Progressive water pollution due to anthropogenic impact on the environment is one of the current problems. One of the main types of wastewater pollutants is organic matter. A relatively simple and cheap method of purifying water from them is its biological treatment with aerobic bacteria. However, there are many highly toxic organic impurities, for the decomposition of which this method is in any case in its aerobic guise is unsuitable, and anaerobic processes require too much time and temperature control of processing processes and also become questionable given the required energy costs. Such complex substances, from the point of view of their biological treatment, include organic dyes, which according to world statistics make up 15% of all harmful substances that must be neutralized before entering the aquatic ecosystem. For such waters, their pre-treatment becomes relevant, which will reduce the load on biological treatment plants by oxidation of toxic substances and a general reduction of the organic component, i.e. reduction of dichromate chemical oxygen demand (HSC). Water treatment with such contaminants can be carried out using technologies that use advanced oxidation processes (AOP). In our work we studied the efficiency of plasma oxidation of wastewater barrier discharge of dye manufacturers, the main component of which is technical 2,4-dinitrotoluene, as well as models of the organic component of NPP wastewater, the main component of which is a phosphate-based detergent containing South Africa - 26.8%. Water films with a thickness of ~ 0.1 mm were treated at a rate of growth of discharge voltage pulses ~ 3 * 1011 V / s. The energy efficiency of the pulsed barrier discharge at different modes of water treatment with different impurities of organic substances has been studied. To obtain high energy efficiency, water treatment should be carried out at such parameters of the pulse barrier discharge (energy and pulse repetition frequency) and air velocity, so that the specific energy input to the air passing through the chamber does not exceed ~ 100 J / L. The highest energy yield of the pulsed barrier discharge, for wastewater samples, at specific energy inputs does not exceed ~ 10 J / ml.

Keywords: plasma, dielectric barrier discharge, water, ozone, hydroxyl radical, dinitrotoluene, methylene, surfactants, energy efficiency

1. Preliminary

One of the main types of wastewater pollutants is organic matter. In the case of a large number of highly toxic organic impurities, the method of anaerobic water treatment does not work and, in addition, anaerobic processes require considerable time and temperature regulation of treatment processes, which also requires significant energy costs.

Organic dyes are undoubtedly persistent biological pollutants, which according to world statistics [1] account for 15% of all harmful substances that must be neutralized before entering the aquatic ecosystem. For such waters, their pre-treatment becomes relevant, which will reduce the load on biological treatment plants by oxidation of toxic substances and a general reduction of the organic component, i.e. reduction of dichromate chemical oxygen demand (COD).

Water treatment with such contaminants can be carried out using technologies that employ advanced oxidation processes (AOP) [1, 2]. AOP is an innovative tool that allows the researchers to enter energy directly into the area where the decomposition of pollutants is re-
required. Plasma is obtained by pulsed dielectric barrier discharge (PDBD) on the water surface. Due to this discharge, a low-temperature plasma is generated at the gas-liquid interface, which is one of the types of AOR, in which highly active particles with oxidizing potentials \( \varphi \) higher than oxygen \( \text{O}_2 \) (1.2 V) are formed: hydrogen peroxide \( \text{H}_2\text{O}_2 \) (1.8 V), ozone \( \text{O}_3 \) (2.1 V), hydroxyl radical \( \text{OH}^* \) (2.7 V) (symbol * means that the particle is in a high-energy excited state). The presence of these substances and their concentration are determining factors for the oxidation of pollutants in water [1, 2]. Since these substances interact with water mainly at the gas-liquid interface, water treatment must be performed at a large ratio of the surface area of the water sample to its volume (~ 10 m\(^2\)/l). This can be achieved when the water is in the film (film thickness \( \approx 0.1–0.15 \) mm) [3] or drip state (the droplet diameter ~ 1 mm) [6]. In recent decades, a study of water treatment by PDBD [1–7] has been performed, which had both scientific and applied orientation.

The main oxidants, which decompose organic impurities in water are \( \text{O}_3 \), \( \text{OH}^* \) and \( \text{H}_2\text{O}_2 \) [1, 2]. Such molecules appear under the action of plasma due to a chain of plasma-chemical reactions in gas and water. These reactions and their intensity are determined by the parameters of the discharge in the gas part of the interelectrode gap. For example, reactions

\[
e + \text{O}_2 \rightarrow \text{O}^* + \text{O}^* + e, \quad (1)
\]

\[
\text{O}_2 + \text{O}^* \rightarrow \text{O}_3 \quad (2)
\]

resulting in the formation of ozone in a gas containing oxygen are possible only when the energy of the electron \( e \), which it receives in an electric field, is somewhere higher than the threshold energy for \( \text{O}_2 \), which is 5.14 eV and is required for the dissociation of oxygen in reaction (1).

