Ultrasonic Irradiation a Chlorinated Organic Compounds (Trichloroethylene, Tetrachloroethene, 1, 1, 2-Trichloroethane) from Water

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The paper describe the sonochemical degradation of organochlorine compounds (Trichloroethylene, Tetrachloroethene and 1, 1, 2-Trichloroethane) from aqueous solutions. The experiments was realized with two types of equipment: ultrasound bath UCD-150 and sonotrode UP 200 Ht. The experimental results showed high efficient removal for all three compounds: Tetrachloroethene 93.8%, 1, 1, 2-Trichloroethane 92.9% and Trichloroethylene 86.6% in bath ultrasound treatment after 50 min. The ultrasound efficiency treatment depend by the sonotronde diameter. The degradation of Trichlorethylene and 1, 1, 2 -Trichloroethane is much better for sonotrode with 14 mm diameter (92.1% respectively 92.7%) than for sonotrode with 40 mm diameter (71.9% and 61.6%), while for Tetrachloroethene values were very close, 88.7% respectively 89.4% for the same above mentioned diameters.

Keywords: chlorinated organic compounds, ultrasonic irradiation, sonochemical processes

The volatile organic compounds are considered among the most dangerous indoor pollutants because of their diffusion properties and their continuous emission from many sources, predominantly from organic compounds and chlorinated and non-chlorinated solvents [1-2].

There is already known that ultrasonic treatment of liquids cause acoustic cavitation and it implosion generate high temperatures and pressures for a very short periods of time, which are responsible for unusual sonochemical effects. In general, the most studies on sonochemistry have adopted the model of *hot spot* to explain the experimental results. In light of this theory there are heterogeneous sonochemical reactions and processes taking place due to heat-formed reactive species and place in a *microreactor* which encompasses three areas: *cavity ultrasonic*, *gas-liquid interface* and the *liquid in the vicinity of the interface* [3-7]. The mechanism of degradation intermediates depend on experimental conditions and oxidation elected. In the light of above mentioned theories there are next processes during the sonochemical water treatment: *oxidation by hydroxyl radicals*, *pyrolytic decomposition or combustion* and *supercritical water oxidation conditions*. The volatile and hydrophobic organic compounds, tend to diffuse into the cavity, where it is degraded mainly by the thermal decomposition resulting in the formation of combustion by products present. The pollutants with high vapor pressure tend to enter the cavity formed by the gas phase more quickly, in which case the vapor pressure is a more important parameter than the hydrophobic or hydrophilic property and the binding energy. At high concentrations the main degradation route is the pyrolysis of the volatiles in the gaseous phase inside the cavity, where they are present in a high proportion. At low concentrations, the volatile substances react with the free radicals in the cavity-liquid interface. The interface region is specific for hydrophobic and low volatile substances. Hydrophilic compounds and non-volatile specifically react with free radicals in the vicinity of the cavity. The thermal decomposition is not important for non-volatile compounds as they do not reach the cavity center in a large quantities [8-11].

Experimental part

The experiments were conducted in aqueous solutions containing the analytical grade quality of Trichloroethylene (TCE), Tetrachloroethene (PCE) and 1,1,2 -Trichloroethane (1,1,2 - TCE). Stock solutions were prepared by dissolving the proper amount of the chemical in water and stored 24 hours in refrigerator. Grade 1 water (resistivity (MÙ.cm) > 18.0, TOC (ppb) < 10, Na (ppb) <1, silica (ppb) <3) was used to prepare the solutions was obtained from water purification system. All other chemicals used were of p.a. grade and purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (Deisenhofen, Germany). The irradiation for all three solutions was performed using an ultrasonic baths UCD-150 type, 35 kHz, 325 W (Raypa Spain) and a sonotrode UP 200 Ht type, 26 kH, 200W (Hielscher, Germany).

Irradiation experiments of the three compounds (Trichloroethylene, Tetrachloroethene and 1, 1, 2 -Trichloroethane) were made using an ultrasonic bath type UCD 150 at a frequency of 35 kHz and power of 325 W. A volume of 2500 mL of aqueous solution was transferred to the ultrasound bath. The aqueous solutions have been irradiated for 10, 20, 30, 40 and 50 min in the ultrasound bath. The next series of experiments have been realised using sonotrodes with two diameters, 14 mm and 40 mm. A volume of 400 mL of aqueous solution was transferred into a Berzelius beakers where then was introduced the sonotrode. The aqueous solutions have undergone to ultrasonic treatment for 2, 4, 6, 8 and 10 min.

