ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Mutual Influence of Hydrogen Peroxide and Guanibifos On Sewage Water Treatment Process Under Aerobic Conditions.

Ilnar A. Nasyrov[1]*, Gennady V. Mavrin[1], Elmira M. Masagutova[2], Tatiana P. Pavlova[3], and Sergei V. Fridland[3]

[1]Assistant professor of KFU, Kazan Federal University, Russia, 423810, Naberezhnye Chelny, Prospect Mira, 68/19
[2]Graduate student of KNRTU, Kazan National Research Technological University, Russia, 420015, Kazan, Karl Marx st., 68
[3]Assistant professor of KNRTU, Kazan National Research Technological University, Russia, 420015, Kazan, Karl Marx st., 68

ABSTRACT

The article presents a study of currently existing systems and wastewater treatment principles. Study of the process of biological treatment of polluted sewage water using stimulant of biocenosis of activated sludge together with an oxidizing agent.Choose a path to stimulate the functioning of biocenosis of activated sludge with biologically active substances. The investigations were carried out on real sewage water produced by JSC "Kazanorgsintez". The hydrogen peroxide was taken as the oxidant purification process. During the experiment, we observed intensification of the wastewater treatment process of organic compounds with the participation in the process of hydrogen peroxide as intensifying the work of activated sludge and protects against the harmful effects generated radical species. The paper showed that the hydrogen peroxide does not decompose under the experimental conditions for radical species. This opens the possibility of penetration in her cell while preserving the molecular structure followed by decomposition, causing the death of the living matter. We present the results of the possibility of sewage water treatment by a combination of several factors at the same time.

Keywords: aerobic biological sewage treatment, activated sludge, chemical consumption of oxygen, biological active substances, low and extremely low concentrations, oxidation of hydrogen peroxide.

**Corresponding author*

INTRODUCTION

Currently used systems and sewage treatment principles are very diverse and a significant place is given to biological methods. [1] At first, the improvement of the methods of biological treatment is associated with the guaranteeing of the destruction of connections which are unusual for natural water. Secondly, there is a very significant economical efficiency of this method since biological treatment is carried out at relatively minimal cost of energy on a mass unit of removed substances.

Aerobic biological sewage water (SW) treatment is the result of the system 'activated sludge -sewage water ", which is characterized by the presence of a complex multi-level structure. Biological oxidation which forms the basis of this process is a consequence of the flow of a large complex of interrelated processes of varying complexity, from the elementary acts of electrons sharing to complex interactions of biocenosis with the environment [2].

Activated sludge (AS) is a complex ecosystem of microflora and microfauna representatives clusters, including flaky accumulation of bacteria (zoogel) and animal and vegetable origin protozoa. The time of the biological treatment of sewage water stream in the aeration tanks is estimated in the range of about 8-16 hours depending on the amount and sewage water composition. The reduction of residence time in the bubbling volume will influence the energy consumption, as power production causes emissions of nitrogen oxides, sulfur, carbon, causing acid rains, the greenhouse effect and contributes to the smog formation.

The way of the functioning biocenosis stimulation of activated sludge by biologically active substances (BAS) has been selected in order to intensify the processes of SW treatment with high content of hydrocarbons. To achieve this goal SW with a high value of chemical oxygen demand (COD) and phosphate anion were selected as objects of a study , and ,N-N-diphenylguanidine salt of dihydroxyphenylphosphinic acid was selected as a biologically active substance (BAS) **1** [3]. It was shown that at the concentrations of 1 10-10-10-11 mole / l **1** can be used as a dietary supplement, intensifying SW treatment [4,5].

