DOI: http://doi.org/10.21698/simi.2017.0015

THE SONODEGRADATION OF ORGANIC COMPOUNDS FROM INDUSTRIAL WASTEWATER

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Abstract
Removal of the organochlorine compounds from industrial wastewater by sonochemical processes was performed in order to evaluate process' efficiency. Sonochemical degradation of the following organochlorine compounds: 1,2 dichloropropane, 1,1,2-trichloroethane, 2 ethylhexanol and β, β'-dichlorodiisopropyl ether was carried out. The experiments was realized with two types of equipment: ultrasound bath UCD-150 and sonotrode UP 200 Ht.
Experimental results showed high efficient removal for all compounds: 1,1,2-trichloroethane and β, β'-dichlorodiisopropyl ether 78.0%, 1,2 Dichloropropane 66.0%, 2 ethylhexanol 35.0 % in bath ultrasound treatment after 60 minutes. Degradation of β, β'-dichlorodiisopropyl ether, 1,1,2-trichloroethane, 1,2 dichloropropane and 2 ethylhexanol performed much better for sonotrode with 14 mm diameter (89.0%, 77.5%, 73.0%, respectively 73.0%) than for sonotrode with 40 mm diameter (64.0%, 64.0%, 53.0% and 48.0%). This difference between the two probes regarding removal efficiency can be explained by different amplitudes of equipment.

Keywords: *organochlorine compounds, ultrasonic irradiation, sonochemical processes, wastewater*

Introduction
The chlorinated volatile organic compounds (Cl-VOCs) including polychloromethanes (PCMs), polychloroethanes (PCAs) and polychloroethylenes (PCEs), are a group of ubiquitous contaminants that have been widely detected in environment media in recent years. These compounds possess high volatility and strong recalcitrance to degradation, for instance, the atmosphere lifetime of carbon tetrachloride and 1, 1, 1 - trichloroethane could reach as high as 100 and 6 years, respectively, allowing them to be transported over long distances in various environment media (Nenciu & Vareanu 2014; Cohl 2015; Iordache 2017).
The ultrasound use in the water and wastewater treatment have acquired considerable attention, mostly due the extreme condition effects during the cavitation collapse. Cavitation collapse generates sites with locally very high temperatures and/or pressures for short periods of time, which are responsible for unusual sonochemical effects. It is now well established that this process is capable of providing very high temperatures (4500 – 5000^{o}K) and very high pressures (aprox. 1000 atm) in extremely short times (in the range of microseconds), thus rendering cavitation a quasi-adiabatic phenomenon (Blume 2000; Leonelli & Mason 2010; Cravotto 2015; Iordache 2017).

Since the beginning of the investigation on sonochemistry processes a lot of works have been published on ultrasound wastewater treatment. The mechanism proposed for the sonochemical degradation of organic pollutants is usually based on the formation of short life radicals generated in violent cavitation events (Suslick 1990; Visscher 2003; Iordache, M. 2009).

$$H_2O \rightarrow HO\bullet + H\bullet \quad (1)$$

The "hot spot" model was adopted to explain the sonochemical effects and results. In light of this theory the reactions caused by ultrasound irradiation of waters are heterogeneous and processes occurred due to the reactive species and heat generated during the cavitation collapse. That can by imagined as a "micro-reactor" which encompasses three areas: the cavity interior, the cavity ultrasonic gas-liquid interface and the liquid from the vicinity of the interface. The next processes are considered for destruction or decomposition of the pollutants: oxidation by hydroxyl radicals, pyrolytic decomposition and combustion and finally supercritical water oxidation conditions (Serpone 1994; Iordache 2016).

Materials and Methods

Sonochemical method

The experiments were conducted in wastewater and irradiation processes were 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).

A volume of 2500 mL of wastewater was transferred to the ultrasound bath. The wastewater have been irradiated for 10, 20, 30, 40, 50 and 60 minutes in the ultrasound bath.

The second set of experiments have been realized using sonotrodes with two diameters, 14 mm and 40 mm. A volume of 400 mL of wastewater was transferred into a Berzelius beakers where then was introduced the sonotrode. The wastewater have undergone to ultrasonic treatment for 2, 4, 6, 8, 10 and 12 minutes.

