

## **NITROGEN REMOVAL STRATEGY FROM BAKER’S YEAST INDUSTRY EFFLUENTS**

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### **Abstract:**

Wastewaters from baker’s yeasts industry effluent have a high organic contamination. The classical biological treatments under aerobic and anaerobic conditions lead to a good efficiency in removing the organic carbon, but regarding nitrogen efficiency is variable. To obtain a good efficiency in removing nitrogen, the effluents must pass through all different stages of nitrogen cycle (i.e. ammonification, nitrification and denitrification), catalyzed by the activated sludge microbiota involved in the bioconversion processes from the organic nitrogen to the gaseous nitrogen. The biological processes involved in nitrogen removal from wastewaters of baker’s yeast industry are also dependent in physical and chemical conditions in which the activated sludge microbiota work to mineralize the organic compounds or to bio-convert them in to gases.

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**Keywords:** wastewater, baker’s yeast industry, nitrogen removal

### **Introduction**

The baker’s yeast industry represents the main source of residual nitrogen compounds in wastewater effluents (Wang *et al.*, 2006b). The most important effects of nitrogen derivates compounds in

water are: dissolved oxygen concentrations changed dramatically by waste oxidation, eutrophication, increase of toxicity in the aquatic media and public health endanger (Raftelis, G., 2005).

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The principal forms of nitrogen from the wastewaters are: ammoniacal nitrogen (N-NH<sub>3</sub> or N-NH<sub>4</sub><sup>+</sup>), nitrite nitrogen (N-NO<sub>2</sub><sup>-</sup>), nitrate nitrogen (N-NO<sub>3</sub><sup>-</sup>) and organic nitrogen (N<sub>org</sub>) (Wang and colab., 2006a).

Organic nitrogen consists of many families of substances: amines, amic acids, herbicides, nitroso derivatives, macromolecular combinations (proteins, peptides, chlorophylls, humic acids etc.).

Ammonia exists in aqueous solutions as gas NH<sub>3</sub> or as ammonium ion NH<sub>4</sub><sup>+</sup> depending on the solution's pH, according to the equilibrium reaction: NH<sub>3</sub> + H<sub>2</sub>O ↔ NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup>. Thereby, at pH levels > 9.25 the ammonia is prevailing and when the pH is < 9.25 the ammonium is prevailing. The toxicity of ammonia comparative to the ionic form is much higher. In neuter solution or slightly alkaline with a pH level of 8.00, where the ionic form is dominant, the NH<sub>3</sub> concentration is only 4.5% (according to NP 107-04 normative, 2005). Ammonium can be found in almost all types of water. Its presence show a recent contamination with cellular degradation compounds, a wastewater discharge or leakage of the rain water from the agricultural fields where fertilizers on nitrogen bases there were used (ammonium nitrate – NH<sub>4</sub>NO<sub>3</sub> and urea).

The nitrites (NO<sub>2</sub><sup>-</sup>) are relatively unsteady and easy to be oxidized to nitrate. They indicate an antecedent pollution and rarely exceed 1.0 ppm in wastewaters or 0.1 ppm in surface waters. Nitrites represent the first oxydization stage of ammonium. Their presence suggests the existence of the reducing agents.

The nitrates (NO<sub>3</sub><sup>-</sup>) represent the most oxydized form of nitrogen that can be found in wastewaters. An older contamination is indicated by their presence.

The nitrogen cycle in wastewater treatment begins with the conversion of organic nitrogen to ammonia by the heterotrophic bacteria that degrade the organic nitrogen and convert it to ammonia nitrogen through ammonification (Figure 1).

Generally, ammonification takes place during the degradation of the animal or vegetal tissue and of the animal excrements which can be carried out even in aerobic or anaerobic conditions by bacteria, such as: *Pseudomonas*, *Vibrio*, *Proteus*, *Serratia*, *Bacillus*, *Clostridium* etc.

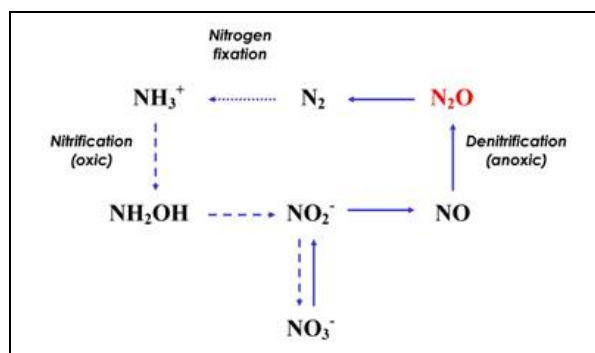
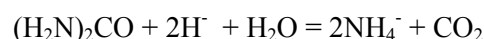


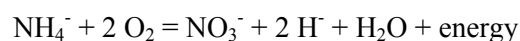
Fig. 1. Activated sludge nitrogen cycle in wastewater

The breakdown proteins in dead organisms and animal waste release the ammonium ions which will be converted to other nitrogen compounds. The main reaction of ammonification is:



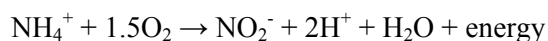
In an aerobic environment the autotrophic bacteria genus *Nitrosomonas* can oxidize the ammonia nitrogen to nitrites (NO<sub>2</sub><sup>-</sup>). Nitrites are unstable compounds and are easily oxidized by *Nitrobacter* bacteria to the nitrate form (NO<sub>3</sub><sup>-</sup>) in the presence of oxygen. This process is catalyzed by two types of chemoautotrophic bacteria (they obtain energy from chemical reactions by aerobic oxydation of inorganic compounds as ammonium, nitrites and sulphides, using for synthesis the inorganic carbon from carbon dioxide). Generally, these two reactions are simultaneous, and the transformation in nitrate is fast, the nitrate level at a certain moment being relatively low.

