

Intensification of biological wastewater treatment using ionic liquids

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Abstract. In this article, biologically active tris-(2-hydroxyethyl) ammonium ionic liquids (IL) of the general formula $[N(CH_2CH_2OH)_3H]^+ \cdot ^-O(O)CCH_2YAr$ (where Ar = aryl, Y = O, S, SO₂) are studied as stimulators of biological wastewater treatment intensification (concentration is 10⁻⁴-10⁻⁸% mass). It was found that ionic liquids being introduced into the active sludge favorably influence the microorganisms of the activated sludge. When biostimulants are used, the biological wastewater treatment passes more intensively, and the indices of contaminants, such as ammonium ions and surfactants, decrease.

1 Introduction

The livelihoods of settlements and the ecological situation of water sources have a close relationship with the technical state of the water disposal system. The urgency of the problem of removing biogenic elements and surfactants from wastewater (hereinafter referred to as surfactants) is due to the ever increasing degree of eutrophication of surface water bodies, which determines the ecological situation, both in Russia and abroad, to a large extent [1].

The most common method for removing organic and biogenic constituents from wastewater is biological treatment in aerated lagoons [2].

Significant reserves for increasing the efficiency of biological treatment processes consist in the use of chemical stimulators of biochemical oxidation. Currently, a search is being carried out for new synthetic bioregulators capable of increasing the rate of wastewater treatment at low and ultra-low concentrations. This approach significantly reduces the consumption of the bioregulator and excludes its effect on purified water [1].

2 Materials and methods studies

In this paper, we analyze the effect of five ionic liquids, the formulas of which are presented in Table 1, on the microorganisms included in the active sludge.

A prerequisite for the work was the investigation of biologically active tris-(2-hydroxyethyl) ammonium ionic liquids (IL) of the general formula $[N(CH_2CH_2OH)_3H]^+$.

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-O(O)CCH₂YAr (where Ar = aryl, Y = O, S, SO₂) as growth stimulators of the *Saccharomyces cerevisiae* yeast (concentration 10⁻⁴-10⁻⁸% mass) [2, 3, 4].

The study was carried out on the actual household wastewater (HW) of urban treatment facilities in the Pravoberezhny District of Irkutsk.

Table 1. Formulas of ionic liquids.

| No. | Gross formula | Mol. the weight | Mp, °C |
|-----|---|-----------------|--------|
| 1 | C ₁₄ H ₂₂ ClNO ₅ S | 351.88 | 77-78 |
| 2 | C ₁₄ H ₂₂ ClNO ₇ S | 383.88 | 92-94 |
| 3 | 2-C ₁₄ H ₂₂ ClNO ₆ | 335.78 | 80 |
| 4 | 4-C ₁₄ H ₂₂ ClNO ₆ | 335.78 | 80-82 |
| 5 | C ₁₆ H ₂₄ N ₂ O ₅ S | 356.45 | 92-93 |

To obtain different concentrations of ionic liquids, a matrix solution (100 mg of IL dissolved in distilled water in a 100 ml volumetric flask) was diluted in distilled water in a ratio similar to that of [4].

The sludge index was calculated by [5], where the influence of IL on sludge is presented in 16 hours.

With the help of such an indicator as dehydrogenase activity, we determined the physiological state of the activated sludge. The dehydrogenase activity is determined by a standard procedure [6].

The effect of ionic liquids on the growth dynamics of the isolate from the active sludge *Micrococcus luteus* was determined by increasing the optical density of the culture fluid, which characterizes the increase in the number of cells of the microorganism (strain) from the active sludge *Micrococcus luteus*. The environment for the transfer of the strain was the meat-peptone medium (MBP). The results of the incubation of the crops for 20 hours in a thermostat at 30 ° C are shown in Table 3.

These ILs were introduced into the flasks of 100 ml of the sludge mixture, reaching concentrations of 1 · 10⁻² % by weight to 1 · 10⁻⁸ % by weight. The control sample was performed without introducing a biostimulator (IL) into it. After determining the initial reading for ammonium and antifreeze, all the flasks (control and with the product) were aerated. The indications of the ammonium and surfactant content on Tables 4 and 5 were determined every two hours, for 4 hours, both in the control experiments and in water with the product

Measurement of the mass concentration of ammonium ions was carried out using a photometric method with a Nessler reagent [7].

