

POSSIBLE WAYS FOR POST-TREATMENT OF BIOLOGICALLY TREATED WASTEWATER FROM YEAST FACTORY

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Abstract. The effluents, which are formed from the waste in the process of production of yeast and molasses, contain a large amount of colouring substances (melanoidins, etc.) and can give dark brown painting to the effluent leading to high organic load on the wastewater treatment plant. The purpose of this study was estimation of the process of coagulation as possible method for the post-treatment of effluents of yeast industry. The experiments on the coagulation were carried out using biologically purified effluents of Salutaguse yeast factory. This effluent had relatively high residual content of COD (with the effectiveness of treatment – 90%) and brown colour. Different coagulants and flocculants were studied under laboratory conditions. The most effective coagulants FeCl₃·6H₂O and Al₂ (SO₄) ₃ were studied additionally. The results of this experiment showed a significant decrease of colour and also concentration of COD. Economic analysis for the possible application of coagulants and ozone for the post-treated effluents of yeast factory was also made. The obtained data showed that coagulants and ozone could be used in the process of the post-treatment of effluents of yeast industry for the purpose of decreasing the colour and general concentration of pollutants, however, these processes are very expensive.

Keywords: baker's yeast wastewater, coagulation, colour, melanoidines, ozonation, post-treatment.

1. Introduction

Yeast production wastewater is a complex mixture. Most of the contaminants in the wastewater are due to the use of molasses as a main raw material. Molasses, being the main by-product of beet sugar process, are also used as raw material for the commercial production of yeast and ethanol. As a by-product of sugar manufacturing, molasses contain from 45 to 50% of residual sugars, 15 to 20% of non-sugar organic substances, 10 to 15% of ash (minerals) and about 20% of water.

Sugar beets contain no colouring materials, but they do contain colour-forming substances. Sugar and nonsugars such as phenol-iron complexes, melanins, that participate in the production of colour (caramel substances, melanoidines) or nonsugars as such (phenol-iron complexes, melanins) are responsible for the change. The degree of discoloration is related primarily to pH and temperature. The discoloration in sugar juices increases threefold for each 10 °C rise in the temperature of processing. Colouring matter is formed not only when bases or acids react, but also, to some extent, from decomposition of saccharose. These mixtures of colour-conferring materials are referred to in the literature under various names, such as caramelan, caramelene, carameline, saccharan and fuscazinic acid. In addition, furfural derivatives are formed simultaneously with volatile compounds (aldehydes, such as acrolein) and also carbon dioxide is being discarged. The colouring matters, that appear in the course of sugar manufacturing, can be divided into the following groups (Olbrich 1973):

A) *Caramel materials.* These substances are the results of thermal decomposition (including loss of water) of saccharose- they contain no nitrogen. At constant pH the formation of caramel is directly proportional to the effective temperature.

B) **Polyphenol-iron complexes.** Pyrocatechol (plant pigment), which occurs in the epidermis and the head of beets (in amounts of about 0.02%), leads to a yellow-greenish discoloration of sugar juices. It is known that the change results from the formation of a pyrocatechol-iron complex. This is not entirely removed during the defecation of the juice and can be found in molasses.

C) *Melanoidines.* Melanoidines are high molecular weight polymers and main coloured compounds (Gonzàlez *et al.* 1999). The formation of melanoidins comprises a set of consecutive and parallel chemical reactions taking place between amino compounds and carbohydrates during a Maillard reaction (Cämmerer and Kroh 1995).

D) *Melanins.* Beet tyrosinase, which belongs to the polyphenol-oxidases, contains copper in its active group. On access with oxygen it can cause oxidation of various aromatic compounds (pyrocatechol, tyrosine) and produce blackish-grey discolorations. This reaction, known as melanin-formation, requires only enzymatically catalyzed oxidation for its initiation and then proceeds as a chain reaction passing through red and red-brown intermediate stages to orthoquinone-like compounds. Since this discoloration can be removed almost completely in the

predefecation of beet-sugar juice, melanins seldom appear in molasses.

During yeast fermentation process sugars contained in molasses are utilized as carbon and energy sources. The major part of the non-sugar substances in molasses (molasses residuals), however, is not utilized by the yeast production and discharged unchanged to the processed wastewater, which represents the principal waste in the yeast production process. Besides molasses' residuals, yeast production wastewater also contains chemicals which are added during fermentation (e.g. various salts, antifoams, propionic acids, brine, etc), yeast metabolites and residual yeast cells.