A series of studies [6-9], [10-13] mainly performed by DLS demonstrated the formation of giant clusters (supramolecular domains) with a size up to hundreds of nanometers (30-500 nm) in aqueous solutions of inorganic and organic compounds with concentrations of $1 \bullet 10^{-6}$—6 mol L^{-1}. Kinetic measurements of the formation of these domains and domain stability demonstrated that depending on the nature of the solute, the time scale of domain formation varies from several minutes to several weeks, and the period of their stability ranges from 1 to 15 months. It was convincingly proven that supramolecular domains are not nanobubbles of the gases present in solutions [13]. In the author´s opinion, [13] the most probable mechanism of domain formation in aqueous solutions is the formation of intermolecular hydrogen bonds between the solute and water molecules [12]. It was suggested [14—15] that protons and hydroxyl ions play a crucial role in the formation of supramolecular and super supramolecular complexes of 3 to 100 µm size. The association of supramolecular structures (ion pairs of hydrated protons and hydroxyl ions) to supersupramolecular complexes, which form chains or 3D fractals, is due to electromagnetic forces. Apparently, isotope modifications of water [30] and *ortho* and *para* modifications of water [16,17] can play a considerable role in the appearance of water nanoheterogeneity. Quite recently, quantum field theory has been invoked to explain experimental data indicating nanoheterogeneity of water and aqueous solutions and formation of structures measuring tens to thousands of nanometers in aqueous solutions [18,19,20].

Organic compounds presenting in the water may undergo not only aerobic biochemical oxidation as a result of bacterias activity, but chemical reactions of oxidation of organic substances as well in the presence of oxidants in water and appropriate conditions.

Current understanding of the mechanism of oxidation is based on the peroxide theory that says that organic compounds react with oxygen, after passing into the active state.

Primary act does not require breaking the link between oxygen atoms, their dissociation energy is very high (117 kcal). The bond dissociation energy O - O in peroxide is significantly lower (30 - 40 kcal) than in the O2 molecule, so peroxides are unstable substances which easily undergo transformations leading to the rupture of the O - O and to the formation of deeper oxidation products .

With the purpose of better understanding of oxidation processes in biological SW treatment the work with the addition of hydrogen peroxide (HP) as an additional agent of cleaning process has been carried out. It was interesting to investigate the possibility of SW treatment using the combination of simultaneously operating factors as HP, AS and AS combined with the HP and **1**.

EXPERIMENTAL PART

Hydrogen peroxide was taken as one of the most effective compound as an oxidant for the cleaning process. The calculation of the peroxide concentration was made from the data of COD of SW. Thus, the initial concentration was calculated amount of peroxide that can carry out complete oxidation for SW being studied.

The experiment was conducted in the following way: 100 ml of the AS and 100 ml of the SW were poured in a 500 ml flasks , then HP and 1 in a concentration of 10-10 mol / l were being added as the most efficient, or distilled water, in case of a control experiment. After that, all flasks were mounted on a rocker. COD was measured every hour of aeration during a control experiment, and in the experiment with 1 and in the experiment combined with the HP with 1 by the method presented in [21].

RESULTS AND ITS DISCUSSION

The results of the SW treatment process of organic synthesis production in the conditions of AS + SW, AS + SW + 1, SW+ HP and as results of the experiments were quite prospective, proceeded evenly, almost in a straight line, there was a reduction of COD of the investigated runoff. After four hours, the COD of SW reduces to the maximum for the biological treatment process stimulated by **1** to the value of 134 mg O_2 / l, in conventional biological treatment process to 224 mg O_2 / l and under the influence of HP in the monitored conditions to 287 mg O2 / l. These results are shown in Figure 1, the kinetic curves 5,1 and 2 respectively. The effects of two factors aimed at the oxidation of pollutants, namely, biocenosis of AS and HP is reflected in Figure 1 estimated by the value of COD determined every hour, showed in zigzag line 3. The concentration of HP added to the system approached the required amount for the oxidation of organic matter in the water drains. The overall picture of the process observed in this experiment can be interpreted as a series of interactions of HP not only by pollutant of SW, but by biocoenosis of AS as well, which undergoes destruction and generates soluble organics.

The process includes a combination of two factors leading to the decrease of the water pollutants and it cannot be predicted in advance. Thus, HP does not act only as the oxidant of pollutants, but as the generator of radical species, and it can be expected that it will act negatively on the biocenosis, destroying it. It is interesting that there is the inhibition of HP degradation into hydroxyl radicals in the presence of **1** in small (1 * 10-10mol / L) concentrations [22].

