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Using the method of chemical dosimetry to evaluate the level of generation of active oxygen forms in advanced oxidation processes based on ultrasound

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Abstract. The widespread use of ultrasound is due to the diversity of phenomena occurring in an ultrasonic field. Ultrasonic vibrations initiate dispersion and emulsification of substances, contribute to coagulation and degassing, affect the processes of crystallization and dissolution. It is known that ultrasound causes various chemical transformations of a substance, including oxidation reactions, reduction, polymerization, etc. Research on the chemical effects of acoustic cavitation is an important task and for this, there are a large number of different chemical dosimeters of organic and inorganic nature. However, the proposed dosimeters have both advantages and disadvantages, including a long analysis time, high measurement errors, cost analysis, the use of expensive equipment. This work shows that the known substance butyl potassium dithiocarbonate can be used as a dosimeter of the effects of acoustic cavitation, in particular, high-frequency ultrasound 1.7 MHz, and has several advantages over the commonly used dosimeters. A large synergistic effect (2.26) was shown in the oxidation of dithiocarbonate from the combined effect of two directed at each other sources of ultrasound.

1. Introduction

Ultrasound, which is actively used in many spheres of human activity, is also used for water purification. However, existing technologies using acoustic cavitation are not widely used due to high-energy costs. Nevertheless, there is a growing interest in high-frequency ultrasound using piezoceramic transducers as an energy-efficient alternative.

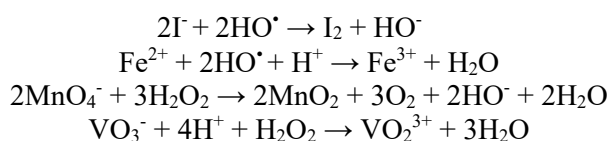
To perform sonochemical reactions, generators of low, medium and high frequency acoustic oscillations from 20 kHz to 2 MHz are used [1]. It should be noted that low- and mid-frequency devices are quite energy-intensive and have a low efficiency, which is a significant disadvantage, and the power consumption of high-frequency counterparts is almost an order of magnitude lower, which makes them promising for industrial use [2-4].

With the passage of an ultrasonic wave in a liquid, areas of tension and compression appear, while in places of rarefaction the process of formation of cavitation bubbles occurs. The collapse of bubbles leads to the pyrolysis of molecules contained in the liquid. So, in the water during the passage of an ultrasonic wave, the pyrolysis of water molecules occurs with the formation of reactive oxygen species (ROS):



ROS are strong oxidizing agents (for example, $E^0(\text{OH}^\bullet) = 2.7 \text{ eV}$). As a result of oxidation reactions, accompanied by elimination reactions, hydroxylation and splitting of C – C bonds, it is possible to achieve complete mineralization of organic micropollutants [5]. However, the flow of oxidative processes under conditions of acoustic cavitation is affected by many parameters, such as the frequency and power of the ultrasonic wave, temperature, viscosity of the liquid, external pressure, impurities, hydrophobicity / hydrophilicity of the solute, etc. [6].

Herewith, it is worth noting that calorimetry is not applicable to estimate the amount of ROS generated, as it reflects only the amount of energy transmitted to the system, and now there is no correlation between the amount of energy transmitted to the system and the ROS generated. To estimate the amount of ROS generated, chemical dosimetry methods are most often used, based on the study of the kinetics of ROS reaction with model substances — chemical dosimeters, for example:



Chloroform, salicylic and terephthalic acids, etc. are used as model substances [7-10]. But the proposed dosimeters have both advantages and disadvantages, including a long analysis time, high measurement errors, cost analysis, the use of expensive equipment (for example, HPLC and spectrofluorimetry), etc.

This study examines the possibility of using potassium butyl dithiocarbonate as a model compound for evaluating the chemical effects of acoustic cavitation. The proposed dosimeter is inexpensive, easy to store, easily soluble in water, and preparation of the working solution is reduced to obtain an aqueous solution of dithiocarbonate of a given concentration (whereas many dosimetric solutions in addition to the target substance contain various additives that ensure measurement accuracy [11]). Potassium butyl dithiocarbonate appears to be a photoactive substance — at 300 nm, the molar extinction coefficient is $1,750 \text{ L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$, while its degradation products do not absorb at 300 nm, which makes it possible to use express and less costly than chromatography.

2. Materials and Methods

Studies were conducted in model aqueous solutions of potassium butyl dithiocarbonate (99%) with a concentration of 10 mg/L. Distilled water with a specific electrical conductivity of less than $2 \mu\text{S}/\text{cm}$ was used to prepare solutions. The experiments were carried out in a thermo-controlled sonochemical reactor with a volume of 400 ml, a ceramic piezoelement with a diameter of 20 mm was used as a source of ultrasound, and the ultrasound frequency was 1.7 MHz. A detailed description of the reactor can be found in [12, 13]. The temperature in the reactor was kept constant at 25°C . The kinetics of the oxidation of dithiocarbonate was investigated by the method of spectrophotometry (Shimadzu UV-1800 spectrophotometer, Japan). A portable Multi 3410 instrument with a SenTix940 electrode (WTW) was used to measure the response of the medium. In order to ensure the efficiency of the acoustic cavitation flow, we used the rate constant of dithiocarbonate destruction.

