.g. H_2O_2/US, O_3/US, UV/US, also concern the opportunities of treatment of specific types of waste, e.g. pharmaceutical or dyeing waste [7, 8]. However, an in-depth economic analysis demonstrated unequivocally that the costs of waste treatment by means of the US method are so expensive that only a combined method can be considered [9]. The investigations of the use of ultrasounds for removal of organic contaminants from water confirm the long contact time required for obtaining substantial effectiveness of the process. This determines high costs of the process; therefore, the independent method is typically excluded. The experiments in this field have used ultrasounds with low frequencies, 20÷40 kHz; however, different concentrations of the solutions, volume of the water samples and ultrasound power do not allow comparison of the obtained effectiveness [10-12].

In some studies [11], use of ultrasounds with the frequency of 20 kHz caused that TOC in the volume of 300 mL was reduced, after 20 minutes, by 24.5%

and 34.9%, respectively for the concentration of 5 and 15 mgHS/L. With power density of 33÷226 W/L, which determined the economical aspects of the process, the authors suggest the method of decomposition of natural organic matter (NOM) as possible to be used in water treatment. In highly concentrated solutions of HS (550 mg HS/L), after initially insignificant increase in UV_{254} absorbance, reduction in this parameter occurred as late as after 60 minutes of solution sonication (35 kHz) [13]. The changes in other parameters measured by these authors (E4/E6, oxidation--reduction potential, pH) confirmed the effect of physical and chemical degradation of humic compounds. The aggregation of high-molecular fraction of HS to colloid form, remaining in the system, was emphasized. Low-molecular fractions, dominant in the solution of extracted HS were decomposed to volatile compounds.

The economical rationale behind the long time of sonication was the reason for the investigations of the effectiveness of NOM removal in the arrangements of ultrasounds/chemical oxidation. In the case of the use of the process of US/H_2O_2 for the solution with concentration of 100 mgHA/L (volume 100 mL, US 20 kHz, H_2O_2 200 mg/L) it was confirmed [14] that the TOC reduction rate was twice slower than the reduction in absorbance (254 nm). After 60 minutes of contact, the degree of HA removal, measured with TOC, amounted to 40%, with this value for UV_{254} being 80%. This observation leads to the presumption that HA decomposition into carbon dioxide and water, as it is the case with ultrasound field, occurs indirectly. At the same time, the effects of ultrasounds and magnetic stirring (50 rev/min) were compared for the same experimental conditions, combining either of the processes with H_2O_2. The use of ultrasounds in HA solution caused 90% decomposition (expressed in TOC), whereas the use of magnetic stirring resulted in 25% decomposition. This finding confirms the effect of ultrasounds on the decomposition of HA and activation of H_2O_2 oxidation potential.

In the aspect of the opportunities of reduction in costs of generating ultrasounds and production of ozone, the process of US/O_3 deserves particular attention. In the context of the above mentioned explorations of opportunities to increase ozone mass transport in water, the results of the studies by [15], which confirmed the effect of ultrasounds on the improvement of the rate of decomposition of ozone in water, are essential. The effect of the combined method (ultrasounds and ozone) on NOM has been rarely researched [16, 17].

The investigations presented below concern the effect of the use of the combined process of US/O_3 (ultrasounds and ozone) in water solutions of HS. The aim of the investigations was to assess the opportunities of application of this method for the removal of humic compounds from water during the process of its treatment.

1. Methods

The investigations were carried out for model water, i.e. solutions of humic acids (manufactured by FLUKA-Aldrich) based on deionised water. The concentrations of the model solutions were 10, 15 and 20 mgHA/L. The contents of HA

were adopted as higher than the typical content found in natural water in order to limit the effect of measurement error. The volume of the water samples was 1000 mL. The parameters of the studied solutions of HA are given in Table 1. High index absorbance suitable $SUVA_{254}$ confirms contents in researched solutions HA high-molecular hydrophobic compounds.

Water samples were subjected to the effect of the three processes: ozonation (O_3), sonication (US) and the combined process of ultrasound and ozonation (US/O_3).

