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# SONOCHEMICAL DEGRADATION OF CARBON TETRACHLORIDE IN AQUEOUS SOLUTION AT TWO FREQUENCIES: 200KHZ AND 600KHZ, 200W ACOUSTIC POWER

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## Abstract

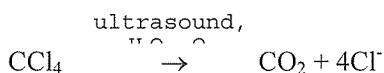
Sonochemical degradation of carbon tetrachloride have been studied at 200, 600 kHz frequencies of 200 w acoustic power source. It is investigated that the degradation rates of carbon tetrachloride solutions with various concentrations seem to be dominant at 200 kHz frequency in comparison with one at 600 kHz. The results of the research have been observed by formed chloride ion parameter which is determined by Standard Method 4500-Chloride B (Argentometric Method). Irradiation time was up to 165 minutes. Carbon tetrachloride decomposed strongly in the first 60 minutes and the degradation rate reached up to 64 percentage.

## 1. Introduction

Chlorinated hydrocarbon contaminants in water are both toxic to human health, other organisms and very persistent in the nature, destroying aquatic world and itself – cleaning of the receiver. Above mentioned chemicals, among them carbon tetrachloride, are widely used as solvents or sources of the industrials, in addition, formed naturally or in accidental conditions, or be as secondary pollutants of the environmental engineering.

Ultrasound using in an effort to degrade carbon tetrachloride in waste water into less harmful compounds has been investigated in decade. Under 30 w acoustic power, the carbon tetrachloride in 0.4 mM solution disappearance ( $\mu\text{M}/\text{min}$ ) enhances when frequency increases from 20 to 200, 500 and 800kHz [5]. The view of carbon tetrachloride destruction for one ultrasonic period is that the parameters of mol destroyed carbon tetrachloride per period vary in inverse proportion to the values of frequency.

The investigated phenomena can explained that the high enough energy to involve pyrolysis of carbon tetrachloride molecules releases due to the phenomenom of cavitation at low frequency, which is the nucleation, growth and collapse of bubbles in a liquid. The results of the research also showed that: the roles of hydroxyl radicals, hydroxide, hydroperoxyl radicals are minor important in frame of carbon tetrachloride destruction; some intermediates formed during carbon tetrachloride pyrolysis in very few amount and very short retention time; the final products of the processes are chloride anion  $\text{Cl}^-$  and carbon dioxide  $\text{CO}_2$  [6]:



In frame of the research, our attention was focused on the study on degradation efficiency of multiconcentration carbon tetrachloride waste water, at two big different frequencies 200 kHz and 600 kHz under 200 w acoustic power, the degradation rate change upon irradiation time.

## 2. Experimental section

### 2.1. Apparatus

100 ml of carbon tetrachloride solution is holding in a reactor which is a cylindrical glass container of 5.5- 6.5 cm diameter, flat bottom, with glass stopper. The model TA-4021 200 W ultrasonic multi-frequency generator, product of Kaijo Denki Corporation, Japan, was used. The transducer's surface was 6.5 cm diameter, the output units were 200 kHz and 600 kHz, the output adjustment was at the 8<sup>th</sup> in 10-position scale. The cooling water's temperature was keeping stable at supplied water temperature of about 15±3 degree C. The experimental set-up has been described in Fig. 1.