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The experiments were repeated for three times and the results indicated are the average value obtained.

The analytical methods

Trichloroethylene, Tetrachloroethene and 1,1,2-Trichloroethane concentrations were determined by gas-chromatography (GC) using flame ionization detection. The GC analyses were designed and performed according to SR EN ISO 10301:2003. The *p*H was measured using the electrochemical method, according to SR EN ISO 10523:2012, and the residual chlorine, according to the SR EN ISO 7393-1:2002, volumetric method.

Results and discussions

Irradiation experiments using ultrasonic bath

The experimental results for Trichloroethylene (table 1) shows its degradation from initial value of 4.22 mg / L to 0.564 mg / L in 50 min that means a degradation efficiency of 86.6%. The *pH* decrease from 6.48 to 4.16 from the same period of time, its variation can be caused by the formation of acidic compounds and free radicals. In contrast with these evolutions, the *residual chlorine* increase in first 30 min from an initial value of 0.048 mg / L to 0.06 and decline to 0.028 mg / L at the end of experiment.

The experimental results for Tetrachloroethene (table 2) points a similar variation of the indicators analysed during the ultrasound treatment. The *pH*, decrease from 6.44 to 4.30; the *residual chlorine* increase from 0.022 to 0.052 mg / L, with a decline at 0.03 mg / L. *Tetrachloroethene*, initial concentration decrease from 5.62 mg / L to 0.35 mg / L, yielding a removal efficiency of 93.8%.

The ultrasound treatment of 1, 1, 2-Trichloroethane aqueous solutions (table 3) follows the same direction: the *pH* decreasing from 6.49 to 5.41, the *residual chlorine* increasing from 0.04 to 0.06 mg / L followed by a decrease at 0.034 mg / L. The initial concentration of 7.13 mg / L reached 0.506 mg / L after 50 min and the treatment efficiency is 92.9%.

In figure 1-2 are resumed the experimental results obtained during sonochemical decomposition of Trichlorethylene, Tetrachloroethene and 1,1,2- Trichloroethane using ultrasonic bath.

Time (min.)	TCE mg/L	pH (Unit.pH)	Cl_2 mg/L
0	4.22	6.48	0.048
10	2.73	6.21	0.052
20	1.91	5.89	0.056
30	1.39	5.11	0.06
40	0.97	4.25	0.04
50	**0.564**	**4.16**	**0.028**

Table 1
RESULTS OBTAINED AFTER IRRADIATION TRICHLORETHYLENE USING ULTRASONIC BATH

Time (min.)	PCE mg/L	pH (Unit.pH)	Cl_2 mg/L
0	5.62	6.44	0.022
10	3.88	6.22	0.040
20	2.52	4.93	0.044
30	1.44	4.63	0.048
40	1.12	4.52	0.052
50	**0.35**	**4.30**	**0.03**

Table 2
RESULTS OBTAINED AFTER IRRADIATION TETRACHLOROETHENE USING ULTRASONIC BATH

Time (min.)	1,1,2 TCE mg/L	pH (Unit.pH)	Cl_2 mg/L
0	7.13	6.49	0.04
10	4.35	6.39	0.044
20	3.57	6.32	0.052
30	2.46	6.11	0.056
40	1.79	5.87	0.06
50	**0.506**	**5.41**	**0.034**

Table 3
RESULTS OBTAINED AFTER IRRADIATION 1,1,2-TRICHLOROETHANE USING ULTRASONIC BATH

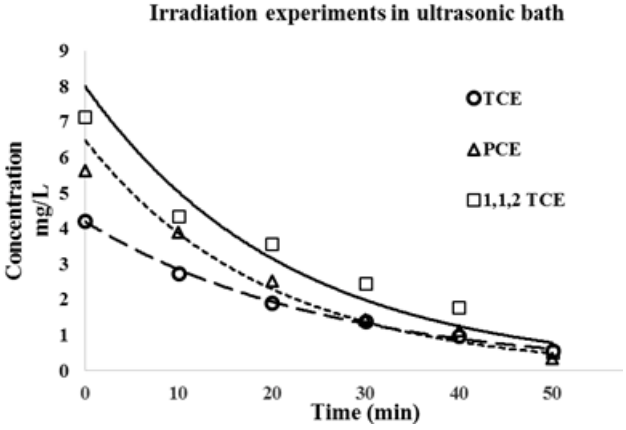

Fig.1 The evolution of concentration on sonochemical decomposition of Trichlorethylene, Tetrachloroethene and 1,1,2-Trichloroethane