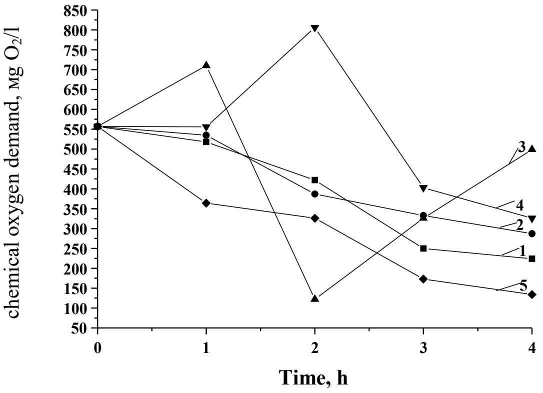

Figure 1 The dependence of the COD of sewage water from the aeration time for different cleaning methods: 1 SW + AS; 2 SW + H_2O_2 (c = 2 * 10-2mol / l); 3 SW + AS + H_2O_2 (c = 2 * 10-2mol / l); 4- SW + AS + H_2O_2 (c = 2 * 10-2mol / l) + BAS 1 (c = 10-10mol / L); 5 SW + AS + BAS 1 (c = 10-10mol / l).

In the absence of **1** there is a sharp jump (line 3), caused by the increase in COD of water flow that can be logically explained by the impact of HP on the biocenosis, which undergoes degradation, causing an increase in organic matter content in the liquid. The reduction of COD by the second hour is associated with a primary process of oxidation in the water volume due to oxidation of organic compounds of HP in the water (in a homogeneous environment, it takes precedence over a heterophase process of liquid - solid), but after the second hour we can observe preferential expansion of the biocenosis caused by adsorbed peroxide particles on the surfaces of the biocenosis components.

Reducing the concentration of oxidized substances in the water after the second hour, quite naturally leads to reduction of COD associated with the revival of biocenosis and intensification of **1** presence. It can be postulated that in the first hour of HP work due to the expansion of AS biocenosis has resulted in easily digestible components. Their disappearance to the second hour, again leads to the destruction of biocenosis components AS and to the appearance of organic matter in solution and therefore there is a reduction in HP concentration.

We can expect the intensification of the SW cleaning process from organic compounds with the participation of **1** in the process as intensifying the AS work and how it would be possible to guess protecting against the harmful effects of the radical particles generated by HP.

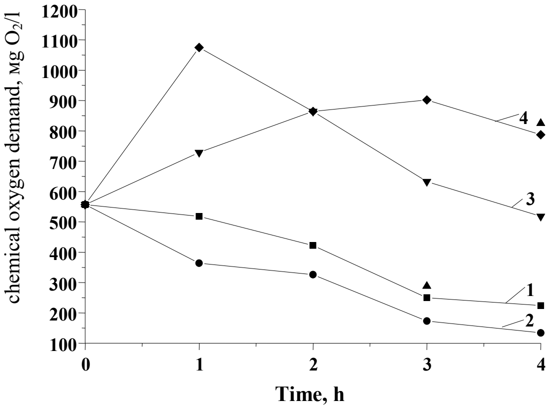

Figure 2. The dependence of COD from sewage water aeration time with the BAC 1 for various concentrations of hydrogen peroxide: control 1. (SW + AS); 2. SW + AS + BAS 1 (c = 10-10mol / l); 3.- SW + AS + BAS 1 (c = 1 * 10-10mol / L) + H_2O_2 (c = 3 * 10-2mol / l); 4.- CB + AS + BAS 1 (c = 1 * 10-10mol / L) + H_2O_2 (c = 3.5 * 10-2mol / l

Indeed at selected concentrations of HP 2* 10-2 mol/l(Fig. 1, lane 4), 3 * 10-2mol / l (Fig. 2, lane 3), 3.5 * 10-2mol / l (Fig. 2, line 4) there is an increase of COD values in the early hours of aeration and subsequent COD gradual decline.

