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USING OF OZONE TECHNOLOGY DURING BIOLOGICAL AND CHEMICAL PROCESSES AND POLLUTED WATER PURIFICATION

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Abstract- This paper deals with the different processes taking place in biological, chemical, and physical systems under the effect of ozone of various concentrations. The results show that ozone technology is able to control the processes of various origin. To study the purification of polluted water as well to compare with theoretical calculations there have been conducted the investigations on ozonation of (C_6H_5OH) phenylic acid water solutions. Suggested ozone technology due to ozone oxidability also the formation of active radicals during the synthesis allows it for the decomposition of a large number of organic substance molecules dissolved in industrial wastewater of petrochemical industry to be used. To preserve the integrity of flora and fauna environment from the destructive effects of industrial wastewater we think what the ozone technology is the most reliable, easily producible. The obtained results and their analysis show that ozone generator plant has the highest paper and the biggest productivity at resonance frequency, respectively. It is show that this ozone generator plant can be used to advantage for waste of small oil processing plants.

Keywords: Ozone Technology, Two-Barrier Discharge, Oil Industry, Ecology.

I. INTRODUCTION

For recent years of researchers being concerned with ozone technology at Physics of Biological System Department with the researchers of NANA Institute of Physics and different Departments of Biology and Chemistry Faculties of Baku State University use the given ozone technology actively in the following leads.

II. CASE STUDY

To study (with the researchers of NANA Institute of Physics) the influence of ozone on the development of oxidizing reactions in erythrocytes and human and animal hemoglobin's (rat, guinea pig and rabbit) substantially differed by selenium metabolism being one of the most important natural antioxidants. There has been studies kinetics of oxidation by ozone generated by two-barrier corona discharge with the concentration 4.6 mkq/l, both the hemoglobin isolated in the in the solution by complete hemolysis of distilled water with the subsequent adjusting 0.1 M buffer solution of sodium phosphate in hematocrit ≈ 1 and hemoglobin in erythrocytes suspension (hematocrit ≈ 1). It is established that accumulation of met hemoglobin (MeTHb) in hemoglobin solutions proceeds much faster than in erythrocytes suspension.

The guinea pig demonstrates the highest immunity to the oxidation, the rat demonstrates the least one, the human and rabbit takes an intermediate position [1]. Investigation of erythrocytes hemolysis induced by ozone shows that type distinction for oxidative hemolysis of erythrocytes are less significant than for MeTHb accumulation rates in them. It turns out that solid erythrocytes of the guinea pig are more resistant to peroxide oxidation than erythrocytes of the rat. For erythrocytes, shadows the distinctions like these are less pronounced.

Obtained data indicate that hemoglobin oxidation (by MeTHb accumulation) is the initial link of oxidative damage of erythrocytes which are as high as Se, (GP) Glutathione Peroxidase activity. In this case, for the guinea pig the antioxidant protection by Se is predominantly carried out by the protection from hemoglobin oxidation. YP membrane protection by mechanism is essential for the rat. As it is known from reference under the normal physiological conditions, the relative constancy of amount of glucose in blood is provided by neuro-humoral process.

Taking into consideration the poor examination of ozone influence on circadian rhythm of glycemic reactions of animals kept in ozone medium, (with the research workers of human and Animal Physiology Department). We have performed experiments with three months old and six months old animals at the ozone concentration in ozone air medium 2.4 mkg/l and 3.4 (ozone half decay time is 15 min). Amount of glucose in blood has been determined by rapid analysis.

The investigation have been made out in accordance with rhythm of day, i.e. at 9:00 am, 13:42 pm, 17:42 pm, 21:42 pm, 01:42 am and 09:42 am. In each case, the blood is taken up from the outer vein of animal's ear to determine glucose level in animal's blood. Experiment results, are adequately verified that at 7-minute contact of animals with ozone the glucose level in their blood as well for intact ones is in agreement with rhythms of the day, but at 15th, 30th and 60th minutes and at 13:42 pm, 17:42 pm and 21:42 pm the given level is slightly excessive.

