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HYBRID SONOLYSIS APPLICATION AS POLISHING STEP FOR REMOVAL OF THMS GENERATED FROM THE DRINKING WATER TREATMENT

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Abstract

Trihalomethanes (THMs) are organic compounds (with toxicity potential) generated during the classical treatment flow of drinking water as a result of reaction between natural organic matter (always present in drinking waters resources) and chlorine, which is the most disinfection reagent on a broad scale, in drinking water treatment plants. Ultrasonic treatment can be feasible for THMs removal for small or medium drinking water treatment plants.

This paper emphasizes the possibility to use sonolysis (chemical oxidation based on active radicals generated during cavitation process) as polishing step in drinking water treatment flow for trihalomethanes (THMs - trichloromethane, tribromomethane and bromodichloromethane) removal (initial concentrations over the admitted limit - 100 µg THM/l).

Four sonolysis systems were tested for synthetic and real surface treated water: direct sonolysis (US), US + H₂O₂, US + H₂O₂ + Fe (Fenton sonolysis), US + H₂O₂ + Fe + UV (low pressure mercury lamp λ = 250 - 400 nm). The variation domains of the main process parameters were as following: THMs concentrations 310 ÷ 3615 µg/L, sonolysis time 1 ÷ 60 min., ultrasonic energy 2x10⁶ J - 8x10⁶ J, ultrasonic amplitude 20 ÷ 80%, oxidant dose 0.6 ÷ 2.1 g H₂O₂/L, catalyst dose 0.25 ÷ 2 mg Fe²⁺/L.

Experimental results showed the evolution of THMs removal depending on sonolysis system: direct sonolysis (US) 56% < sonolysis and hydrogen peroxide (US + H₂O₂) 59% < foto Fenton sonolysis (US + H₂O₂ + Fe + UV) 63% < Fenton sonolysis (US + H₂O₂ + Fe) 73% emphasizing that bromoform are more difficult to remove compared to other.

Keywords: *cavitation, drinking water, direct sonolysis, hybrid sonolysis, THMs*

Introduction

Ultrasonic radiation is a vibration of an elastic medium (water, gases, solids) having over 16 kHz frequency with many application in medicine, industry, biology as well as in water/wastewater treatment (Ashokkumar 2011).

Since 1990s ultrasound has been widely used in water and wastewater treatment processes as an emerging advanced oxidation process (AOP) technology, applicable for a wide range of contaminants with various initial concentrations (Mahammumi & Adewuyi 2010).

Generation, combination and recombination of free radicals, very reactive, able to degrade pollutants from water are the base of aqueous solutions sonochemistry (Ashokkumar 2011; Mahammumi & Adewuyi 2010; Naddeo & Belgiorno 2007). Scientifically research in this field proved that direct sonolysis is efficient for

advanced degradation of organic pollutants in water. Ultrasounds become more efficient in both pollutants degradation and economical if sonolyse is associated with other classical and AOPs methods for water treatment: US + H₂O₂, US + H₂O₂ + Fe, US + O₃, US + UV, US + electrochemical oxidation, US + adsorption (Joseph et al. 2009).

Natural organic matter from drinking water sources reacts with chlorine generating THMs. Over the limit of 100 µg/L THMs became toxic for human so, should be avoided their generation and diminished the concentrations below admitted limit if their formation cannot be prevented (Shemmer & Narkis 2005; Stefanescu et al. 2015).

Chlorine is still the most efficient and economical disinfectant having remanence in drinking water pipes. Because of this last reason chlorine cannot be totally replaced by ozone or/and UV radiation in the drinking water treatment plants.

Sonolysis could be an alternative option for THMs advanced removal from drinking water.

Experimental

This paper emphasizes the possibility to use sonolysis (chemical oxidation based on active radicals generated during cavitation process) as polishing step in drinking water treatment flow for trihalomethanes (THMs) removal (concentrations over the admitted limit - 100 µg THM/L).

