Nitrophenol Oxidation in Water with the Use of Hydrodynamic Cavitation

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Abstract

The role of the hydrodynamic cavitation for initiating and supporting chain-radical reactions of oxidation of organic substrates, among them 4-nitrophenol (4-NP), with Fenton's reagent (H_2O_2 + Fe^{2+}) has been shown. Fe^{2+} ions were supplied into solution by dissolving split steel shot or steel chips in cavitation reaction vessel. At initial concentrations of 4-NP and H_2O_2 of $6.7 \cdot 10^{-5}$ and $4.02 \cdot 10^{-4}$ mol/L, respectively, the degree of phenol conversion at pH 3.4 reaches 98 %. The diagram of the set-up designed to treat sewage with productivity 0.5 m^3/h and the description of the equipment for cavitation generation are presented.

INTRODUCTION

4-Nitrophenol (4-NP) is the priority toxicant that is liable, when being brought into the human body even in small amount, to attack liver, kidneys, and central nervous system. For the most part, it enters the ambient medium with wastewater of commercial processes for production of herbicides, insecticides, and synthetic dyes [1]. High stability and considerable solubility in water are the cause of much of the trouble in the destruction of this toxicant in the course of the sewage purification.

The use of cavitation reaction vessels [2–9], where oxidation processes are initiated and maintained, may be promising in the destruction of 4-NP and other phenols.

Cavitation (generation, growth, and collapse of bubbles of gas or vapour in liquid) is the familiar phenomenon that is generally attended with physical and chemical effects. Cavitation can be of acoustic origin (during propagation of ultrasonic waves in the liquid) and of hydrodynamic one (in turbulent streams at instants of discontinuity of the liquid).

Chemical processes proceeding in aqueous solutions under the action of acoustic cavitation are well understood [2–5]. Cavitation in aqueous solutions is accompanied by rise of pressure and temperature at the boundary of microcavities (cavitation bubbles) and liquid on their collapse. The maximum pressure $P_{\max}$ at the instant a spherical bubble collapses in liquid under the action of external pressure P_{amb} is determined from the relation [3]

$$P_{\max} = P_{g0} \left[\frac{P_{\mathrm{amb}}(k-1)}{P_{g0}} \right]^{k/(k-1)} \qquad (1)$$

where P_{g0} is the initial pressure of gas within the bubble; k is the coefficient now taken for water as 4/3.

The maximum temperature generated at the instant of the bubble collapse ($T_{\max}$) is determined from the relation

$$T_{\max} = T_0 \left[\frac{P_{\mathrm{amb}}}{3P_{g0}} \right] \qquad (2)$$

where T_0 is the initial temperature within the bubble.

For P_{amb} = 0.1 MPa and P_{g0} = 1 kPa , the quantity P_{max} may run to $1.2 \cdot 10^3$ MPa and the temperature may rise to 10 000 K. In such a situation, the cavitation is accompanied by the decomposition of H_2O and by the formation of H_2O_2, radicals $^{\bullet}OH$ and $^{\bullet}H$ that are capable to generate a variety of redox reactions.

The hydrodynamic cavitation in the liquid of density c at external pressure P_{amb} is commonly characterized by a dimensionless parameter − cavitation number σ:

$$\sigma = (P_{amb} - P_v)/0.5\rho v^2 (P_{amb} - P_v)/\Delta P \qquad (3)$$

where P_v is the pressure of the saturated vapour (gas); v is the speed of turbulent flow of the liquid; ΔP is the pressure difference at the output of liquid flow from the nozzle.

The effect of such parameters as P_{amb}, ΔP, temperature, volume and composition of the solution on the rate and mechanisms of redox reactions has not been adequately investigated. As illustrated in [6−9], the rate of oxidation reactions of inorganic (KI [6], As(III) [7]) as well as organic compounds (1,4-dichlorobenzene [8], 4-nitrophenol [9]) increases during hydrodynamic cavitation practically linearly with the decrease in quantity σ. In this case the efficiency of oxidation of substrates rises with decreasing P_{amb}, because the expenditure of energy for the performance of the reaction is lowered, other factors being the same. It is also found that the oxidation rate of substrates falls with a rise in temperature of the treated solution.

