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NOVEL N REMOVAL WITH SOME INDUSTRIAL REALISATION IN HUNGARY

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Continuous decrease of discharge limits of purified wastewater and the demand for minimization of investment and treatment costs resulted in new discoveries and technological developments in nitrogen removal from sewages and industrial wastewaters. Almost all the newly recognised processes are based on the NO_2^- route of the nitrogen removal. The SHARON process comprises an autotrophic and a following heterotrophic nitrogen transformation step. The ANAMMOX process however requires around 1:1 NH_4^+:NO_2^- ratio in its influent. Besides the N_2 gas production in the process, a small portion of the nitrogen turns into NO_3^-. Nowadays the practical importance of the aforementioned processes is unfortunately limited to some special wastewater streams, but the utilization of this shortcut of the nitrogen removal in municipal sewage treatment would also be highly beneficial. It appears that according to our practical data collected in specially designed treatment plants for the purification of the wastewater of some animal waste rendering plant and two-stage activated sludge municipal sewage treatment plants the new technologies can easily be realized. The two-stage systems contain two separate sludge cycles in series. Both cycles comprise an aerobic bioreactor and a following mainly rectangular clarifier. The first stage is specially designed for COD removal while the second for autotrophic nitrification. The highly overloaded first stage can remove of the main portion of the influent COD. This way the sludge of the second stage contains 5-10 times more autotrophic microorganisms than the conventional A2/O systems. This results in similar increase in the specific nitrification capacity, while significant simultaneous denitrification can occure.

Keywords: nitrogen removal, nitrit route, two sludge cycle, animal waste rendering industry

Introduction

Nowadays wastewater treatment is the essential part of the environmental infrastructure. As a result of the centralization, the wastewater treatment has become an inevitable task since the middle of the last century. One of the biggest challenge of the future in this field is to increase the specific efficiency, besides the cut of the usage of the external energy sources.

The issue of this paper is to point out the collected national and international experiences, and to introduce one possible way of the future development to remove the nitrogen from domestic and special industrial wastewater streams in a cost-effective way.

The realization of the nitrogen removal in the past

The recognition of the special ways of nitrogen elimination in the wastewater treatment and the experimental results in the same field have resulted in the development of new wastewater treatment strategies. One of the most important results of the last 2-3 decades was the discovery of the nitrit route [1] in nitrogen removal. International research groups have identified the fully autotrophic way of nitrogen removal besides the autotrophic/heterotropic nitrate route [2, 3]. It came to the light that nitrogen removal over nitrite can take place in treatment plants that operate with special, concentrated (TKN), warm (>35 °C), wastewater streams [4, 5]. The aforementioned process was implemented mainly for the treatment of the sludge liquor of the anaerobic sludge digestion [6], however some publications are existing concerning similar processes for the treatment of special wastewater streams [6].

The researchers and the engineers have implemented some full scale technologies for the side stream of the communal wastewater treatment starting out from the laboratory scale [7, 8]. At first these plants were able to convert the ammonium to nitrite autotrophically and in a subsequent heterotrophic reaction into nitrogen gas (with external carbon source addition) (SHARON). The stoichiometry of the first step is presented in Equation 1 [9]. At the beginning of the operation of the SHARON-ANAMMOX technology the operators could stop the oxidation of the ammonium at nitrite but the autotrophic reduction of the nitrite wasn't carried out in the second anoxic reactor [10]. The second step of the process (ANAMMOX, Equation 2 [11]) was successfully developed in the year of 2006. As a result of their success the autotrophic conversation of the nitrite and the ammonium of the effluent of the SHARON reactor were realised [8].