Nitrification is the ammonium oxidation process. The general reaction is:

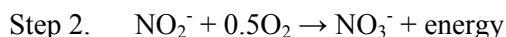


This process is a two-step autotrophic process carried out by aerobic bacteria from the family *Nitrobacteraceae*. The first step is carried out by ammonia oxidizing bacteria such as: *Nitrosomonas*, *Nitrosococcus*, *Nitrospira*, *Nitrosolobus* and *Nitrosovibrio* (Herbert, 1999), which oxidize ammonium into nitrite.

Step 1.



The second step of nitrification is carried out by nitrite oxidizing bacteria, such as: *Nitrobacter*, *Nitrosococcus*, *Nitrospina* and *Nitrospira*, which oxidize nitrite into nitrate.

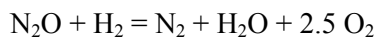
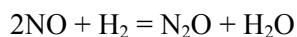
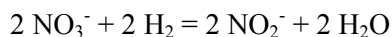


A predominance of nitrite/nitrate forms of nitrogen in the wastewater indicate that the waste has been stabilized with respect to oxygen demand.

The second part of the nitrogen cycle is the denitrification process which converts the nitrates back to nitrites in the absence of available oxygen by heterotrophic bacteria (those that use organic carbon for building cell tissue) in an anoxic environment. It can be made in many steps, in a biochemical way with gaseous nitrogen production. A large range of anoxic heterotrophic bacteria participate in this process. These bacteria need organic carbon as a source of energy. If in a wastewater there are nitrates and oxygen, at the same time, the bacteria will use the oxygen for the organic matter oxidation as more energy is produced in this way. The anoxic conditions must be created in order that the denitrification should take place, the oxygen being used from the nitrates chemical bounds. This process is carried out by bacteria such like: *Thiobacillus denitrificans*, *Micrococcus denitrificans*, *Serratia* sp., *Pseudomonas aeruginosa*, *Achromobacter* sp., etc. The general denitrification reaction expressed as a redox reaction is:



The following reactions can be developed only under anoxic conditions:



Nitrogen removal through biological nitrification and denitrification processes, as practiced in wastewater treatment, is generally classified as an advanced treatment process (Rittmann and McCarty, 2001; Metcalf and Eddy, 1991).

Baker's yeast industry produces a great amount of nitrogen compounds as a result of the use of water in biotechnological processing. Removal of nitrogen

from baker's yeast wastewater is a complex process, even for large wastewater treatment plants. Quality control of nitrogen removal processes from individual onsite wastewater systems is even more difficult to manage.

Treatment systems that are most commonly used are relatively efficient in the removal of biological oxygen demand (BOD<sub>5</sub>) and total suspended solids (TSS) from wastewater, but provide less than optimal removal of nitrogen (10-30 %).

In this study a strategy for nitrogen removal from baker's yeast wastewater is made in order to increase the yield and rate of nitrogen compounds bioconversion.

## Materials and Methods

The researches were made on baker's yeast wastewater plant of RomPak Baker's Yeast Company, Pascani, Romania.

The quality indicators analyzed were:

- *pH measurement* – the pH was determined according to SR ISO 10523-97 with a pH-meter which preliminary calibrated with buffer solution: potassium phthalate with pH = 4.00 at 25°C, phosphate with pH = 6.87 at 25°C and borax with pH = 9.18 at 25°C. The pH is also measured on-line, in the nitrification tank, with the help of a pH transducer.
- *TSS measurement* – the measurement is made according to STAS 6953-81. The suspended solids are separated through filtration followed by the drying and the weighing of the residue to constant mass (1h at 105 ± 3°C). Filtration is made through filter paper.
- *Chemical oxygen demand (COD) measurement* – COD is determined according to SR ISO 6060/96. The COD determination by potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) method is considered to be an approximate value of the theoretical oxygen demand which represents the quantity of oxygen consumed through total chemical oxidation of organic matter to inorganic. In a vessel 10 ml of waste water are mixed with 5 ml of potassium dichromate.

15ml of sulphuric acid – silver sulphate is added with caution in the same vessel. The mix is brought to boiling in 10 minutes and it is kept 110 minutes further more. The boiling temperature has to be  $148^{\circ}\text{C} \pm 3^{\circ}\text{C}$ . The vessel is immediately water cooled at about  $60^{\circ}\text{C}$ . The mix is diluted with about 75 ml water and it is cooled to the room temperature. The potassium dichromate excess is titrated with iron and ammonium sulphate in the presence of an indicator.