From Eq. (3) follows that the experimental data obtained in studies of processes under cavitation conditions are bound to be dependent on the type of cavitation generating equipment, temperature, and the bulk of the treated solutions. Analysis of the available literature on the oxidation of various materials in aqueous solutions under the action of cavitation confirms this assumption.

For comparison of efficiency of various technical decisions met with in cavitation oxidation in aqueous solutions of different substances the integral parameter $m(t)$ (the mass of oxidized substance on a per-unit of expended energy, mg/J) has been proposed in [9]:

$$m(t) = (C_0 - C(t))V/tP \qquad (4)$$

where C_0 is the initial concentration, mg/L; $C(t)$ is the concentration at instant t, mg/L; P is the consumed power, W; V is the volume of the solution, L.

The quantity of energy expended on doing oxidation of substance in unit volume may be considered as the parameter that allows the oxidation efficiency to be estimated at given temperature with regard to the influence of the solution volume and constructional features of different experimental arrangements.

The object of this work is to investigate the role of the hydrodynamic cavitation for initiating and sustaining chain-radical reactions of oxidation of phenols, among them 4-NP, by hydrogen peroxide in the presence of Fe^{2+} ions as are supplied into the solution through dissolving split steel shot or steel chips in the cavitation reaction vessel.

EXPERIMENTAL

Experiments on 4-NP oxidation were conducted in the set-up represented schematically in Fig. 1. Operating pressure in liquid stream $P_{amb} = 2 \cdot 10^5$ Pa at a flow rate of 0.5 m^3/h. The volume of circulating solution was 26 L. The solution temperature ((20±0.2) °C) was maintained with the help of a heat exchanger. The initial concentration of 4-NP ("pure") made up 9.3 mg/L, and pH in solution was in the range from 3.3 to 3.4. Concentration of 4-NP was determined with the help of a KFK-3 spectrophotometer at a wavelength of 402 nm after alkalifying the sample to pH 11 and isolating the precipitate of iron hydroxides. Photometric evaluation was carried out in cells 1 cm thick under change of optical density from 0.05 to 0.4. The overall iron concentration was determined by standard procedure using a KFK-3 spectrophotometer with sulphosalicylic acid [10]. A general purpose a Delta 320 pH meter Mettler Toledo was used for monitoring temperature and pH values determined by acidifying the solutions with sulphuric acid.

Cavitator [11] diagrammed in Fig. 2 has a body *1*, an inlet *2*, toroidal chamber *3*, cone diffuser *4*, and also a niche in the form of turning *5*, which encloses a ring *6*. The passages *7* are found in the body for feeding air (gas) or liquid. The flow of working fluid, which is pumped under pressure, is fed into inlet *2*, and a part of the flow finds its way into the toroidal chamber *3*, whereas the remainder leaves
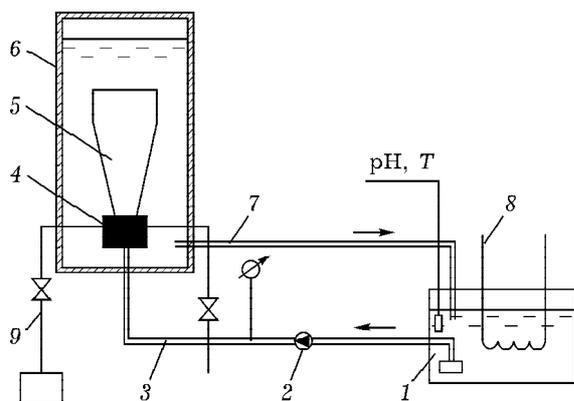
Fig. 1. Schematic diagram of experimental set-up: *1* – tank with model solution; *2* – feed pump; *3* – feed line; *4* – cavitator; *5* – reaction vessel with suspended feed bed; *6* – reaction zone of set-up; *7* – recovered solution; *8* – refrigerator; *9* – input of oxidizing agent.