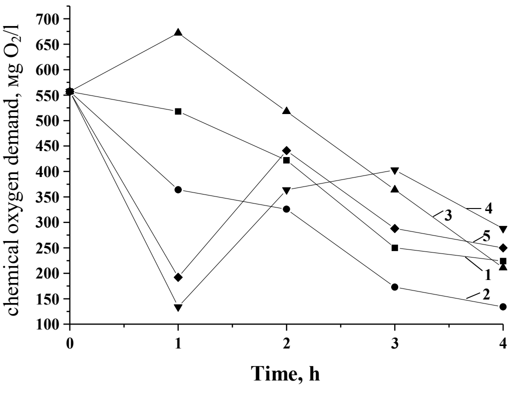

Figure 3 The dependence of the COD of waste water from the aeration time with the addition of BAS 1 for different concentrations of hydrogen peroxide: 1 control (SW + AS); 2 BAS 1 (c = 10-10mol / l); 3 SW + AS + H^2O_2 (c = 1.5 * 10-2mol

/ L) + BAS (c = 1 * 10-10mol / l); 4- SW + AS + H_2O_2 (c = 0.5 * 10-2mol / l) + BAS 1 (c = 1 * 10-10mol / L); 5 SW + AS + H_2O_2 (c = 1 * 10-3mol / l) + BAS 1 (c = 1 * 10-10mol / L).

The results further reduction of the HP concentration in the experiments, are reflected in Figure 3 (the HP concentration 0,5 * 10-2mol / l and 1 * 10-3mol / l) lead to a sharp COD decline in the first hour of the experiment. After the first hour as the concentration of HP is very low the oxidation process is not as intense as it is observed in the previous experiments, but it is possible to postulate the occurrence of two processes: the continued AS destruction and the desorption of organic matter that occurs in the first hour.

Thus, the general conclusion is that the presence of AS and HP at high concentrations primarily acts upon it, and breaks up the components to the compounds which are soluble in water, that increases the COD in its turn. And such picture is similar for the both mixtures the one with **1** and the one without it. The absence of radical particles, defined by the presence of **1** leads to the process in the early hours to the characteristics of the curves resulting only from not decomposed into radicals of HP or transformation scheme H2O2 H2O + O2 and further decline to the AS functioning with **1**.

The results of the test can be explained basing on the previously studied behavioral processes of hydrogen peroxide in the presence of **1** [23]. The study has shown that hydrogen peroxide does not decompose into radical particles under the experimental conditions. Thus it opens the possibility of penetration into the cell while preserving the molecular structure followed by decomposition, causing the death of the living matter. This process can be imagined at a relatively high concentration of hydrogen peroxide. And as in Fig. 1 in the presence of **1** the expansion of the biocenosis components is sustained in the first and in second hour at most(lane 4), but without **1** it is already slow during the first hour (line 3). Further explanation of the dynamics of the process, namely the accelerated oxidation in the absence of **1** is associated with the formation of active radical particles , leading to the oxidation of the contaminants that end by the second hour, but there is an active destruction of the biocenosis living matter. The presence of **1** stabilizes the process (prevents destruction outside the cells of biocenosis) and there is only the oxidation of soluble organics. From the same point we can explain the SW treatment process with high HP (look at and lines 3and 4 in Fig. 2). "Excess" of HP enters the cell and leads to its degradation within the first hours, and in large quantities (line 3 to COD 1100 mg O_2 / l and Line 4 to COD 850 mg O_2 / l) and then the process of SW treatment from organics.comes

Reducing the HP concentration 1.5 * 10-2 g / L we observe the same picture with COD increasing in the first hour, and after the consumption of PV there is a normal process of reducing the organic content. Lines 4 and 5 in Fig. 3 repeat the process trend.

ACKNOWLEDGEMENTS

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

REFERENCES

[1] Galantseva L.F., Fridland S.W., Some shortcomings in the analysis of sewage water for phosphates. The bulletin of Kazan State Technical University, 2011- P. 204-207.

[2] Higins I. Bost J., Jones J. Biotechnology: Principles and Applications; Moscow, 1988. 480 p.

[3] The patent of the Russian Federation. 2404964 (2010).

[4] Pavlova T.P., Masagutova E.M., Pantyukova M.E., Friedland S.V. The Effect of N, N- diphenylguanidine salt bis (hydroxymethyl) phosphinic acid in the nanoconcentration on aerobic treatment of industrial sewage water. The Bulletin of Kazan Technological University. 7, 2012 – P. 40-42.