In order to produce ozone, OPTEL (IMPOZ Mini 2) ozone generator was used. The process of ozonation was carried out with ozonated air flow rate adjusted by means of the ROS-06 rotameter. Ozone was introduced to the water samples in the form of an ozone-air mixture with ozone concentration determined each time (up to 10 gO_3/m^3). A specific parameter of the process was the ozone doses of 1, 3 and 5 mg/L. Based on the ozone concentration, the mean ozonation time was determined, which amounted to 1, 3 and 5 minutes, respectively.

Table 1

Characteristic of researched water samples

Parameter	Unit	Concentration of HA, mg/L		
		P10	P15	P20
humic acids	mgHA/L	10	15	20
colour	mgPt/L	60	85	110
oxygen cons.	mgO_2/L	2.88	4.16	8.32
TOC	mgC/L	3.68	5.17	6.89
DOC	mgC/L	3.42	4.88	6.05
UV_{254}	1/m	23.6	35.6	48.3
$SUVA_{254}$	$m^3/gC\text{-}m$	7.5	7.3	7.9
turbidity	NTU	3.95	5.50	7.15
pH	–	6.07	5.94	5.70

In the US system water samples were sonificated with the use of the Hielscher UP400S high power ultrasonic generator with fixed frequency of 24 kHz and maximum effective power in water of 300 W. An ultrasound device equipped with a titanium sonotrode H 14 of 1.54 cm^2 surface. The process variables included the vibration amplitude (in the range of A = 18÷90 μm) which determines intensity of ultrasonic field. With the UP-400S the obtained intensity was high and ranged from 20 to 105 W/cm^2 (the density of power - to 0.16 W/mL). According to the theoretical fundamentals, the increase in the ultrasound field intensity (the occurrence of cavitation phenomenon) improves the sonochemical processes. The sonification of the water samples was conducted for a period of t = 5, 10 and 20 minutes. In the US/O_3 configuration, ozone was introduced to a water sample, which was then subjected to sonication (1 US/O_3). In the second variant (2 US/O_3), ozone was introduced to water samples in the beginning of sonication, simultaneously with sonication.

The effect of sonification was defined as the effectiveness of the removal of investigated organic contaminants from water during the oxidation process. Efficiency of researched process was analysed on the basis of change, before and after process, of following parameters: TOC, UV_{254}, $SUVA_{254}$, colour, oxygen consumption, pH.

The concentration of ozone in the gas was measured with iodometric titration method. The TOC and DOC were determined with the use of Analyzer Multi N/C 2100S Analytic Jena (with autosampler) employing a method according to the standard PN-EN 1484:1999. The $SUVA_{254}$ index was calculated as the UV_{254}/DOC. The UV_{254} index was determined from the measurement of absorption at the wave length of $\lambda = 254$ nm (with a cuvette optical path length of 1 cm). In addition, colour measurement was taken by the spectrometric method to determine the absorbance at the wavelength of $\lambda = 436$ nm (5 cm absorption cell). The measurement was made with the use of HACH DR/4000U Spectrophotometer apparatus. The remaining water quality indices were determined with standard methods, as adopted in water analyses.

All experiments were carried out in three repetitions for data of process parameters. Average values are shown on diagrams (Figs 2-4).

2. Results and their discussion

The analysis of the studied processes was based on the two basic parameters which determine the content of organic compounds in solutions, i.e. TOC and UV_{254} absorbance. The dependencies on HA content determined based on their measurements are given by the regression line (Fig. 1).