In other time intervals, this level measures up to the previous values. Tran the obtained results it follows that for animals kept in ozone medium the role of epiphysis in neuro-humoral regulation of the circadian rhythm of glycemic reactions is doubtless [2, 3]. For toxic ozone, its effect on the germination of mono-lobe seeds of wheat is little studied. Wheat seeds as the subject of inquiry have been selected (with the research workers of Physiology of Plants Department). First, the seeds are soaked for 24 hours, and then kept in chamber with contact time from 1 min. up to 210 min. Ozone concentration changes within 3.4-7.2 mkg/l.

Experiment results show that ozone affects the germination in different ways. At low concentrations, the germination increases by 3% but at high ones, the decrease of the germination has been observed. While processing wheat seeds by hydroquinone (with research workers of Genetic and Darwinism Department), after processing them under the conditions of ozone at different exposures the ozone behaves itself in two ways, at low exposures as an anti-mutagen and at high ones as mutagenic substance.

Investigations show that at low exposures (up to 3 min) the ozone effect is slight or in some cases it decreases the germination of seeds and fissility of cells comparing with the test seeds. The decrease of germination is related to the formation of negative oxygen ions beyond the cell membrane by ozone decay and change of membrane potential of rest. Further with the increase of exposure time (15-18 min) the straight growth of seed germination, number of fissile cells and chromosomal changes, i.e. change of cell activity has been observed.

These experiments show that ozone behaves to specific value as an antioxidant, i.e. as an anti-mutagen substance. Ozone can interact for practical purposes with all types of organic compounds (with radical formation) [5, 6]. In this paper, process of phenylic acid decomposition under the effect of ozone (the work has been fulfilled by the researchers of Department Physics of Biological Systems in Research Institute of Physical Problems). Phenylic acid are aromatic compounds where hydroxyl group substitutes the hydrogen atom for benzol ring. By the number of hydroxyl, group the phenylic acid divided into monoatomic, diatomic and hex-atomic ones (for benzol).

Particular physical and chemical properties of naphthol, phenanthrol and other multinuclear atomic compounds confirm with phenylic acids and therefore they are named as multinuclear phenylic acids [7]. MPC for phenylic acid is 0.001 mg/l, but index of phenylic acid is 0.25 mg/l, therefore it is clear how it is important the purification of polluted water from phenylic acids [1, 2]. Mixture of phenylic acids is more toxic than phenylic acids itself and has a synergistic effect, also products of high oxidation of phenylic acids by ozone are essentially non-toxic and noncumulative [7].

In Table 1 there has been presented the amount of phenylic acids in underground water of oil and gas territories of the Azerbaijan Republic [7] amount of phenylic acids in underground water of oil and gas territories of the Azerbaijan Republic. At it is known [7, 8] phenylic acids decomposition under the effect of ozone is due to the temperature. Optimum conditions of wastewater ozonation involving phenylic acids are observed in alkaline medium (pH≈12) and within elevated temperature (50-55 °C).

Table 1. The quality of the phenol in the ground water of the oil and gas territory of the Azerbaijan Republic

The area	Phenol, mg/l	
	Volatile	Nonvolatile
Garadagh	13.77	0.5
Lok-batan	2.53	3.37
The Yasamal valley	7.31	15.69

As for the present one of the most effective method of decontamination is ozonation we make out investigations on ozonation of phenylic acid water solutions (C_6H_5OH) to study the purification of polluted water as well to compare theoretical calculations [7, 8]. As it seen from Table 2 the increase of ozone concentration in ozone-air mixture decreases the time of ozonation process.

