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Possibilities of using ozone for the treatment of wastewater from the yeast industry

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Abstract. The purpose of the study was to establish if ozonation can be used to enhance the process of purifying wastewater from the yeast industry. The results of the experiments indicate that ozonation can be used in the tertiary treatment of yeast wastewater for the reduction of colour, odour, and the overall concentration of contaminants. During ozonation, the biodegradability of the wastewater increased; therefore it is possible to include ozonation into the combined purification process simultaneously with anaerobic and aerobic bio-oxidation. In addition, the application of ozonation as a pre-treatment method for anaerobic digestion of excess sludge from wastewater treatment plants was studied. Ozonation of the excess sludge resulted in a reduction of the sludge amount and increased the solubility of sludge organic matter. Although the solubility of sludge increased, the process of anaerobic mesophilic digestion was not improved.

Key words: ozonation, yeast wastewater, excess sludge, anaerobic digestion.

INTRODUCTION

The food industry is one of the contributors of wastewater pollution. The total amount of the wastewater is not large but the level of its contamination is very high. Also, the composition of wastewater varies considerably with each branch and mill type of the industry.

The wastewater from the yeast industry is characterized by a high chemical oxygen demand (COD), dark colour, and high concentrations of total nitrogen (N_{tot}) and non-biodegradable organic pollutants. Most of the contaminants in the

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wastewater are due to the use of molasses as a main raw material. As a by-product of sugar manufacturing, molasses contains 45–50% residual sugars, 15–20% non-sugar organic substances, 10–15% ash (minerals), and about 20% water. During yeast fermentation, the sugars contained in the molasses are a source of carbon and energy. However, a major part of the non-sugar substances in the molasses are not assimilable by the yeast and are released unchanged to the processing wastewater. These compounds represent the principal waste from the yeast production process. In addition, the chemicals added during fermentation (e.g. antifoams, propionic acids, brine, etc.), yeast metabolites, and residual yeast cells are in the wastewater.

In Estonia, Salutaguse Yeast Factory produces about 330 m^3 of wastewater per day, which is currently treated with a combination of anaerobic/anoxic biological oxidation followed by aerobic stages with activated sludge (Fig. 1). The raw wastewater contains high concentrations of organic pollutants (25 020 mg L^{-1} total chemical oxygen demand, COD_{tot}; 23 420 mg L^{-1} soluble chemical oxygen demand, COD_{sol}), nutrients (1470 mg L^{-1} of total nitrogen, N_{tot}; 100 mg L^{-1} of total phosphorus, P_{tot}), and sulphates (2940 mg L^{-1} SO_4^{2-}).

Salutaguse Yeast Factory has developed and improved its biological wastewater treatment process during the last years to reach effluent targets. However, the current technology is still not optimal as the total treatment efficiency in terms of COD is only about 80%. Even after multi-step biological treatment, the wastewater contains a relatively high amount of pollutants – mainly slowly biodegradable or non-biodegradable compounds such as melanoidins. Melanoidins are the high molecular weight polymers responsible for the brown colour, residual COD, and nitrogen in baker's yeast effluent [1].