The equation

\[
d[\text{O}^*]/dt = k[n_e][\text{O}_2]. \quad (3)
\]

determines the rate of generation of \( \text{O}^* \) where \([\text{O}^*] \), \([\text{O}_2]\) and \([n_e]\) are concentration of \( \text{O}^* \), \( \text{O}_2 \) and electrons \( e \), respectively; \( k \) is the rate constant of the reaction that has an exponential dependence on the electric field strength \( E \) in the gas [6].

The contribution of reaction particles \( \text{O}_3 \), \( \text{OH}^* \) and \( \text{H}_2\text{O}_2 \) to the decomposition of impurities in water depends not only on their potential \( \varphi \), but also on their concentration. For example, in the oxidation reaction of an impurity \( \text{D} \) by ozone

\[
D + \text{O}_3 \rightarrow \text{products of the reaction (4)}
\]

according to the basic equation of chemical kinetics, the rate of decrease of the impurity concentration \([D]\) will be equal to

\[
d[D]/dt = -k_0[D][\text{O}_3], \quad (5)
\]

where \( k_0 \) is the rate constant of the reaction (5), which depends on the oxidative potential of ozone and the type of impurity, \([\text{O}_3]\) is the concentration of ozone, \( t \) is time. Thus, it follows from equations (3)–(5) that the electric field strength \( E \) is one of the main parameters that determines the rate of degradation of impurities under the action of PDBD.

The energy efficiency \( Y \) is a criterion for the practical use of technologies with AOR in water treatment. The parameter \( Y \) determines the mass of decomposed pollutant at 1 kWh of energy consumed for this purpose; it is called the energy output [1, 2]. The value of \( Y \) depends on many factors [1–8]: parameters of PDBD (voltage, growth rate, pulse repetition frequency), type and geometry of the discharge chamber in which the water is treated, the method of introduction of liquid and gas and their types, concentration and the type of impurity, the presence of a catalyst and other conditions.

The purpose of this work is to achieve the most energy-efficient treatment of the film of an aqueous solution of organic matter under the action of PDBD plasma.

2. Experimental set-up

The equipment includes: pulse generator (PG), discharge chamber (DC), ozone generator (OG), facility for diagnostics of parameters of discharge pulses and measurement of impurity concentrations in water and ozone in gas, as well as devices for pumping water and gas through the DC and measuring their costs.

The PG provided unipolar voltage pulses with amplitude up to 30 kV with their growth rate about \( 3 \cdot 10^{11} \) V/s and repetition frequency \( f \) up to 1 kHz. The pulse energy was regulated by changing the voltage \( U_0 \) of the DC source that supplied the PG. The DC was coaxial type with an inner electrode in the form of a stainless steel tube, which had an outer diameter \( d_1 = 32.6 \) mm. The role of the dielectric barrier was performed by a tube made of electrical glass with inner and outer diameters \( d_1 = 37.4 \) mm and \( d_2 = 39 \) mm, respectively. A layer of aluminium foil was tightly applied on top of the DC, which served as the second (high-voltage) electrode. The length of the electrodes was \( L = 250 \) mm. After entering the vertically installed DC, water flowed down the inner electrode as a uniform film (~ 0.1 mm). More detailed information on PG and DC is presented in [8]. Oscillograms of voltage and current through the
DC were recorded using an oscilloscope TDS 1012 and voltage sensors P6015 and current P6021.

Samples of wastewater typical for harmful plants were processed by PDBD plasma. The wastewater was:

1. Models of the organic component of cooling waters of nuclear power plants based on a solution of phosphate salts, which in terms of P$_2$O$_5$ was 16.2% and surfactants 26.8%. The initial concentration of COD was 462 mg O$_2$/dm$^3$.

2. Real wastewater from plants that produce dyes, the main component of which is technical 2,4-dinitrotoluene CH$_3$C$_4$H$_3$(NO$_2$)$_2$ (DNT); its structural formula is

![Structural formula of DNT](image)

The first sample of DNT solution had an initial COD equal to 1978 mg O$_2$/dm$^3$, dark gray colour and the inclusion of solid particles with the diameter of 0.1-0.4 mm, and a persistent odour. The second sample of DNT solution had an initial COD equal to 503 mg O$_2$/dm$^3$, almost yellow colour and had no visible solid fractions and persistent odours.