Table 2. Ozonation of phenylic acid water solutions

t (min)	C_{phenol} (C_{ozone} = 4 mg/l)	C_{phenol} (C_{ozone} = 4.5 mg/l)
0	45.5	45.5
5	34.3	32.93
10	27.28	22.89
15	21.01	15.68
20	15.68	10.04
25	10.66	6.27
30	7.21	3.14
35	4.39	1.57
40	2.51	0.31
45	1.25	0.016
50	0.63	0.0003
55	0.31	0
60	0.16	0
65	0.09	0
70	0.05	0
75	0.003	0
80	0.001	0
85	0	0

By investigating the influence of various activating factors on surface tension of dissimilar water the decrease of surface tension by water ozonation has been found out [9, 10]. Before ozonation the natural water has $\sigma = 68.9\times10^{-3}$ N/m and after ozonation $\sigma = 57.6\times10^{-3}$ N/m, that suggests the presence of dependence of phenylic acid decomposition rate on the magnitude of water surface tension, which in turn can lead to the decrease of the ozone specific consumption. From the familiar table of dependence of water surface tension coefficient of temperature it is seen that at T = 55 °C the water surface tension coefficient $\sigma = 66.9\times10^{-3}$ N/m.

In further experiments, one should monitor the temperature and magnitude σ simultaneously. With the decrease of value σ the decrease of ozone conception for the decomposition of equal amount of phenylic acid has been also expected. In [11, 12] ozone technology has been used for water purification polluted by oil products.

In specific cases profitable to build small oil-processing plants producing from ten to hundred tons of oil products in a day. Great expenses for large plant construction are not only profitable but strategically impracticable. While planning the construction of any industry it is necessary to estimate the existed ecological situation beforehand. To preserve the integrity of flora and fauna from destructive effects of industrial wastewater we think that the ozone technology is most reliable easily producible. At any oil-processing plant outlet the water polluted by toxic substances (phenylic acid, pesticides, cyanides, NO_2^-, NO_3^-, NH_4^+) can find its way into rivers, lakes or seas ultimately.

All production waste can cause irreparable harm to the environment. Purification of the polluted water is urgent requirement of the time. Disposal of wastewater into the body of water can be permitted by reducing the concentration of pollution down to maximum permissible concentration (MPC). Our suggested ozone technology for the great ozone oxidability as well the formation of active radicals during the synthesis allows it for the decomposition of great number of molecules of organic substances soluted in production wastewater of oil-chemical industry to be used.

In [1] it is shown that after cycles of biological and physico-chemical purification the use of ozone for oxidizing the rest of molecules of soluted organic substances allows the complete elimination of pathogenic bacteria, microbes and toxic components of purified water to be achieved. The ozone technology enables the degree of purification in many properties to be increased. At the Experimental Industrial Plant (EIP) of Oil-Chemical Process Institute of Azerbaijan National Academy of Sciences with the scientists of Baku State University the multi element ozonizer has been designed and operated.

On average EIP has nearly 150÷200 m^3/day of production polluted water to be subject to the purification. The maim pollutants are hydrocarbons, NH_4^+, NO_2^- ions and small amount of phenolic acids. At it is known the ozone oxidizes efficiently phenolic acid and splits the hydrocarbons of the aromatic ring, as a result their toxic effect is lost. In all purification systems, the wastewater first undergoes mechanical purification according to the familiar scheme passing through the grates, sand-and oil catchers and initial settler.

Then it heads for the biological purification works, after which it finds its way into the flocculating chamber and secondary settler. After all these operations, the more or less purified water for decontamination from toxic components heads for the camera of ozone contact. While polluting wastewater by oil to reinforce bacteriological purification process by small ozone doses one can promote the process of overdoing the bacterially [2]. Functional structural diagram of wastewater organization is given in Figure 1.

The diagram includes three modules. The first one involves, 1 is the frother cell of ozone, 2 is the foam collector, 3 is the stepwise reducer, 4 is the motor, 5 is the aerator, 6 is the water tank, 7 is the rotameter, 8 is the compressor, 9 is the porous disperse divider. 10 is the air gap, 11 is the collector of surface-active substance, and float fractions, 12 is the valve of settling removal. The second module involves, 13, 14 are the reactors of absorbents, 15 is the withdrawal pump. The third module involves, 16 is settling chamber, 17 is the air preparation unit, 18 is the ozonizer, and 19 is the splash lubrication.