Fig. 1 and Fig. 2 show the ultrasonic reactor (SONICS Vibracell 500) and photolytic reactor (Haereus) respectively which are used in sonolysis and hybrid sonolysis tests.



Figure 1. Ultrasonic reactor

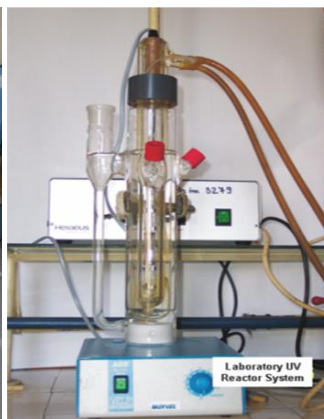


Figure 2. UV Reactor

Preliminary experimental tests were performed on synthetic water (deionized water and THMs dosage: trichloromethane, tribromomethane and bromodichloromethane) in order to establish the influence of THMs initial concentration, type of sonolyse system, ultrasonic irradiation time, ultrasonic energy and amplitude. Ultrasonic frequency was constant - 20 kHz.

Four sonolysis systems were tested both for synthetic water and real surface treated water: direct sonolysis US, US + H₂O₂, US + H₂O₂ + Fe (Fenton sonolysis), US + H₂O₂ + Fe + UV (low pressure mercury lamp $\lambda = 250 - 400$ nm).

The variation domains of the main process parameters were as following: THMs concentrations 310 ÷ 3615 µg/L, sonolysis time 1 ÷ 60 min., ultrasonic energy 2×10^6 J - 8×10^6 J, ultrasonic amplitude 20 ÷ 80%, oxidant dose 0.6 ÷ 2.1 g H₂O₂/L, catalyst dose 0.25 ÷ 2 mg Fe²⁺/L.

Results and Discussion

Sonolysis of synthetic solutions with THMs content

Experimental tests were performed for synthetic solutions with CHCl₃, CHBr₃, CHBrCl₂ in the following concentrations domain: CHCl₃ = 131 – 1536 µg/L, CHBr₃ = 71 – 827 µg/L, CHBrCl₂ = 108 – 1252 µg/L, TTHMs (Total THMs) = 310 – 3615 µg/L. Sonolysis time was 1 ÷ 60 min. Ultrasonic energy field varied in the range of $2 \div 8 \times 10^6$ Joule and waves amplitudes were between 25 ÷ 80%.

The influence of the above mentioned experimental parameters was determined (Tables 1 - 4).

Residual concentrations of THMs species were measured and removal efficiencies were calculated for each one and for total content (Tables 1 - 4 and Figures 3 - 5).

Regarding the influence of ultrasonic irradiation time, sonolysis time between 30 – 60 min. leads to total residual THMs ≤ 100 µg/L (below admitted limit).

Fig. 3 shows that 78% is maximum removal efficiency of total THMs and CHCl₃ is the most removable THM (86% for 60 min. irradiation time).

Table 1. The influence of sonolysis time to remanent THMs concentrations

Sample	Time, min	Residual THMs concentrations, µg/L			Residual Σ THMs concentrations, µg/L
		CHCl ₃	CHBr ₃	CHBrCl ₂	
T1	1	94	49	73	216
T2	5	90	51	77	218
T3	15	58	50	53	161
T4	30	31	37	32	100
T5	45	29	33	28	90
T6	60	14	23	15	52

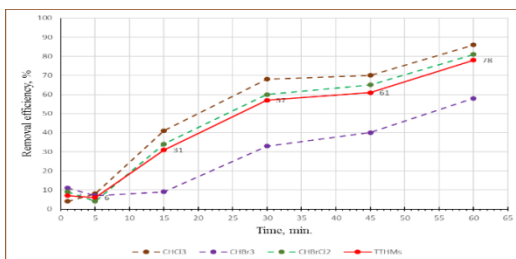


Figure 3. The influence of sonolysis time to THMs removal efficiencies

Concerning the influence of initial THMs concentration, for the same irradiation time, energy and amplitude the lowest residual THMs concentration was for sample C1 having THMs initial concentration 310 µg/L. Over this initial value the sonolysis process is not efficient in the selected operational conditions.