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \rightarrow C_5H_7NO_{2\ biomassza} + + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3 \quad (1)$$

$$NH_4^+ + 1{,}31\ NO_2^- + 0{,}066\ HCO_3^- + 0{,}13\ H^+ \rightarrow 1{,}02\ N_2 + + 0{,}26\ NO_3^- + 0{,}0066\ CH_2O_{0,5}N_{0,15} + 2{,}03\ H_2O \quad (2)$$

The advantages of the nitrogen removal over nitrite have been mentioned several times [12, 13] but the remained nitrogen (nitrate) compounds of the treated wastewater haven't been emphasized. It is known that about 10% of the influent ammonium is remained in the effluent as nitrate. The unconverted ammonium is added to the total effluent nitrogen based on the practical experiences, consequently the effluent of the ANAMMOX reactor always contains ammonium and nitrate as well [8]. It is easily countable that with the typical concentration of the reduced nitrogen form in the raw communal wastewater and without post-denitrification or the recycle of the treated wastewater, the nitrate content of the effluent couldn't be lower than 5–7 mg NO_3-N/l. That characteristic of the process can limit the application or it requires another treatment step that can convert the above mentioned pollutants into gas or solid phase.

As a consequence of the slow growing and the specific environmental inquiries of the ANAMMOX bacteria it seems as if these species could exclusively be suitable in the practice only for the treatment of the side streams of the communal wastewater treatment or for special industrial wastewaters.

The supernatant of the anaerobic sludge treatment contains about the 15–25% of the total nitrogen load of the communal treatment plants [14] and these surplus of the load arises only at those plants where anaerobic sludge treatment is operated. Thus the practicable realization of the similar system configuration and its output are limited (>50 000 population equivalent). Moreover the total nitrogen load of these plants could be reduced by more simply controllable, more competitive methods as well [15].

In case of these specifications of the reactions one should find a suitable combination of the conventional and the novel conversation routes of nitrogen.

In our opinion the real question is how to combine the above mentioned processes so as to be suitable for the treatment of the mainstream of the wastewater treatment plant.

The development of the wastewater technologies yielded numerous results in the operation of the non-activated sludge processes like granular sludge technologies (anaerobic [8], aerobic [16]), and technologies containing artificial or natural biofilm carriers [17, 18]. In this respect the most important advantage of these technologies in contrast to the activated sludge (AS) processes is that these provide suitable selection for the slow growing micro-organisms. This way simultaneous processes (for example: nitrification/denitrification) can take place in the different layers of the granule or the biofilm [18]. Under suitable process control nitrification and denitrification can occur in the same bioreactor simultaneously.

It is interesting to see the duplicate role of the aerated bioreactors nowadays: the carbon and the ammonium oxidation. As the carbon oxidation is a heterotrophic, the ammonium oxidation is an autotrophic process, the control of the sludge retention time has an important function in the treatment. To achieve a suitable nitrification rate the sludge residence time must be around 14–15 days in the AS systems in winter time. From the personal equivalent and the specific sludge yield of the above mentioned two biochemical processes it is easily countable that the ratio of the autotrophs in the activated sludge is around 3–5%. Based on the ratio of the nitrifiers in these AS systems assuming the usual sludge concentrations (3–6 g MLSS/l) the expected maximal volumetric nitrification rate could be around 0,06–0,12 kg NH_4-N/m^3d. Consequently it is unambiguous that the volumetric capacity can be increased with the increase of the sludge concentration (UF membrane, improvement of the sludge settling) [19], but in our opinion there is another option to improve the volumetric nitrification capacity.

This solution could be the well-known spatial separation of the heterotrophic carbon and the autotrphic ammonium oxidation in the treatment of communal wastewater streams (two sludge cycles) *(Fig. 1)*. The disadvantages of these technologies are easily solvable. The chemical phosphorus removal and the reduction of the oxidised nitrogen with the recirculation of a certain amount of the effluent can result in effective treatment technologies. The adoption of the experiences of the past decades in the sphere of special nitrogen removal ways and the combination with other newly applied devices could result in an effective solution in small reactor volume treating the mainstream of communal wastewater.

The two sludge cycle systems contain continuously aerated AS tanks with rectangular clarifiers and sludge recycle. The two activated sludge culture formed are not mixed with each other (just in the first stage) so the efficient carbon oxidation in the first stage provides favourable conditions for the selection of the autotrophs in the second stage [19].

