NITROGEN COMPOUNDS REMOVAL FROM MUNICIPAL WASTE WATER

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Abstract. The paper is a short review on nitrogen compounds removal, as ammonia, nitrate, nitrite, from municipal waste water, containing primary information of nitrogen chemistry, consideration on the physical-chemistry methods of removal and also on the most popular wastewater nitrification systems[1].

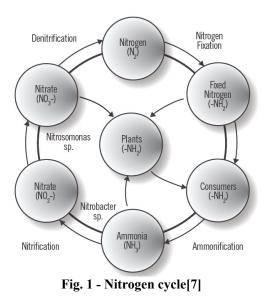
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1. INTRODUCTION

The use of water becomes in time more impractical but the water resources. Human activities, from cities, industry or irrigation systems are discharging effluent which becomes the supply of water for other users. Not only intensive agriculture [2,3], but also the nuclear industry[4] are the main pollution source for the drinking water. The admission levels for nitrate in CE is 50 mg.L⁻¹ (adults) -15 mg.L⁻¹ (children) [3,5,6], high levels of nitrate concentration leading to serious medical problems.

Chemicals as metallic salts or complex organic compounds are increasing frequency in the waterways. They enter the drinking water and eventually end up in the wastewater. Primary and secondary waste treatment processes could be not very effectively in removing these chemicals. For years, dilution and purification of the effluent in the receiving stream was considered acceptable. Because these streams have more pollutant loadings, natural processes are not enough in these days. Often is necessary some more treatment than primary and secondary wastewater. In the last years, some physical, chemical, and biological processes come into light in the technology. wastewater Currently wastewater technologies which have been used for advanced wastewater treatment are the following: filtration, adsorption, chemical oxidation, reverse osmosis, nitrate removal by denitrification, phosphorus removal.

Ammonia removal could be done by the biological nitrification of wastewater and after that the denitrification, which involves the conversion of nitrate nitrogen ions (NO_3) to gaseous nitrogen (N), as shown on the left side of nitrogen cycle (figure 1).



2. EXPERIMENTAL AND DISCUSSION

The removal of ammonia from wastewater treatment becomes a a very important operation in special for the lands where agriculture is done intensively. One method of ammonia removal is the biological nitrification of wastewaters, a process where ammonia is converted to nitrate using aerobic autotrophic bacteria in the treatment process. The process of nitrification is a two-step process for removing ammonia from wastewater and this is done by the utilization of two types of autotrophic bacteria that oxidize ammonia to nitrite (nitrosomonas) and then oxidize nitrite to nitrate (nitrobacter). Biological nitrification systems are projected to convert the entire amount of ammonia into nitrate[1,7].

The two types of autotrophic bacteria need proper biomass concentrations, in a specific environmental conditions (temperature, pH, alkalinity, etc.), enough time for the treatment process, and an increased amount of air, more that requires, for the treatment of biochemical oxygen demand only. A different factor that should be take in consideration in projecting of wastewater treatment plants, that assure biological nitrification is the low alkalinity. Adding sodium hydroxide or other chemicals in order to increase the alkalinity may be needed.

The treatment processes which are recomended for biological nitrification at wastewater treatment plants are :

- conventional activated sludge system(figure 2)
- extended aeration treatment systems(figure 3).

- sequencing batch reactor(figure 4)
- fixed film (figure 5)
- membrane bioreactor(figure 6)
- lagoon systems (figure 7)

The **conventional activated treatment** process (figure 2) has the advantage that the proven treatment process is able of treating many types of wastewater and is easier to operate, comparative with other treatment processes.



Fig. 2 - Wastewater conventional system[1].

Conventional activated sludge treatment processes that were projected for biochemical oxygen demand removal only could be changed to assure biological nitrification, too. Constructing conventional activated sludge treatment processes have the disadvantage of being are very expensive. Aeration basins and clarifiers are usually built of concrete and demand expensive mechanical equipment (blowers, pumps, clarifier mechanisms, etc). Conventional treatment processes are also more sensizitive to bulking sludge from filamentous organisms.

Extended aeration treatment processes (figure 3) are similar to conventional activated sludge treatment processes and involve: aeration basins, clarifiers, return activated sludge, and waste activated sludge processes. The most important difference is the longer hydraulic and solids residence times in the process. The hydraulic residence time is typically around 24 hours and the sludge residence time is over 20 days at design flow rates and organic loadings [1]. Having sufficient air, the nitrification will take place faster in extended aeration processes.