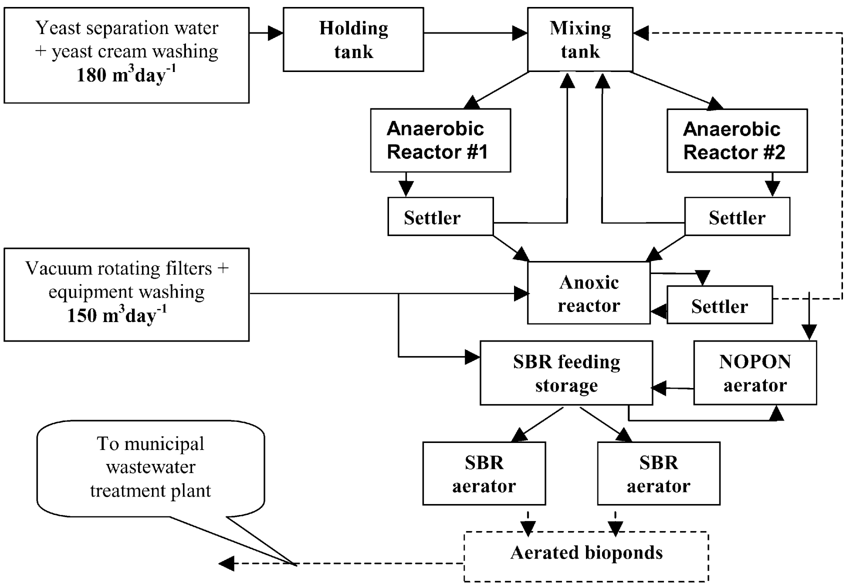

Fig. 1. The technological set-up used in Salutaguse Yeast Factory (Kohila, Estonia).

In summary, the main problems in the treatment of yeast wastewater are high concentration of COD in the effluent, colour, odour, and a high amount of excess sludge generated in the wastewater treatment process.

If a higher degree of purification is required, biological purification can be used in combination with other processes such as physico-chemical, chemical, or advanced oxidation processes [2]. Advantages of ozonation in treatment applications are removal of toxicity, destruction of organic matter, and enhancement of the biodegradability of recalcitrant wastewaters [3]. Ozone pre-treatment has been used to improve subsequent biodegradation [4–6]. In addition, ozonation can also increase the biodegradability of previously biologically treated wastewaters [7], thus enabling the use of an additional biological treatment stage, and repetitive treatment schemes. Presently, special attention is paid to the recycling combinations of biological treatment and ozonation [8, 9] where increased discharge quality at decreased oxidant consumption was obtained. It has been shown that a combined method, aerobic bio-oxidation with ozonation of recycled biologically treated wastewater, enabled improvement in purification efficiency at low ozone dosages [10, 11].

Another concern is the reduction of the excess sludge. According to new regulations, in effect since 2001, the priority is to develop new ways to reduce the amount of waste (excess sludge) on-site and to recycle biomass as much as possible [12]. Anaerobic digestion is an economical and environmentally friendly strategy for solving this problem. At present, a million tonnes of organic wastes are digested per year [13]. These are converted to biogas and to a stabilized residual matter. Today the anaerobic digestion method for sludge stabilization is used in Estonia too.

Anaerobic digestion of excess sludge is a multi-stage process and it is generally limited by the rate of hydrolysis of suspended matter and organic solids [13]. This stage of digestion is very important and therefore it is reasonable to carry it out in a separate reactor as a pre-treatment process. There are several methods that can be used: mechanical methods, ultrasonic disintegration, chemical methods, thermal pre-treatment, and aerobic and anaerobic pre-treatment [14]. Most of these methods have an influence on mesophilic anaerobic digestion and result in a better supply of soluble substrate to methanogenic bacteria.

The aim of this study was to establish if the application of ozone can enhance the purification of yeast wastewater, and improve the pre-treatment of excess sludge.

MATERIALS AND METHODS

Post-ozonation of biologically treated wastewater

In the experiments of post-ozonation, biologically treated yeast wastewater from Salutaguse Yeast Factory was used. Samples of wastewater were taken over a period of two months. This biologically treated wastewater had a relatively