Phenolic compounds responsible for beet molasses wastewater colour are partly removed (63% removal) during aerobic-anoxic treatment process, but the colour removal accounts for only 8–23% (Kalyuzhnyi *et al.* 2005). In accordance with other literature data (Francisca Kalavathi *et al.* 2001) the visible colour is mainly asociated with other substances than phenolic compounds namely, with persistent to biodegradation melanoidins.

Conventional anaerobic-aerobic treatment processes can accomplish the degradation of melanoidins only up to 6% or 7% (Gonzàlez *et al.* 1999; Guimaraes *et al.* 1999).

Therefore, it is necessary to study additional treatment mehods to remove colour from molasses` effluents. This can prevent serious environmental problems such as reduction of both photosynthetic activity and dissolved oxygen concentration that coloured wastewaters can raise in river courses.

Technologies for treatment wastewaters can be divided into three types- chemical, physical and biological methods. The processes of biological and physicalchemical purification of wastewater were investigated by G. Vabolienė, A. Matuzevičius (2007), A. Riauka *et al.* (2006); A. Mazeikiene *et al.* (2005) and G. Vaboliene, A. Matuzevičius (2005).

Melanoidins can be removed by:

1) Biological treatment with certain bacteria and fungi have also been applied, leading to lower colour removal efficiencies (Miyata *et al.* 2000).

Many reseachers have tried to isolate microorganisms, which have the ability to decolorize melanoidins. Melanoidins have antioxidant properties and are toxic to many microorganisms in wastewater treatment (Frankel et al. 1978). It has been reported that basidiomycetes including Corius sp. No. 20 (Watanabe et al. 1982), dueteromycestes including Aspergillus fumigatus G-2-6 (Ohmomo et al. 1987), Aspergillus oryzae Y-2-32 (Ohmomo et al. 1988b) and bacteria including Lactobacillus hilgardi (Ohmomo et al. 1988a) showed melanoidindecolorization properties. Although the potential of these microorganisms to remove melanoidin from molasses wastewater is clear, their actual use for molasses' wastewater treatment processes might be difficult from the viewpoint of the stability and maintanace of colour removal activity. Operation of proposed biological process will be difficult due to the contamination with competetive microorganisms.

2) Chemical oxidation with ozone.

Ozone has been used in many countries for the treatment of drinking water. Ozonation processes are particularly attractive because ozone can destroy hazardous organic contaminants. In the last years ozone has successfully been applied to the treatment of specific compounds such as dyes, phenolic compounds, pesticides and organochlorides (Wu and Masten 2002; Kamenev 2003). Neverless, oxidation of molasses wastewater with ozone is rather limited to a few investigations. In these studies synthetic solutions or very diluted wastewater were oxidized with ozone (Kim et al. 1985; Gehringer et al. 1997). The chemical oxidation of biologically purified effluents of Salutaguse yeast factory with ozone was investigated in 2005 (Blonskaja et al. 2006). The research data showed that 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.

3) Physical-chemical treatments.

These methods require high reagent dosages and generate a large amount of sludge (Gonzàlez *et al.* 1999). It was reported (Gladchenko *et al.* 2004, Kalyuzhnyi *et al.* 2005) that application of iron and aluminium coagulation for molasses wastewater post-treatment of biofilter effluents showed that color, COD, nitrogen and phosphate decreased with incressing acting Fe and Al concentrations and the discharge limits were already archievable under iron concentrations around 200 mg/l and aluminium around 540 mg/l.

Zak (2005) showed, that the using of hydrogen peroxide and iron (II) sulfate or chloride in the chemical pretreatment of *Saccharomyces cerevisae* yeast industry wastewater can be effective.