- *Biochemical oxygen demand (BOD<sub>5</sub>) measurement* – BOD<sub>5</sub> is determined according to STAS 6560-82. The BOD<sub>5</sub> gives indications about the approximate content of organic biodegradable matter. The biochemical oxygen demand represents the quantity of oxygen consumed for the biochemical decomposition in aerobic conditions of the organic matter contained in 1 ml water in standard conditions (5 days at  $20^{\circ}\text{C}$ ). The test shows the microorganisms ability to oxidize the organic matter to CO<sub>2</sub> and H<sub>2</sub>O using the molecular oxygen as oxidizing agent. The reaction develops in a closed vessel and that is how the oxygen quantity used during the reaction can be easily measured. The BOD<sub>5</sub> is a result of the difference between the dissolved oxygen level in the sample at the beginning and at the ending of thermostatic period. The dilution of the sample is made when the content of organic matter is higher and after 5 days the biochemical oxygen demand is higher than 70% from dissolved oxygen at saturation initially contained. The dissolved oxygen level before and after the incubation period is made by an oximeter.
- *Total nitrogen measurement (N<sub>tot</sub>)* – The cuvette tests Hach Lange were used for the total nitrogen determination; TNT828 for influent determination, and TNT827 for effluent determination. The difference between these and the following reagents is that the nitrogen cuvette tests must be kept at high temperature in a special thermoreactor.
- *The ammonium, nitrites and nitrates level* was determined by spectrophotometric methods on

Hach Lange cuvette tests at specific wave length. The used cuvette tests were TNT823 for influent ammonium, TNT831 for effluent ammonium, TNT385 for influent and effluent nitrate, and TNT839 for influent and effluent nitrite.

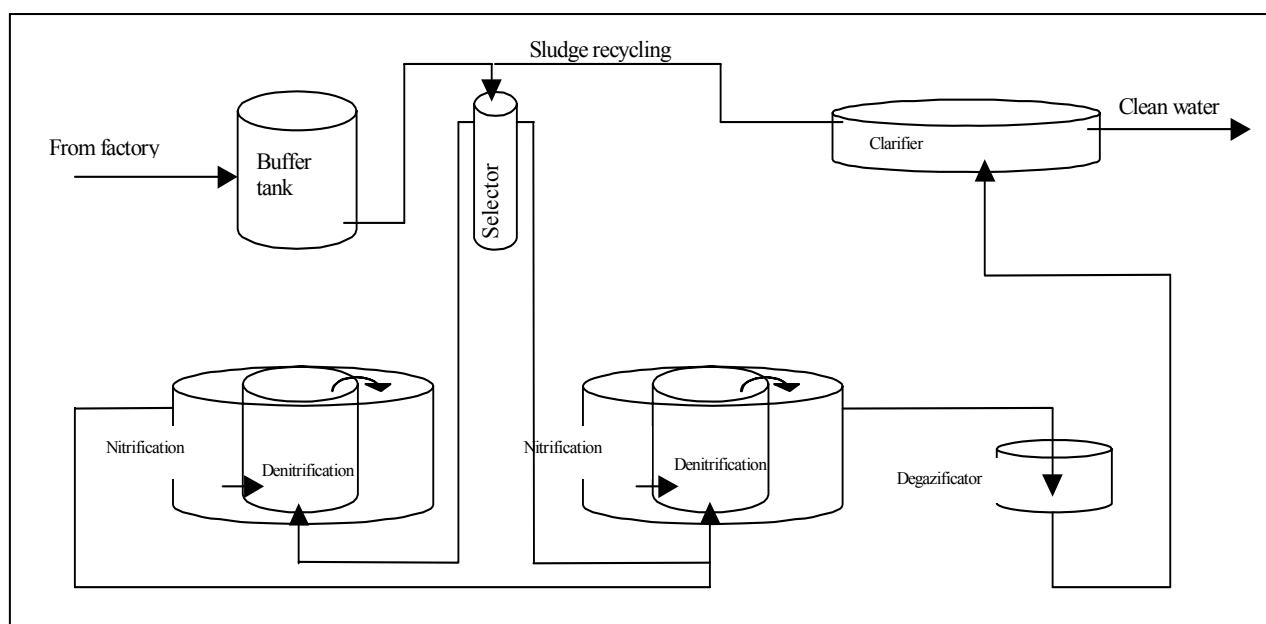
- *The total phosphorus and the phosphates* were also determined by means of Hach Lange cuvette tests: TNT845 for influent and TNT845 for effluent.

The analyses for COD, BOD<sub>5</sub>, TSS, total nitrogen, nitrites and nitrates were made on average samples. Every two hours 100 ml of water that was kept in cold conditions was sampled. The samples from 24 were mixed and the analyses were made on this “average sample”. For phosphorus and phosphates the average samples are not suitable because even at cold temperature some changes may appear; as a result the samples for this application were instantaneous, one per day.

The results were obtained in 4 weeks (28 days) of sampling and analyses. The below values are average values for an entire week or for the entire period.

## Results and discussions

The effluent of the baker's yeast wastewater treatment plant - WWTP (Figure 2) meets the requirements of NTPA 002/2002 normative being sent to the municipal plant. The wastewaters resulted from all factory sectors are stocked in 4 tanks of a total capacity of 3200 m<sup>3</sup>. One of the four tanks plays the role of a buffer tank. Here the wastewaters are mixed and conditioned to obtain a constant loading. The conditioning consists in pH adjustment to neuter. This tank is also provided with recirculation pump for mixing. Because this type of wastewater is alkaline the pH will be adjusted with H<sub>2</sub>SO<sub>4</sub>. The maximum flow of the WWTP is ~4000 m<sup>3</sup>/day. From the buffer tank the wastewater goes to the selector. The selector is a small tank (60 m<sup>3</sup>) that allows the distribution of the wastewater to two tanks simultaneously. In the selector the wastewater is mixed with the recycled sludge from the clarifier.