The ozonizer is the main element of the given system. The filtered air after draining by dehydrator finds its way into the ozonizer under the pressure of about 1.5×10^5 Pa where ozone generation in barrier discharge is taken place. It should be noted that nowadays at world market various types of ozonizer with different production rate reaching several kilograms per/hour have been available.

Taking into consideration that in research laboratory "Ozone generators" of Baku State University the ozonizer with rather low manufacturing cost have been developed [3]. Some specifications of the ozonizer of average power like this are presented in Table 3.

Table 3. Some specifications of the ozonizer of average power

Number of active elements	100
Operating voltage	380 V
Energy input	3 kWt
Output in ozone	30 g/h
Amount of water being worked	25 t/h
Amount of forced air	10 m^3/h
Energy consumption for synthesis of 1 kg ozone	22 kWth/kg
Time of continuous work	8 h
Mass without compressor	60 kg
Cooling method	air-water

The ozonizer provided for using in pilot systems of water purification has output of about 30 g/h that fully meets requirements of EGP in purification of processing wastewater. The given preliminary experiments in purification of processing wastewater, shows the number of microbes of investigated samples coli index under the effect of ozone drops by a factor of 1000, from 1,900,000 down to 220. Multi-element ozonizer runs on the base of two barrier discharges.

The two-barrier ozonizer first receive attention by their electrodes that are covered with qualitative dielectric or they are separated by a glass tube with rather high dielectric constant and at the outlet lack of dangerous heavy atoms and inclusions of electrode erosion materials and are suitable for drinking water. Barrier discharges falls into the most complex types of discharges [4, 6, 7]. The advent mechanism of similar discharges and their structures are not investigated fully.

Therefore, to find out main regularities of ozone synthesis calls for the study of physical processes doing in discharge gaps of barrier discharges in each specific case. It is also necessary to determine and establish link of active power added to discharge gap with different parameters, instance with the ozonizer output. However, it is not easy for nonlinearity of resistance of discharge gap of barrier discharges. To develop the electric theory of ozonizers and estimate their output parameters the study of their Volt-Ampere Characteristics (VAC) is of great importance. Dependence of VAC of experimental conditions and design features of ozonizer is the subject matter of many investigations [4].

In paper [5] there have been experimentally taken and studied VAC of one active element of multi-element ozonizer within supply voltage frequencies 250-1000 Hz.

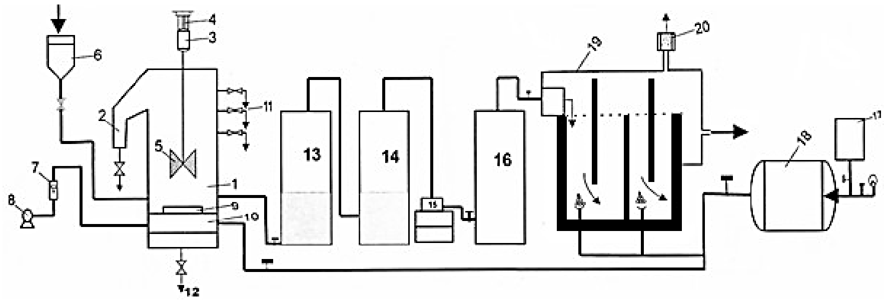

Figure 1. Functional structural diagram of wastewater organization

VAC of the element at issue has a very specific form. According to VAC added powers into the frequency response have defined. By reaching the certain value of voltage (~10^4 V) on the electrodes the discharge current increases almost linearly and be of maximum value ~1 A. It should be noted that the displacement currents defined by total capacity of active element play a significant part and so with the increase of frequency the added powers to the discharge rises too.

