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Prospects for the Use of the “Wet” Combustion of Organic Wastes in Hydrogen Peroxide for Closed Life Support Systems

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Abstract

The dynamics of processes of mineralization of basic types of organic wastes of biotechnical systems of bioengineering systems of the life support in the medium containing hydrogen peroxide, under the action of the alternating electric current was described. Time and electroenergy were evaluated, as well as the degree of mineralization of wastes at the regime of oxidation corresponding to the maximally effective transition of mineral elements into the form, available to plants. The reverse dependence between the intensity of the mineralization process and such parameters, as the degree of waste mineralization, effectiveness of H_2O_2 and energy use was established.

Key words: life support system, mineralization of organic wastes, hydrogen peroxide

INTRODUCTION

Physicochemical methods of wastes utilization differ favourably from biological methods by short times of processing and the ease of the process control. The “wet” method of combustion in the water medium under the action of the alternating electric current is based on the fact that the molecule of H_2O_2 is a dipole, and it begins to fluctuate and become activated when applying an alternating electromagnetic field. This method of hydrogen peroxide activation eliminates the need to use elevated temperatures and different from the atmospheric pressure for the initiation and maintenance of the process of the oxidation of waste. This gives it undeniable advantages over other physicochemical methods, such as the supercritical water oxidation, Zimpro process or dry combustion under a reduced pressure [1, 2].

The possibility of the efficient use of products of mineralization of organic wastes by the method of “wet” combustion [6] for harvesting the acceptable harvest of higher plants in terms of biotechnical life support systems (BTLSS) was shown in the multi-year research [3–5]. The gas and mineralized solution of some composition obtained as a result of this method do not have a toxic effect on plants and may be involved in turnover mass transfer processes inside the system [7].

The issue regarding the synthesis of hydrogen peroxide within the system is being effectively being solved [8], however, for the process of oxidation of various types of organic wastes there is still no quantitative assessment of its energy consumption, time characteristics and dynamics. Further, the oxidation degree of various types of organic wastes was not established. The goal of this work is the determination of these parameters for processes of mineralization of two types of organic wastes, basic for BTLSS: of the human exometabolites and inedible vegetation of the biomass. The data received can be useful at projecting such systems, building mathematic models of mass exchange flows within the system and searching for ways to improve this method.

RESEARCH METHODS

As mineralized wastes, human exometabolites are taken relatively to the daily allowance norm (10 mL of urine per 1 g of dense wastes), straw of wheat as a model mixture of the plant biomass and mixture of vegetable wastes, similar in composition to the actually obtained vegetable wastes in BTLSS, the so-called working mixture. Straw was selected as a model mixture assuming that about 60 % of all inedible plant biomass in BTLSS is wheat straw, which is characterized by the highest content of cellulose and lignin, in comparison with vegetable wastes of other crops [9]. These compounds are hardly amenable to the radical chain mechanism of oxidation by hydrogen peroxide. Straw and the aboveground part of plants radish and chufa in a weight ratio of 5.31 : 2.25 : 1 became a part of the working system. This ratio was chosen on the ground of the data of experiments with Bios-3 on the productivity of various crops [10] taking into account that up to 50 % of the crop area in BTLSS will be given for wheat, 30 % for chufa and 20 % for other vegetable crops (in this experiment, for radish plants).

The whole inedible plant biomass was dried, grinded and mixed in the dry form in a certain proportion. The dry mass of roots is an insignificant proportion in the total mass of plants, so, leaves only were grinded when working with the inedible biomass. Their quantity corresponded to the total mass of leaves and roots.

Human exometabolites and a model mixture of plant biomass were mixed with hydrogen peroxide (33 %), according to data [6], 4 mL of H_2O_2 per 1 g of dense human wastes, 0.5 mL of per 1 mL of urine and 18 mL per 1 g of straw. Dense and liquid human waste were mixed in the daily ratio (150 g and 1500 mL, correspondingly), therefore, 15 mL of H_2O_2 (33 %) was accounted for 1 g of the dry substance of exometabolites. At mixing peroxide with straw, 50 mL of urine per 1 L of peroxide was added to accelerate up the process of mineralization. At the mineralization of the working mixture of the inedible plant biomass, 33 % H_2O_2 in amount of 10 mL per 1 g of the dry biomass of plants was used, and also distilled water in amount of 7 mL per 1 g of the dry plant biomass was poured to liquefy the mixture. Urine or some salts were not added to improve its electric conductivity were not added into the mixture. Solutions prepared in such a way were kept for 1 day and then mineralized.