through the cone diffuser *4*. Cavitator inlet is displaced relative to the rotational axis of toroidal chamber, resulting in a build up of liquid bulk finding way into the chamber. Owing to this, the contact duration of transit stream with whirlpool zones and the friction force curving liquid in the hollow of generator, with a consequent decrease of the magnitude of σ. Owing to the availability of recavitation unit built in the form of a ring, an added rotation of liquid takes place in the space between walls of ring and turning. As this takes place, a region of reduced pressure is formed, and air (gas) and/or other liquid, which are required for mixing two media, are drawn into this region through passages in the body of generator. Cavitation number σ = 0.18. The calculated value for P_{max} in liquid is equal to $14.3 \cdot 10^8$ Pa, and the maximum temperature $T_{max} = 739$ K.
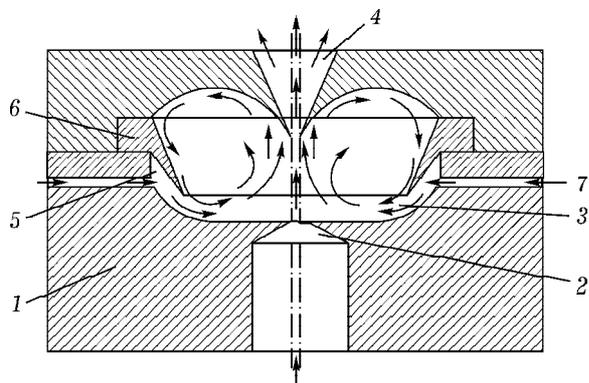
Fig. 2. Schematic diagram of cavitator: *1* – cylindrical body; *2* – inlet; *3* – toroidal chamber; *4* – cone diffuser; *5* – niche in the form of turning; *6* – ring; *7* – passages for feeding air (gas) or liquid.

RESULTS AND DISCUSSION

Influence of cavitation on the kinetics of 4-nitrophenol oxidation

The direct oxidation of 4-NP by peroxide of hydrogen at room temperature is impracticable, whereas in cavitation stream it is relatively slow (Fig. 3, curve *1*). The constant of action k_5 calculated in the approximation of the first-order reaction with respect to nitrophenol

$$dC_{4\text{-NP}}/dt = -k_5 C_{4\text{-NP}} \qquad (5)$$

accounts $5 \cdot 10^{-5} \text{s}^{-1}$.

In the absence of cavitation, the rate of nitrophenol oxidation may be two orders of magnitude higher (see Fig. 3, curve *2*) with the use of Fenton's reagent ($H_2O_2 + Fe^{+2}$) that generates active hydroxyl radicals $^\bullet OH$ according to equation [12]

$$Fe^{2+} + H_2O_2 = Fe^{3+} + {}^\bullet OH + OH^-,$$
$$k_6 = 51 \text{ mol}^{-1} \cdot \text{s}^{-1} \qquad (6)$$
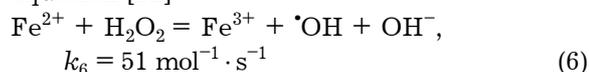
The resulting ions Fe^{3+} are reduced by hydrogen peroxide, however the rate of this reaction is well below that corresponding to Fe^{2+} expenditure in the reaction (6) [12]:

$$Fe^{3+} + H_2O_2 = Fe^{2+} + HO_2^\bullet + H^+,$$
$$k_7 = 0.001 - 0.01 \text{ mol}^{-1} \cdot \text{s}^{-1} \qquad (7)$$
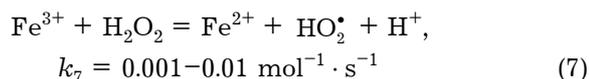
The rate constant (k) of 4-NP oxidation by Fenton's reagent, when calculated by equation (5), was equal to $2.95 \cdot 10^{-3} \text{ s}^{-1}$. At 4-NP starting concentration of $6.7 \cdot 10^{-5}$ mol/L, H_2O_2 – $4.02 \cdot 10^{-4}$ mol/L, Fe^{2+} – $1.66 \cdot 10^{-4}$ mol/L, the maximum degree of 4-NP conversion was 63 %.