The investigation proved that the use of Fenton's system permitted a high reduction of sugar-like substances and total decolorizing of non-sugar compounds. The level of COD reduction depended on the amount and mutual proportions of COD:Fe(II):H₂O₂, as well as a type of the applied salt Fe(II). For iron concentrations: 1000-4000 mg l^{-1} with molar excess [H₂O₂]:[Fe(II)] - 2-14:1 and reaction pH - 3.1-3.4, very high reproducibility of results and the COD reduction exceeding 75% were obtained, but the concentration of iron was very high. For this range of the reagent concentrations, the distribution of COD reduction values correlated with the equation: $COD = -Ax^4 + Bx^3 - Cx^2 + Dx - E$ (where: x = [H₂O₂]:[Fe(II)]). Additional neutralization with the use of lime milk made the secondary reduction of $\text{COD}_{r(CaO)}$ value possible, which resulted in the reduction of the total COD_T above 90%.

Salutaguse WWTP

The most common of all the treatment methods is biological treatment, because it is more economical than any other types. Therefore, it can successfully be implemented for wastewater treatment (Tables 1 and 2).

Wastewater (up to 350 m³/d) from the yeast production plant processing beet sugar molasses was treated with anaerobic sludge in modified anaerobic/anoxic reactors system. The anaerobic reactors were fed with mixture of raw wastewater and recycled anoxic sludge. The temperature of the anaerobic stage was kept between 30 and 36 °C, the pH of between 7.2 and 7.5 and was self-regulated by the biological process without neutralization. Both anaerobic reactors were operating with COD loading of 12–16 kg COD·/m³/d. During the last six years technological scheme was the following (Fig. 1).

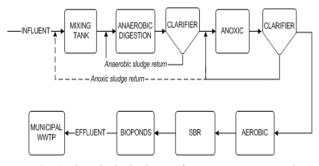


Fig. 1. The principal scheme of wastewater treatment in Yeast Factory (Estonia)

According to the technological set-up presented in Fig. 1, the biological processes in the anaerobic reactors and in the anoxic reactor are inter-related with the returned sludge from the secondary sedimentation tank (by the anoxic reactor) to the inlet of the mixing tank.

Evaluation of the efficiency of anaerobic and anoxic stages as well as the total efficiency of the system has demonstrated that leading the wash waters back to the mixing tank improved the efficiency of the anoxic stage. The results proved that the success of this type of purification process, based on the recirculation system with the use of returned sludge, depends significantly on the sludge loss prevention from the anaerobic reactors. The main results of wastewater treatment from yeast industry are given in Tables 1 and 2.

The general effluent from the yeast factory usually contains 22-35 g COD/*l*, 1.7-2.7g/*l* total N and sulphate as well a significant amount of recalcitrant for biodegradation and highly coloured melanoidins.

Wastewater treatment plant was working in the optimum regime, but concentration of effluent pollutants was very high, therefore the post treatment was required.

The wastewater from molasses processing presents a large amount of coloured substances that give dark brown colour and high organic load to the effluents. After a multistage biological treatment most of the organic load was removed. Although the treatment results showed that the brown colour does not disappear and it can even increase because of the repolymerization of coloured compounds.

The aim of this study was to investigate the precipitation of coloured substances with coagulation (as one of possible ways for post-treatment) of highly polluted biologically pre-treated wastewater from Salutaguse Yeast Factory where beet molasses are being processed. Successful implementation of treatment measures will prevent serious environmental problems, such as reduction of both photosynthetic activity and dissolved oxygen concentration, that colored wastewaters can cause in river courses.