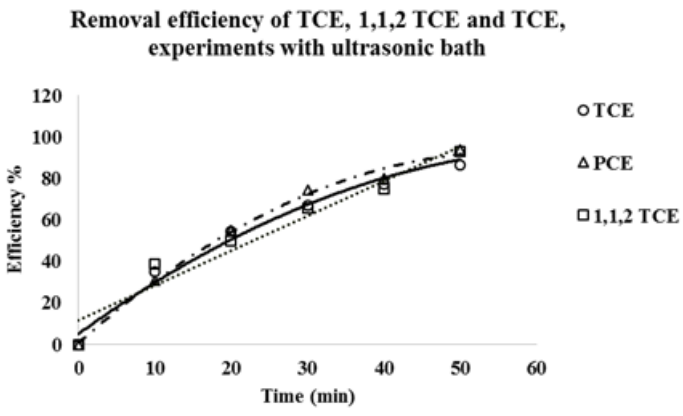

Fig. 2. The evolution sonochemical decomposition efficiency of Trichloroethylene, Tetrachloroethene and 1,1,2-Trichloroethane

Irradiation experiments using ultrasonic processor

In tables 4 - 6 are presented experimental results obtained during sonochemical decomposition of Trichlorethylene, 1,1,2-Trichloroethane, and Tetrachloroethene using sonotrode having a diameter of 14 mm and 40 mm. Because the efficiency is higher in this case, the irradiation time was limited to a maximum of 10 min.

The ultrasound treatment of Trichloroethylene aqueous solution using sonotrodes (table 4, fig. 3) satisfactory efficiency after 10 min. The best results are indicated by sonotrode with small diameter (14 mm) compared to bigger diameter (40 mm). The final concentration of *Trichloroethylene* reached 0.384 mg / L for first experiment and 1.34 mg / L for second, the efficiency is 92.1% respectively 71.9%. In contrast with that the differences

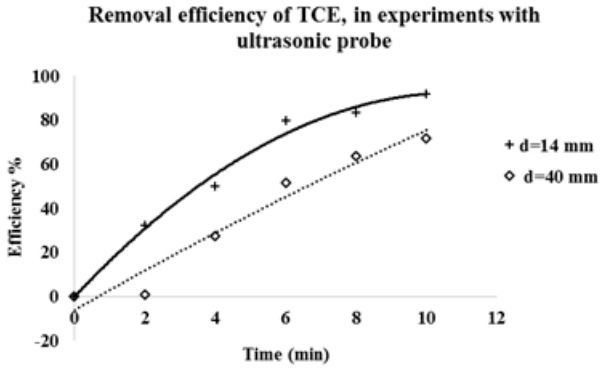

Fig.3 The evolution sonochemical decomposition efficiency of Trichloroethylene

Time (min.)	TCE mg/L		pH (Unit.pH)		Cl_2 mg/L	
	d=14 mm	d=40 mm	d=14 mm	d=40 mm	d=14 mm	d=40 mm
0	4.85	4.77	6.43	6.51	0.046	0.046
2	3.29	4.48	5.53	6.04	0.048	0.048
4	2.43	3.45	4.43	5.16	0.052	0.050
6	0.96	2.31	4.20	4.43	0.058	0.054
8	0.8	1.74	4.08	4.06	0.048	0.052
10	**0.384**	**1.34**	**3.98**	**3.92**	**0.034**	**0.04**

Table 4
RESULTS OBTAINED AFTER IRRADIATION TRICHLOROETHYLENE USING SONICATION PROBE

Time (min.)	PCE mg/L		pH (Unit.pH)		Cl_2 mg/L	
	d=14 mm	d=40 mm	d=14 mm	d=40 mm	d=14 mm	d=40 mm
0	4.24	4.76	6.33	6.42	0.036	0.038
2	2.27	2.65	4.57	5.84	0.044	0.048
4	1.53	1.76	4.21	5.15	0.058	0.052
6	1.06	1.62	4.07	4.32	0.068	0.056
8	0.8	1.06	3.98	4.0	0.052	0.050
10	**0.45**	**0.54**	**3.91**	**3.98**	**0.044**	**0.04**