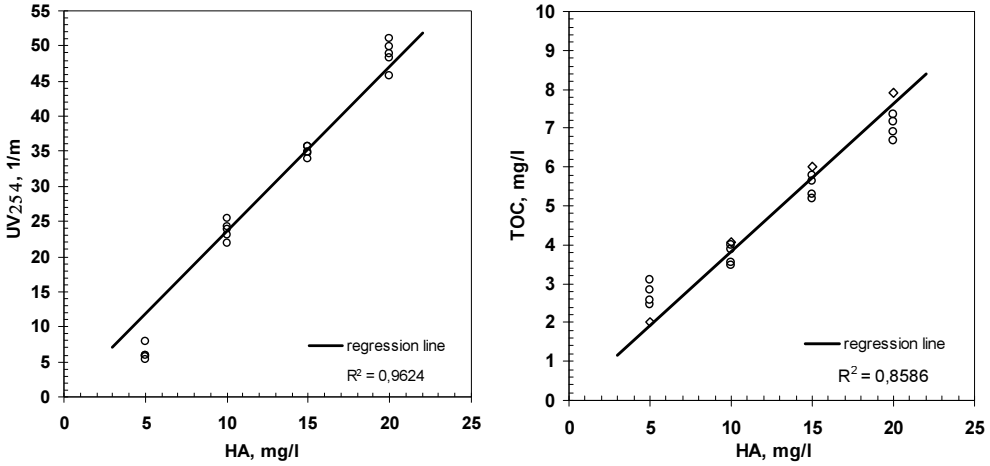

Fig. 1. Correlations between the TOC, UV_{254} and HA contents in the investigated water

High correlation coefficients for HA-TOC and HA-$UV_{254,}$ being r = 0.9786 and r = 0.9934, respectively, confirm a close relationship between these parameters. Simultaneously, as [16] claims, the decrease of HA content after US/O_3 process in solutions with higher HA content HA (64 mgHA/L), does not correlate with full organic compounds mineralization. Effect of HA mineralization confirms the drop of TOC index, which is indicated by previously cited research [13].

2.1. Comparison of methods with the use of ultrasounds and ozone

During the first stage of the investigations, the experiments with water containing of 10 mgHA/L were carried out using selected parameters of the US/O_3 process (amplitude: 45 μm, time: 10 minutes, ozone dose: 3 mg/L). In the first variant of the combined process, sonication of water samples was carried out after ozonation (3 minutes), whereas during the second time it was carried out during ozonation. The effects of these combined processes, compared to the results obtained by means of the O_3 and US alone methods, were presented in Table 2. These results of the investigations point to a reduction in parameters determining the content of humic compounds (TOC, UV_{254} absorbance), which is confirmed by removal of HA or their transformation. The effect of ozone on reduction in the colour and UV_{254} absorbance was observed, but TOC level barely changed. It is noticeable that humic compounds are resistant to direct ozone effect, whereas radical reactions in acid environment of the solution are not effective.

Table 2

The changes of water parameters in the researched processes (HA = 10 mg/L, A = 45 μm, t = 10 minutes, O_3 = 3 mg/L)

Parameter	Unit	before	US	O_3	1 US/O_3	2 US/O_3
TOC	mgC/L	3.68	3.18	3.25	2.75	2.62
DOC	mgC/L	3.42	2.90	2.98	2.58	2.54
UV_{254}	1/m	23.6	18.8	16.4	14.2	13.3
$SUVA_{254}$	m^3/gC-m	7.5	6.7	5.5	5.5	5.3
pH	–	6.57	6.08	5.62	6.28	6.35
oxygen cons.	mgO_2/L	2.88	2.30	2.40	2.20	2.05
colour	mgPt/L	60	35	25	25	20

A similar effect was observed when using only ultrasounds. Considerably lower values of TOC and UV_{254} were obtained with combined methods, whereas more favourable levels were observed for 2 US/O_3 arrangement. Removal of humic acid from water in the process of ozonizing is connected with oxidizing of these compounds (direct and indirect). However, taking the low pH of HA solutions into consideration, direct action of molecular ozone mainly takes place. Ultrasonic catalysis of ozone reactions in HA solutions in the US/O_3 system concerns the initiation of

hydroxyl radicals creation. Effects of radical HA oxidation was proved as growth of the efficiency of US/O_3 process in respect of O_3 process. The effect of reduction of pH in O_3 method can be connected with the decomposition of HAs, which are transformed into low-molecular acids with high content of acid functional group. In US/O_3 arrangements, HA are partially removed from water, which reduces the effect of substantial reduction in pH. The decrease in UV_{254} absorbance confirms chemical modification of aromatic structures of HA. Therefore, in the case of additional sonochemical effect (US/O_3), these changes were the highest. This fact also confirms the reduction in $SUVA_{254}$ index, i.e. reduction of particles, size and reduction of the share of aromatic carbon in the solved components, defined by DOC (Tab. 2). These effects are reflected by the results of other studies concerning the effect of ultrasounds on natural organic matter [16].