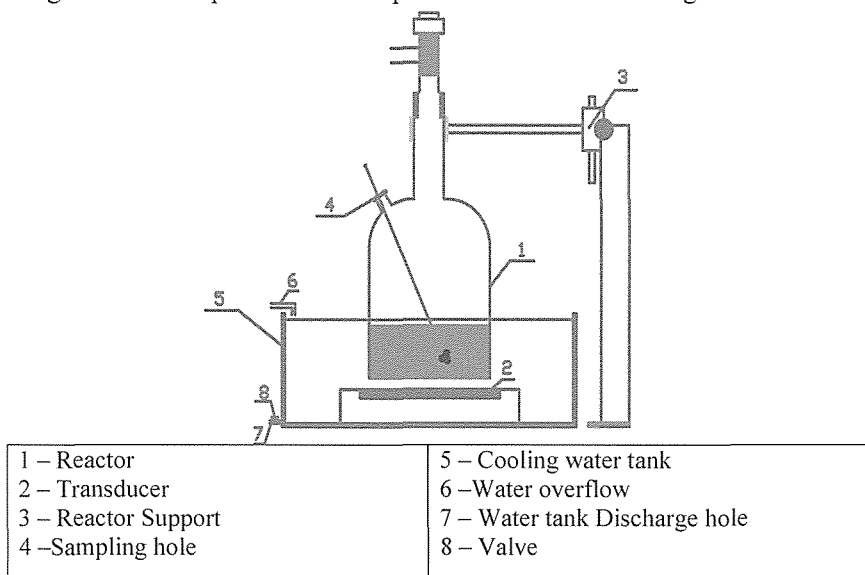


Fig. 1: Reaction scheme of carbon tetrachloride waste water treatment by ultrasound

### 2.2. Materials and experiments

Table 1: Samples and experimental conditions of carbon tetrachloride solutions

Num.	Concentration (ppm)	Frequency , kHz	Irradiation time, min.
1	Saturated (~800)	200	60
2	Saturated (~800)	600	60
3	4-time diluted saturated (~200)	200	120
4	4-time diluted saturated (~200)	600	120
5	8-time diluted saturated (~100)	200	165
6	8-time diluted saturated (~100)	600	165
7	16-time diluted saturated (~50)	200	165
8	16-time diluted	600	165

	saturated (~50)		
9	40-time diluted saturated (~20)	200	165
10	40-time diluted saturated (~20)	600	165
11	80-time diluted saturated (~10)	200	165
12	80-time diluted saturated (~10)	600	165

Chinese carbon tetrachloride with purity 99.5%, density  $d=1.592-1.598$  g/ml at  $20^{\circ}\text{C}$ , was used in the research. The saturated carbon tetrachloride solution ( $\sim 800$  ppm at  $18^{\circ}\text{C}$ ) was prepared by the way: pour an amount of pure carbon tetrachloride into a bottle, shake in 5 minutes, then put it on the table, 5 seconds later incline the bottle and pour 100 ml into 100-ml volumetric flash, shake and transfer to the reactor with stopper. The 200ppm, 100ppm, 50ppm 20ppm, 10ppm were prepared by the way: transfer amounts 25,12.5,6.25,2.5,1.25 ml saturated solution respectively to the 100-ml volumetric flashes, then add pure water to each until reach 100 ml mark..

Table 1 give some samples and experimental conditions of carbon tetrachloride solutions.

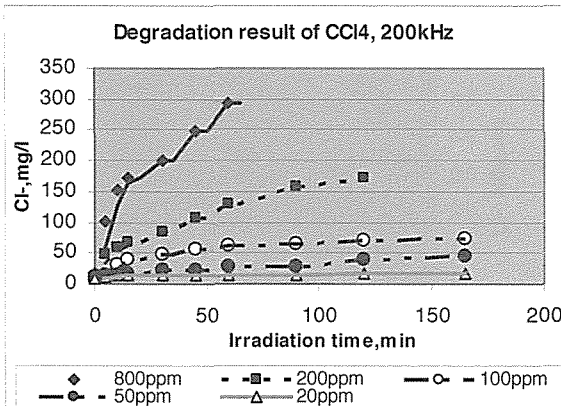
### 2.3. Analysis

Anion chloride formed concentration was a main parameter in assessment the efficiency of carbon tetrachloride destruction by ultrasound. Standard Method 4500-Chloride B (Argentometric Method) was used for anion chloride concentration determination. The sampling is as following: 5-ml samples were taken out via main entrance of the reactor after 5,10,15,20,30,45,60,90,120,165 minutes of irradiation time. The solutions irradiation were implementing in airtight space.

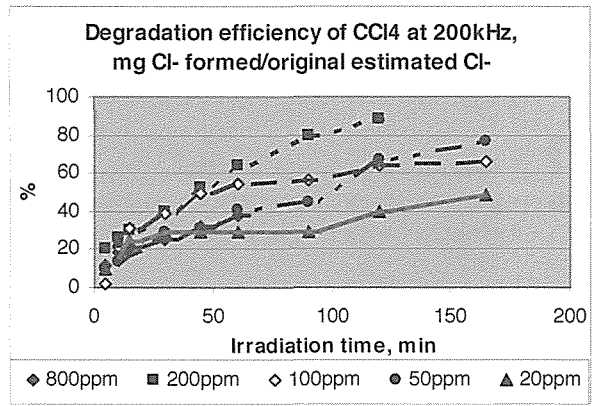
## 3. Results and discussions

a/ At 200 kHz frequency:

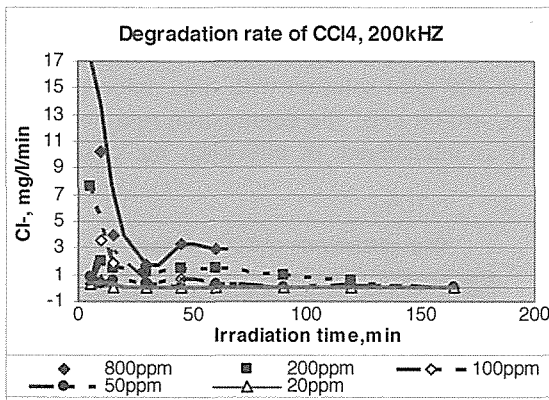
At 200 kHz frequency, the dependent diagram in fig.2 and fig.3 showed that, in higher concentration solutions, the destroyed carbon tetrachloride amounts bigger under the same acoustic power source (200 W). The aspect of the irradiation time on carbon tetrachloride destruction efficiency (mg/l in fig.2 and % destroyed in fig.3) depend on the original concentration of the experimental solutions. It means: apart from acoustic power source value, the destroyed pollutants amount depended on their element's density in the solution. The destruction rate (fig.4 and 5) give more clarity of pollutant concentration changes in time, by the way, we can investigate the period of time when the destruction efficiency of carbon tetrachloride solutions by acoustic power reaches the maximum. That is: the degradation quickly slowed down in the first 60 minutes of irradiation to 1 % Cl<sup>-</sup> formed per minute and reaches 60 % efficiency in case of 200 ppm and 100 ppm solutions, then fluctuated and slowly decreased. This parameters are 0.63%/min and 37.85% respectively in case of 800 ppm solution.



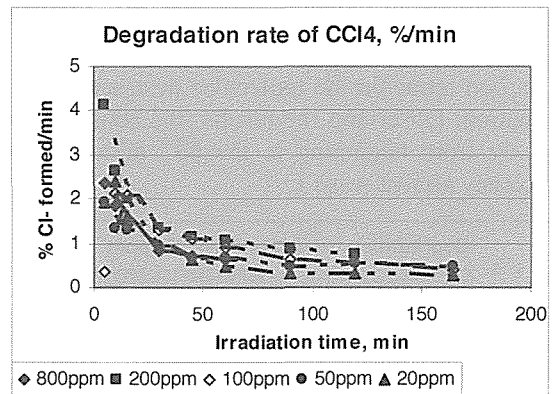
**Fig. 2:** Cl<sup>-</sup> concentration formed upon irradiation time at 200kHz of various CCl<sub>4</sub> concentration solutions



**Fig.3:** Degradation efficiency (%) of various CCl<sub>4</sub> concentration solutions upon irradiation time



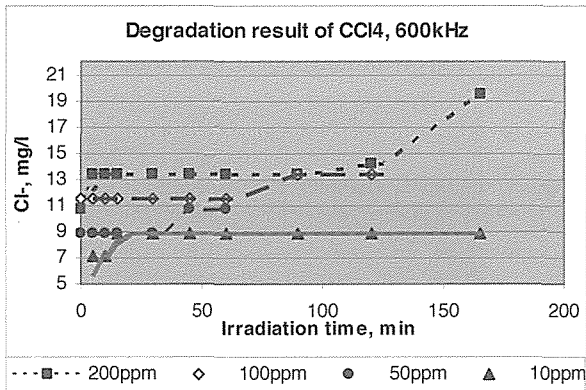
**Fig.4:** Degradation rate of CCl<sub>4</sub> upon irradiation time at 200kHz of various CCl<sub>4</sub> concentration solutions