The effectiveness of processing of the samples was assessed by changing the COD. The study was performed at room temperature and atmospheric pressure in the DC. The initial volume of the untreated water was 150 ml. This volume was passed through the DC several times. The number $n$ of such cycles varied from 1 to 25.

The thickness of the water layer $\delta$ and the time $\tau_o$ of processing PDBD were found from equations (6):

$$\delta = \left( \frac{3 \nu_k Q_w}{\pi \rho g d} \right)^{1/3} , \quad \tau_o = \frac{nLd_1\delta n}{Q_w}$$

where $\nu_k$, $Q_w$ are the kinematic viscosity of water and the water consumption, respectively; $g$ is the acceleration of gravity.

The results of calculations according to the expressions (6) show that with increasing water consumption within the limits at which the study was conducted ($Q_w = 15-75$ ml/min), the value of $\delta$ increased in the range of 0.1-0.15 mm, and its processing time for one cycle decreased from 8.8 to 3 s.

3. Results

**Discharge parameters.** The type of oscillograms of current $i(t)$ and voltage $u(t)$ characteristic of PDBD is shown in Fig.1. They were obtained under the following conditions $U_0 = 240$ V, $f = 48$ Hz, water and air consumption, respectively, are $Q_w = 0.03$ l/min and $Q_a = 0.8$ l/min.

Curve $i(t)$ shows that the current pulse consists of two parts: the direct current with amplitude $I_{m1} = 190$ A with duration $\tau_1 \approx 120$ ns and the reverse current $I_{m2} = 70$ A and $\tau_2 \approx 150$ ns. The rate of voltage increase during a direct current pulse is $\approx 3 \cdot 10^{11}$ V/s and its amplitude is $U_{m1} = 9.4$ kV. The energy released in this interval per one discharge pulse, $W_p = 88$ mJ. This value was obtained on the basis of the method described in [9]. Within the variation of parameters $f = 10-250$ Hz, $Q_w = 0.015-0.07$ l/min, $Q_a = 0.1-2$ l/min and types of gases for which the research was conducted, the values of $W_p$ changed insignificantly ($< 5\%$).

Under these conditions, each time the water sample passes through the DC, its treatment time according to (6) was 4.6 s. The effect of reducing the concentration of impurities in water after the end of the action of PDBD is explained [3, 4] by the presence in water of a stable oxidizing substance (hydrogen peroxide H$_2$O$_2$) compared to OH$^*$ and O$_3$, which was formed during PDBD.

For the convenience of further consideration and analysis of the obtained results, it is advisable to use the parameter $\eta$, which describes the relative degree of water treatment and is calculated by the expression $\eta = \frac{\Delta K}{K_0 - K_o}$, in which $\Delta K = K_o - K_n$ is the reducing the impurity concentration after $n$ treatment cycles.

We have already noted that the generally accepted indicator of energy efficiency of water treatment is the energy yield $Y = \Delta K \cdot \frac{Q_w}{W_p}$, which was determined by the expression in which $\Delta K_1$ is the decrease in concentration per one treatment cycle. This value is 20–60% higher than that obtained in similar conditions of PDBD treatment of water with methylene blue admix-
ture in [3–5]. As the number of cycles increases, the value of $Y_t$ decreases sharply, which can be explained by a decrease of almost three times after the first cycle of concentration, as a result of which the rate of oxidation of the impurity according to (5) must fall as many times.

**PDBD in a gas containing nitrogen generates oxides of NO, NO$_2$, which initiates the formation of nitrates (ions $\text{NO}^-_3$) in water** [1]. The dependence of their concentration $K_n$ on the specific energy $W'_p = n f W_p Q_w^{\prime -1}$ that was spent on the treatment of distilled water, has a linear nature, Fig. 2.

![Fig. 2. Dependence of the concentration $K_n$ of ions $\text{NO}^-_3$ vs. specific energy spent on distilled water treatment.](image)

The presence of nitrates in water is undesirable because they interact with oxidants that enter the water under the action of PDBD. This reduces their concentration and hence reduces the rate of decomposition of the impurity [1]. In addition, in accordance with the requirements for drinking water existing in the EU, the content of nitrates in it should not exceed $K_{nd} = 45 \text{ mg/l}$.