Fig. 3 - Conversion of ammonia in a diffused aeration system [1].

Because of these longer times for hydraulic and solids residence, the extended aeration treatment processes can assure the better quality effluent for any kind of wastewater. Extended aeration processes are easier to operate than conventional activated sludge treatment process. With a sufficient amount of oxygen, extended aeration treatment processes can assure raised levels of biological nitrification. The main disadvantage to extended aeration treatment processes consist in the dimension of the facilities that are required to guarantee longer times for the hydraulic and solids residence. The cost of building these types of processes is bigger because the aeration basins and clarifiers are mainly made of concrete and because of the costs of the mechanical equipment.

Sequencing batch reactors (figure 4) are using extended aeration activated sludge treatment process, the difference being that the aeration and clarification processes are taking place in the same reactor basin, having the next steps: fill, react/aeration, settle, and decant. Wasting usually occurs during the react/aeration step[1]. Having sufficient air, the hydraulic and solids residence times could be changed in such a manner to activate the nitrification in the reactor basin.



Fig. 4 - Photo of sequencing batch reactors[8].

The most important advantage of the treatment process is the lower dimension of the treatment system. Using the combination of the aeration and clarification steps into one basin, the processes can be controlled, measuring the time for each step to assure the required quality of the treated effluent. This type of treatment process, to be performance requires professional operations personnel, with long practice in working and maintenance of these devices. The majority of the municipal systems also need multiple reactor basins and equalization tanks.

Biochemical oxygen demand removal and biological nitrification could be done by **fixed film treatment**[1] process: trickling filter/activated sludge treatment process, rotating biological contactors, or moving bed bioreactors. In the place of the microorganisms that treat the wastewater suspended in the liquid, the microorganisms are placed to fixed media and treat the wastewater as it flows through the reactor. The trickling filter/activated sludge treatment process also includes plastic media for the microorganisms to develop on packed inside a tower where wastewater is used for treatment. The trickling filter is followed by a conventional activated sludge process. Fans, blowers, clarifiers and pumps are

necessary. Rotating biological contactors are made of a series of closely packed plastic circular disks that are partially submerged and rotated through the wastewater to be treated. Microorganisms develop on the disks and aeration is accomplished as the disks are exposed to the air during rotation.



Fig. 5 - Fixed film treatment system.[9].

Moving bed bioreactors include plastic media that is immersed in the wastewater in a separate basin with screens to keep the media in the basin. They are built in the manner of conventional aeration basins for biochemical oxygen demand removal and are projected specifically for biological nitrification only. Utilization of the trickling filters/activated sludge treatment process have the advantage of both processes. Trickling filters are more energy efficient and the activated sludge process holds off scaling material from creating lower effluent quality. These types of systems can also reduce the footprint necessary for the conventional activated sludge treatment processes. The main disadvantages to fixed film treatment technologies are the increased high solids retention time requirements, pumping energy required, the potential for rotten egg odors, and the potential for snails and filter flies. The moving bed bioreactors treatment process also requires higher levels of dissolved oxygen.(up to 7 mg/L)[1].

The membrane bioreactor treatment process[1] have three mainly components: 1) anoxic basins, 2) preaeration basins, and 3) the membrane bioreactor basins. Rough wastewater have to be screened through a fine screen prior to the anoxic basin. From the anoxic basin, mixed liquor goes into the pre-aeration basins and then into the membrane bioreactor basins. The membranes are placed in the membrane bioreactor basins where wastewater is passed through the membranes and permeate pumps deliver the effluent to the disinfection process prior to discharge[1]. The membranes eliminate the necessity for secondary clarification, Pumping is required as in the same way as in conventional treatment processes. The membrane bioreactor treatment process produces a high quality of the effluent, without any additional operations, will assure both biological nitrification but also nitrogen removal, fitting into a less area, but there are outgoing costs connected to the operation devices and also with purchasing replacement membranes.



Fig. 6 - Membrane bioreactor treatment system[10].

The costs of operation and maintenance of these systems are higher because they need more power and more operator attention.

Lagoon treatment systems [1] are not projected to provide more than biochemical oxygen demand and total suspended solids removal. Biological nitrification takes place, having enough long hydraulic and solids residence times, the proper temperature and sufficient oxygen. Hydraulic residence times have to be extended to at least five to seven days in the aeration process, higher temperatures must be maintained, and enough oxygen have to be assured. A mixed liquor recycle system could be involved to keep a high enough biomass to promote the growth of nitrifying bacteria.