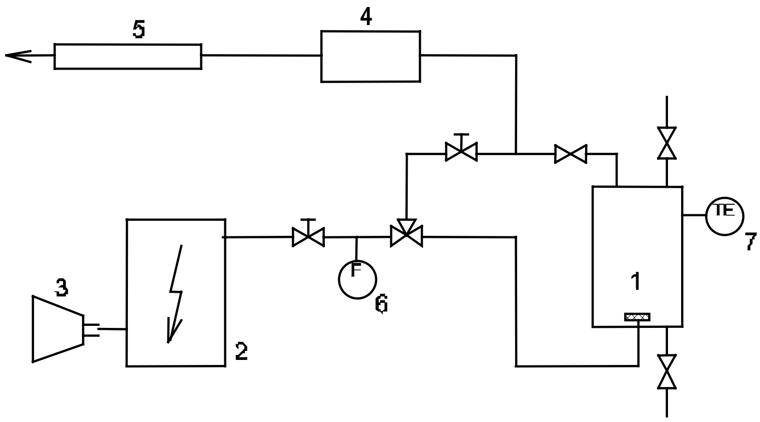

Fig. 2. Laboratory set-up for batch ozonation. 1 – semi-batch reactor, 2 – ozone generator Ozon-2M, 3 – air compressor, 4 – ozone analyser Anseros GM-6040, 5 – residual ozone destruction unit, 6 – flow meter, 7 – thermometer.

high residual COD and brown colour. The values of the most important parameters were: COD – 1500–2200 mg L^{-1}, BOD – 160–310 mg L^{-1}, pH – about 8.

Figure 2 illutrates the laboratory set-up used in the experiments of post-ozonation. Ozonation of wastewater was conducted in a 0.9-L semi-batch glass reactor with a continuous gas flow through the liquid. This ozone–air gaseous mixture was generated in the ozone generator OZON-2M. The ozone–air mixture was introduced to the bottom of the reactor through a ceramic diffuser. Wastewater was ozonated until an ozone breakthrough was observed after a period of complete ozone absorption by the wastewater. The experiments were carried out without adjusting the pH.

Pre-ozonation of excess sludge

In this part of the study, the influence of pre-ozonation of excess sludge on its anaerobic mesophilic digestion was tested.

The ozonation of the sludge was carried out in a laboratory set-up analogous to that shown in Fig. 2. The batch reactor was a 1.3-L glass reactor supplied with a foam destructor. The sludge was ozonated for 20, 105, and 240 min, with the corresponding consumed ozone doses of 23.8, 89.0, and 313.3 mgO_3 L^{-1}.

In the following tests of anaerobic digestion, mesophilic anaerobic inoculation sludge (10% of the total volume of the reactor) was added to the pre-ozonated sludge to initiate a mesophilic anaerobic digestion process. Flasks (volume 1.0 L) containing sludge mixture were then placed into an air-thermostat at mesophilic temperature conditions (35 ± 1 °C). Anaerobic digestion was carried out for 27 days. The flux of the generated biogas, a criterion for the evaluation of the process efficiency, was measured continuously.

Analyses

The amount of total organic matter in the wastewater was determined as chemical oxygen demand of unfiltered sample COD_{tot}, the amount of soluble organic matter as COD of filtered samples COD_{sol}, and the amount of bio-degradable organic matter as seven-day bio-chemical oxygen demand BOD. In addition, the pH of the wastewater was measured.

For sludge, the following concentrations were measured: COD of sludge mixture (COD_{tot}) and its supernatant, the solubilized fraction (COD_{sol}), and total suspended solids (TSS).

Analyses of COD were conducted using HACH reagents and equipment according to the standard methods. BOD was determined using procedure 5210 of the Standard Methods for the Examination of Water and Wastewater. The pH was measured with an Evicon E6121 pH-meter. Ozone concentration in gaseous phase was measured with an ozone analyser Anseros GM-6040.

RESULTS AND DISCUSSION

Post-ozonation of biologically treated wastewater

The results of the post-ozonation of biologically treated yeast wastewater are presented in Table 1. The experiments indicated that the efficiency of post-ozonation in terms of COD (COD removal) ranged from 30% to 49%, and the ratio dn/ΔCOD, consumed ozone dosage mg of ozone per mg of COD removed, ranged from 1.2 to 2.5.