		Influent,	mg/l			Effluent, mg/l					
COD	COD	TSS	N tot	Р	SO_4	COD	COD	TSS	Ν	Р	SO_4
tot				tot		tot			tot	tot	
22 650	20 185	2 391	1 702	60	2 207	2 723	2 183	486	395	45	343
22 975	20 542	2 433	1 853	32	2 475	2 504	2 038	466	463	33	343
24 207	21 545	2 661	1 645	52	1 879	4 368	3 555	813	533	29	235
31 798	29 330	2 468	2 706	81	3 521	4 348	3 931	416	394	15	94
32 587	30 388	2 174	2 6 2 5	50	2 360	2 744	2 446	314	490	20	20
34 945	31150	3 795	-	-	2 250	4 330	3 825	505	-	-	_
						250			10	2	
	tot 22 650 22 975 24 207 31 798 32 587	tot 22 650 20 185 22 975 20 542 24 207 21 545 31 798 29 330 32 587 30 388	COD tot COD 22 650 TSS 22 975 20 185 2 391 22 975 20 542 2 433 24 207 21 545 2 661 31 798 29 330 2 468 32 587 30 388 2 174	tot 22 650 20 185 2 391 1 702 22 975 20 542 2 433 1 853 24 207 21 545 2 661 1 645 31 798 29 330 2 468 2 706 32 587 30 388 2 174 2 625	COD tot COD COD TSS N tot P tot 22 650 20 185 2 391 1 702 60 22 975 20 542 2 433 1 853 32 24 207 21 545 2 661 1 645 52 31 798 29 330 2 468 2 706 81 32 587 30 388 2 174 2 625 50	COD tot COD COD TSS N tot P tot SO ₄ 22 650 20 185 2 391 1 702 60 2 207 22 975 20 542 2 433 1 853 32 2 475 24 207 21 545 2 661 1 645 52 1 879 31 798 29 330 2 468 2 706 81 3 521 32 587 30 388 2 174 2 625 50 2 360	COD tot COD COD TSS N tot N P tot SO ₄ COD tot 22 650 20 185 2 391 1 702 60 2 207 2 723 22 975 20 542 2 433 1 853 32 2 475 2 504 24 207 21 545 2 661 1 645 52 1 879 4 368 31 798 29 330 2 468 2 706 81 3 521 4 348 32 587 30 388 2 174 2 625 50 2 360 2 744	COD tot COD 22 650 COD 20 185 TSS 2 391 N tot 1 702 P tot SO ₄ COD tot COD tot COD tot 22 650 20 185 2 391 1 702 60 2 207 2 723 2 183 22 975 20 542 2 433 1 853 32 2 475 2 504 2 038 24 207 21 545 2 661 1 645 52 1 879 4 368 3 555 31 798 29 330 2 468 2 706 81 3 521 4 348 3 931 32 587 30 388 2 174 2 625 50 2 360 2 744 2 446 34 945 31150 3 795 - - 2 250 4 330 3 825	COD tot COD COD TSS N tot N tot P tot SO ₄ COD tot COD tot TSS 22 650 20 185 2 391 1 702 60 2 207 2 723 2 183 486 22 975 20 542 2 433 1 853 32 2 475 2 504 2 038 466 24 207 21 545 2 661 1 645 52 1 879 4 368 3 555 813 31 798 29 330 2 468 2 706 81 3 521 4 348 3 931 416 32 587 30 388 2 174 2 625 50 2 360 2 744 2 446 314 34 945 31150 3 795 - - 2 250 4 330 3 825 505	COD tot COD COD TSS N tot N P tot SO ₄ COD tot COD tot TSS N tot 22 650 20 185 2 391 1 702 60 2 207 2 723 2 183 486 395 22 975 20 542 2 433 1 853 32 2 475 2 504 2 038 466 463 24 207 21 545 2 661 1 645 52 1 879 4 368 3 555 813 533 31 798 29 330 2 468 2 706 81 3 521 4 348 3 931 416 394 32 587 30 388 2 174 2 625 50 2 360 2 744 2 446 314 490 34 945 31150 3 795 - - 2 250 4 330 3 825 505 -	COD tot COD COD TSS N tot 1700 P tot SO ₄ COD tot COD tot TSS N tot P tot 22 650 20 185 2 391 1 702 60 2 207 2 723 2 183 486 395 45 22 975 20 542 2 433 1 853 32 2 475 2 504 2 038 466 463 33 24 207 21 545 2 661 1 645 52 1 879 4 368 3 555 813 533 29 31 798 29 330 2 468 2 706 81 3 521 4 348 3 931 416 394 15 32 587 30 388 2 174 2 625 50 2 360 2 744 2 446 314 490 20 34 945 31150 3 795 - - 2 250 4 330 3 825 505 - -

Table 1. The results of the treatment process

- not detected

 Table 2.
 Treatment effect during 6 years

Removal %	2003	2004	2005	2006	2007	2008
COD	88	89	85	86	92	88
H.a		90	84	87	92	87
Sulphate	84	86	88	97	99	-
N tot	77	85	68	85	81	-
P tot	25	-	25	81	60	-

2. Method

Post-treatment of biologically treated wastewater

Chemical methods are one of the possible ways for the post treatment process (for removal of non-biodegradable substances). These methods include chemical precipitation, chemical oxidation reduction, formation of an insoluble gas followed by stripped gas, and other chemical reactions that involve exchanging or shaping electrons between atoms.