Fig. 7 - Lagoon treatment system [11]

Lagoon treatment systems have the primary advantage of having building low costs and they are easier to operate and maintain comparative to mechanical wastewater treatment systems. Basins are built mainly by excavation , very little concrete is required. In this case, expensive mechanical equipment (pumps, clarifier mechanisms) are not required. Unfortunately, it is harder to control the parameters that influence effluent quality such as wastewater temperature, wasting, return rate, and oxygen levels in lagoon treatment systems [1].

The effluent quality may fluctuate, that means there are needed facilities projected to be be more versatile in design and operation. The facilities use very large areas, these kind of system is recommended only for small treatment systems.

After ammonia was converted in nitrate/nitrite, the denitrification treatment will be applied following the cycle below:

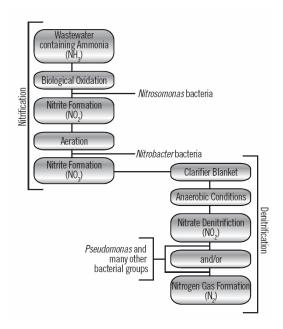


Fig. 8 - Nitrification-Denitrification Cycle [7].

Biological denitrification [7] is realized in anaerobic conditions by heterotrophic bacteria that use nitrate during the fermentation of organic carbon materials. Contrary to nitrification, in which only Nitrosomonas and Nitrobacter bacteria are necessary, a relatively large range of bacteria could done the denitrification. These include Pseudomonas Micrococcus, Achromobacter, and Bacillus. These groups accomplish nitrate reduction through the process of nitrate dissimulation[1]. In nitrate dissimulation, nitrate or nitrite replaces oxygen in the respiratory processes of the organism under anoxic conditions. Due to the ability of these organisms to "eat" either the oxygen bound in nitrate or free oxygen, these organisms are named facultative heterotrophic bacteria. Denitrifiers are able of an assimilation process where nitrate/nitrite is converted to ammonia. Ammonia is then utilized for the bacterial cell's nitrogen requirements. If ammonia is already present, assimilation of nitrate need not occur to satisfy cell requirements. Electrons pass from the carbon source (the electron donor) to nitrate or nitrite (the electron acceptor) to promote the conversion to nitrogen gas. This involves the nitrifiers' "electron transport system" and releases energy from the carbon source for use in organism growth. This electron transport system is similar to that used for respiration by organisms oxidizing organic matter aerobically, except for one enzyme. Because of this close relationship, many facultative bacteria can shift between using oxygen or nitrate (or nitrite) rapidly and without difficulty[7].

In wastewater treatment, organic carbon is the pollutant to be removed, and oxygen must be added. In denitrification, it is nitrate that is removed, and a carbon source must be available. If an insufficient amount of organic carbon is available for denitrification, sufficient carbon (such as methanol) is added to accomplish the nitrate removal.

For the nitrates removal from the potable water, various methods have been proposed: chemical reduction [12,13],physical-chemical processes [14-16], biological

methods [17,18], electrochemical reduction of nitrates on different electrodes: Pt [19,20], Pd[21, 22], Cu[23-28], Ag[27], Ni [29,30], Rh[31], Sn[32], Pb [33], binary alloys [34], CuSn [35] CuZn [36], PdRh1.5/Ti [37], metallic electrodes modified by *upd* deposition [38-41] or *opd* deposition [20,26,42–35].

Transforming nitrate/nitrate in nitrogen gas, could also be a challenge using electrochemical treatment methods, based on nitrogen cicle, but taking in consideration the reactions with electron transfer.

3. CONCLUSIONS

Removal of nitrogen compounds from municipal wastewater, but also resulting mainly from agriculture, animal farms or nuclear industry is following the scheme :

ammonia→nitrate→nitrite→nitrogen gas

As it could be seen there are many types of conventional activated sludge treatment processes for the nitrification process as: complete-mix, plug flow, and step feed treatment. They all have the same basic layout of an aeration basin and secondary clarifier with return and waste activated sludge pumps. The conversion of ammonia occurs in the aeration basins. Because the duration of the required time for nitrification, more than for biochemical oxygen demand removal, there are not recomanded high-rate and contact stabilization activated sludge treatment processes. All the presented method has advantages or disadvantages, and one option is not the best solution for all systems and a good consulting engineer can assist with evaluating all of the options before recommending the best solution for each system. The gaseous product is primarily nitrogen gas, but some nitrous oxide or nitric oxide may also result during denitrification.

