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Ultrasonic intensification of ozone and electrochemical destruction of 1,3-dinitrobenzene and 2,4-dinitrotoluene

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Abstract

The removal of nitroaromatics from polluted water is difficult due to their high stability to conventional treatment methods. This paper presents a method for the destruction of 1,3-dinitrobenzene and 2,4-dinitrotoluene in aqueous solutions. The compounds are shown to be stable to reaction with ozone, even under ultrasonic activation. The use of ultrasound enhances the rate of electrochemical reduction but the overall rate of reaction is still slow. However, the simultaneous application of ultrasound and ozonation to the electrochemical reaction allows virtually complete destruction of the compounds in short times. The effect is attributed to the ultrasonic enhancement of the electrochemical process giving intermediates that are susceptible to ozone oxidation. While further analytical work is needed to deduce the exact contributions of the various possible degradation mechanisms, the work demonstrates the synergies that can be gained by using combined techniques for the destruction of these difficult compounds.

Keywords: nitroaromatics; sonoelectrochemistry; ozone.

Introduction

Nitroaromatics are commonly used chemicals, for example in explosives or rocket fuels. They are also used as intermediates in the production of medicinal products and dyes [1, 2]. More than thirty different nitroaromatic compounds are formed as by-products of the industrial synthesis of trinitrotoluene (TNT). In the production of dyes, explosives and rocket fuel components, a considerable amount of these compounds can get into effluent waste and sewage. A large number of toxic and carcinogenic nitroaromatics [3] find their way into soil and groundwater during rocket launches and around military firing ranges. Therefore, the removal and neutralization of nitroaromatics from industrial effluents and other environments is an important problem.

There has been tremendous interest in the use of 'advanced oxidation processes' such as treatment with high-energy radiation, ozone, ultraviolet radiation or electric discharge for the detoxification of waste waters and sewage and other environmental remediation. Oxidation of toxic components using strong but environmentally-friendly oxidants such as hydrogen peroxide or ozone in combination with additional physicochemical processes is considered to be promising [1, 2]. Among these, the use of ultrasound has been explored; a number of studies of the combined use of ozone with sonication having been reported. For example, Weavers *et al.* [4] studied the decomposition of pentachlorophenol (PCP) by sonication where parallel reaction pathways of pyrollysis within the cavitation bubble and reaction in solution with OH• radicals were noted.   Ozone was added to the system but this did not affect the first-order degradation constant for PCP compared with the combination of separate sonication and ozonation experiments. In a study of the potential of combined ultrasound and ozone to oxidize natural organic matter, Olson and Barbier showed [5] that total organic carbon (TOC) removal rates were enhanced by ultrasound. Under the conditions used, 91% of the TOC in a fulvic acid solution was removed with 87% being converted to carbon dioxide

gas compared with 40% and 28% respectively by treatment solely with ozone. Direct combustion of volatile intermediates in the cavitation bubble partially explained the improvement while hydroxyl radical scavengers were found to inhibit TOC removal. Most advanced oxidation processes (AOP) readily decolorize, but are unable to mineralize, aqueous azo dye solutions. As a final example of the combined application of ozonation and sonochemistry, Destaillats and co-workers reported [6] that TOC losses during sonication of azobenzene or methyl orange solutions increased from 20% to more than 80% in the presence of O_3. The increase in TOC loss was attributed to the fast oxidation by ozone of free radical or unsaturated species generated by OH• radical attack on otherwise refractory products. Significantly for this work, nitrobenzene was rapidly and completely mineralized by the combined oxidation treatment.

The application of sonochemical methods to electrochemical processes has provided many benefits, [7]. In early work, Zhang and Coury [8] reported that irradiated glassy carbon electrodes exhibited enhanced heterogeneous electron-transfer rates for a variety of aqueous redox probes. Their results indicated the effects were most likely due to surface cleaning. However, Benahcene and co-workers showed [9] that enhancement of the diffusion to the electrode occurred during sonication of methylviologen and ferricyanide reductions and pyrrole oxidations along with suppression of passivation at a glassy carbon electrode. Malins and co-workers [10] investigated the influence of ultrasonic irradiation on the electrochemiluminescence from the oxidation of several ruthenium complexes and noted an increase in the luminescence yield of over 100%. These effects resulted from changes in mass transport of reactants through the bulk solution and modification of the electrode diffusion layer.