The presence of organic matter in effluent from Salutaguse WWTP generally increases the required coagulant dosage and therefore it is always necessary to confirm a chemical treatment process by laboratory experimentation. Laboratory experimentation is always required to determine the optimum doses of coagulants.

In order to obtain more accurate data, the research group was testing the effect of different dose concentrations of coagulants on the performance of biologically treated wastewater. The coagulation process usually uses pH adjustment, addition of chemical precipitant, and flocculation. Flocculation was used as the further agglomeration of slowly-settling coagulated particles into large rapidly-settling flock and precipitation mainly had to convert dissolved ionic species into solid-phase particulates. In the precipitation process, coagulants and flocculation were used to increase particle size through aggregation and be removed from aqueous phase by coagulation and filtration. A suggested procedure for determining, optimum doses of reagent chemicals in the laboratory is as follows:

- 1. Place wastewater from effluents of Salutaguse WWTP in a glass.
- Determine reagent doses to bracket the anticipated optima, regarding pH precipitant/coagulant/flocculants.
- 3. Mix rapidly for 30 seconds.
- 4. Mix slowly, so as to achieve good coagulation. Carry on for up to 30 minutes.

- 5. Allow settling.
- 6. Measure results.

Addition of coagulants was carried out less than 200 rpm and then intensity of stirring was reduced to 40 rpm to complete a flocculation process during which pH was maintained at 7.2–7.5 by addition of sodium hydroxide. All experiments were performed with 200 ml of anaerobic/aerobic pre-treated effluent in a laboratory glass under continuous stirring and pH control (Fig. 2).

All analyses (COD_{tot}, COD, phenols, P_{total} , N_{total} , SO₄, TSS and VSS) were performed by Standard Methods for the Examination of Water and Wastewater (1998).

The colour was determined using a UV spectrophotometer.

3. Results and discussion

Some non-biodegradable substances, that are resistant to biodegradation, can be chemically altered to yield the material that is biodegradable. Hydrolysis, under either acidic or alkaline conditions, can be used to break up many large organic molecules into smaller segments that are amenable to biological treatment.

Hydrolyses derives its name from the chemical reaction when a carbon-carbon bond is broken, a hydrogen atom attached to the site on one of the carbon atoms, and OH group attaches to the site on the other carbon atom.

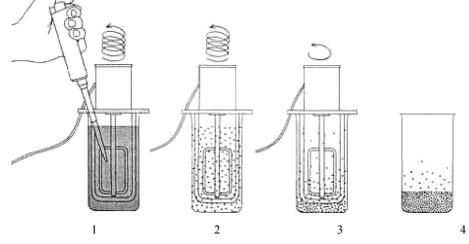
The basic reaction, when the AL^{3+} ion is added to water, consists of the formation of aluminium hydroxide precipitate and release of a degree of acidity (hydrolysis):

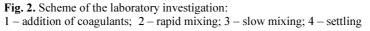
$$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^{-}$$
. (1)

Each mole of cation should react with three moles of water to produce one mole of metal hydroxide and three moles of hydrogen ions. This acidity reacts with certain species in solution, especially bicarbonate ions.

$$HCO_3^- + H^+ = H_2O + CO_2,$$
 (2)

$$Al^{3+} + 3HCO_3^{-} = Al(OH)_3 + 3CO_2.$$
 (3)





Type of coagulants/floculants	Acting Fe(Al) concentration, mg/l			The COD removal, %				
FeCl ₃ ·6H ₂ O	65	200	375	535	45	54	28	26
$Al_2(SO_4)_3$	80	150	250	350	36	38	31	43
$Fe_2(SO_4)_3$	150	350	450	700	10	30		
Al ₂ (OH) _{6-x} Cl _x *YH ₂ O	125	200	300	350	7	4	-	-
Zetak 7563*	5				0			
Zetak 7587*	5	1	0,5		57	50	44	
Zetak7635*	5				20			
Magnofloks10*	5				29			

Table 3. The results of experiments with coagulants

*Were used for sludge setting

2

Ferric salts are the most frequently used iron salts. Overall reaction is the same as that for aluminium salts

$$Fe^{3+} + 3HCO_3^{-} = Fe(OH)_3 + 3CO_2.$$
 (4)

And for instance, with ferric chloride in water with calcium alkalinity

$$2\text{FeCl}_3 + 3\text{Ca}(\text{HCO}_3)_2 =$$
(5)

$$2Fe(OH)_3 + 3CaCl_2 + 6CO_2.$$

With iron salts we have the same problems relating to the consumption of alkalinity products that have to be added in order to maintain pH within the optimum range.