However, the discharge power reaching its maximum value 26.5 Wt at frequency 750 Hz drops rapidly. Probably the maximum power is added to the discharge at the limiting resonance frequency. At this power value, the ionizer has most output equal to about 30 g/h. The given paper is the continuation of investigation of the physical processes proceeding in ozonators with two-barrier discharge, stated in [10] where it has been shown. The active power put in discharge interval, ceases to depend on the frequency if the applied voltage in the certain interval is 500-900 Hz, and then decreases with frequency increase (Figure 2).

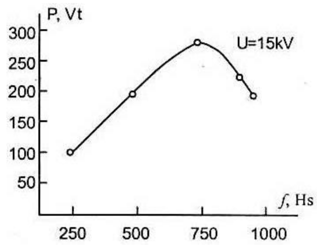

Figure 2. Dependence of active power including to discharge interval of the ozonator on the frequency of the applied voltage

Power is determined from VAC of discharge by the Equation (1) as follow:

$$P = [I_{av} \;\; I_{av.f}]U_c \tag{1}$$

where, I_{av} is the average current, $I_{av.f}$ is the average current of firing voltage, U_c is the voltage of discharge combustion.

We note that while increasing the frequency up to values exceeding 1000 Hz the discharge ceases. Given conclusion disagrees with the calculation Equation (1) fixed in theory of ozonizer. According to this Equation (1), the power increases with the frequency growth as:

$$P = \frac{2}{\pi}\omega U_C\left[C_B\left(U - U_C\right) - U_C C_G\right] \tag{2}$$

where, $\omega = 2\pi f$ is the circular frequency, U_C is the voltage of discharge combustion, U is the applied voltage, to the ozonizer, C_B is the barrier capacity, C_G is the discharge gap capacity.

To clear up above mentioned deviation of experimental results from the theoretical Equation (2) in paper [5] there has been made out the full equivalent circuit of ozonizer plant operating on two-barrier discharge under pulsed conditions (Figure 3). In this circuit, the ozonizer plant is presented as a system of two-coupled circuits. Supply voltage is transmitted from the initial circuit to the secondary one by the use of pulse transformer.

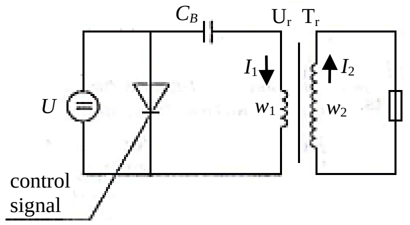

Figure 3. Equivalent circuit of ozonizer plant

The initial one affects the form of pulses by transferring speedy processes formation of their fronts but the second one has an influence by transferring slowly changing part of pulses and forms their peaks. The discharge current has two half-periods and strongly damped behavior. It can be presented in the integral form as $I_1 = I_{m1}e^{j\omega t}$ for the initial and $I_2 = I_{m2}e^{j\omega t}$ for the secondary circuits. I_1 is created by the effect of $e_1(t)$, i.e. EMF of the first circuit. As a results the initial circuit is added to the certain complex resistance being equal to Equation (3).

$$\dot{Z} = \frac{\omega^2 M^2}{\dot{Z}_2} \tag{3}$$

where, M is the mutual inductance.

Reactance part of what is termed as added resistance compensates the reactance of the initial circuit, as a result the resistance of system becomes active and independent of frequency. Independence of added power to the discharge on the frequency in neighborhood of resonance frequency (ω_0 = 750 Hz), observed in experiments has been explained. It is obvious in this case, there have been changed other characteristics, particularly transmission factor of the coupled circuit system under investigation.

III. CONCLUSIONS

A- It is shown that suggested ozone generator plant has the highest power and the biggest productivity at the resonance frequency, respectively.

B- Given preliminary experiments on the purification of production waste water show that microbe number of investigated samples under the effect of ozone drops by a factor 1000 but Coli index drops from 1,900,000 down to 220.

C- Ozone generator plant can be used to advantage for the purification of wastewater at small oil-processing plants.

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