Table 5
RESULTS OBTAINED AFTER IRRADIATION TETRACHLOROETHENE USING SONICATION PROBE

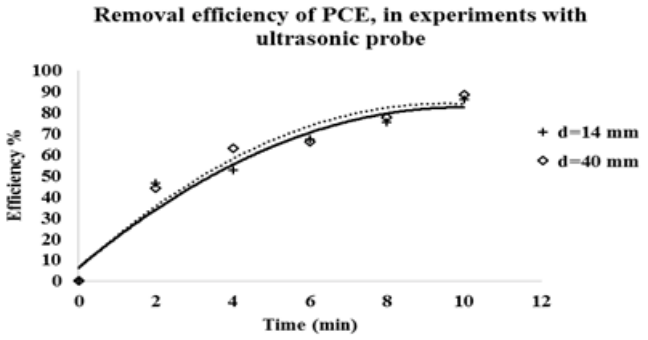

Fig. 4 The evolution sonochemical decomposition efficiency of Tetrachloroethene

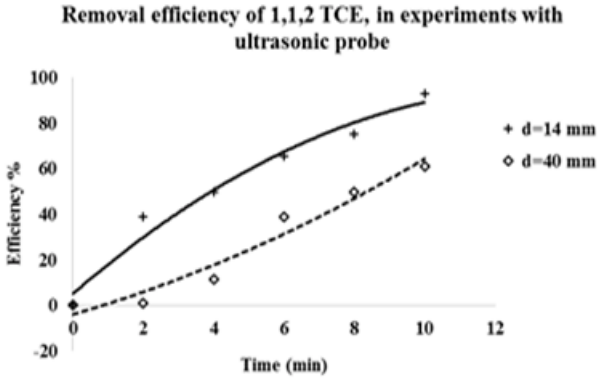

Fig. 5 The evolution sonochemical decomposition efficiency of 1,1,2-Trichloroethane

are not so evident for: the *pH* and *residual chlorine*. The initial *pH* (6.43 and 6.51) became acid with appropriate values in both situations, 3.98 respectively 3.92. The *residual chlorine* follow the same trend like in bath ultrasound treatment, increase initial from 0.046 mg/ L until 0.058 mg/L and 0.054 mg/L and decrease at the end of experiments, 0.034mg / L and 0.04 mg / L.

The efficiency degradation of *Tetrachloroethene* from aqueous solutions using sonotrode irradiation are showed in table 5 and figure 4. In this situation the sonotrode with the smallest diameter (14 mm) indicated the best results like bugger one (40 mm) but the differences are not so evident like in above descripted experiment, the degradation efficiency is 89.4 and 88.7%. It is found that the initial *pH* (6.33 and 6.42) become acidic (3.91 and 3.98) and the *residual chlorine* follow the same trend like in bath ultrasound treatment, increase initial from 0.036 mg / L and 0.038 mg / L until 0.068 mg / L and 0.056 mg/ L and decrease at the end of experiments, 0.044mg / L and 0.04 mg / L

The experimental results for 1,1,2-Trichloroethane, detailed presented in table 6 and figure 5, showed a similar trend like for Trichlorethylene. The efficiency removal of the 1,1,2-TCE with small diameter sonotrode (14 mm) was 92.7% while 40 mm sonotrode was 61.6%, the difference is more evident now. The *pH* decreasing from 6.66 and 6.68 to 4.10 and 4.67, and the *residual chlorine* increasing from 0.04 mg / L and 0.038 mg / L to 0.058 mg / L and 0.056 mg / L followed by a decrease at 0.038 mg / L and 0.04 mg / L.