The main results of experiments are given in Table 3.

Table 3 shows that the best results were obtained with the following coagulants $FeCl_3.6H_2O$ and $Al_2(SO_4)_3$.

Performance of iron and aluminium coagulation step

Coagulants $FeCl_3 \cdot 6H_2O$ and $Al_2(SO_4)_3$ were analyzed additionally.

The results on efficiency of Fe³⁺ and Al⁺³ coagulation step for treatment of aerobic SBR effluent are presented in Tables 4 and 5. It is noticeable that all parameters (COD_{total}, N_{total}, P_{total} and color) decrease with the increase of acting Fe and Al concentrations and the discharge limits are already achievable under iron concentrations around 200 mg/l and aluminium around 400 mg/l.

The performance of colour removal by chemical coagulation depends on the characteristics of both colour substances and coagulants.

Acting Fe concentration, mg $/l$									
	0	50	100	150	200	500			
$COD_{tot}, mg / l$	2120	1750	1350	1040	830	710			
Phenols, mg /l	288	260	224	178	125	99			
P _{total} , mg / <i>l</i>	21	18.3	15,2	10,2	4,5	2.1			
$N_{total}, mg /l$	310	245	125	101	78	61			
OD ₅₈₀	0.414	0.380	0.331	0.250	0.165	0.067			
Sludge percentage, % vol*.	—	ND	ND	5.4	15.8	63.4			
SVI, ml g ⁻¹ TSS	—	ND	ND	210	270	420			
Sludge VSS/TSS, %	_	ND	ND	90	88.9	33.5			

Table 4. Performance of iron coagulation stage

*after 30 min of settling; ND-not detected

Table 5. Performance of aluminium coagulation stage

Acting Al concentration, mg /l									
	0	100	200	400	600	800			
$COD_{tot}, mg/l$	2120	1910	1690	1270	800	760			
Phenols, mg $/l$	288	144	82	67	64	59			
$P_{total}, mg /l$	21	15.7	7.2	4.5	3.4	1.5			
N _{total} , mg / <i>l</i>	310	180	112	74	65	54			
OD ₅₈₀	0.414	0.361	0.139	0.112	0.076	0.065			
Sludge percentage, % vol*.	_	35.5	91.4	93.5	94.4	96.3			
SVI, ml g ⁻¹ TSS	_	655	615	545	355	341			
Sludge VSS/TSS, %	_	42	52.4	56.5	52.2	39.8			

Gel-filtration of untreated yeast wastewater revealed that the substances responsible for visible colour (OD580) have symmetrical Gauss-type distribution of their molecular weights (MW) in the range of 0–30 kDa with a maximum at 6–7.8 kDa (>60% of colour is associated with the substances having MWs in the range of 2.6–14 kDa). On the contrary, substances with aromatic structures (OD280) have non-symmetrical distribution of their MWs with a clear prevalence of low MW molecules (maximum at 2.6–4.5 kDa; > 82% of UV-absorption is associated with MWs < 8 kDa). These data show that the visible colour yeast wastewater is not closely associated with the aromatics like phenolic compounds.

The colour of wastewater underwent dramatic changes from deep brown to pastel yellow after coagulation. These results are superior (with regard to coagulant added) to those reported in the literature for anaerobically treated baker's yeast wastewater (Kalyuzhnyi *at al.* 2003).

Varying ferrous chloride concentration (from $50\text{Fe}^{3+} \text{ mg/}l$ up to $500 \text{ Fe}^{3+} \text{ mg/}l$) and keeping pH constant were applied for the treatment of wastewater. A ferrous chloride concentration of 200 mg/l was necessary for an efficient COD removal to 830 mg/l and for colour removal by 60%, but did not significantly catalysed P tot and N tot removal.