Figures 3 to 7 express the dependence of COD_{tot}, COD_{sol}, BOD, and BOD/COD, the biodegradability of the wastewater, on the consumed ozone dose dn (mg of ozone per litre of treated wastewater). The ozone dosage required to decrease the residual COD noticeably was about 1000–1500 mg L^{-1}, and both COD_{tot} and COD_{sol} decreased. This indicates that during post-ozonation the particulated organic matter in the wastewater was partly solubilized and the soluble matter was being oxidized.

Table 1. Results of post-ozonation of biologically treated wastewater

Run	Parameters of biologically treated yeast wastewater			Consumed ozone dosage, dn/ΔCOD, mgO_3 $mgCOD^{-1}$	Efficiency of post-ozonation ΔCOD, %	Parameters of wastewater after post-ozonation		
	COD_{tot}, mg L^{-1}	BOD, mg L^{-1}	BOD/COD			COD_{tot}, mg L^{-1}	BOD, mg L^{-1}	BOD/COD
1	2055	161	0.08	2.45	30	1460	317	0.22
2	2120	579	0.27	2.47	31	1470	381	0.26
3	1480	204	0.14	2.2	34	970	310	0.32
4	1860	308	0.17	1.2	49	940	297	0.32
5	1940	147	0.08	1.6	30	1430	250	0.17

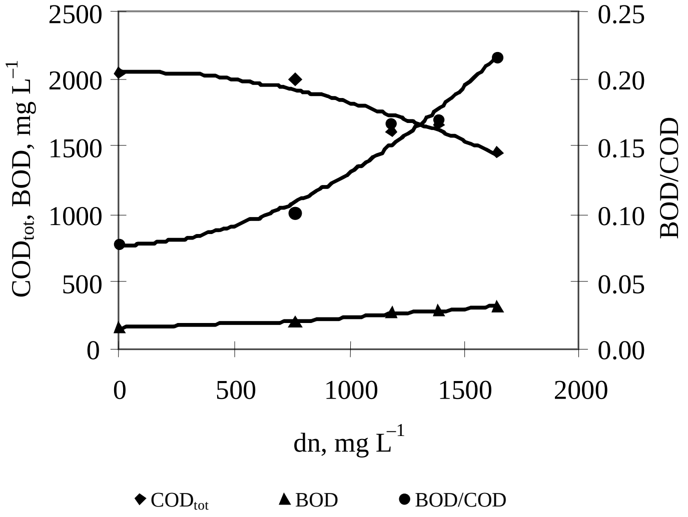

Fig. 3. The effect of ozone dosage (dn) on COD_{tot}, BOD, and the ratio BOD/COD of biologically treated yeast wastewater (run 1). The pH rose from 7.3 to 7.9.

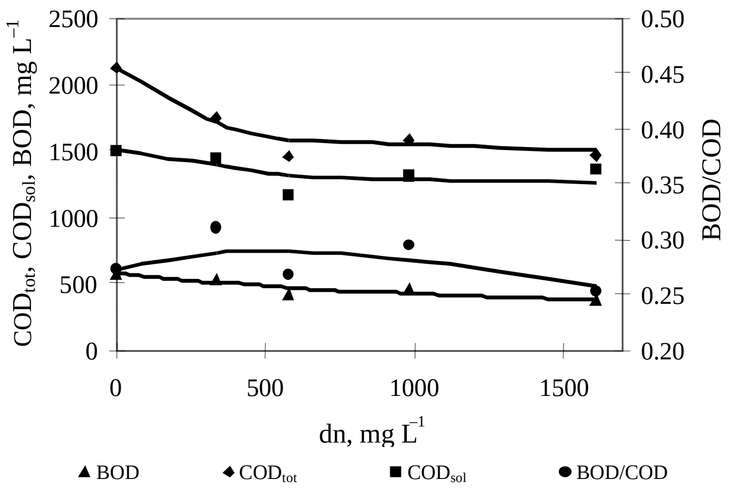

Fig. 4. The effect of ozone dosage dn on COD_{tot}, COD_{sol}, BOD, and BOD/COD of biologically treated yeast wastewater (run 2). The pH fell from 8.3 to 8.1.