For the conditions of this work for each treatment cycle at $U_0 = 240 \text{ V}$, $f = 48 \text{ Hz}$, $Q_w = 0.03 \text{ l/min}$, $Q_a = 0.8 \text{ l/min}$ ($W_p = 8 \text{ J/ml}$), the value of $K_n$ increases by 7.2 mg/l. It turns out that at $n = 6$, when $W_p = 48 \text{ J/ml}$, the concentration of nitrates becomes greater than the allowable value $K_{nc}$. This should be borne in mind when treating PDBD with drinking water. In the case of wastewater, the permissible nitrate content can be much higher.

The increase in the number of ions $\text{NO}^-_3$ in water under the action of PDBD is evidenced by a 40-fold increase in the relative value of the specific conductivity $\sigma^* = \sigma/\sigma_0$ (where $\sigma_0$ and $\sigma$ are specific conductivity of the untreated and treated methylene blue solution, respectively) when changing $W_p$ in the range 0 – 200 J/ml as well as its acidity [1], which is characterized by the pH value. This parameter has a significant effect on the course of oxidative reactions in water [1, 2]. Estimates based on the results [1] showed that when $W_p$ increases to 200 J/ml, the pH value decreased from 6.3 to 3.5.

**Treatment of the solutions.** The solutions were treated at a flow rate of 0.03 l/min of water and flow rate of 0.2 l/min and flow rate of air by passing them several times through the discharge chamber at a repetition frequency of PDBD of 95 Hz and their energy of 88 mJ. The change in COD depending on the specific energy $W_p$ for solutions 1–3 is shown in Fig. 3 (respectively, curves 1–3, which demonstrates that the COD decreases with increasing $W_p$).

![Fig. 3. The change in COD depending on the specific energy $W_p$: 1 – solution of NPP detergent; 2 – DNT 1; 3 – DNT 2](image)

Fig. 3 exhibits a particularly rapid drop in COD at relatively small values of $W_p$. This can be explained by the fact that in solutions at high $W_p$ the concentration of nitrates increases, which not only neutralize the oxidants generated by PDBD, but also by the fact that they lead to an increase in COD. This explains why at low concentrations of DNT (Solution 3, curve 3), when the reaction rate decreases according to expression (5), the effect of PDBD on the solution becomes smaller.

In the process of wastewater treatment of plants producing dyes containing dinitrotoluene, i.e. molecules of DNT1 and DNT2, a persistent odour disappeared and the liquid from the dark brown opaque became much lighter and more transparent.

4. **Conclusion**

The energy efficiency of the pulsed dielectric barrier discharge at different modes of water treatment with different impurities of organic substances has been studied. To obtain a high energy efficiency of water treatment, the specific energy consumption has to be about 100 J/l at which the parameters of energy and pulse repetition of PDBD, and rates of water and air movement passing through the chamber are self-consistent.
ДОСЛІДЖЕННЯ ОБРОБКИ ВОД З ПІДВИЩЕНИМИ КОНЦЕНТРАЦІЯМИ ХСК ПЛАЗМОЮ ІМПУЛЬСНОГО БАР'ЄРНОГО РОЗЯДУ НА ПОВЕРХНІ РІДИНІ

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Прогресуючи забруднення води через антропогенний вплив на навколишнє середовище відноситься до актуальних проблем сучасності.

неннями можна проводити за допомогою технологій, що використовують передові окисні процеси (advanced oxidation processes – AOP). В нашій роботі вивчалась ефективність окиснення плазмою бар’єрного розряду стічних вод підприємств виробників барвників головним компонентом яких є технічний 2,4-динітротолуол, а також моделі органічної складової стічних (трапних) вод АЕС головною складовою яких є миючий засіб з на фосфатній основі з вмістом ПАР – 26,8%. Оброблялись плівки води товщиною ~0,1мм при швидкості наростиання імпульсів розрядної напруги ≈3·1011В/с. Досліджено енергоефективність імпульсного бар’єрного розряду при різних режимах обробки води з різними домішками органічних речовин. Для отримання високих показників енергоефективності оброб- 
кі води треба проводи при таких параметрах імпульсного бар’єрного розряду (energia та частота повторення імпульсів) та швидкості руху повітря, щоб питомий енерговнесок у повітря, що проходить через камеру, не перевищував ~ 100Дж/л. Найвищий енергетичний вихід імпульсного бар’єрного розряду, для зразків стічної води, при питомих енерговкладах не перевищують ≈10Дж/мл.

Ключові слова: плазма, імпульс, бар’єрний, розряд, вода, озон, гідроксильний радикал, динітротолуол, ПАР, енергоефективність.