It is noticed that there are better results for the situation in which it is used sonotrodes than ultrasonic bath, but in

Time (min.)	1,1,2 TCE mg/L		pH (Unit.pH)		Cl_2 mg/L	
	d=14 mm	d=40 mm	d=14 mm	d=40 mm	d=14 mm	d=40 mm
0	9.27	10.51	6.66	6.68	0.04	0.038
2	7.17	9.47	6.59	6.47	0.046	0.048
4	4.48	9.30	6.0	6.27	0.052	0.052
6	2.74	6.43	5.81	6.12	0.056	0.056
8	1.12	5.27	5,09	5.45	0,058	0,050
10	0.68	4.1	4.67	4.87	0.038	0.04

Table 6
RESULTS OBTAINED AFTER IRRADIATION 1,1,2-TRICHLORO-ETHANE USING SONICATION PROBE

first situation there are only 400 mL and in second series of experiments are 2500 mL. The power density can be one reason, for sonotrode there are 200 W for 400 mL and for ultrasound bath are 325 W for 2500 mL. Of course, the frequency and the geometry of bath and Berzelius glass can also play an role, but there is not enough data to made more detailed discussions or comparisons.

In the situation of ultrasound treatment using sonotrodes can be realised another comparison. There was observed that for sonotrode with smaller diameter (14 mm), implicitly smaller surfaces, the results are better than for equipment with bigger diameter (40 mm). Because the characteristic of equipment are the same, power and frequency, can be deduced that the reason for the different performance is power intensity at the contact between aqueous solution and ultrasound irradiation surface. That imply higher amplitude and more sonochemical processes. The best results are for smaller surfaces, where the ultrasound source with 200 W power are distributed on contact surface between aqueous solution and ultrasound irradiation representing 154 mm^2, in contrast with 1256 mm^2 for second sonotrode.

Conclusions

The ultrasound degradation of Trichloroethylene, tetrachloroethene and 1, 1, 2 -Trichloroethane from aqueous solutions can be realised into a success manner using both ultrasound bath and sonotrodes. The efficiency degradation indices good values for all components: 93.8% (Tetrachloroethene), 92.9% (1,1,2-Trichloroethane) and 86.6% (Trichloroethylene) after 50 min of treatment in ultrasonic bath.

The process is faster with sonotrodes regardless them diameter. One reason is the quantity of ultrasound treated aqueous solution. In the ultrasonic bath there are 2500 mL and in Berzelius glass there are only 400 mL. Of course the geometry of equipment play also an important role, but it is difficult to prove for all these experiments, excepting sonotrode diameter. The experiments showed the best results for sonotrode with smaller diameter implicitly smaller surfaces. The explanation can be the power intensity at the contact between aqueous solution and ultrasound irradiation surface. That imply higher amplitude and more sonochemical processes. The efficiency of Trichlorethylene and 1, 1, 2-Trichloroethane degradation is much better with 14 mm diameter sonotrode (92.1 and 92.7 %) than with diameter of 40 mm (71.9 and 61.6%). In the experiment where was used Tetrachloroethene the efficiency was appropriate 88.7 and 89.4%.

Sonochemical processes represents a promising energy intensive technique that can successfully contribute to the detoxification of waters containing organic compounds and required time can be shorter compared with classical methods.

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References

1.NENCIU, F., VAIREANU, D. I., Rev. Chim. (Bucharest), **65**, no. 5, 2014, p. 565
2.COHL,M., LAZAR,L., CRETESCU, I. BALASANIAN,I., Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1282
3.N. SERPONE, P. COLARUSSO, SONOCHEMISTRY I. RES. CHEM. INTERMED., 20, 1994, p. 635-679
4.M. IORDACHE, I. IORDACHE, L. R. POPESCU, D. SCHITEA, L. F. PASCU, PROGRESS OF CRYOGENICS AND ISOTOPES SEPARATION, 19, (1), 2016, 91-98
5.P. R. GOGATE, A. B. PANAIT, ADV. ENV. RES., 8, 2004, 553-597
6.J. LIFKA, B. ONDRUSCHKA, J. HOFMANN, ENG. LIFE. SCI., 3, 6 2003, 253-262
7.Y. G. ADEWUYI, ENVIRON. SCI. TECHNOL., 39, (10), 2005, 3409-3420
8.Y. G. ADEWUYI, ENVIRON. SCI. TECHNOL., 39, (22), 2005, 8557-8570
9.M. GOEL, H. HONGIANG, A. S. MUJUMDAR, M. B. RAY, WATER RES., 38 (2004) 4247-4261
10. H SHEMER, N. NARKIS, ULTRASON. SONOCHEM, 12, 2005, 495-499
11. R. J. EMERY, M. PAPADAKI, L. M. ENVIRON. INT., 31, 2005, 207-211

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