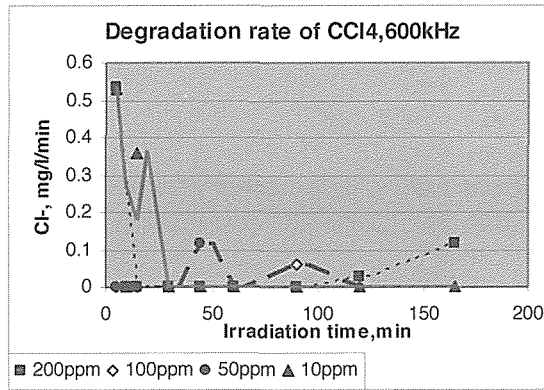
**Fig.5:** Degradation rate (% Cl<sup>-</sup> formed/min) of various CCl<sub>4</sub> concentration solutions upon irradiation time

b/ At 600 kHz frequency:

Observing the degradation results of carbon tetrachloride solutions in fig.6 and 7 upon irradiation time, the changes were very small, that means the effect of this acoustic frequency in the role of pyrolysis agent wasn't considerable. In case of slower concentration solutions, the destruction token appeared earlier: at 5<sup>th</sup> minute of 10 ppm soln., at 120<sup>th</sup> minute of 200 ppm soln.



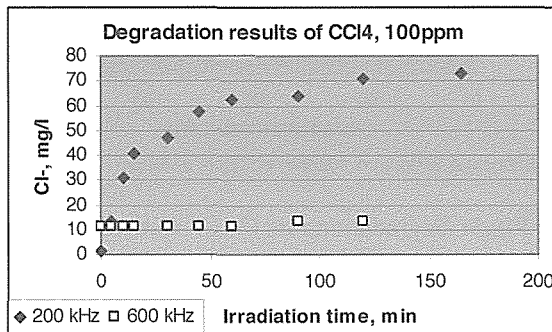
**Fig.6:** Cl<sup>-</sup> concentration formed upon irradiation time at 600kHz of various CCl<sub>4</sub> concentration solutions



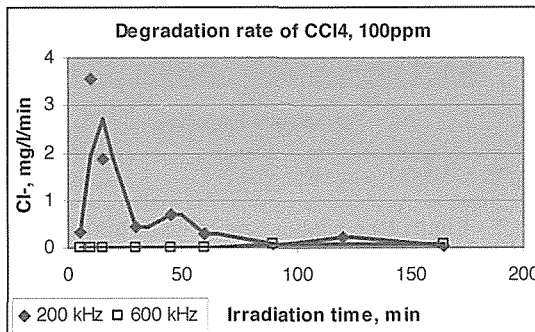
**Fig.7:** Degradation rate of CCl<sub>4</sub> upon irradiation time at 600kHz of various CCl<sub>4</sub> concentration solutions

c/ Comparisons of degradation efficiency at frequencies 200 kHz and 600 kHz:

The diagrams of fig.8 and 9 showed the big differences between the effects of the acoustic frequencies in carbon tetrachloride molecules destruction processes in 100 ppm solution with final anion chloride formation. Observing the results, the confirmation is that, at 200 kHz, the degradation rate decreased quickly from beginning to the 60<sup>th</sup> minute, then nearly is unchanged; at 600 kHz, the destruction efficiency almost wasn't.



**Fig.8:** Cl<sup>-</sup> concentration formed upon irradiation time at 200kHz and 600kHz of 100 ppm solution



**Fig.9:** Degradation rate of CCl<sub>4</sub> 100 ppm soln. upon irradiation time at 200kHz and 600 kHz

#### 4. Conclusions

- Under 200 W acoustic power source, at 200 kHz frequency, carbon tetrachloride in water solution destructed vigorously much more than at 600 kHz frequency.
- The destructed amounts (mg) didn't absolutely proportional to the energy of the acoustic power sources but was characteristic of each frequency of the source. They were not fixed in case of the different concentration solutions even under the same frequency and acoustic power source, but

varied in direct proportion to the concentrations of solution. The degradation efficiency (percentage of anion chloride formed on original estimated) was also proportional to the solution's concentration excepting 800 ppm soln., this parameter of which was lower by far than of 200 ppm soln., was approximately to that of 50 ppm soln.

- At 200 kHz frequency, the degradation rate decreased quickly from beginning to the 60<sup>th</sup> minute, then nearly is unchanged; at 600 kHz, the destruction efficiency almost wasn't. At 600 kHz frequency, the destruction token appeared earlier in case of slower concentration solutions, it happen at 120<sup>th</sup> minute of 200 ppm soln..

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