For the above experimental conditions, the effectiveness obtained for individual processes is compared in Table 3.

Table 3

Effectiveness (%) of the investigated processes

Parameter / Process	US	O_3	1 US/O_3	2 US/O_3
TOC	13.6	11.7	25.3	28.8
UV_{254}	20.3	30.5	39.8	43.6

Comparison of the effectiveness of the two combined arrangements reveals an insignificant advantage of the process where US effect was enabled during water ozonation. At the same time, in consideration of the effect of entire decomposition of HA, quantitative determination of TOC should be emphasized (effectiveness of 28.8%). Hence, in the case of 2 US/O_3 arrangement, an insignificant (3.5%) synergic effect of ozone and ultrasound on removal of HA was confirmed.

2.2. Influence of amplitude of vibrations and sonification time

Further investigations involved the verification of the effect of ozone and ultrasounds on HA, depending on the ultrasound parameters (Figs 2 and 3). The increase in the amplitude of vibrations is connected with an increase in ultrasound field intensity. The results (Fig. 2) demonstrated that this fact causes an increase in the effectiveness of removal of HA. The highest grade of HA removal with the use of $2US/O_3$ method was obtained while using the maximum ultrasound amplitude - 90 μm. However, it can be observed that this effect in UV_{254} decreases with amplitude above 45 μm.

Independent ultrasound process with low amplitude of 18 μm was less effective than the use of ozone only with chosen dose. Additional use of ultrasound (2 US/O_3) with the amplitude over 18 μm increased the effectiveness of the ozone dose. Increase in the intensity of the used ultrasounds for elevated amplitude was particu-

larly important for reduction in the TOC index. Obtaining the effectiveness of the combined process over 40% in the case of UV_{254} required the use of ultrasounds with the amplitude of 45 μm whereas for TOC the required amplitude was twice higher.

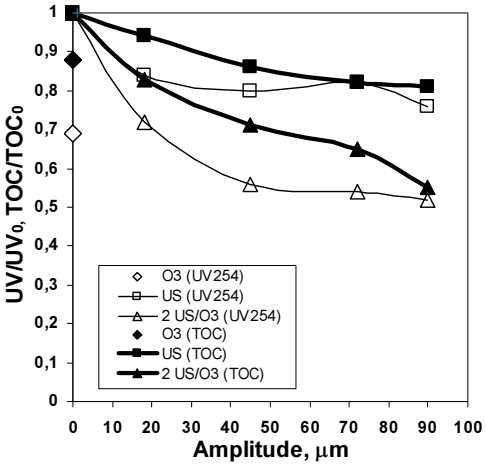

Fig. 2. Efficiency of interaction of ozone and ultrasound on HA removal from water depending on amplitude (t = 10 min, O_3 = 3 mg/L, HA = 10 mg/L)

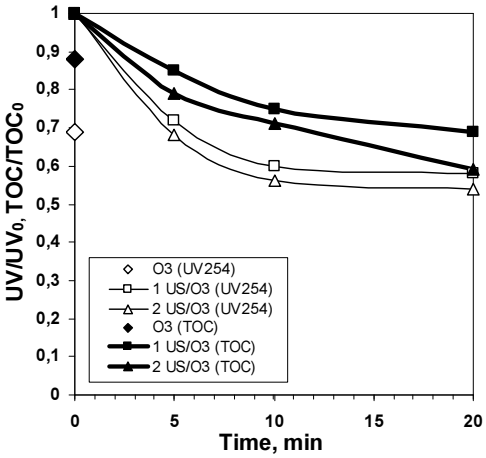

Fig. 3. Efficiency of interaction of ozone and ultrasound on HA removal from water depending on time (A = 45 μm, O_3 = 3 mg/L, HA = 10 mg/L)

Elongation of the contact time contributed to a greater reduction of the studied parameters (see Fig. 3). A noticeable reduction in TOC and UV_{254} can be observed in the first phase of the process (2 US/O_3) when the sonication was accompanied by introduction of ozone into the water. This confirms a favourable effect of ultrasounds on decomposition of ozone and generation of radicals. In [16] research also, better efficiency of US/O_3 system was confirmed, in which simultaneously

ozonization and sonification were performed. The obtained efficiency of associated system (HA concentration 64 mgHA/L) was in the initial phase of the process (after 30 minutes) much higher (30% TOC) than in O_3 match (10% TOC). At lower HA concentration in this researched solution (10 mgHA/L) a better effect is noted in 2US/O_3 system also (40% TOC after 20 minutes). Extending the time from 10 to 20 minutes for this method (2 US/O_3) resulted in the increase in reduction of TOC. It can be assumed that for the acclaimed conditions of the experiment it is economically justified to employ ultrasounds with amplitude of 45 μm for the time of 10 minutes (together with ozonation).