*Fig. 2.. Baker's yeast wastewater biological treatment plant*

From the selector, water is distributed to both nitrification/denitrification tanks. A percentage of 60% of the wastewater goes to the first nitrification/denitrification tank and the rest to the second one. The nitrification/denitrification tank is, in fact, an assembly of two concentric tanks. In the middle there is the denitrification zone and in the outside there is the nitrification area. The volume of these areas is:

- Denitrification zone – 960 m<sup>3</sup>
- Nitrification zone – 2880 m<sup>3</sup>

The effluent from the selector enters in to the denitrification area first through the bottom. On the first stage, the ammonification process takes place. The zone is provided with a powerful mixer that doesn't allow the sludge sedimentation. In this area there are also anoxic conditions. Created the ammonifying bacteria will rip off the organic nitrogen from macromolecules and convert it into ammonium.

From the denitrification area the liquid falls into the nitrification area through the upper part. This area is aerobic the air being provided continuously by the blowers. Here the ammonium formed in the first stage will be converted in to nitrates and nitrites under the influence of bacteria.

At the bottom of the nitrification area a pump sends the water back to the denitrification area. In the denitrification area under the influence of the denitrifying bacteria the nitrates, formed on the second stage, will be converted into gaseous nitrogen. The nitrification and ammonification processes take place simultaneously in the same area under the influence of specific bacteria.

From the third stage of advanced treatment on the water goes into a small tank named degasificator. The role of this tank is to force the gases to pass off from the water. Because of high gases concentration the further sludge sedimentation can be disturbed. As denitrification is being promoted, rising nitrogen gas can create a potential problem with sludge bulking. This is also a problem with large-scale systems.

The degasification tank volume is 80 m<sup>3</sup>. The clarifier holds a 1211 m<sup>3</sup> capacity, is a horizontal one and it is provided with a scraper bridge. The treated water mixed with sludge from the degasificator enters in to the clarifier at the bottom side. The scraper bridge collects the sludge from the bottom of the clarifier and by suction the sludge is sent to the sludge pit. It is from here a part of the sludge is recycled and another part removed from



the system. The clean water is collected in a discharge channel and then sent out of the WWTP.

### Nitrogen removal during oxidative biological transformations

Table 1 shows the COD and BOD<sub>5</sub> values for the entire sampling period stated in weekly averages. The maximum COD load that can be absorbed by

the design of the WWTP is 7168 kg / day and for the BOD is 4928 kg. According to the values from Table 1, a very organic removal efficiency is observed according to values of BOD and COD. The real loadings are lower than the maximum one but in most cases the WWTP are sized by at least 20% higher capacity.

The modifications of the nitrogen compounds level during biological treatment are presented in Table 2.

*Table 1. Wastewater indicators (COD, BOD<sub>5</sub>) at inlet and outlet of the biological treatment process*

Week	Wastewater inlet flow, m <sup>3</sup> /h	COD inlet		COD outlet		BOD <sub>5</sub> inlet		BOD <sub>5</sub> outlet	
		ppm	kg/day	ppm	kg/day	ppm	kg/day	ppm	kg/day
1	1615	3806	6028	333	537	1813	2908	189	304
2	1427	3878	5522	374	533	1789	2550	213	303
3	1567	3976	6219	413	648	1936	3029	210	329
4	1414	3709	5248	392	554	1827	2582	217	307
Average	1506	3842	5755	378	568	1841	2767	207	311

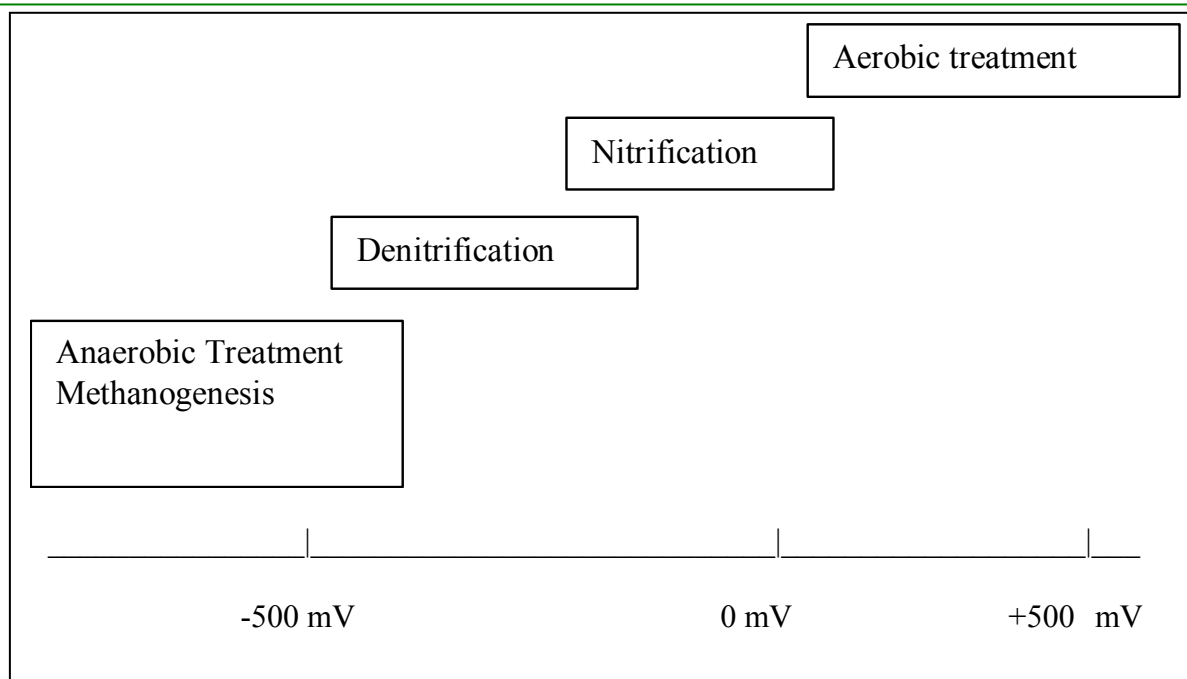
*Table 2. Waste water indicators (N<sub>tot</sub>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>) at inlet and outlet of the biological treatment process*