Table 2. The influence of initial THMs concentrations on residual organic content

Sample	Initial THMs concentrations, µg/L			Initial ΣTHMs conc., µg/L	Residual THMs concentrations, µg/L			Residual ΣTHMs conc., µg/L
	CHCl ₃	CHBr ₃	CHBrCl ₂		CHCl ₃	CHBr ₃	CHBrCl ₂	
C1	131	71	108	310	12.9	23.9	12.5	49.3
C2	237	135	196	568	52.5	84.9	57.2	194.6
C3	607	307	468	1382	144	147	133	424
C4	1048	531	820	2399	165	225	162	552
C5	1536	827	1252	3615	294	387	295	976

Time = 60 min, Energy = 4 x 10⁶J, Amplitude = 25%

The lowest value of total THMs residual content was determined for the highest value of ultrasonic energy (sample E4).

Regarding the influence of ultrasonic energy. Maximum efficiency for total THMs removal was 91% and bromoform has the lower value – 86%.

Table 3. The influence of ultrasonic energy to residual THMs content

Sample	Energy, J	Residual THMs concentrations, µg/L			Residual ΣTHMs concentrations, µg/L
		CHCl ₃	CHBr ₃	CHBrCl ₂	
E1	2x10 ⁶	26.3	35.5	25.4	87.2
E2	4x10 ⁶	12.9	23.9	12.5	49.3
E3	6x10 ⁶	11.3	17.4	10.4	39.1
E4	8x10 ⁶	9.7	10.2	6.9	26.8

ΣTHMs = 310 µg/L (CHCl₃ = 131 µg/L, CHBr₃ = 71 µg/L, CHBrCl₂ = 108 µg/L), Time = 60 min., Amplitude = 25%

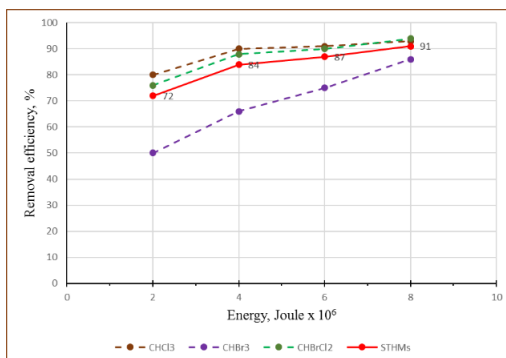


Figure 4. The influence of ultrasonic energy to THMs removal efficiencies

From the point of view of *the influence of ultrasonic waves amplitude*, the increase of ultrasonic amplitude has not a significant influence on residual THMs concentrations, which were in the domain of 26 – 30 µg/L.

Table 4. The influence of ultrasonic waves amplitude on residual THMs concentrations

Sample	Amplitude, %	Residual THMs concentrations, µg/L			Residual ΣTHMs concentrations, µg/L
		CHCl ₃	CHBr ₃	CHBrCl ₂	
A1	25	9.7	10.2	6.9	26.8
A2	40	9.9	11	7.2	28.1
A3	60	8.9	9.7	7.5	26.1
A4	80	10.5	11.8	8.1	30.4

ΣTHMs = 310 µg/L (CHCl₃ = 131 µg/L, CHBr₃ = 71 µg/L, CHBrCl₂ = 108 µg/L), Time = 60 min., Energy = 8x10⁶ J

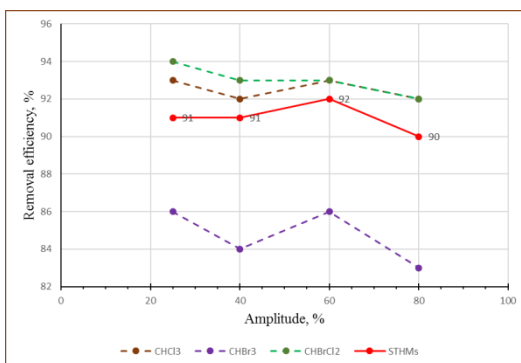


Figure 5. The influence of ultrasonic amplitude to removal efficiency of THMs

This tests confirm that bromoform had the lower removal efficiency (83% for the maximum amplitude of 80%).