3. Results and discussion

Like all compounds containing divalent sulfur, dithiocarbonates are reducing agents. They are easily oxidized by reactive oxygen species and other oxidizing agents (Figure 1). The oxidation in aqueous solutions appears to be very easy and convenient. Among the decomposition products are thiosulfate, sulfate, carbonate. When exposed to mild oxidizing agents (air oxygen, halides, nitrites, Fe^{3+} ions, Cu^{2+} , etc.), dioxanthogen disulfide (dioxanthogenide) is formed in aqueous solutions [14].

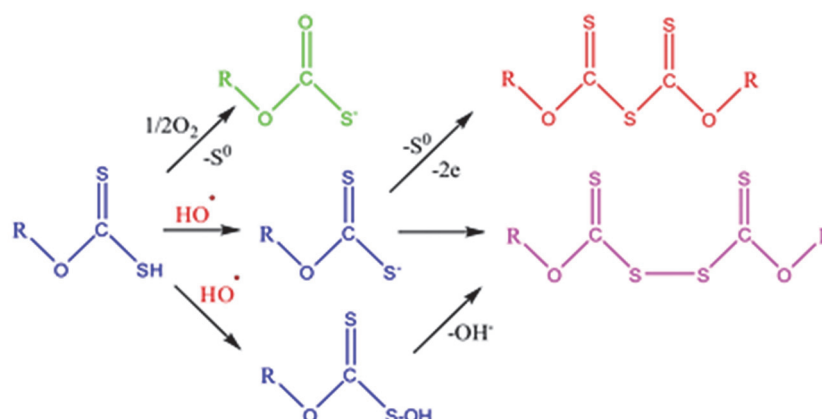


Figure 1. Some reactions with ROS.

The study of the absorption spectra showed that the reaction products practically did not contribute to the peak of interest in the region of 300 nm (Figure 2). At the same time, an increase in optical density was observed in the region with a maximum of 207 nm, which was probably caused by the accumulation of carbon disulfide CS₂ (peak 207 nm, $\epsilon = 60\text{-}70 \cdot 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ [14]):

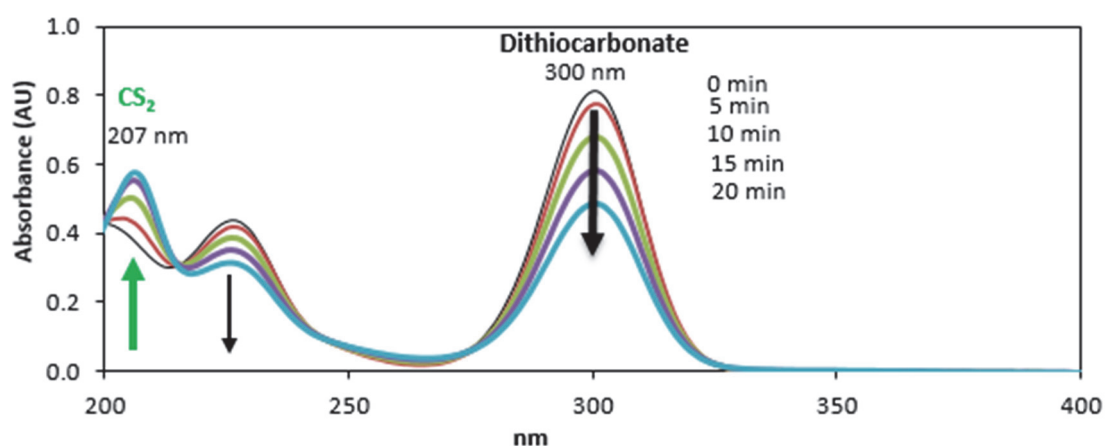


Figure 2. Absorption spectra of Dithiocarbonate under conditions of high-frequency ultrasonic (1.7 MHz).

Dithiocarbonate is oxidized by oxygen dissolved in water, but this process is much slower than the oxidation of dithiocarbonate under high-frequency ultrasound conditions (Figure 3).

Establishing the order of dithiocarbonate sonolysis reaction (in the concentration range 28–90 $\mu\text{mol/L}$) showed that the reaction is close to zero order, which suggests that the destruction probably mainly proceeds due to pyrolysis of the dithiocarbonate molecule in a cavitating bubble (reaction 1), and that reactions with $\text{HO}\cdot$ and $\text{H}\cdot$ radicals (reaction 2) also contribute. The reaction order was determined graphically in the coordinates $\ln t_{1/2} - \ln C_0$ by the slope of the line $\text{tg } \varphi = 1-n$, we get $n = 0.42$ (Figure 4).