The working volume of the solution that was used for the mineralization of human exometabolites is 1200 mL. The oxidation of the model and working mixtures of the plant biomass occurred in the volumes of 1000 and 800 mL, respectively, what is conditioned by the release of large amounts of thick foam and the danger of breakthrough of the reactor.

A series of experiments was preliminary carried out, as a result of which the optimal regime of waste mineralization was selected. The optimality means the process time and degree of mineralization of wastes providing the receipt of acceptable crops of plants [3–5, 7]. Three voltage values for the mineralization of exometabolites and the model mixture (Table 1) were selected: initial (for the process initiation), working (for the process sustaining) and final (for the decomposition of residual quantities of hydrogen peroxide). At the mineralization of the working mixture of the plant biomass the voltage was 200 V during the whole process.

At the mineralization of wastes the voltage and current were recorded, the energy consumption of the process was calculated on their basis. The oxidation degree of the solutions was determined according to the decrease of the total content of residual organic compounds that is indirectly determined according to the value of chemical oxygen demand (COD), as well as the mineralization degree of organic nitrogen

TABLE 1

Energetic characteristics of the mineralization reaction of organic wastes in the reactor of the "wet" combustion

Parameters	Exometabolites	Plant biomass	
		Model mixture	Working mixture
Reaction time, min	150	780	748
Voltage, V:			
initial	100	200	200
working	70	150	200
final	100	200	200
Average current strength, A	4.50	3.96	2.66
Specific energy consumption, W · h/L	776	7950	8450
Efficiency coefficient of the use of H_2O_2, %	15.3	26.6	71.8

(the transition into the ammonium form). When calculating the efficiency coefficient of the use of H_2O_2 the amount of oxygen escaping with a reactor gas mixture as a result of the "parasite" decomposition of H_2O_2 (without oxidation of the organic substrate) was compared with its content in the initial amount of hydrogen peroxide.

RESULTS AND DISCUSSION

The process of wastes mineralization proceeded to the complete decomposition of H_2O_2. Oxidation of human exometabolites lasts almost 2.5 h, the process of oxidation of the inedible plant biomass takes a longer time (see Table 1). To associate such a long reaction time only with low the current strength is impossible. The amount of H_2O_2 (100 %) per 1 L of a solution in case of the mineralization of the model mixture of the inedible plant biomass is three times higher, therefore, this also cannot be the reason of significant differences in time. Besides, almost 0.1 vol. % H_2O_2 remains in solutions with the plant biomass even for 3 to 4 h before the end of the mineralization process. Probably, the duration of the process in this case is due to the fact that when mineralizing compounds that have the inhibiting effect on the oxidation reaction or the stabilizing effect on H_2O_2 are formed (or were present). The inhibition of the oxidation process of organic compounds of H_2O_2 can be achieved by unsaturated monomers and other acceptors of free radicals in a solution [11]. Stabilizers of H_2O_2 can be both metals and organic compounds [12]. It can be seen from Table 1 that at a less intense process, *i. e.* at a lower amperage hydrogen peroxide is used more effectively. For this reason, under conditions of BTLSS it is necessary to select between the rate of the mineralization process and efficiency of the H_2O_2 flow. For energy saving one can increase the electrical conductivity of the solution by adding salts or mixing wastes of different types.

The dynamics of the current strength change (Fig. 1) displays well the change in the electrical conductivity of the solution over time and some processes occurring in the reactor. The current strength correlates with indications of the voltage: stepwise amperage increase and decrease in case of the mineralization of exometabolites and the model mixture of the plant biomass is due to switching voltage. Zigzagging oscillations in the graph of the model mixture are caused by strong foaming of the solution and its transfusion from the capacity of the reactor into the foam tank and back

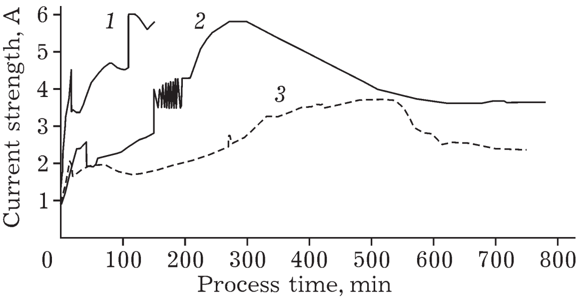

Fig. 1. Dynamics of the change of the current strength when oxidizing the wastes in the reactor of the «wet» combustion: *1* – exometabolites, *2* – model mixture, *3* – working mixture.