Directly related to the current work, Marken *et al*. [11] applied ultrasound to the four-electron reduction of nitrobenzene in alkaline aqueous media. The reaction mechanism is

complex and both surface and solution pathways may be observed. The results suggested that the homogeneous pathway was dominant under applied ultrasound. Both under silent and ultrasonic conditions, nitrobenzene was reduced on glassy carbon electrodes in a chemically reversible one-electron process followed by an irreversible three-electron reduction. Del Campo *et al*. [12] also reported an investigation of the reduction of nitrobenzene and *p*-chloronitrobenzene at low temperatures in liquid ammonia. Sonication resulted in sizable mass transport enhancements and a reduced diffusion layer thickness. Ultrasound was beneficial by causing extremely fast mass transport, enhancing mixing and dissolution kinetics and affecting the formation of solid products at the electrode surface.

The various effects caused during sonication of an electrochemical system serve to accelerate the reactions at the electrode. Sonication can also enhance oxidation by ozone. The presence of the electron-withdrawing nitro group substantially reduces the susceptibility of nitroaromatics to oxidation [13] so that even when using ozone, it is not possible to achieve an acceptable rate of destruction of some compounds such as 1,3-dinitrobenzene (DNB), 2,4-dinitrotoluene (DNT) or TNT [1]. It has previously been found that the oxidation of organic compounds by ozone or a combination of ozone with hydrogen peroxide in an ultrasonic field is enhanced in a low electric field [14]. The objective of the present work is to study the possibility of the oxidation of DNB and DNT by ozone in an electrochemical cell under ultrasonic irradiation.

Experimental

Reagents and materials. Commercial DNB and DNT with purity not less than 99 % by g.l.c., tetradecane (97 % by g.l.c.), chromatographic-grade dichloromethane, analytical-grade acetic acid and sodium hydroxide were used as received.

Apparatus and equipment. The reactions were conducted in a thermostatted glass cell with a capacity of 100 cm^3 into which was fitted a gas-supply tube. A titanium ultrasonic horn radiator was used as a cathode; an anode was introduced through a side wall of the cell, and the anode and cathode compartments separated by MA-40 membranes as shown schematically in Fig. 1. A B5-49 power supply was used to control the potential during the electrochemical experiments. As a source of ultrasound, a piezoceramic transducer equipped with a titanium horn waveguide with a working surface area of 5 cm^2 and powered from an ultrasonic generator UD-11 was used. The intensity used in all sonochemical experiments, measured in the usual calorimetric method [15], was 5 W cm^{-2}.

A gas-discharge generator was used to produce ozone from oxygen. The amount of ozone supplied to the reactor was controlled by varying the oxygen feed to the generator, flow rates in the range of 0.1 to 3 dm^{-3} hr^{-1} were used. The ozone concentration in the ozone-oxygen mixture, determined by iodometry, was 3 - 10 %.
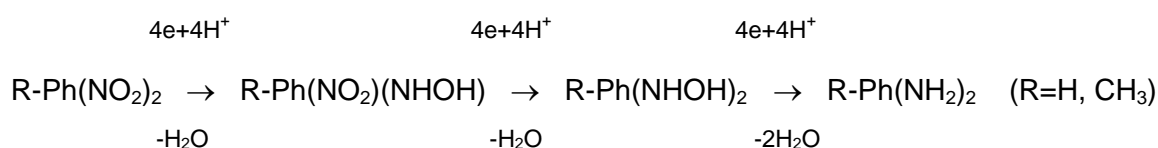
Oxidation Procedures for DNB and DNT. 100 cm^3 of 1 % acetic acid solution containing DNB and DNT at concentrations of 100 mg dm^{-3} were introduced into the cathode compartment and 1 % aqueous solution of sodium hydroxide into the anode space. Oxygen or oxygen-ozone mixture was bubbled into the lower section of the cell through a capillary. A direct current of 50 mA was maintained during the process of electrochemical treatment with the voltage varying between 3 V and 5.5 V. The temperature was maintained between 20 – 25 °C.