As a rule, the results of the post-ozonation of yeast wastewater depend on the wastewater composition and consequently on the previous process of biological purification. BOD and biodegradability (BOD/COD) of the wastewater increased during ozonation, as shown in Figs 3, 5, and 7. In run 2, illustrated in Fig. 4, BOD decreased. This can be explained by the low efficiency of the biological treatment before ozonation. The biologically treated water contained a large amount of biodegradable compounds – COD_{tot} was 2120 mg L^{-1} and BOD was 580 mg L^{-1}. Even in this case, the biodegradability was initially enhanced by ozonation (at ozone dose of 300 mg L^{-1}) followed by a decrease. In run 4 (Fig. 6), BOD decreased slightly, and the biodegradability increased in this case due to a faster decrease in COD.

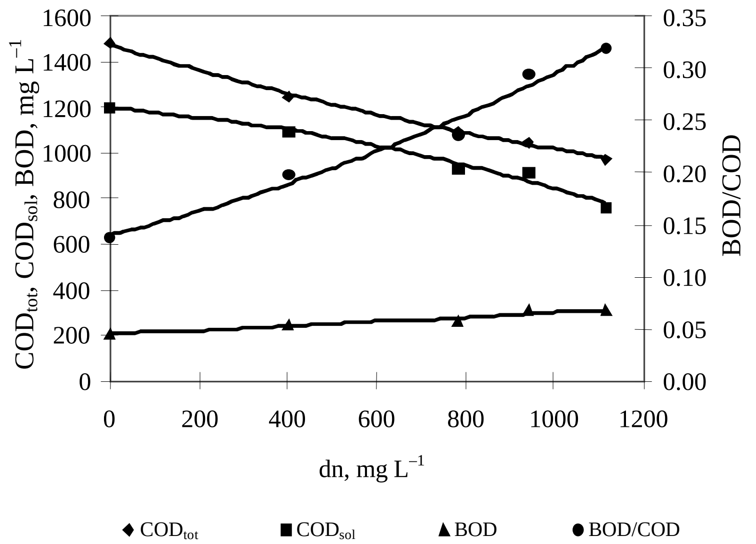

Fig. 5. The effect of ozone dosage dn on COD_{tot}, COD_{sol}, BOD, and BOD/COD of biologically treated yeast wastewater (run 3). The pH rose from 7.3 to 7.9.

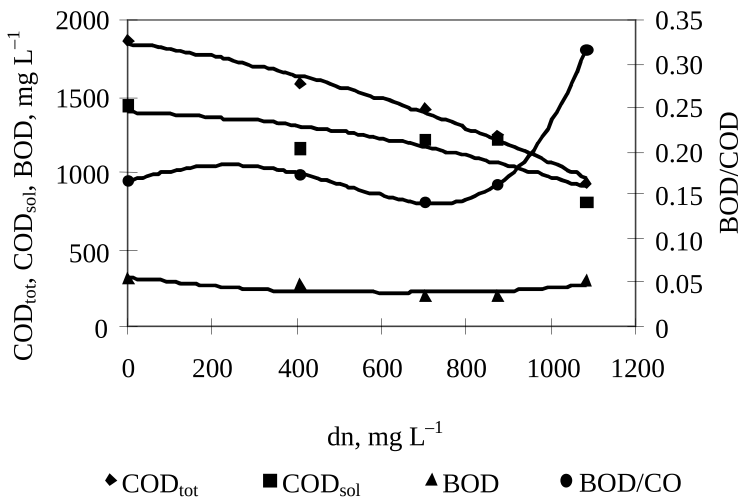

Fig. 6. The effect of ozone dosage dn on COD_{tot}, COD_{sol}, BOD, and the ratio BOD/COD of biologically treated yeast wastewater (run 4). The pH rose from 7.3 to 7.9.