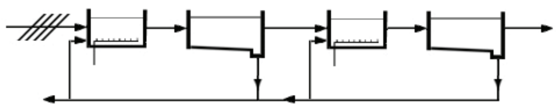

Figure 1: The scheme of the 2AB system

After the collection and evaluation of the operational data of such treatment plants in Hungary [19] it can be concluded that the 2AB systems operate with a high loaded first stage to oxidise the maximal portion of the organic carbon in the raw wastewater. Due to the short hydraulic retention time (HRT), law dissolved oxygen concentration (DO), and the high sludge concentration, small SRT is formed. Under these circumstances only the organic carbon oxidation can take place in this step resulting in high sludge yield so that the decrease of the nitrogen and phosphorous concentration of the wastewater is the effect of the growing of micro-organisms [19].

It is noticeable that in one Hungarian treatment plant (2AB configuration) the specific sludge yield of the organic carbon removal (in the 1st stage) is around 0,4–0,5 kg MLSS/kg BOD_5 due to the high organic load, low DO level and the over-designed intermediate clarifier. So in this plant such specific sludge yield is formed as in the fixed film systems [20].

Typically the effluent of the first stage contains small amount of biodegradable COD and nearly the total TKN. In consequence of the small COD/TKN ratio of the influent wastewater of the second stage the ratio of the autotrophs could be higher than in the conventional A2/O treatment plants. It is easily countable that the ratio of the autotrophs could be around 20–25% if the intermediate clarification and the first aerobic stage work properly. So no wonder that the nitrification rate of this stage can reach the 1 kg NH_4-N/m^3d in summer with 3–4 mg/l DO level, and 3–4 g MLSS/l sludge concentration at the same time [19]. This is clearly due to the increase of the ratio of autotrophs in the sludge.

More surprising is that besides the above mentioned nitrification capacity around 0,6 kg NOx-N/m^3d denitrification rate can be observed in the second AS stage. From the small COD/TKN ratio it is indirectly suspectable that the nitrogen removal must happen via nitrite heterotrophically or only autotrophically [13].

In our opinion the nearly forgot 2AB technology in combination with the research experiences of the past decades could be one direction of the further development to purify the main communal and industrial wastewater streams.

An opportunity presents itself to recycle a certain portion of the treated wastewater to be denitrified. So in the first step due to the low DO level the denitrification of the remaining NO_x-N can occur as well. Moreover the combination of the 2AB system with the biofilm processes could result in more efficient technologies to treat the also communal and industrial wastewater.

One possible way for the purification of the liquid waste of the rendering industry

One can find some of the above mentioned 2AB or similar treatment technology in the rendering industry treating the 1-3rd. class animal waste in Hungary.

In Hungary the ATEV co. carries out the elimination of the animal waste ranked into 3 classes:

- specified risk material (SRM) based on the Hungarian regulations (1st class),
- fatty sludges, manure, dead domestic/farm animals (2nd class),
- slaughterhouse waste that is not used for food-production (3rd class),

The various elimination strategies result in different amount of wastewater with different quality. The wide-spread strategies for the elimination of the animal waste are the wet and the dry technologies. The decision between the two technologies is based mainly on the type of the animal waste. The product of the dry technology is the meat flour that can be used as a fodder or it can be burned up. The product and the by-product of the wet technology could be used in the biogas and compost production.

In the so-called wet fat extraction technology the fat is extracted from the wet meet paste. The heat-consuming drying and the pressing or the grinding and classification of the meat flour and the packaging do not happen in this technology.

In the classical meat flour production (dry technology) after the boiling of the raw material the pasta is transported to the dryer and the fat is extracted with pressing from the dried material. The subsequent step is the grinding (in a mill), where the dried material is grinded into flour, and packed into sacks (50 kg) or into big-bags.