The rate of 4-NP oxidation by Fenton's reagent is fast reduced with decreasing concentration of Fe^{2+} ions in solution, even with H_2O_2 present. A deficiency of Fe^{2+} ions is commonly compensated through regular addition of Fe^{2+} salt solution to reaction mixture, or, alternatively, through Fe^{3+} reduction by ultraviolet radiation treatment of solutions [13], or through Fe^0 electrochemical [14] or galvanochemical [15] dissolving.

The iron galvanochemical dissolving initiated by hydrodynamic cavitation forms the basis for the method of oxidation of organic compounds that is proposed in our work.

If steel chips or split steel shot are placed in the reaction vessel *5* (see Fig. 1), the feed bed (50–100 g of fragments irregular in shape of size 1.5–2 mm) transforms into suspension under the action of a stream of water pumped
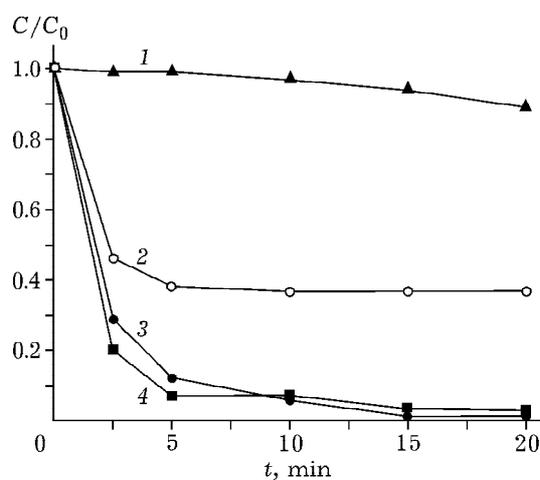
Fig. 3. 4-Nitrophenol oxidation kinetics with peroxide of hydrogen in cavitation stream (*1*), with Fenton's reagent (*2*), with peroxide of hydrogen in cavitation stream and Fe^0 dissolving (*3*), with Fenton's reagent in cavitation stream (*4*). Initial concentrations, mol/L: 4-NP $6.7 \cdot 10^{-5}$, H_2O_2 $4.02 \cdot 10^{-4}$, Fe^{2+} $1.66 \cdot 10^{-4}$; temperautre 20 °C, pH 3.4.

from the cavitator. An added collapse of gas bubbles contained in a liquid stream and preserved intact in the inner space of cavitator is in progress at the surface of metallic feed. At that time, cavitation provokes an intensive corrosion and solution of iron with the formation of Fe^{2+} ions as well as of Fe(II) and Fe(III) hydroxy compounds of different composition depending on pH. Iron solution occurs with an increase of pH that is compensated by more sulphuric acid.

The results of 4-NP oxidation by peroxide of hydrogen in cavitation stream with simultaneous solution of iron in the reaction vessel *5* (see Fig. 1) and by Fenton's reagent in cavitation stream are presented in Fig. 3 (curves *3* and *4*).