Week	Total nitrogen inlet		Total nitrogen outlet		N-NH <sub>4</sub>		N-NO <sub>3</sub>		N-NO <sub>2</sub>	
	ppm	kg/day	ppm	kg/day	inlet, ppm	outlet, ppm	inlet, ppm	outlet, ppm	inlet, ppm	outlet, ppm
	1	266	482	28	50	30	6	6	1	0.27
2	220	305	32	46	22	1	4	2	0.30	0.12
3	240	393	32	52	26	2	5	3	0.39	0.31
4	240	352	33	48	31	2	4	4	0.21	0.10
Average	241	383	31	49	27	3	5	3	0.29	0.16

The ammonium level is drastically decreased between inlets to outlets. The total amount of ammonium in kg/day can be calculated with the daily flow rate (the same for nitrate and nitrite). If it is subtract from the total nitrogen the inorganic forms of nitrogen (ammonium, nitrate and nitrite) the rest means organic nitrogen that represents more than 80%. The efficiency in nitrate and nitrite removal can not be taken in consideration as these two compounds are continuously formed, in the presence of oxygen, at every stage of the process.

In the denitrification tank it is mounted an oxido-reducing power transducer (ORP) that sends to the process computer valuable data about the treatment development (Stumm and Morgan, 1996; Byl and Williams, 2000). The ORP is given in mV and depends on the treatment solution (Figure 3).

In the nitrification tank there was installed a dissolved oxygen transducer that is also connected to the process computer. The values of oxido-reducing power (ORP) from the denitrification tank and the values of dissolved oxygen from the nitrification are revealed in the Table 3.



*Fig. 3.. ORP values for different treatment processes*

**Table 3.** Dissolved oxygen and oxido-reducing power (ORP) variations during the biological treatment process

Day	Dissolved oxygen, ppm	Oxido-reducing power, mV	Day	Dissolved oxygen, ppm	Oxido-reducing power, mV	Day	Dissolved oxygen, ppm	Oxido-reducing power, mV
1	1.05	-374.68	11	1.74	-338.79	21	1.99	-348.14
2	0.16	-387.67	12	0.96	-344.57	22	0.80	-362.12
3	1.00	-354.51	13	1.98	-362.40	23	3.02	-341.73
4	1.32	-352.69	14	1.07	-349.48	24	1.73	-354.56
5	0.41	-379.41	15	1.38	-349.93	25	1.17	-366.22
6	2.12	-341.73	16	0.89	-375.89	26	1.51	-350.75
7	1.71	-335.65	17	0.38	-394.08	27	1.99	-354.98
8	1.16	-347.56	18	1.81	-353.90	28	1.66	-348.82
9	0.84	-367.58	19	1.55	-356.04			
10	2.47	-338.58	20	2.12	-345.25			

The ORP is directly related to the dissolved oxygen values as we can see in Figure 4

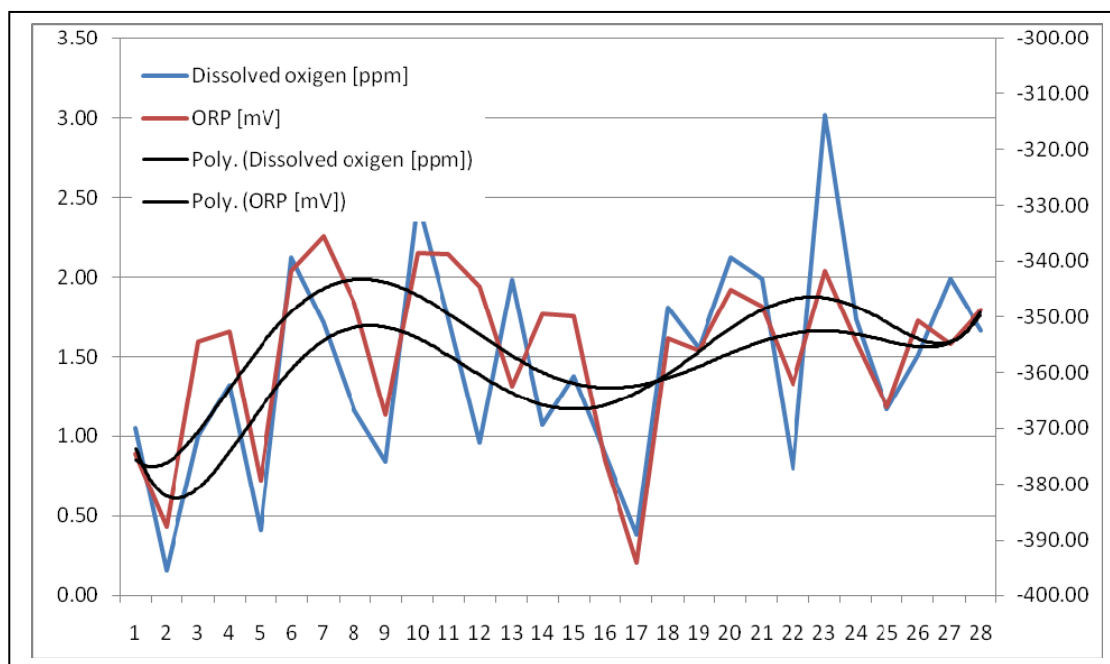
In the denitrification tank there take's place, at the same time, two important reactions: the ammonification of the organic nitrogen and the denitrification of the nitrogen oxides come from the nitrification tank. The process is a complex one and involves three steps. Because of the two simultaneous reactions (ammonification and denitrification) the ORP value is very low and it can