[5] Ryzhkina I.S., Murtazin L.I. , Masagutova E.M, Mishina O.A, Pavlov S.V. Friedland, academician Konovalov A.I.. The self-organization of sodium chloride solutions in the absence of a low concentration active compound in normal and hypoelectromagnetic conditions. DAN. T. 446, 2012 - P.646-652.

[6] D. Subramanian, D. A. Ivanov, I. K. Yudin, M. A. Anisimov, J. V. Sengers, J. Chem. Eng. Data, 2011, 56, 1238.

[7] D. Subramanian, M. A. Anisimov, J. Phys. Chem. B, 2011,115, 9179.

[8] P. Bharmoria, H. Gupta, V. P. Mohandas, P. K. Ghosh, A. Kumar, J. Phys. Chem. B, 2012, 116, 11712.

[9] D. Hagmeyer, J. Ruesing, T. Fenske, H.W. Klein, C. Schmuck, W. Schrader, M. E. M. da Piedade, M. Epple, RSC Adv., 2012, 2, 469.

[10] M. Sedlak, J. Phys. Chem. B, 2006, 110, 4329.

[11] M. Sedlak, J. Phys. Chem. B, 2006, 110, 4339.

[12] M. Sedlak, J. Phys. Chem. B, 2006, 110, 13976.

[13] M. Sedlak, D. Rak, J. Phys. Chem. B, 2013, 117, 249.

[14] A. N. Smirnov, A. V. Syroeshkin, Zh. Vsesoyuz. Khim. Ovaim. D. I. Mendeleeva, 2004, 48, No. 2, 125 [Mendeleev Chem. J. (Engl. Transl.), 2004, 2004, 48, No. 2].

[15] D. M. Kuznetsov, A. N. Smirnov, A. V. Syroeshkin, Zh. Vsesoyuz. Khim. Ova im. D. I. Mendeleeva, 2008, 52, No. 1, 114 [Mendeleev Chem. J. (Engl. Transl.), 2008, 52, No. 1.

[16] S. M. Pershin, Mezhdunar. konf. "Struktura vody: fizicheskie ibiologicheskie aspekty" [Intern. Conf. "Structure of Water: Physical and Biological Aspects"] (StPetersburg, September 12—16, 2013), Abstrs., StPetersburg, 2013, 46 (in Russian).

[17] A. A. Khamzin, R. R. Nigmatullin, Dokl. Phys. Chem. (Engl. Transl.), 2013, 452, 247 [Dokl. Akad. Nauk, 2013, 452, 534/

[18] N. Marchettini, E. Del Giudice, V. Voeikov, E. Tiezzi, J. Theoret. Biol., 2010, 265, 511.

[19] T. Yinnon, C. Yinnon, Modern Phys. Lett. B, 2012, 26, 1150006.

[20] T. Yinnon, V. Elia, Int. J. Modern Phys. B, 2013, 27, 1350005/

[21] Lurie Y.,Y., Rybnikov A.M. Chemical analysis of industrial sewage water. Chemistry. Moscow, 1974 - 336p.

[22] Ryzhkina I.S. Murtazin L.I., Savelyev IA,. Pavlova M.E., Pantyukova, A.Ayu Lapin, Friedland S.W., Konovalov A. The study of the mechanism of solutions actions of low concentration bioregulaters of active microorganisms. Abstracts from the 8th International Conference "Bioantioxidants." - Moscow, 2010. –P.409-419.

[23] Mishina O.A., Murtazina L.I., Ryzhkina I.S., Lapin A.A., Pavlov T.P, Friedland S.V., The relationship of self-organization, and the antioxidant activity of water solutions of N, N-diphenylguanidine salt of dihydroxylphosphinic acid in a wide range of concentrations. The materials of scientific and practical conference. The scientific questions of current interest: reality and prospects. Tombov, 2012 P.93-94.

[24] Ryzhkina I.S., Murtazin L.I., Sherman E.D., Pantyukova M.E., Masagutova E.M. Pavlov T.P., Friedland S.V, academician Konovalov A.I. Physical and chemical substantiation of a hormetic response of biosystem sewage water treatment solutions to the action of N, N- diphenylguanidine salt of dihydroxylphosphinic acid. DAN, 2, 2011-T.438, P. 207-211.