(see the device of the reactor in [6]), as a result of which the solution level and current strength range. The continuous increase in the current strength at the constant voltage is due to the fact that the electrical conductivity of the solution first increases when heated (the temperature increased from 18 to almost 100 °C for 30–40 min and remained constant at this level until the process end) and then at the release of ions in the mineralization process. It is obvious that as ion release, the availability of mineral elements for the plant nutrition increases. With a greater intensity the mineralization process occurred in the solution of exometabolites, what is associated with the absence of such difficultly oxidizable compounds, as lignin and cellulose.

With a certain moment, the current strength decreases gradually to a certain value and then does not change. This is conditioned by the growth of the precipitation degree and salts contained in it as a result of the fact that processes of mixing caused by the convection and formation of gas slow down. In the reactor, this picture can be observed through the quartz body. In order to establish the cause of the degree of deposition increase we carried out experiments, where the dynamics of pH was determined. Samples were taken every 30 min at mineralizing exometabolites and every hour at mineralizing the model mixture of vegetable wastes; the sample volume was 40 mL. Before the analysis samples were cooled and then returned to the reactor.

It has been established that increasing the degree of deposition of precipitation is due to the increase of the value of the pH of the solution (Figs. 2, 3). The mineralization time of exometabolites exceeds 2.5 h, since the samples returned to the reactor cool the solution and thus decrease the process intensity. With time, ammonia volatilized from the solution and the pH value decreased to 6.9. As a consequence, the deposition degree of the precipitate did not increase and current strength did not change. In the control variant (the mineralization of exometabolites without measuring the pH dynamics) the factors indicated above are absent and the dynamics of the current strength did not differ from the one presented in Fig. 1. A small increase of the current strength at the end of the reaction is apparently associated with a partial output of ammonia from the solution. The acidity of the control solution was pH 8.3. The fact that volatilization of NH_3 affects the pH value is evidenced by the difference in the content of ammonia: for the test and control variants it is 1000 and 1200 mg/L, correspondingly.

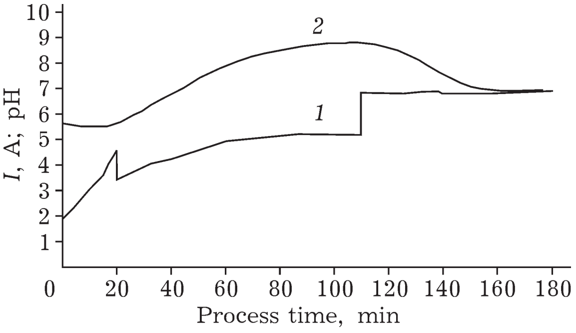

Fig. 2. Dynamics of the change of the current strength (*I*) (*1*) and pH (*2*) at oxidation of exometabolites.

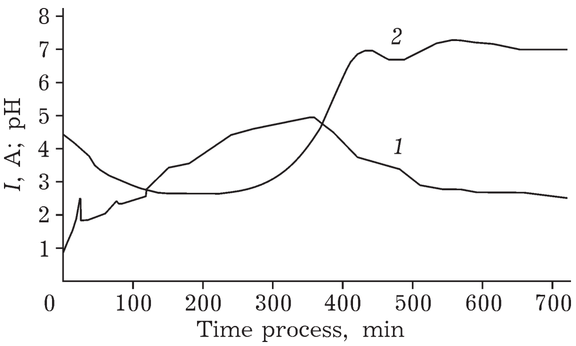

Fig. 3. Dynamics of the change of the current strength (*I*) (*1*) and pH (*2*) at oxidation of model mixture of vegetable wastes.

In case of mineralizing the model solution of vegetable wastes, the dependence between increasing pH and decreasing the electrical conductivity with the increase of the precipitation degree is obvious (after 350 min).