The mass concentration of surfactants was determined by the extraction-photometric method according to [8]. For the colorimetric determination, sodium lauryl sulfonate (dodecylsulfonate) C₁₂H₂₅SO₃Na.

3 Results and analysis

The effect of the compounds studied on the intensification of biological purification can be seen through the range of changes in the sludge index after the addition of IL to the samples of the mud mixture and is presented in Table 2.

The range of values of the sludge index within 150 - 200 characterizes the normally operating sludge, therefore, the use of all ionic liquids, except IL No. 2, has a beneficial effect on the sedimentation characteristics of the mud.

The dehydrogenase activity of the sludge was carried out for each test sample, the data are presented in Figure 1.

Table 2. Results of determination of the sludge index of activated sludge with addition IL at a concentration of $1 \cdot 10^{-6}$ % of the mass.

| Sample No. | Filter weight, g | Filter weight with dried precipitation, g | Silt dose by volume, cm^3/dm^3 | Silt dose by weight, g/dm^3 | Sludge index, cm^3/g |
|------------|------------------|---|--|---|--------------------------------------|
| Control | 1,12 | 1,55 | 800,00 | 4,30 | 186,05 |
| IL No. 1 | 0,86 | 1,31 | 830,00 | 4,50 | 184,44 |
| IL No. 2 | 1,20 | 1,59 | 835,00 | 3,90 | 214,10 |
| IL No. 3 | 1,00 | 1,41 | 820,00 | 4,10 | 200,00 |
| IL No. 4 | 0,96 | 1,40 | 760,00 | 4,40 | 172,73 |
| IL No. 5 | 1,18 | 1,62 | 840,00 | 4,40 | 190,91 |

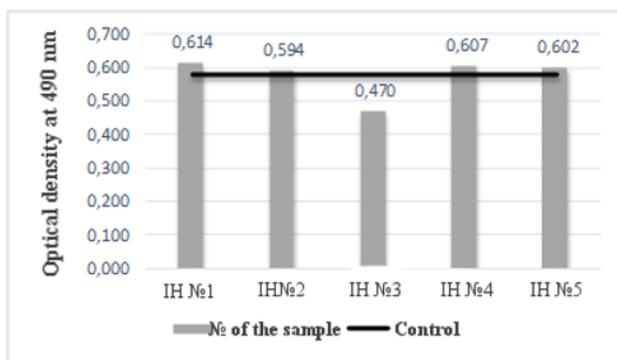


Fig. 1. Effect of ionic liquids on dehydrogenase activity of sludge.

By dehydrogenase activity, it is seen that the optical density of all samples, except IL No. 3, exceeds the optical density of the control. This factor indicates that in these samples the number is higher and the work of microorganisms is more effective.

The results of the study of the determining the effect of ionic liquids on the dynamics of growth of the isolate from the active sludge *Micrococcus luteus* are given in Table 3.

Table 3. Determining the influence of IL on the dynamics of growth of the isolate from the active sludge *Micrococcus luteus*.

| Sample No. | The results of spectrophotometric determination of the optical density at the concentration of IL 10^{-6} in the MPB medium through | | | | | |
|------------|---|---------|---------|----------|----------|----------|
| | 0 hours | 2 hours | 4 hours | 16 hours | 17 hours | 20 hours |
| Control | 0,245 | 0,282 | 0,312 | 0,344 | 0,381 | 0,474 |
| IL No. 1 | 0,250 | 0,298 | 0,305 | 1,133 | 1,190 | 1,372 |
| IL No. 2 | 0,259 | 0,350 | 0,343 | 1,142 | 1,103 | 1,236 |
| IL No. 3 | 0,239 | 0,282 | 0,302 | 0,330 | 0,413 | 0,655 |
| IL No. 4 | 0,268 | 0,300 | 0,315 | 0,856 | 0,842 | 1,672 |
| IL No. 5 | 0,262 | 0,316 | 0,316 | 0,605 | 0,777 | 1,022 |

Comparing the rate of growth of the strain number, it can be concluded that microorganisms in samples with ionic liquids already at the sixteenth hour begin to manifest themselves as a good stimulant for increasing the number of microorganisms.

Based on the results of these experiments, the IL No. 1 and No. 4 were chosen, because they proved to be good stimulants of activated sludge. Subsequently, studies were conducted with concentrations ranging from 10^{-2} to 10^{-4} % mass.