The rate of oxidation reaction and the respective degrees of nitrophenol conversion in cavitation stream are nearly 1.6 times greater than it is in 4-NP oxidation with Fenton's reagent and air dispersion. 4-NP oxidation in the course of initial five minutes is accompanied by turning the solution to a brown colour, which suggests the preferential formation of *p*-dihydroxybenzene, *p*-benzoquinone, and quinhydrone that is an intermediate product of *p*-dihydroxybenzene oxidation. The constant of action calculated in the approximation of the first-order reaction by Eq. (5) is equal to $4.73 \cdot 10^{-3}$ s^{-1}. The maxi-

mum degree of 4-NP conversion in cavitation stream at indicated above initial concentrations of 4-NP and H_2O_2 is equal to 98 %.

High degree of 4-NP conversion is explained both by activation of 4-NP molecules with collapsing gas bubbles and by availability of Fe^{2+} ions in reaction mixture that support chain-radical mechanism of phenol oxidation in both cases and whose necessary concentration is provided by way of high-rate reduction of Fe^{3+} with intermediates. Experimental verification of the function of intermediates in Fe^{2+} regeneration during the oxidation of phenol compounds by Fenton's reagent in aqueous solutions has recently been reported in [16]. In addition, the continuous Fe^{2+} supply during 4-NP oxidation in the reaction vessel with steel feed is also provided by dissolving this feed.

The results of investigations [13, 16−19] suggest that the oxidation of nitrophenol by a variety of processes with the participation of H_2O_2 (ultraviolet rays − H_2O_2 [13, 16], ultrasound − Fenton [17], electro-Fenton [18]) proceeds with the formation of identical products: *p*-dihydroxybenzene, 4-nitro-*o*-dihydroxybenzene, *p*-benzoquinone, 1,2,4-trihydroxybenzene, fumaric and oxalic acids. The oxidation procedure determines only the relative content of intermediate products in the reaction mixture.

Analysis of literature and obtained experimental data suggests the most probable ways of 4-NP oxidation by Fenton's reagent under the action of hydrodynamic cavitation (Fig. 4). In the first stage of oxidation the activation of 4-NP molecules in *ortho*- and *para*-positions, hydroxylation and formation of 4-nitro-*o*-dihydroxybenzene and *p*-dihydroxybenzene take place, whereupon these compounds are subjected to ˙OH radicals and oxidized initially to 1,2,4-trihydroxybenzene and then to fumaric (maleic) and oxalic acids given sufficient amount of H_2O_2 in the reaction mixture. However there are only 6 mol of H_2O_2 for 1 mol of 4-NP in the early stage of the process, which is why the speedy accumulation of primary intermediates and following oxidation of *p*-dihydroxybenzene to *p*-benzoquinone and formation of quinhydrone take place. The sufficiently stable equilibrium between these secondary products of 4-NP oxidation is established.
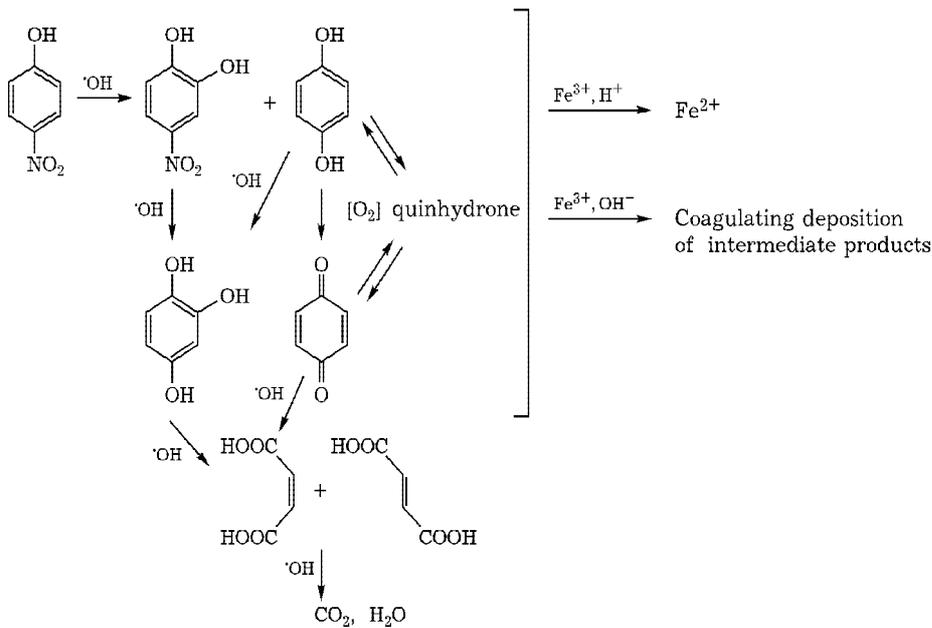
Fig. 4. Scheme of 4-nitrophenol oxidation with peroxide of hydrogen in cavitation stream.