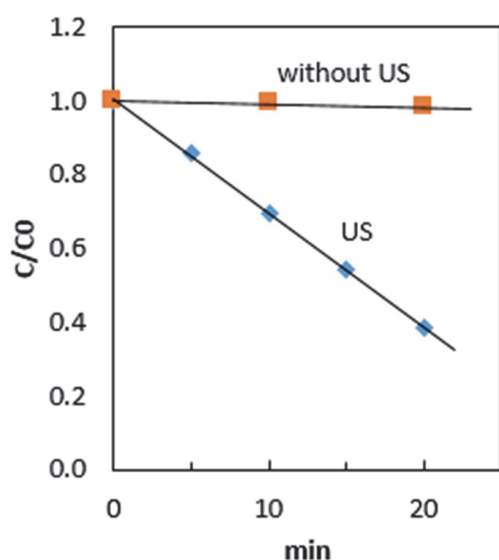
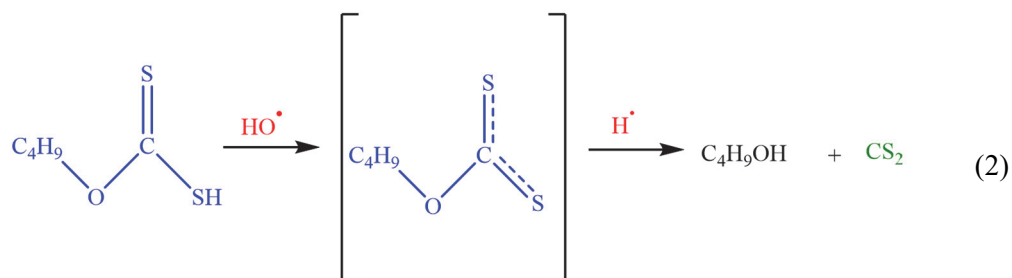
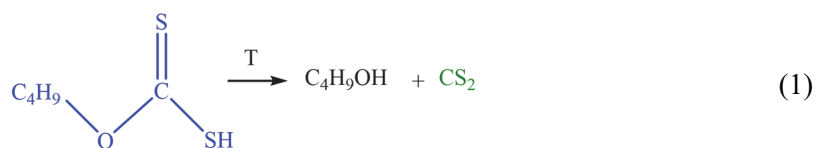


Figure 3. Kinetics of dithiocarbonate destruction under ultrasound conditions and without.

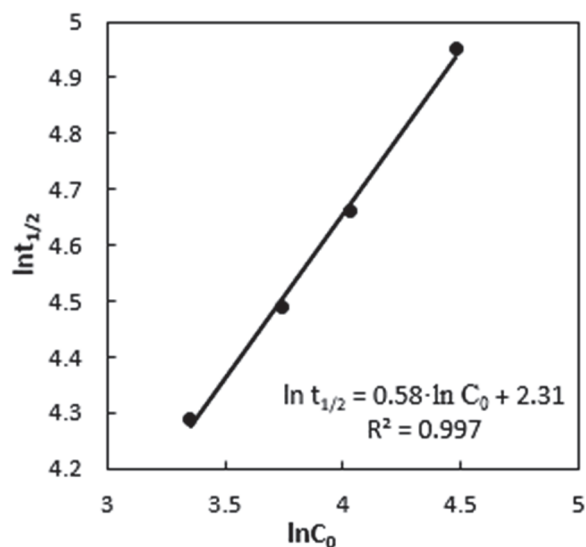


Figure 4. Graph of $\ln t_{0.5}$ versus $\ln C_0$.

When using together two coaxially aligned and face-to-face ultrasonic emitters (emitter diameter 20 mm, distance between emitters 10 mm), a significant synergistic effect was found (Table 1), which was found by the formula:

$$\varphi = \frac{k_{\text{together}}}{k_1 + k_2} = \frac{0.4501}{0.0926 + 0.1065} = 2.26$$

Table 1. Experimental results V (reactor) = 400 ml.

	k ($\mu\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)
Ultrasound transducers №1	0.0926
Ultrasound transducers №2	0.1065
Together №1 + №2	0.4501

The generated microbubbles fluctuate intensely in response to pressure disturbances caused by ultrasound [15]. At relatively low acoustic pressures, microbubbles oscillate in a symmetric radial mode with periodically varying volumes of bubbles. Probably, in the interval between the "face to face" emitters, conditions are created under which bubble oscillations in both modes (volume and shape) persist for hundreds of acoustic cycles, determining steady cavitation.

4. Conclusion

The results indicate that it is possible in principle to use potassium butyl dithiocarbonate as a chemical dosimeter of reactive oxygen species formed in aqueous solutions under acoustic cavitation conditions. It was shown that dithiocarbonate is oxidized under high-frequency ultrasound conditions of 1.7 MHz, kinetic regularities were determined, including the order of reaction. It has been established that with the use of two coaxially aligned and face-to-face ultrasonic emitters, a significant synergistic effect was revealed (synergistic index $\phi = 2.26$).

Acknowledgements

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