Analytical methods

1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-Ethylhexan-1-ol, β,β'diclordiizopropilic ether 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 pH was measured using the electrochemical method, according to SR EN ISO 10523:2012. Determination of the chemical oxygen demand (COD-Cr) was performed according to SR ISO 6060:1996 and the chloride, according to the SR ISO 9297:2001, volumetric method.

Results and Discussion

The sonodegration experiments were carried out on industrial water (P1 and P2) containing 1, 2 Dichloropropane, 1, 1, 2 Trichloroethane, 2 Ethylhexanol, and β,β' diclordiizopropilic ether. From the analysis results shown in Table 1 it has been found that industrial wastewater is highly alkaline with a pH between 11.47 and 11.88. For the analyzed wastewater samples, the inorganic charge expressed in chlorides took values in the range of 18081.0 mg/l and 18258.3 mg/l while the organic load expressed

in COD-Cr was in the range of 1094.4 mg O_2/l and 1920.0 mg O_2/l. Waste water samples were analysed by gas chromatography to determine the organochlorine compounds, and have found values between 0.444 and 0.48 mg/l for ββ'diclordiizopropilic ether, values between 0.15 and 0.64 mg/l for 1,1,2 Tricloroethane, values between 13.88 and 17.61 mg/l for 1,2 Dichloropropane, and values between 0.81 and 1.38 mg/l for 2 ethylhexanol.

Table 1. Physical and chemical characterization of industrial wastewater

Crt. No.	Polluted	U.M.	P1	P2
1	pH	Unit. pH	11.88	11.47
2	COD-Cr	mgO_2/l	1094.4	1920.0
4	Cl^-	mg/l	18081.0	18258.3
5	1,1,2 TCE	mg/l	0.64	0.15
6	1,2 DCP	mg/l	13.88	17.61
7	2 EH	mg/l	1.38	0.932
8	β β' eter	mg/l	0.444	0.48

Irradiation experiments using ultrasonic bath

Since the pH was located in the highly alkaline zone: pH 11.47 and 11.88, the pH adjustment to neutral pH with H_2SO_4 was used and the irradiation was performed using an ultrasonic baths UCD-150 type, 35 kHz. Experimental results for 1, 2 Dichloropropane (Table 2) show its degradation from the initial value of 17.61 mg/l to 6.07 mg/l in 60 minutes, which means a degradation efficiency of 66.0%. For 1,1,2 trichloroethane the initial value was 0.15 mg/l and after 60 minutes it reached 0.033 mg/l, with a removal efficiency of 78.0%, a similar removal with ββ' ether, in while removal efficiency for 2 Ethylhexanol was 35%.

Irradiation experiments using ultrasonic processor

In Tables 3 and 4 are presented the experimental results obtained during sonochemical decomposition of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode with a diameter of 14 mm and 40 mm. The ultrasound treatment of 1,2 Dichloropropane using sonotrodes reached satisfactory efficiency after 12 minutes. The best results were obtained using thesonotrode with small diameter (14 mm) compared to bigger diameter (40 mm). The final concentration of 1,2 Dichloropropane reached 3.8 mg/l for first experiment (14 mm) and 7.77 mg / L for second (40 mm), the efficiency is 73.0% respectively 53.0%. The experimental results for 1,1,2 Trichloroethane, showed a similar trend like for 1, 2 Dichloropropane. The efficiency removal of the 1,1,2 Trichloroethane with small diameter sonotrode (14 mm) was 77.5% while 40 mm sonotrode was 64.0 %, the difference is more evident now. The efficiency degradation of 2-ethylhexan-1-ol from waste water using sonotrode irradiation are showed in Tables 3 and 4, also. In this situation the sonotrode with the smallest diameter (14 mm) presented the best results compared to bigger one (40 mm), for which the degradation efficiency was 73.0% and 48.0%. For the ultrasound treatment of β,β'diclordiizopropilic ether, best results were obtained using thesonotrode with small diameter (14 mm) compared to bigger diameter (40 mm). The final concentration of β,β'diclordiizopropilic ether reached 0.444 mg/l for first experiment (14 mm) and 0.46 mg / L for second one (40 mm), the efficiency was 89.0% respectively 64.0%.