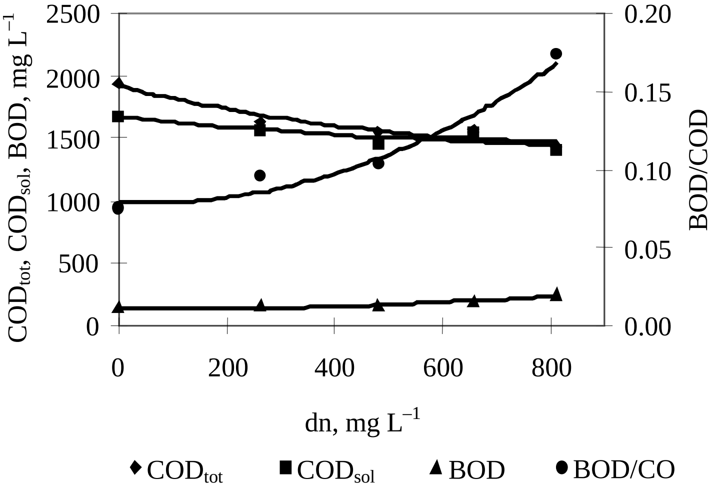

Fig. 7. The effect of ozone dosage (dn) on COD_{tot}, COD_{sol}, BOD, and the ratio BOD/COD of biologically treated yeast wastewater (run 5). The pH rose from 7.9 to 8.4.

Generally, during ozonation the pH decreases as a result of the formation of carboxylic acids. However, in the experiments of post-ozonation of the yeast wastewater, the pH decreased only in run 2. In all other runs the pH increased. The reason could be that acidic products of biochemical oxidation had been degraded by ozone.

In all cases, ozonation removed the colour and distinct odour of the treated wastewater. Initially, the biologically treated wastewater was dark brown and had a distinct odour, and after ozonation it was practically transparent and colourless with no odour specific to this wastewater.

The post-ozonation experiments indicate that ozonation can be used in the tertiary treatment of yeast wastewater for the reduction of colour, odour, and overall concentration of organic contaminants and matter. Since the biodegradability of the yeast wastewater increased during the ozonation, or at least at the beginning of post-ozonation, it is possible to include ozonation into the combined purification process simultaneously with anaerobic and aerobic bio-oxidation. In the combined process, the goal of ozonation is enhancement of biodegradability and removal of colour and odour. Taking into account that ozonation is still an expensive technology, the last option – application of ozonation in combinations with biological methods – may be more economical for yeast wastewater purification than ozonation alone.

Pre-ozonation of excess sludge

During the experiments raw sludge (COD_{tot} 85 000 mg L^{-1}, COD_{sol} 5300 mg L^{-1}, and TSS 39 200 mg L^{-1}), sludge after pre-treatment and after anaerobic mesophilic digestion process were analysed.

Table 2. Main results of sludge pre-treatment with ozone

Consumed ozone dosage, mgO_3 L^{-1}	Sludge characteristics								
	COD_{tot}, mg L^{-1}			COD_{sol}, mg L^{-1}			TSS, mg L^{-1}		
	Raw sludge	After pre-treat-ment	ΔCOD, %	Raw sludge	After pre-treat-ment	ΔCOD, %	Raw sludge	After pre-treat ment	ΔTSS, %
0	85 000			5300			39 200		
23.8	85 000	64 000	25	5300	7000	–32	39 200	34 100	13
89.0	85 000	70 000	18	5300	6500	–23	39 200	35 900	8
313.3	85 000	73 000	14	5300	7500	–42	39 200	36 200	8

The main results of the pre-ozonation of excess sludge are shown in Tables 2 and 3. These tables contain a control experiment without ozonation for direct comparison.