Analytical methods. Analysis of volatile organic compounds in samples was carried out using either a Varian Star 3600 chromatograph (Varian, USA), with a type 1040 PID injector and 15 m, 0.53 mm i.d. quartz capillary column with 0.5 μm SPB-1 stationary phase (Supelco, USA) or an Automass 150 gas chromatograph - mass spectrometer (Delsi Nermag, France) fitted with 25 m 0.25 mm i.d. capillary column with 0.3 μm of OV-101. 0.5 cm^3 of reaction solution

was extracted for 2 min with 0.5 cm^3 of dichloromethane containing 100 mg dm^{-3} of tetradecane as an internal standard. The organic phase was recovered and 0.5 μL injected into the chromatograph with injector, column and detector temperatures of 250 °C, 140 °C and 290 °C respectively. The concentrations of DNB and DNT were determined by comparison with the internal standard using a calibration over the concentration range 1-100 ppm. The mean deviation of the analyses did not exceed 5-7 %.

Results and Discussion

It is known [16] that the cathodic reduction of DNT and DNB in an acid medium occurs in three stages according to scheme **(1)**

$$\underset{\text{-H}_2\text{O}}{\overset{\text{4e+4H}^+}{}} \qquad \underset{\text{-H}_2\text{O}}{\overset{\text{4e+4H}^+}{}} \qquad \underset{\text{-2H}_2\text{O}}{\overset{\text{4e+4H}^+}{}}$$

$$\text{R-Ph(NO}_2)_2 \;\rightarrow\; \text{R-Ph(NO}_2)(\text{NHOH}) \;\rightarrow\; \text{R-Ph(NHOH)}_2 \;\rightarrow\; \text{R-Ph(NH}_2)_2 \quad (\text{R=H, CH}_3)$$

Scheme (1)

Thus DNB can be reduced sequentially to *m*-(nitrophenyl)hydroxylamine and further to *m*-di(hydroxyamino)benzene. The final product of electrochemical reduction is the corresponding diamine.

Under the conditions used here, a current of 50 mA passed through the cell for 30 min should be sufficient for the complete reduction of DNT and DNB to the corresponding dihydroxylamines. The reduction in concentration of DNB and DNT is shown in Figure 2. It is clear that in the absence of ultrasound (curves a and b), relatively little reaction took place and over the initial 10 min period the system was operating at a current efficiency of ~15%. (It should be noted that the electrochemical cell used was not optimized in terms of the

electrode material, potential, current, etc. However, the relative results from each series of experiments should be valid and demonstrate any enhancement due to ultrasound.) Figure 2 also shows that operation under 5 W cm^{-2} of ultrasound significantly enhanced (curves c and d) the reaction of DNB and DNT. Under ultrasonic treatment the current efficiency during the first 10 min increased to 55-57 %. The observed increase in current efficiency compared with the corresponding unsonicated reactions can be attributed to the speeding-up of mass transfer processes in the aqueous medium.

The rate of electrochemical reactions is usually limited by diffusion of reactants and products to and from the electrode surfaces. It is known that ultrasonic irradiation leads to an increase in the effective diffusion of both ions and molecules in a liquid [17] so that, in an ultrasonic field, an acceleration of redox processes is observed. The reported effect of reducing the diffusion layer near the electrode [7] will also have a role in the observed acceleration.

If the reaction is carried out under oxygen rather than air during electrolysis, the rate of the consumption of DNT and DNB is relatively insensitive to the ultrasonic field after the initial stages of the reaction. Figure 3 shows that it is initially faster under sonication but reaches the same level of reaction after a short time. Significantly, it was at the same value as in Figure 2 showing that availability of the oxidant is not a limiting factor in these reactions. It can be assumed that during the passage of oxygen, the primary process occurring at the cathode is the reduction of oxygen rather than the dinitrocompounds. In the ultrasound field, acceleration of the reduction of both oxygen and dinitrocompounds at the cathode can occur. However, with a decrease in the relative concentration of DNT and DNB, the rate of their reduction decreases (Fig. 3 c, d). Thus, ultrasonic treatment does not significantly change the rate of DNT and DNB reduction when oxygen is bubbled through the solution. Other effects that have been observed in sono-electrochemical reactions are the prevention of fouling or

passivation of the electrode by reaction products and the removal of gas bubbles from the electrodes. The results in Figure 3 suggest that these play at best a minor role in the systems studied here.