be interpreted as an incipient anaerobic process, but it is not.

The ammonification process takes place even in anoxic or aerobic conditions; in this case it develops in anoxic conditions together with the denitrification process. The wastewater organic load is very high, the tank is of 8 m high, the activated sludge concentration is also high and all these three conditions lead to a low ORP value. The ammonification process does not necessarily need

oxygen in the air and the denitrification process take's oxygen from nitrogen oxides. In the technical literature the recommended dissolved oxygen level for the denitrification process is a rate of maximum 0.1 ppm (according to NP 107-04 normative, 2005). To obtain this small value the air administration must be limited in the nitrification area to a rate of maximum 2 ppm or lower, depending on the

treatment plant constructing peculiarity. Because the dissolved oxygen level depends on many factors, between changing one of the factors and obtaining a quantified result some time can pass, so the reaction is not an immediate one. The entire plant (activated sludge) acts as an ecosystem and, the same as in the nature, the results can not be seen immediately.



*Fig. 4. ORP and dissolved oxygen correlation*

Another important factor that easily modifies the ORP value is the COD. If the organic load is variable then the dissolved oxygen value will be variable too, the same as the ORP value.

In this case to keep the process in normal condition the ORP value can not decreased under -450 mV. Under this value the anaerobic process will take place and the sludge will became black from brown, with an awful smell and also bulking at the surface that will affect the sedimentation stage.

Higher ORP values (positive ones) mean higher dissolved oxygen values and, in this case, the denitrification process will stop. In the oxygen presence, the denitrifying bacteria prefer to take the oxygen from the water and not from the nitrogen oxides. The result will be high nitrates and nitrites levels in the effluents. Another reason for the high

ORP value is the low nitrogen level in the influent and, in this situation, the operating condition of the plant shall be reconsidered because is possible for the aeration system to be oversized, leading to unjustified electrical consumption.

The nitrogen from the wastewater is returned to the environment in three ways:

- In air (the air contains 78% nitrogen), by effect of denitrifying bacteria.
- In soil, by sludge disposal as fertilizer.
- In water, in small amount because the effluent still contain nitrogen, but in concentration that does not affect the aquatic life.

Every day the WWTP is filled up with 383 kg of nitrogen on average and the outlet register only 49



kg (table 2). It means that 334 kg of nitrogen is retained by the plant.

The nitrogen concentration embedded in the biomass that leave the bioreactor – clarifier system by excess sludge is considered to be, in the technical literature, 0.04 ÷ 0.05 from BOD<sub>5</sub> (according to NP 107-04 normative, 2005).

In this case, 0.045 x BOD<sub>5</sub> = 0.045 x 1841 = 82.85 ppm

If the excess sludge volume in a day is: 130.79 cubic meters per day result that the amount of nitrogen removed with the biomass is:

$$130.79 \text{ m}^3/\text{h} \times 82.85 \text{ ppm} / 10^6 = 10.84 \text{ kg}$$

So, the nitrogen that is set free out in the atmosphere sum 323.16 kg/ per day. If we extend this value to an entire month the amount will become huge, almost 10 tons of pure N<sub>2</sub> reenter in the nature cycle, a big achievement for the treatment techniques.

### Oxygen demand for an efficient biological treatment of baker's yeast wastewaters

The oxygen requested to fulfill this entire process can be calculated. The oxygenation capacity represents the amount of oxygen needful for biochemical processes that take place in the bioreactor for:

- Organic carbon removal (including the endogenous breathing)
- Nitrification (ammonium conversion to nitrites and nitrates)
- Denitrification that represents the economy of oxygen by absorbing it from nitrites and nitrates in biomass development.

The oxygen specific consumption for removing the organic carbon (OSC<sub>C</sub>) is stated in kg O<sub>2</sub> / kg BOD<sub>5</sub> and it is determined according to the formula:

$$OSC_C = 0.56 + \frac{0.15 \cdot T_N \cdot F_T}{1 + 0.17 \cdot T_N \cdot F_T} = 0.8 [\text{kgO}_2 / \text{kgBOD}_5]$$

where: F<sub>T</sub> - 1.072<sup>(T-15)</sup> – temperature factor for summer

T - 25 ...27 (wastewater temperature in summer), °C

T<sub>N</sub> – sludge age, days

The oxygenation capacity for organic carbon removal is:

$$\overline{OC}_C = OSC_C \cdot BOD_{5-load} = 2213.6 [\text{kgO}_2 / \text{day}]$$