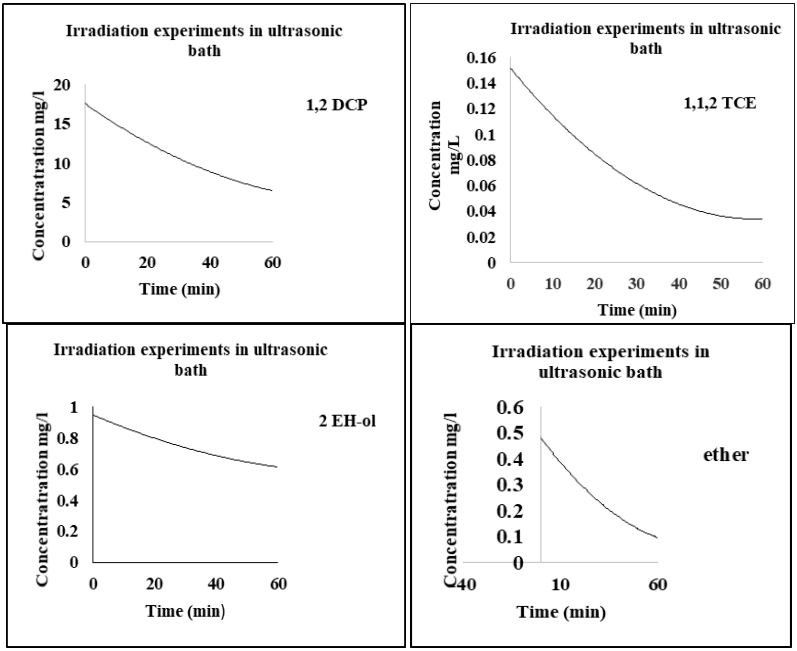

Figure 1. The evolution of concentration on sonochemical decomposition of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Table 2. Results obtained after irradiation 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using ultrasonic bath

Time	pH (U. pH)	COD-Cr mgO_2/l	Cl^- mg/l	1,2 DCP mg/l	1,1,2 TCE mg/l	2 EH mg/l	Eter ββ' mg/l
0	6.87	1920.0	18258.3	17.61	0.15	0.932	0.48
10	6.86	1824.0	18258.3	15.13	0.12	0.91	0.39
20	6.61	1728.0	18258.3	12.27	0.082	0.77	0.282
30	6.53	1632.0	18081.0	10.44	0.056	0.732	0.266
40	6.47	1536.0	18081.0	8.7	0.052	0.69	0.167
50	6.38	1536.0	18081.0	8.46	0.036	0.65	0.115
60	**6.31**	**1440.0**	**18081.0**	**6.0**	**0.033**	**0.61**	**0.104**

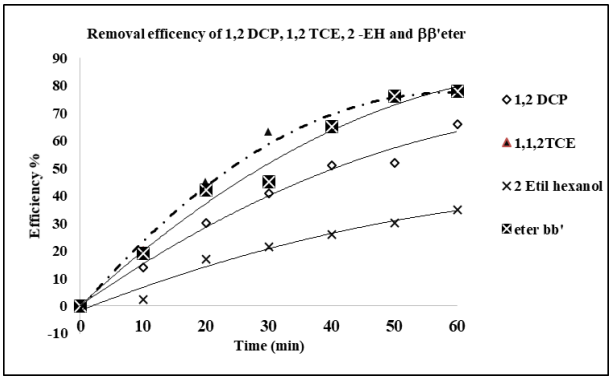

Figure 2. The evolution sonochemical decomposition efficiency of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Table 3. Results obtained after irradiation 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode having a diameter of 14 mm

Time	pH (U.pH)	COD-Cr mgO_2/l	Cl^- mg/l	1,2 DCP mg/l	1,1,2 TCE mg/l	2 EtH mg/l	Eter ββ' mg/l
0	6.95	1094.4	18081.0	13.88	0.64	1.38	0.444
2	6.93	1048.8	18081.0	12.63	0.484	1.114	0.329
4	6.77	1003.2	17726.5	9.58	0.344	0.93	0.222
6	6.70	912.0	17372.0	8.35	0.267	0.746	0.148
8	6.64	866.4	17372.0	6.58	0.192	0.62	0.112
10	6.53	820.8	17372.0	5.35	0.154	0.41	0.066
12	**6.44**	**775.2**	**17372.0**	**3.8**	**0.144**	**0.37**	**0.049**

Table 4. Results obtained after irradiation 1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether using sonotrode having a diameter of 40 mm