Varying aluminium sulphate concentration (from $100 \text{ Al}^{3+} \text{ mg/}l$ up to $800 \text{ Fe}^{3+} \text{ mg/}l$) and keeping pH constant were applied for the treatment of wastewater. Aluminium sulphate concentration of 400 mg/l was necessary for an efficient COD removal for 1270 mg/l and for colour removal by 73%, but did not significantly increase P tot and N tot removal.

The sludge formed under an acting Fe concentration of 200 mg/l was relatively large (SVI = 270 ml/l TSS). The acting Al concentration of 400 mg/l produced much more sludge (SVI = 545 ml/l TSS). The iron sludge had higher (~90%) VSS content compared to the sludge obtained during Al coagulation step (56, 5% VSS) showing the significant removal of organic COD and nitrogen during the iron coagulation step.

Fig. 3 shows the evolution of colour removal and COD decrease for experiments carried out at different Fe3+ and Al3+ dosages.

As the result of coagulation, absorbance at 580 nm decreased significantly. Applied concentration of Fe^{3+} and Al^{3+} had positive effect not only on colour removal but also on COD. Melanoidins are responsible for the brown colour and included in COD.

Results of coagulations

- Application of iron chloride and aluminium sulphate coagulation for post-treatment of anaerobic-aerobic effluents may fulfil the discharge limits to the sewer under iron concentrations of around 200 mg/l and aluminium concentrations around 400 mg/l.
- Significant decrease of colour substances could be achieved by using coagulation. It is very important to meet biological standards when final effluent is treated with ultraviolet radiation.
- Generated during coagulation sludge could be the problem when full scale process applied. The iron sludge had much better SVI which is an important parameter for further handling of sludge (separation, de-watering).
- Considering that Salutaguse Yeast Factory has daily 330 m³/d of wastewater to be treated using coagulation process it could be proposed that up to 426 kg TSS/d would be generated additionally if Fe3+ was used and up to 281 kg TSS/d in case of Al³⁺. It corresponds to amount of sludge 1.27– 1.94 m³/d (at 22% DS after sludge dewatering).
- Installation of flotation unit is needed before sludge de-watering.

Ozonation

Chemical oxidation of biologically purified effluents of Salutaguse yeast factory with ozone was investigated for the period from 2005 to 2008. Some results of the experiments with ozone are presented in Table 6 (Blonskaja *et al.* 2006). The experiments indicated that the efficiency of post-ozonation in terms of COD (COD removal) ranged from 30% to 49%, and the ratio dn/ Δ COD, consumed ozone dosage mg of ozone per mg of COD removed, ranged from 1.2 to 2.5. The best result with COD removal was received in run 4.

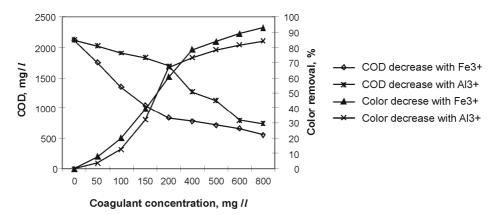


Fig. 3. Decreasing COD and colour during experiments

	WWTP effluent, mg/l			Consumed ozone dos-	Efficiency of	Effluent after post-ozonation mg/l			
Run	COD _{tot}	BOD	BOD/COD	age, dn/∆COD, mgO ₃ /mgCOD	post-ozonation ΔCOD, %	COD _{tot}	BOD	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	

Table 6. Results of post-ozonation of biologically treated wastewater

During ozonation, pH decreases as a result of formation of carboxylic acids. However, in the experiments of post-ozonation of the yeast wastewater, pH decreased only in the run 2 (from 8.3 up to 8.1). In all other runs (1, 3, 4, 5) pH increased (from 7.3 to 7.9). 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. Studies on the ozonization of effluents of yeast industry continue and the results of this study will be presented in the near future.

First results of ozonation

- 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 in the beginning of postozonation, it is possible to include ozonation into a combined purification process simultaneously with anaerobic and aerobic bio-oxidation.
- In the combined process, the goal of ozonation is the 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 combination with biological methods may be more economical for yeast wastewater purification
- The ozone dosage required to decrease the residual COD noticeably was about 1000– 1500 mg/l, and both CODtot and CODsol decreased. Haapea *et al.* 2002 reported, that electrical power consumption to produce pure ozone from air is 17–30 kWh/kgO₃.