In the absence of an electric field, the destruction of DNT and DNB by ozone is slow, as shown in Figure 4. The rate is faster when under sonication but the level of conversion without the use of electrochemical treatment does not exceed 15-20 % for 30 min of treatment. Thus, DNT and DNB are fairly stable to oxidation destruction by ozone, even with the use of additional ultrasonic treatment.

However, carrying out simultaneous electrochemical and ozone treatment in an ultrasonic field leads to a dramatic increase in the rate of DNT and DNB consumption as demonstrated in Figure 5. Almost complete destruction can be achieved with this combined treatment. This large enhancement of nitroaromatic destruction can in part also be attributed to an increase in the rate of diffusion processes and, as a consequence, speeding-up of the process of electrochemical reduction of ozone.

It is known that molecular ozone in aqueous solutions is one of the most active oxidizing agents. Interaction of ozone with an electron donor, D, or by reduction at a cathode, leads to the formation of the O_3^- ion [18].

$$O_3 + e\text{-} \ (D) \ \rightarrow O_3^- \ \ (+ D^+) \tag{2}$$

The O_3^- ion is a stronger oxidant than molecular ozone and, and in acid media rapidly undergoes reaction with the formation of the $O^{-\bullet}$ anion-radical and oxygen:

$$O_3^- \rightarrow O^{-\bullet} + {}^1O_2 \tag{3}$$
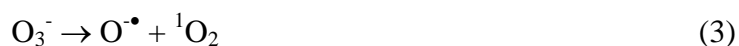
Alternatively, it can interact with water, giving oxygen, hydroxyl ion and radical $OH^{\bullet}$ [18]:

$$O_3^- + H_2O \rightarrow HO^{\bullet} + {}^1O_2 + HO^- \tag{4}$$

Thus, the cathodic reduction of ozone yields highly active oxidizing agents. During the passage of ozone, its reduction at the cathode rather than that of the nitrocompounds most

probably occurs. This is suggested by the decrease in the rate of consumption (a combination of the processes of oxidation by ozone products and electrochemical reduction) of the reactants during the passage of ozone (Fig. 5 a, b) in comparison with simple electrochemical reduction (Fig. 2 a, b). Despite the probable formation of more reactive O_3^- ions at the cathode, the oxidation destruction of DNT and DNB occurs very slowly without the use of ultrasonic treatment (Fig. 5 a, b). This could be due to the high activity of O_3^- anions which are unstable in acidic or neutral media and very rapidly consumed, for example, by to reaction (4).

However, in an ultrasonic field during the passage of ozone, a significant increase in the rate of consumption of DNT and DNB is observed, so that in 30 min of such treatment the original products are virtually completely consumed (Fig. 5 c, d). This effect could be due to the local heating of the medium during the collapse of cavitation bubbles but it is mainly due to the enhanced mixing, diffusion and mass transfer. The most favourable conditions for this are established directly near the surface of ultrasound horn. Since the horn also acts as the cathode where molecular ozone is reduced to the O_3^- ion, the relative concentration of O_3^- near its surface can be significantly higher than that without ultrasonic treatment. Such a local rise in the concentration of O_3^- in turn leads to an acceleration of the oxidation of DNT and DNB. Thus, only in the simultaneous use of ultrasonic and electrochemical treatment during the passage of ozone through the solution, is a noticeable rate of DNT and DNB consumption achieved.

Conclusions

This work has shown that ultrasonic treatment increases the current efficiency of the reaction of cathodic reduction of DNT and DNB to 55-57 % from ca. 15% in the absence of ultrasound. This effect is apparently due to the enhancement of diffusion and mass transfer

processes which limit the electrochemical reduction of DNT and DNB under silent conditions. It was found that combined electrochemical and ozone treatment with simultaneous ultrasonic irradiation led to virtually complete consumption of DNT and DNB within a short time. The intensification of the cathodic process during the passage of ozone can be attributed to increases in the rate of the electroreduction of the nitroaromatics with the formation of products that have significantly higher reactivity to ozone. More work is needed to determine the precise mechanisms for the sonochemical enhancements reported here but the clear synergies achieved by the use of combined techniques are worthy of further study and may form the basis of important techniques for environmental remediation.