During sludge pre-treatment COD_{tot} decreased by up to 25% as a result of the oxidation of organic materials. COD_{sol} of the pretreated sludge was higher than that in the control reactor because the products of ozonation (alcohols, aldehydes, organic acids) are more soluble than the initial organic material. Thus ozonation enabled us to transfer more organic matter into soluble form (the COD_{sol} increase 42%) and as a result the amount of sludge (as TSS) decreased by up to 13%.

The results of the anaerobic digestion process are shown in Table 3.

During the mesophilic anaerobic stage of digestion, the best results were achieved in the control sample without ozonation. The decomposition of organic matter was 70%, the amount of total suspended solids decreased by up to 35%, and as a result, the best biogas production occurred (up to 0.01 m^3 kg^{-1} COD_{tot} removed).

The pre-treatment has to be evaluated by its effects on the overall process. The ozone pre-treatment did not improve the mesophilic anaerobic digestion process (COD_{tot} and TSS removal and biogas production were lower than in the control experiment) and therefore cannot be used for this purpose.

Table 3. Main results of the anaerobic sludge digestion process

Consumed ozone dosage in sludge pre-treatment, mgO_3 L^{-1}	Sludge characteristics								
	COD_{tot}, mg L^{-1}			COD_{sol}, mg L^{-1}			TSS, mg L^{-1}		
	Before MAD	After MAD	ΔCOD, %	Before MAD	After MAD	ΔCOD, %	Before MAD	After MAD	ΔTSS, %
0	85 000	25 400	70	5300	3470	35	39 200	25 400	35
23.8	64 000	30 700	52	7000	8220	17	34 100	28 800	15
89.0	70 000	26 900	62	6500	5030	23	35 900	27 400	24
313.3	73 000	25 800	65	7500	3920	48	36 200	27 000	25

MAD – mesophilic anaerobic digestion of the sludge.

CONCLUSIONS

It was established that the post-ozonation of biologically treated yeast wastewater resulted in the reduction of COD by 30–49%, and the consumed ozone dosage (mg ozone per mg of COD removed) ranged from 1.2 to 2.5. The biodegradability of the wastewater, expressed as BOD/COD ratio, generally increased during the ozonation. Also, the colour and odour problems of the yeast wastewater were eliminated. Thus, it is possible to use ozonation in the tertiary treatment of yeast wastewater or to include ozonation into the combined purification process simultaneously with anaerobic and aerobic bio-oxidation. Application of ozonation in a combined process seems to be promising for yeast wastewater purification; in this case, the target of ozonation is the enhancement of biodegradability and removal of colour and odour.

Although the pre-treatment of the excess sludge with ozone resulted in a reduction of the sludge amount and increased the solubility of sludge organic matter, the following process of mesophilic anaerobic digestion was not improved.

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Osooni kasutamise võimalustest pärmitööstuse reovee töötlemisel

Viktoria Blonskaja, Inna Kamenev ja Sergei Zub

Töö eesmärgiks on hinnata osoonimise rakendamise võimalikkust pärmitööstuse reovee puhastusprotsessi parandamiseks.

Katsetest on selgunud, et osoonimist on võimalik kasutada bioloogiliselt puhastatud reovee süvapuhastuses värvuse ning lõhna kõrvaldamiseks ja reoainete kontsentratsiooni vähendamiseks. Kuna osoonimisel suureneb reovee biolagundatavus, on otstarbekas kasutada osoonimist reovee puhastamisel kombineeritult koos anaeroobse ja aeroobse biooksüdatsiooniga.

Samuti on uuritud reovee puhastusprotsessis tekkinud jääkmuda osoonimist enne selle anaeroobset kääritamist. Jääkmuda eeltöötlemine osooniga vähendab muda hulka ja suurendab selle orgaanilise aine lahustuvust. Muda lahustuvus küll suureneb, kuid sellele järgneva muda mesofiilse kääritamise protsessi efektiivsus ei parane.