The biggest amount of the wastewater is produced during the pressure compensation of the boiled (sterilized) meat paste. The boiler operates at 3 bar pressure, 135 °C temperature minimum 20 minutes long. The wastewater has high TKN concentration that is produced during the pressure compensation (condensation). The average parameters of the condensate are the following:

- high temperature (40–60°C),
- high pH (8–9,5),
- high COD concentration (~3–6 g/l),
- high TKN concentration (depending on quality of the raw material 1–3 g/l).

The other considerable wastewater stream is the water leakage of the raw material terminal station that has varying composition (greasy, fatty). The average parameters of the leakage are the follows

- high COD concentration (depending on quality of the raw material ~10–30 g/l),
- high suspended solid content (1–2 g/l) ,
- high TKN concentration (depending on quality of the raw material 0,5–2 g/l).

Most often the mentioned wastewater streams are treated together. This mixed wastewater is pumped through an oil and fat separator, and the next step is usually the air flotation with chemicals. In case of efficient flotation the physically and chemically treated water's COD/TKN ratio is about 1–4 (~2,5–4 g/l COD/1–2 g/l TKN). The pH and the temperature of the pre-treated water remains high after the physical and chemical treatment, too.

The treatment plants with different configurations built in the 90's are operated properly with these wastewaters, due to the regular reconstruction and careful operation. Almost all of them were built in 2AB or similar configuration. For example one of them operates with a high loaded trickling filter in combination with an AS second stage (Bőny), an other one is a modified 2AB AS configuration (Debrecen).

In *Table 1* one can see the nitrification rates are close to the well-known design data for the communal wastewater, but significant denitrification activity with low COD/TN ratio can be observed. The high denitrification activity can prove the nitrit route under these circumstances (high temperature even in winter, high NH_4-N concentration, small COD/TN ratio).

Table 1: Operational data of some Hungarian ATEV co. wastewater treatment plants

Plant	Treatment plant		Wastewater					Operational parameter							
	Pretreatment	Biology	Q m^3/d	COD g/l	NH4-N g/l	BOD5 g/l	COD/TN	LSP KOI kg/m^3*d	LSP BOI5, kg/m^3*d	LSP NH4-N kg/m^3*d	ηKOI %	ηNH4-N %	ηTN %	Vox(anox) m^3	x gSS/l
BO	Oil- and grease separation	Trickling filter/ AS (cyclic aeration)	60-80	0,5-0,7*	0,4-0,5*	n.a.	1,3-1,8	0,4-0,6*	n.d.	0,3-0,4*	90-95	60-70	70-75	60/-	~6
DEB	Oil- and grease separation, Flotation	2AB AS	120-150	~6/~4**	~1/~0,7**	~4/~2**	~6/~2**	1,5/0,75**	1,1/0,4**	0,3/0,13**	35/85**	25/30**	40/90**	525/720**	3/5**
MD	Flotation	A/O	150	~4	~1,2	~2	~3	0,3	0,15	0,09	98-99	95-99	85-95	1600 (400)***	4-5
HMVH	Flotation		250	~6	~0,8	~3	~7,5	1,1	0,55	0,19	98-99	95-99	90-95	1000 (400)	6,5

n.d.: no data
BO: wastewater treatment plant of Bőny
DEB: wastewater treatment plant of Debrecen
MD: wastewater treatment plant of Mátyásdomb
HMVH: wastewater treatment plant of Hódmezővásárhely
* wastewater that goes in to the AS stage
** first stage/second stage (efficiency is calculated from the influent and the effluent concentration of the given stage)
*** cyclic aeration in the aerobic basin (1,5 hours aeration - 1 hour mixing)

Summary

Based on our practical experiences it is clear that there is significant simultaneous denitrification in all of the observed industrial wastewater treatment plants (Bőny, Debrecen, Sárvár, Mátyásdomb). The NO_3^- concentration in the effluent is lower than it should be in NO_3^- route (stochiometrically). Without detailed researches the data support that the simultaneous nitrit route can take place in these industrial wastewater treatment plants.

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