Acknowledgements

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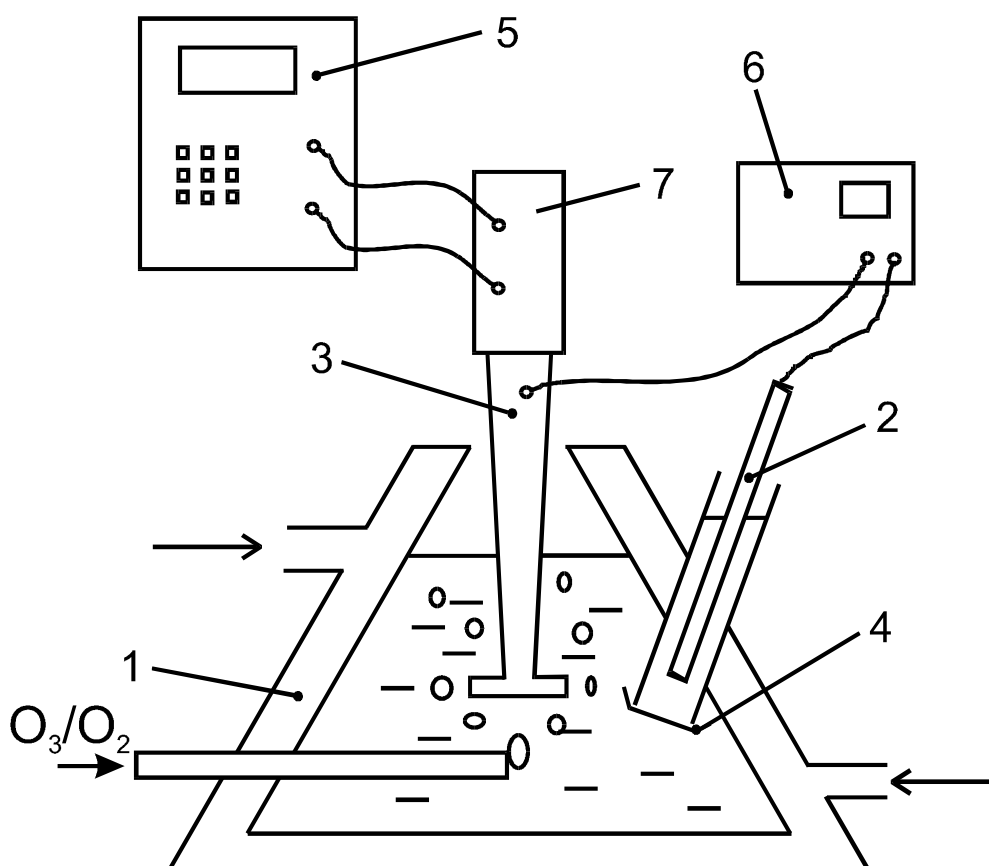
Fig. 1. Setup for simultaneous ozone and electrochemical treatment of solutions in ultrasonic field:

1 – thermostated vessel, 2 – anode, 3 – waveguide-cathode, 4 – diaphragm, 5 – ultrasonic generator,   6 – source of direct current, 7 – piezoceramic transducer.
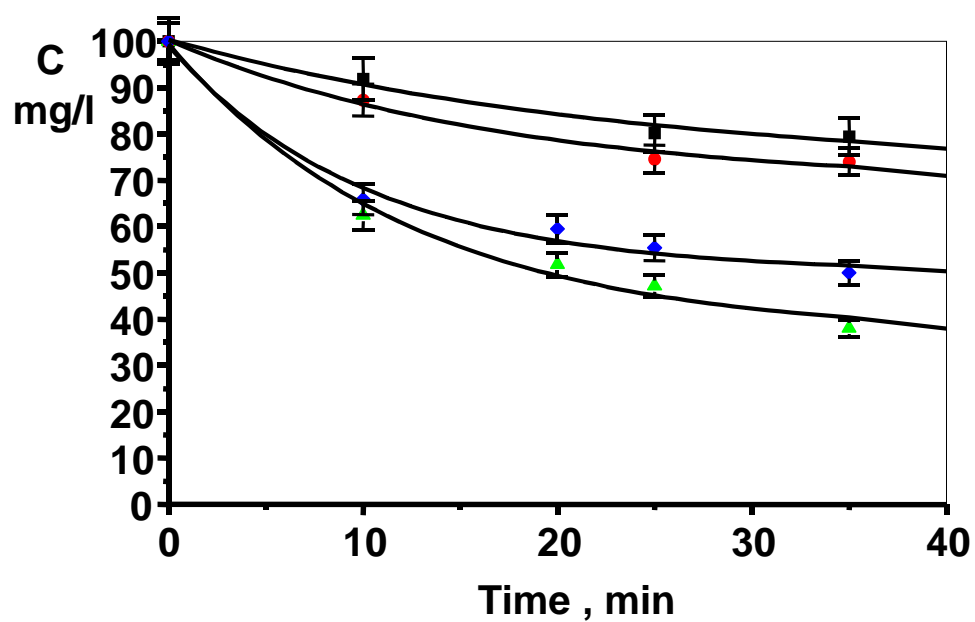
Fig. 2. Effect of ultrasonic treatment on process of electrochemical reduction of DNT and DNB at cathode (J = 50 mA, air):

a - (   ) – DNB, ref.; **b** - (   ) – DNT, ref.; **c** - (   ) – DNT, US; **d** - (   ) – DNB, US.

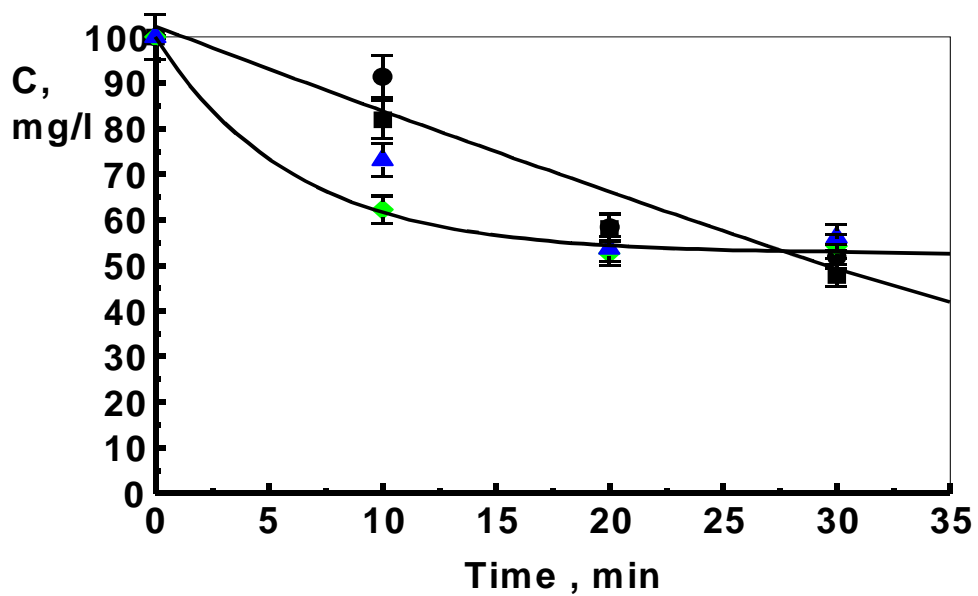Fig. 3. Effect of ultrasonic treatment on process of electrochemical reduction of DNT and DNB at cathode during passing of oxygen (J = 50 mA):