Time	pH (U.pH)	COD-Cr mgO_2/l	Cl^- mg/l	1,2 DCP mg/l	1,1,2 TCE mg/l	2 EH mg/l	ββ' ether mg/l
0	6.84	2016.0	18435.6	16.55	0.147	1.09	0.460
2	6.81	1920.0	18435.6	15.09	0.132	1.0	0.440
4	6.68	1824.0	18453.6	12.78	0.121	0.835	0.380
6	6.54	1728.0	18258.3	12.17	0.105	0.705	0.210
8	6.48	1632.0	18081.0	10.35	0.084	0.676	0.190
10	6.41	1536.0	18081.0	9.13	0.066	0.611	0.172
12	**6.37**	**1536.0**	**18081.0**	**7.77**	**0.053**	**0.564**	**0.167**

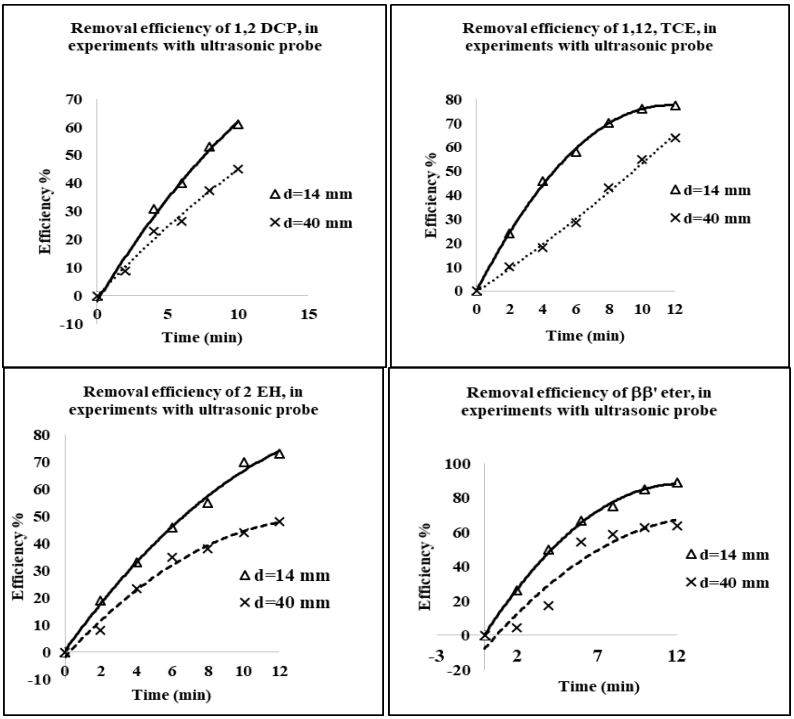

Figure 3. The evolution sonochemical decomposition efficiency of 1,2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether

Conclusions

The ultrasound degradation of 1, 2 Dichloropropane, 1,1,2 Trichloroethane, 2-ethylhexan-1-ol, β,β'diclordiizopropilic ether from wastewater can be realized into a success manner using both ultrasound bath and sonotrodes. The efficiency degradation indicates good values for all components: 78.0% (1,1,2 Trichloroethane and β,β'diclordiizopropilic ether), 66.0% (1, 2 Dichloropropane) and 35.0 % (2-ethylhexan-1-ol) after 60 minutes of treatment in ultrasonic bath.

The experiments showed the best results for sonotrode with smaller diameter implicitly smaller surfaces. The explanation is the power intensity at the contact between wastewater and ultrasound irradiation surface. That imply higher amplitude and more sonochemical processes. The efficiency of β,β'diclordiizopropilic ether and 1,1,2 Trichloroethane degradation is much better with 14 mm diameter sonotrode (89.0% and 77.5%) than with diameter of 40 mm (64.0% and 64.0%). The experimental results for 1,1,2 Trichloroethane, showed a similar trend like for 1, 2 Dichloropropane. The degradation efficiency of 1,2 Dichloropropane and 2-ethylhexan-1-ol, showed a similar trend like for β,β'diclordiizopropilic ether and 1,1,2 Trichloroethane, 73.0% and 53.0% respectively 73.0 and 48.0%.

It can be concluded that sonochemical processes represents a promising technique that improves the detoxification of waters containing organic compounds especially considering the time required for detoxification (few tens of minutes) compared with conventional methods.

Acknowledgements
The authors acknowledge the financial support from the Ministry of Education - State Authority for Research Scientific, technological development and innovation through the Project PN 16-25 03 10, "Research on application procedures sonochemical the degradation of organic compounds from wastewater".

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