2.3. Influence of HA concentration and ozone dose

Another stage of the investigations concerned the effect of HA content in the studied solution on the effectiveness of the process of US/O_3. The investigations in US/O_3 arrangement, and, for comparison, in US and O_3 arrangement, were carried out for selected concentrations of HA, 10, 15 and 20 mg/L. The obtained process effectiveness (Fig. 4) exhibits an insignificant decrease in the effects (defined as TOC) with an increase in HS concentration. A double increase in HA concentration (from 10 to 20 mg/l) caused that the previous effect (28.8%, Table 3) was reduced to 26%. However, the synergic effect was not confirmed with the same ozone dose. Effects of the researched processes concerning solutions with the selected HA concentration are important from the point of view of water treatment. Effectiveness of US/O_3 process is higher than obtained in similar research, which, as it was indicated, connected with higher HA concentration, 64 mgHA/L [16]. The results confirm that the effectiveness of chemical effect of ozone reduces with the increase of concentration of HA in water. The opposite relationship is observed in the case of the ultrasound effect. Consequently, in the US/O_3 method, it can be observed that the influence of HA concentration on the effectiveness of the process is reduced.

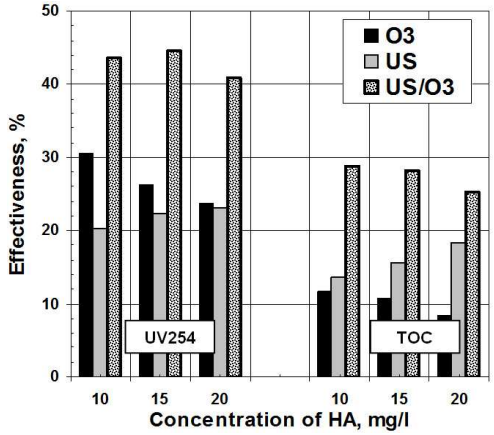

Fig. 4. Influence of HA contents in water on efficiency of researched process (t = 10 min, A = 45 μm, O_3 = 3 mg/L)

In the final part of the investigations, the effect of the ozone dose on the effectiveness of US/O_3 was analysed. The results presented in Figure 5 show that the effectiveness of ozone method and the process connected with US was high in both cases.

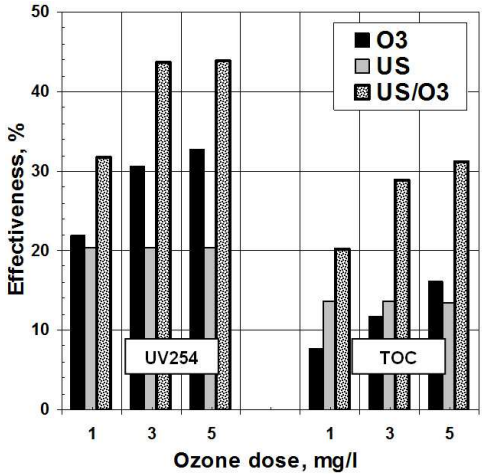

Fig. 5. Influence of ozone dose on efficiency of researched process in water (t = 10 min, A = 45 μm, HA = 10 mg/L)

In consideration of TOC index, almost twofold increase in the effectiveness of ozone dose after additional use of ultrasounds was observed. This points to a beneficial effect of ultrasounds, particularly in the process of mineralization of HA. The synergy in the combined process analysed in the study, understood as an increase in total effectiveness of ozone and ultrasounds, was in this case insignificant.

Increasing the ozone dose gave in general an increase in the effectiveness of both studied processes (O_3, US/O_3). The use of the lowest dose of ozone in the arrangement with US, allowed for obtaining comparable effects of removal of humic compounds, as well as for ozone alone in the dose of 5 mg/L.