The effect of the compounds studied on the intensification of biological wastewater treatment in determining the mass concentration of surfactant and ammonium using the ILs No. 1 and No. 4 is presented in Tables 4 and 5.

Table 4. Determining the mass concentration of ammonium, mg / dm³ in domestic HW during its purification by means of active silt with adding the ILs No. 1 and No. 4.

| Samples | 0 hours | 2 hours | 4 hours |
|---------------------------|---------|---------|---------|
| Control | 3,81 | 3,69 | 2,86 |
| IL No. 1·10 ⁻² | 3,81 | 3,50 | 2,19 |
| IL No. 1·10 ⁻³ | 3,81 | 2,85 | 2,76 |
| IL No. 1·10 ⁻⁴ | 3,81 | 2,99 | 2,33 |
| IL No. 4·10 ⁻² | 3,81 | 2,00 | 1,86 |
| IL No. 4·10 ⁻³ | 3,81 | 2,80 | 2,54 |
| IL No. 4·10 ⁻⁴ | 3,81 | 2,68 | 1,56 |

The content of ammonium gradually decreases over 4 hours, especially with the IL No. 1 in concentrations of 10⁻³ – 10⁻⁴ % mass and the IL 4 in the concentration of 10⁻⁴ % mass.

Table 5. Determining the mass concentration of surfactants in domestic HW during its purification by means of active silt with adding the ILs No. 1 and No. 4.

| Sample No. | Concentration of surfactants, mg / dm ³ | | |
|---------------------------|--|---------|---------|
| | 0 hours | 2 hours | 4 hours |
| Control | 20,56 | 18,36 | 17,49 |
| IL No. 1,10 ⁻² | 20,56 | 18,47 | 17,49 |
| IL No. 1,10 ⁻³ | 20,56 | 15,00 | 16,91 |
| IL No. 1,10 ⁻⁴ | 20,56 | 16,45 | 18,59 |
| IL No. 4,10 ⁻² | 20,56 | 19,28 | 18,30 |
| IL No. 4,10 ⁻³ | 20,56 | 18,53 | 17,43 |
| IL No. 4,10 ⁻⁴ | 20,56 | 15,69 | 14,77 |

The content of surfactants for 4 hours is gradually reduced in samples with the IL No. 4, especially the concentration of 10⁻⁴ % by weight. Samples with IL No. 1 are significantly less for 2 hours, better at 10⁻³ %.

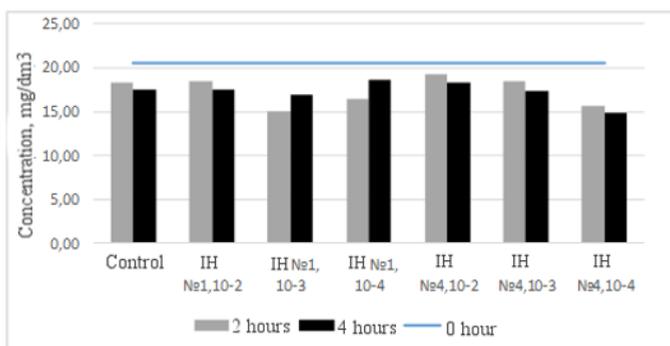


Fig. 2. The diagram of the determination of the mass concentration of surfactants in the domestic and domestic HW during its purification by means of active silt with the addition of ILs No. 1 and No. 4.

4 Conclusions

Based on the results of the experiments, it can be concluded that, with the use of ionic liquids, the HW biological purification is more intensive, and the pollution indices decrease

(in comparison with the parameters of control samples) [2]. The obtained data add a list of previously studied safe methods of activation of biological wastewater treatment [2, 10, 11]. Within the framework of our research, the ILs have been tested for toxicity by various biotests [2, 12].

The advantage of the biostimulants studied is their availability, low cost, good water solubility, storage stability, non-toxicity, efficacy at low concentrations ($1 \cdot 10^{-4}$ - $1 \cdot 10^{-8}$ %)

Analyzing the research results, it can be concluded that, due to the use of ionic liquids (especially No. 1 and No. 4), it is possible to shorten the time of biological purification from biogenic elements and surfactants to about two hours, thus reducing the volume of aerated lagoons when used in new treatment facilities.

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