The oxygenation capacity for nitrification is determined according to the formula, where oxygen specific consumption (OSC<sub>N</sub>) was approximated to 4.3 kg O<sub>2</sub> / kg oxidized nitrogen:

$$\overline{OC}_N = 4.3 \cdot Q_i \cdot (c_{N-NO_3}^D - c_{N-NO_3}^i + c_{N-NO_3}^{eff}) / 1000 = 972.34 [\text{kgO}_2 / \text{day}]$$

where: Q<sub>i</sub> - wastewater influent flow, m<sup>3</sup>/h

c<sub>N-NO<sub>3</sub></sub><sup>D</sup> - daily average concentration of the nitrogen that must be denitrified, mg N-NO<sub>3</sub>/liter,

c<sub>N-NO<sub>3</sub></sub><sup>i</sup> - nitrogen from nitrate concentration in influent to the WWTP, mg N-NO<sub>3</sub>/liter

$$c_{N-NO_3}^D = c_{N_{tot}} - c_{N_{org}}^{efl} - c_{N-NH_4}^{efl} - c_{N-NO_3}^{efl} - c_{N_{org}}^{BM} = 152.15[mg / liter]$$

where:  $c_{N_{tot}}$  - total nitrogen concentration in influent, mg N<sub>2</sub>/liter

$c_{N_{org}}^{efl}$  - organic nitrogen concentration in effluent, mg N<sub>org</sub>/liter

$c_{N-NH_4}^{efl}$  - nitrogen from ammonium concentration in effluent, mg N-NH<sub>4</sub><sup>+</sup>/liter

$c_{N-NO_3}^{efl}$  - nitrogen from nitrate concentration in effluent, mg N-NO<sub>3</sub><sup>-</sup>/liter

$c_{N_{org}}^{BM}$  - nitrogen concentration embedded in the biomass that leave the bioreactor, mg N<sub>org</sub>/liter

In the denitrification process the “gain” of oxygen from the nitrites, is approximated to be 2.9 kg O<sub>2</sub> / kg nitrogen from the nitrites and nitrates that should be denitrified. Minus sign reflect that the oxygen is gained from the nitrification stage.

$$\overline{OC}_D = -2.9 \cdot Q_i \cdot c_{N-NO_3}^D / 1000 = 664.5[kgO_2 / day]$$

The hourly oxygenation capacity for the entire process will be:

$$\overline{OC}_{h.nec} = \frac{(\overline{OC}_C - \overline{OC}_D) + \overline{OC}_N}{24} = 105.06[kgO_2 / hour]$$

The needed air flow that will be blown in (to ensure the hourly oxygenation capacity) includes in its equation, the wastewater temperature, the oxygen transfer from air to water efficiency, the air maximum temperature, the blowing depth, etc. The relation for expressing the oxygenation capacity in real condition is Arrhenius type.

$\overline{OC}_{h.nec} = AOR$  (Actual Oxygen Requirement)

$$SOR = \frac{AOR}{\alpha \left( \frac{\beta \cdot C_{sw} - C_L}{C_{ss}} \right)} \cdot \theta^{(T-20)} = 310[kgO_2 / hour]$$

where: SOR - Standard Oxygen Requirement

$\theta = 1.024$  - temperature correlation factor

$t$  - wastewater temperature (will take in to consideration summer temperature = 27°C), in °C

$\alpha$  – oxygen transfer coefficient = 0.6, for  $t=27^\circ\text{C}$

$\beta$  – oxygen solubility coefficient = 0.95

$C_L$  – aeration basin dissolved oxygen level = 2 ppm

$C_{sw}$  – Oxygen average concentration at saturation in clean water in working conditions at 27°C

$C_{ss}$  – Oxygen average concentration at saturation in clean water in standard conditions

$$C_{sw} = C_{SM} T \cdot \left( \frac{BP + 0.4335 \cdot DWD \cdot f}{14.7} \right) = 10.9[mg / l]$$

$$C_{ss} = 9.092 \cdot \left( \frac{BP + 0.4335 \cdot DWD \cdot f}{14.7} \right) = 12.3[mg / l]$$

were:  $C_{SMT}$  - oxygen saturation value at atmospheric pressure and  $27^{\circ}C = 8.08$  ppm

9.0292 - oxygen saturation value at standard conditions

BP - barometric pressure = 14.7, psi – pound/square inch

DWD– air release or diffuser water depth = 26.25, feet

f – effective depth factor = 0.45

The value of standard oxygen requirement must be turned in air flow. Based on this air flow we can peak the suitable blower for the WWTP.

$$Q_{Nair} = \frac{SOR}{SOTE} \cdot \frac{1}{\gamma_{air}} \cdot \frac{1}{c_{SO}} = 2295 [Sm^3 aer / hour]$$

where: SOTE – oxygen transfer efficiency in clean water, under standard conditions, at  $H_i$  blowing depth,

$$SOTE = \eta_1 \cdot H_i = 0.4[\%]$$

$\eta_1$  – oxygen transfer specific efficiency in clean water, under standard conditions, for 1 meter blowing depth = 5%

$\gamma_{aer}$  – air specific weight = 1.206 kg / m<sup>3</sup>

$C_{SO}$  - oxygen content from 1 m<sup>3</sup> air under standard conditions= 0.28 kg / m<sup>3</sup>

The 2295 Sm<sup>3</sup> / hour are needed for a daily average of 2762 kg BOD<sub>5</sub>, but the WWTP was designed for 4928 kg BOD<sub>5</sub> / day and the blowers should be sized for maximum load, meaning 4094 Sm<sup>3</sup> / hour.