   a - (   ) – ■NB, ref.; **b** - (   ) – ●NT, ref.; **c** - (   ) – ◆NT, US; **d** - (   ) – ▲NB, US.
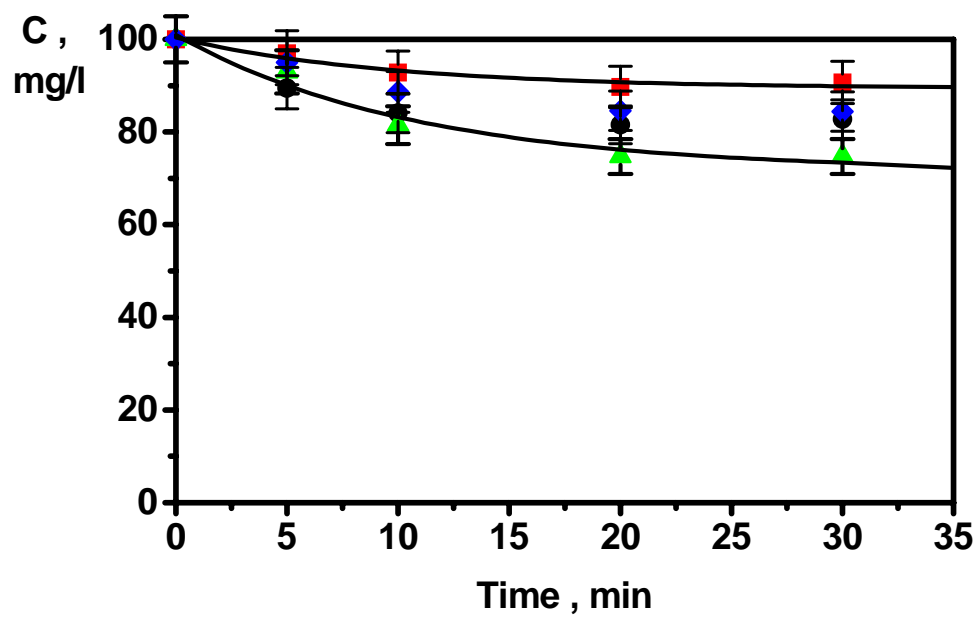
Fig. 4. Effect of ultrasound on oxidation destruction of DNT and DNB using ozone:

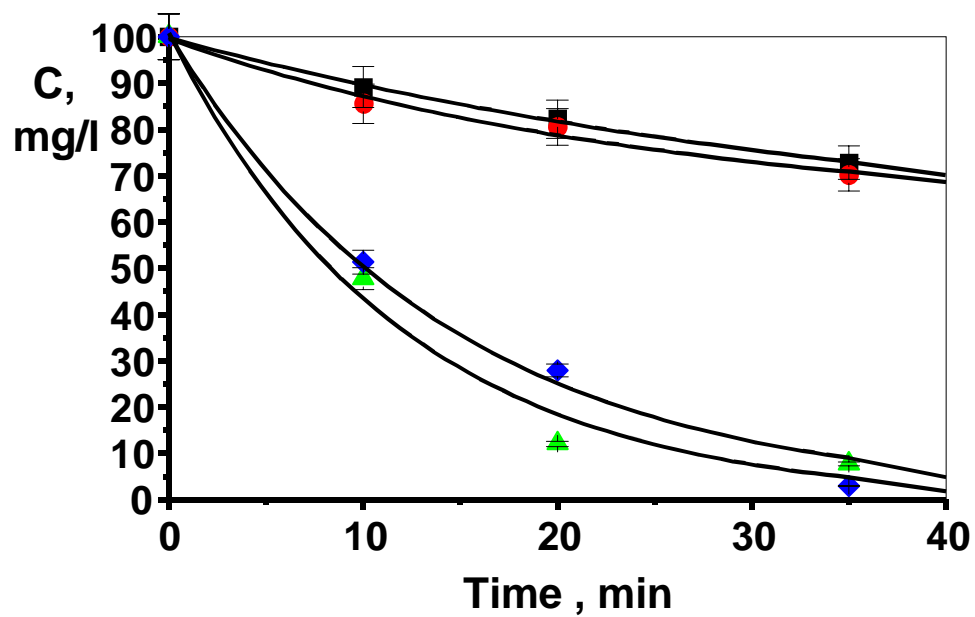**a** - (   ) – ■NB, ref.; **b** - (   ) –●NT, ref.; **c** - (   ) –◆NT, US; **d** - (   ) – ▲NB, US.

Fig. 5. Effect of ultrasound on oxidation destruction of DNT and DNB during passing of ozone through solution treated in cathode space (J = 50 mA):

    a - (   ) – ■NB, ref.; **b** - (   ) – ●NT, ref.; **c** - (   ) – ◆NT, US; **d** - (   ) – ▲NB, US.