Sonolysis of real drinking water with THMs content

In case of real drinking water which was pretreated by coagulation – flocculation (2 mg Al/L dose, 10 minutes stirring), flocculation with a flocculant based on starch and acrylamide (containing silver) 0.1% d.wt., 2 mL/L dose, TTHMs content was ~350 µg/L. These reagent doses and reaction times were established to be optimal based on previous research experiments (only the reaction time was halved).

The best results for the sonolysis tests were obtained in the following experimental conditions (Table 5):

- *direct sonolysis*: pH 7, time 30 min., energy 8x10⁶ J, amplitude 25%;
- *hybrid sonolysis* US + H₂O₂: similar with direct sonolysis + 1,7 g H₂O₂/L;
- *hybrid sonolysis* US + H₂O₂ + Fe: similar with previous system + 1 mg Fe/L;
- *hybrid sonolysis* US + H₂O₂ + Fe + UV: pH 7, sonolysis time 30 min., UV irradiation time 30 min., 1,7 g H₂O₂/L, 1 mg Fe/L, energy 8x10⁶ J, amplitude 25%, iron catalyst

and oxidant have put together in the photolytic reactor, after direct sonolysis phase.

Table 5. THMs removal efficiencies in different sonolysis systems

No.	Sonolysis system	$\eta_{\text{THM}}, \%$			$\eta_{\text{TTHM}}, \%$
		CHCl_3	CHBr_3	CHBrCl_2	
1	US	70	48	65	56
2	US+H ₂ O ₂	70	51	66	59
3	US+H ₂ O ₂ +Fe	82	67	80	73
4	US+H ₂ O ₂ +Fe+UV	63	66	59	63

Conclusions

Experimental results showed the evolution of THMs removal depending on sonolysis system: direct sonolysis (US) 56% < sonolysis and hydrogen peroxide (US + H₂O₂) 59% < foto Fenton sonolysis (US + H₂O₂ + Fe + UV) 63% < Fenton sonolysis (US + H₂O₂ + Fe) 73% emphasizing that bromoform are more difficult to remove compared to other.

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References

- Ashokkumar, T 2011, 'The characterization of acoustic cavitation bubbles – An overview', *Ultrasonic Sonochemistry*, vol. 18, pp. 864 – 872.
- Mahamuni, N & Adewuyi, YG 2010, 'Advanced oxidation processes (AOPs) involving ultrasound for wastewater treatment: A review with emphasis on cost estimation', *Ultrasonic Sonochemistry*, vol. 17, pp. 990 – 1003.
- Naddeo, V & Belgiorno, V 2007, 'Behaviour of natural organic matter during ultrasonic irradiation', *Desalination*, vol. 210, pp. 175 – 182.
- Joseph, CG, Puma, GL, Bono, A, Krismaiah, D 2009, 'Sonophotocatalysis in advanced oxidation process: A short review', *Ultrasonic Sonochemistry*, vol. 16, pp. 583 – 589.
- Shemmer, H & Narkis, N 2005, 'Trihalomethanes aqueous solutions sono – oxidation', *Water Research*, vol. 39, pp. 2704 – 2710.
- Stefanescu, M, Cosma, C, Cristea, I, Ionescu, I & Bumbac, C 2015, 'Degradation of natural organic matter from Surface Water Using Sonolysis', *International Symposium The Environment and Industry*, SIMI 2015, National Research and Development Institute for Industrial Ecology ECOIND, pp. 47-54.