Three blowers for this application with the capacity of 2511 Sm<sup>3</sup> / hour were selected. One of the blowers is provided with frequency converter to obtain the wanted dissolved oxygen level. In normal conditions one blower is enough but at high loadings another blower should be started (the one with frequency converter).

### **Phosphorus addition for increase organic nitrogen bioconversion to gaseous form**

Acting like an ecosystem the microorganisms from the activated sludge (especially bacteria) need nitrogen beside carbon and phosphorus to grow (Spellman, 2003). For mineralizing of the organic matters the bacteria needs all these three macro elements in well defined proportions. The recommended ratio for a classical treatment is revealed below

(according to NP 107-04 normative, 2005):

CBO <sub>5</sub>	:	N	:	P
100	:	5	:	1

In many cases, this ratio is not met and the treatment technologies become more sophisticated. The wastewater from the baker's yeast industry is unbalanced from this point of view; it contains a big quantity of nitrogen, a very small amount of phosphorus. The ratio for this type of water looks as follows:

CBO <sub>5</sub>	:	N	:	P
100	:	13.8	:	0.4

It is understood that the classical treatment system can not be efficient in this job, but the advanced treatment techniques can deal with it.

The phosphorus is an important growth factor for the microorganisms from the activated sludge. The lack of phosphorus leads to bad efficiency and unbalance the trophic pyramid. As showed above the phosphorus concentration is very small and to obtain good results for nitrogen and organic carbon removal it must be furthermore administrated. Besides, a big part of the total phosphorus (almost 30%) can not be assimilated and, it precipitates. The

easy digested compounds are the phosphates ( $PO_4^{3+}$ ) and these will be taken into account (Table 4).

**Table 4.** Wastewater indicators ( $P_{tot}$ ,  $PO_4^+$ ) at inlet and outlet of the biological treatment process

Week	Influent total phosphorus, mg/l	Influent soluble phosphorus - $PO_4$ -P, mg/l	Effluent total phosphorus, mg/l	Effluent soluble phosphorus - $PO_4$ -P, mg/l
1	6.21	4.74	1.79	0.57
2	8.02	4.92	0.99	0.52
3	6.14	5.19	1.48	0.71
4	7.63	5.15	0.84	0.51
Average	7.00	5.00	1.27	0.58

The added phosphorus comes from the phosphoric acid ( $H_3PO_4$ ) which is a molecule easy to assimilate. It is administrated in the external recirculation pipe of the activated sludge with two dosing pumps.

To find out the phosphoric acid quantity that must be supplied we will use the following relations:

The ratio  $\frac{BOD_5}{PO_4 - P} = 100/1$ , is imposed

Thereby:

- $BOD_5 = x[mg/l] = 1544[mg/l]$
- $PO_4 - P = \left(\frac{x}{100}\right) = y[mg/l] = 15.44[mg/l]$
- Effective concentration from effluent  $PO_4 - P = z[mg/l] = 5[mg/l]$
- Phosphorus need  $y - z = a$   $15.44 - 5 = 10.44[mg/l]$
- Daily wastewater flow to WWTP =  $1506 m^3$
- Loading  $PO_4 - P = \frac{1506 \cdot a}{1000} = b[kg/day] = 15.72[kg/day]$
- Atomic mass of P = 31
- Atomic mass of  $H_3PO_4 = 98$
- Pure phosphoric acid daily need  $H_3PO_4(100\%) = b \cdot (98/31) = c[kg/day] = 49.7[kg/day]$
- Technical phosphoric acid need  $H_3PO_4(75\%) = \frac{c}{0.75} = d[kg/day] = 66.26[kg/day]$ 
  - Volume  $H_3PO_4(75\%) = 1.75(kg/l) \Rightarrow H_3PO_4(75\%) = \frac{d}{1.75} = 37.86(l/day)$

In these conditions the treatment efficiency is sustainable by:

Nitrogen removal efficiency:

$$\eta_N = 100 - \frac{N_{tot-efluent} \cdot 100}{N_{tot-influent}} = 100 - \frac{49 \cdot 100}{383} = 87.20\%$$

Organic carbon removal expressed by COD – chemical oxygen demand:

$$\eta_{COD} = 100 - \frac{COD_e \cdot 100}{COD_i} = 100 - \frac{568 \cdot 100}{5755} = 90.13\%$$

Organic carbon removal expressed by BOD - biochemical oxygen demand:

$$\eta_{BOD} = 100 - \frac{BOD_e \cdot 100}{BOD_i} = 100 - \frac{311 \cdot 100}{2767} = 88.76\%$$

## Conclusions

1. The nitrogen removal can not be done in a classical aerobic or anaerobic WWTP.
2. The best efficiency, almost 90%, is obtained on nitrification/denitrification processes.
3. Every month 10 tons of pure nitrogen reenter in the nature cycle.
4. In the classical aerobic treatment systems the more dissolved oxygen bubbled in the pools the better process works, but in the advanced treatment techniques the dissolved oxygen control is a key to nitrogen removal efficiency.
5. Beside nitrogen the WWTP has a 90% efficiency in removing organic carbon.
6. The ORP from denitrification area has a precise correlation with the dissolved oxygen value from the nitrification area.
7. If the oxygen level in the nitrification area is too high the denitrification process can be disturbed. The denitrifying bacteria prefer the free dissolved oxygen rather than bounded oxygen from nitrites as energy is higher.
8. The advanced biological treatment is completely ecological and it does not needs chemicals for pretreatment processes.

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