Considering that Salutaguse Yeast Factory has daily $350 \text{ m}^3/\text{d}$ of wastewater to be treated using ozonation process it could be proposed that up to $495 \text{ gO}_3/\text{d}$ is required. It corresponds to 8415-14850 kWh/d of electrical energy consumption. In addition to the above mentioned installation a modern ozone generator is needed.

4. Conclusions

1. The results of coagulation-significant decrease of colour substances and also COD concentration could be achieved.

2. Colour removal by coagulation process using aluminium sulphate and ferrous chloride was more than 80%.

3. The most effective coagulants were $(FeCl_3 \cdot 6H_2O)$ and Al_2 $(SO_4)_3$ however, the required amount of inorganic coagulants was relatively high.

4. The post-treatment method of yeast factory effluent with coagulants and ozone can be used in the tertiary treatment of yeast wastewater, but the treatment is very expensive.

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GALIMI PAPILDOMI MIELIŲ GAMYKLOS BIOLOGIŠKAI VALYTŲ NUOTEKŲ VALYMO BŪDAI

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Santrauka

Nuotekų, susidarančių pramoniniuose procesuose naudojant mieles bei melasą, sudėtyje esti dideli kiekiai dažančių medžiagų (melanoidų). Jie nuotekas nudažo tamsiai rudai, o valymo įrenginiams tenka didelės organinių medžiagų apkrovos. Tyrimo tikslas buvo įvertinti koaguliacijos procesą kaip galimą papildomą mielių pramonės nuotekų valymo metodą. Koaguliacijos eksperimentams buvo naudojamos biologiškai valytos Salutaguso mielių gamyklos nuotekos. Nustatyta didelė šių nuotekų liekamoji organinių medžiagų vertė (valymo efektyvumui esant 90 %), nuotekos buvo rudos. Laboratorinėmis sąlygomis ištirta įvairūs koaguliantai ir flokuliantai. Efektyviausieji koaguliantai – FeCl₃ · $6H_2O$ ir $Al_2(SO_4)_3$ buvo išanalizuoti papildomai. Eksperimento rezultatai – žymiai pašviesėjo nuotekų spalva, sumažėjo organinių medžiagų koncentracija. Atlikta ekonominė analizė, įvertinta koaguliantų ir ozono taikymas biologiškai išvalytoms mielių gamyklos nuotekoms valyti papildomai, kad pašviesėtų nuotekų spalva, ir suminė organinių medžiagų koncentracija būtų mažesnė. Šie procesai yra itin brangūs.

Reikšminiai žodžiai: koaguliacija, spalva, ozonavimas, papildomas valymas, mielių pramonės nuotekos.

ВОЗМОЖНЫЕ ПУТИ ДООЧИСТКИ БИОЛОГИЧЕСКИ ОЧИЩЕННЫХ СТОЧНЫХ ВОД ДРОЖЖЕВОГО ЗАВОДА

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Резюме

Сточные воды, образующиеся от использования в процессе производства дрожжей мелассы, содержат большое количество красящих веществ (меланоидинов), которые придают сточной воде темно-коричневую окраску и приводят к высокой органической нагрузке на очистные сооружения. Целью исследования была оценка процесса коагулирования как возможного метода доочистки сточных вод дрожжевой промышленности. В экспериментах по коагулированию была использована биологически очищенная сточная вода Салутагуского завода по производству дрожжей. Сток имел относительно высокое остаточное содержание органических веществ (при эффективной очистке в 90%) и коричневый цвет. Различные коагулянты и флокулянты были изучены в лабораторных условиях. Наиболее эффективные коагулянты FeCl₃·6H₂O и Al₂ (SO₄)₃ были изучены дополнительно. В результате эксперимента удалось добиться значительного уменьшения интенсивности цвета и концентрации органических веществ. Был произведен экономический анализ с целью возможного применения коагулянты и озон можно использовать в процессе доочистки стоков биологически очищенных вод дрожжей. Коагулянты и озон можно использовать в процессе доочистки стоков биологически очищенных вод дрожжей промышленности для уменьшения цветности и общей концентрации органических веществ. Эти процессы, однако, очень дороги.

Ключевые слова: коагуляция, цвет, озонирование, дополнительная очистка, сточные воды дрожжевой промышленности.

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