It is noteworthy that the dynamics of the change of pH at the mineralization of exometabolites and vegetable wastes differs considerably. When oxidizing plant wastes the initial decrease of the value of pH is more pronounced. In order to explain this fact, all processes occurring in the reactor can be divided into two types: the first ones lead to the decrease of the pH, second ones result in its growth. Processes of the first type can be related to: 1) the release of organic acids and inorganic acidic residues into the solution ac-

TABLE 2

Characteristics mineralized of solutions of organic wastes

Parameters	Exometabolites	Plant biomass	
		Model mixture	Working mixture
COD, g/L	7.901	1.847	4.417
Degree of mineralization, %	60.7	95.8	94.1
Content of organic nitrogen, g/L	4.0*	0.3	0.3
Degree of mineralization of organic nitrogen, %	38	45	55
Content of lipids, g/L	0.7	0.1	0.3
pH	8.6±0.1	7.2±0.1	6.6±0.1
Content of the precipitate, g/L	4.7	3.7	5.8

Note. Relative error of the determination does not exceed 10 %.

* 3.5 g/L in the form of urea.

companied by its oversaturation with carbon dioxide as the oxidation of the organic substance; 2) the formation of organic acids in the process of oxidation and hydrolysis of various compounds. Processes of the second type include the release of metals ions at the oxidation of the organic substance and deamination of amino acids. Processes of the first type prevail initially due to the destruction of easily oxidizable compounds and initial formation of organic acids; then CO_2 volatilizes gradually, acids are destroyed, as a result, the value of pH increases. Human exometabolites are initially more oxidized products than vegetable wastes, therefore, processes of the formation of organic acids in this media and the decrease of pH is likely to manifest themselves here weaker. For a definite answer to this question it is necessary to further explore the chemism of the process.

Almost 0.1 vol. % of hydrogen peroxide still remains in solutions by the moment of the strength of current decrease, however, the reactor gas ceases to release. Therefore, at the moment of the decrease of the electric conductivity oxidative processes are practically terminated and then only the decomposition of residual amounts of H_2O_2 occurs. Oxygen evolved at the decomposition of residual H_2O_2 is likely to interact with metals in a solution forming bases and therefore, is not allocated, which also increases the alkaline reaction of the medium (see Figs. 2, 3 and Table 2) and promotes the volatilisation of ammonia. Nevertheless, in order to check this assumption, the profound analysis of processes occurring at mineralization is necessary.

It follows from the data obtained that energy flows in BTLSS should be established thus to provide preliminary heating of the solution with wastes to the working temperature or close to it. The intensity of mineralization process can be judged about by the change of the strength of current and if necessary H_2O_2 should be added by portions releasing metal ions into the solution, what probably will allow using it more efficiently.

The highest oxidation state has been achieved in case of the working and model mixtures of vegetable waste (see Table 2) due to the fact that the intensity of this process is lower, in comparison with the mineralization of exometabolites. The reverse dependence of the oxidation state products from the intensity of the mineralization process is confirmed by the fact that the degree of exometabolites mineralization in tests on the determination of dynamics of pH (*i. e.* when the oxidation process slowed down as a result of periodical cooling) is equal to 74.3 %.

The value of COD (70–75 % falls on the residue) depends on the ratio of the classes of organic compounds present in the solution [13] and it is more interest in terms of the study of cycles of H, C and O in the system, since according to it one cannot judge of the availability of mineral elements for plants. The highest content of lipids almost completely remaining in the residue is observed for mineralized exometabolites, what explains partially the high value of COD. Herewith, the degree of nitrogen mineralization in exometabolites is lowest, however, 65 % of initial nitrogen remains in the composition of urea, no less than 80 % of which is saved after oxidation. The amount of unavailable nitrogen in all cases reaches around 180 mg/L, about the availability of other mineral elements can be indirectly judged by the effective growing harvests [3–5, 7].

CONCLUSION

The reverse dependence between the efficiency coefficient of H_2O_2 use and energy consumption, on the one hand, and intensity of the course of the process, on the other hand, was established. The depth of mineralizing wastes also has the reverse dependence from the process intensity and increases with increasing the availability of the material for the oxidation with hydrogen peroxide. In all cases of recycling organic wastes the mineralization regime has been worked out that allows converting maximally efficiently mineral compounds into the form, available to plants. Further attempts to lower values of COD of wastes will result in a decrease in the efficiency coefficient of the use of H_2O_2 and increase of the process time and energy consumption.

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