Conclusions

1) The ozonation combined with ultrasound can be a promising method of AOPs. Comparing with ozonation or ultrasound alone, it appears to be more effective and uses less energy. In the process of ozone/ultrasound, ultrasound can be responsible for sonolytic degradation of the organic molecule and causes sonolysis of the oxidant molecule to create potent oxidizing free radicals.
2) In effect of US/O_3 process at set up parameters, the TOC and UV_{254} were considerably low in comparison with the effect of ozonation alone. It indicates on more forceful HA mineralization process as a result of the application of ultrasound.

3) The better efficiency of US/O_3 system was confirmed in the second variant ($2US/O_3$), in which ozone was introduced in the beginning of sonification (simultaneously with sonification).
4) The most favourable reduction of the content of HA compounds was observed for the higher intensities of the ultrasonic field, estimated by the vibration amplitude and at the longer sonification time.
5) Additional employment of ultrasonic field in the process of HA removal with the ozone method has enabled to increase the efficiency of US/O_3 process which amounts to 10÷18%, depending on the concentration of HA and the dose of ozone. The synergy in the combined process analysed in the study, understood as an increase in total effectiveness of ozone and ultrasounds, was in this case insignificant.
6) What has been observed is that the use of ultrasounds in the combined systems US/O_3 decreases the influence of HA concentration on the removal of these compounds from solutions in comparison to the O_3 method. The effects of the researched processes concerning solutions with the selected HA concentration are important from the point of view of water treatment. Effectiveness of US/O_3 process is higher than the one obtained in a similar research, which, as it was indicated, was connected with higher HA concentration.

Acknowledgements

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Ultradźwięki i ozon w usuwaniu substancji humusowych z wody

Substancje humusowe (SH) występują w środowisku wodno-gruntowym. SH, będąc podstawowym składnikiem humusu glebowego, odgrywają ważną rolę w glebie; kondycjonują, stabilizują i poprawiają jej strukturę. SH przenikają również do wód naturalnych, w których składzie stanowią 60÷80% całkowitej naturalnej materii organicznej. SH ze względu na swoją zdolność sorpcyjną wielu uciążliwych zanieczyszczeń organicznych antropogenicznych, jak również zdolność do tworzenia kompleksów z metalami ciężkimi muszą być usuwane z wody podczas jej uzdatniania. Również w efekcie końcowego chlorowania są przyczyną tworzenia się THM-ów.

W artykule przedstawiono wyniki badań nad zastosowaniem połączonej metody ultradźwięków i ozonu UD/O_3 do usuwania substancji humusowych z wody. Jako urządzenie wytwarzające ultradźwięki wykorzystano generator UP-400S (24 kHz) o mocy 300 W. Ilość energii ultradźwiękowej wprowadzanej do ośrodka i wysokość natężenia pola ultradźwiękowego były kontrolowane poprzez zmienny czas nadźwiękawiania (t = 5÷20 minut) i zmianę amplitudy drgań w zakresie A = 18÷90 μm. Natężenie pola ultradźwiękowego wynosiło powyżej 100 W/cm^2. Dawka ozonu wynosiła 1÷5 mg/dm^3. Jako próbki przygotowano roztwór preparatu handlowego kwasów humusowych (FLUKA) w dejonizowanej wodzie (stężenie roztworu 10÷20 mg/dm^3). Skuteczność badanego procesu analizowano na podstawie zmiany, przed procesem i po nim, następujących parametrów: OWO, RWO, absorbancja UV_{254}, barwa, utlenialność. W wyniku zastosowania procesu UD/O_3 obserwowano zmniejszenie badanych parametrów. Na podstawie otrzymanych wyników potwierdzono, że metoda połączona UD/O_3 była bardziej skuteczna w degradacji badanych związków humusowych niż każdy z procesów oddzielnie (efekt synergiczny). Najkorzystniejszy efekt redukcji zawartości tych związków odnotowano dla wyższych wartości natężenia pola ultradźwiękowego.

Słowa kluczowe: oczyszczanie wody, substancje humusowe, ultradźwięki, ozon