Efficiency of 4-nitrophenol oxidation by Fenton's reagent under conditions of hydrodynamic cavitation

Efficiency of 4-NP oxidation by Fenton's reagent, by peroxide of hydrogen in cavitation stream with suspended bed of iron feed, without reagents under conditions of hydrodynamic cavitation or acoustic one [9] was estimated by calculation of integral parameter $m(t)$ using equation (4). The obtained data are presented in Fig. 5. As to expenditure of energy for 4-NP destruction, the combination of galvanochemi-cal solution of Fe^0 with oxidation of p-nitrophenol by Fenton's reagent under the action of hydrodynamic cavitation appears to be most useful. Process of 4-NP (and other phenols) oxidation can be stopped at the stage of formation of intermediate products by way of dosing H_2O_2, alkalization of the solution and following coagulating precipitation of formed compounds by iron hydroxides. This makes it possible to cut essentially the time of processing of solutions and oxidant consumption in the realization of oxidation of impurities in the waste water.
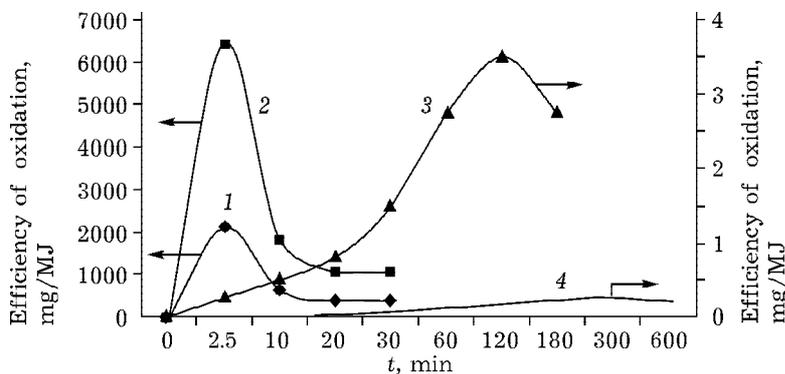
Fig. 5. Efficiency of 4-nitrophenol oxidation by Fenton's reagent (1), by peroxide of hydrogen in cavitation stream with suspended bed of iron chips (2), without reagents under conditions of hydrodynamic cavitation (3) [8], on acoustic cavitation (4) [8].

CONCLUSION

The role of hydrodynamic cavitation in initiating and supporting of chain-radical reactions of 4-NP oxidation by Fenton's reagent has been shown. Fe^{2+} ions were supplied into solution by dissolving split steel shot or steel chips in cavitation reaction vessel. The reaction between Fe^{2+} and H_2O_2 gives rise to $^{\bullet}OH$ radicals that attack a molecule of phenol in *ortho*- and *para*-positions. Thereupon stable intermediates are generated by free-radical reactions, which can be removed from the solution by means of coagulation. In our opinion the first stage – initiation – is due to cavitation as a great deal of energy is liberated on collapsing bubbles. At initial concentrations of 4-NP ($6.7 \cdot 10^{-5}$ mol/L), H_2O_2 ($4.02 \cdot 10^{-4}$ mol/L) and pH 3.4 the degree of phenol conversion reaches 98 %.

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