REFERENCES:

- [1]. www.waterworld.com
- [2]. The Nitrate Directive of European Council 91/676/EHS.
- [3]. N.F. Gray, DrinkingWater Quality: Problems and Solutions, John Wiley and Sons Ltd., Chichester, 1994, p. 21.
- [4]. J.O'M. Bockris, J. Kim, J. Appl. Electrochem. 27 (1997) 623.
- [5]. EEC Council Recomandations, 1987.
- [6]. WHO, Guidelines for Drinking Water Quality, vol. 2 (and Addendum) (World Health Organisation, 1996, 1998).
- [7]. cursuri pdf-www.waterworldce.com
- [8]. www.esi.info
- [9]. www.aquatechsys.com
- [10]. www.constructionweekonline.com
- [11].www.wmfhillinc.com
- [12].F. Gauthard, F. Epron, J. Barbier, J. Catal. 220 (2003) 182.
- [13].K. Inazu, M. Kitahara, K. Aika, Catal. Today 93–95 (2004) 263.
- [14].L. Panyor, C. Fabiani, Desalination 104 (1996) 165.
- [15]. K.N. Mani, J. Membr. Sci. 38 (1991) 117.

- [16]. J.J. Shoeman, A. Steyn, Desalination 155 (2003) 15.
- [17].V. Mateju, S. Cizinska, J. Krejei, T. Ianoch, EnzymeMicrobiol. Technol. 14 (1992) 170.
- [18].C.-P. Huang, H.-W.Wang, P.-C. Chiu, Wat. Res. 32 (1998) 2257.
- [19].G. Horanyi, E.M. Rizmayer, J. Electroanal. Chem. 188 (1985) 265.
- [20].O.A. Petrii si, T.Ya. Safonova, J. Electroanal. Chem. 331 (1992) 897.
- [21].J.F.E. Gootzen, L. Lefferts, J.A.R. Veen, Appl. Catal. 188 (1999) 127.
- [22].G.E. Dima, A.C.A. Vooysde, M.T.M. Keper, J. Electroanal. Chem. 554 (2003) 15.
- [23].G.E. Badea, T. Badea, Sci. Technol. Environ. Prot. 5 (1998) 42.
- [24].G.E. Badea, T. Badea, U.P.B. Sci, Ser. B: Chem. Mater. Sci. 63 (2001) 493.
- [25].K. Bouzek, M. Paidar, A. Sadilkova, H. Bergmann, J. Appl. Electrochem. 31 (2001) 1185.
- [26].M. Paidar, I. Roušar, K. Bouzek, J. Appl. Electrochem. 29 (1999) 611.
- [27].S. Cattarin, J. Appl. Electrochem. 22 (1992) 1077.
- [28].G.E.Badea, Electrochimica Acta , 54(2009), 996-1001.
- [29].Li Hu Lin, D. Robertson, J. Chambers, D. Hobbs, J. Electrochem. Soc. 135 (1998) 1154.
- [30].J.O'M. Bockris, J. Kim, J. Electrochem. Soc. 143 (1997) 3801.
- [31].Ph. M. Tucker, M.J.Waite, B.E. Hayden, J. Appl. Electrochem. 34 (2004) 781.

- [32].I. Katsounaros, D. Ipsakis, C. Polatides, G. Kyriacou, Electrochim. Acta 52 (2006) 1329.
- [33].J.D. Genders, D. Hartsough, D.T. Hobbs, J. Appl. Electrochem. 26 (1996) 1.
- [34]. T.Ya. Safonova, O.A. Petrii, J. Electroanal. Chem. 448 (1998) 211.
- [35].C. Polatides, G. Kyriacou, J. Appl. Electrochem. 35 (2005) 421.
- [36].Z. Mácová, K. Bouzek, J. Appl. Electrochem. 35 (2005) 1203.
- [37].H. Cheng, K. Scott, P.A. Christensen, J. Appl. Electrochem. 35 (2005) 551.
- [38].Ma Ling, Li Hu Lin, Cai Cheng-Liang, Electrochim. Acta 38 (1993) 2773.
- [39]. H. Huang, M. Zhao, X. Xing, I.T. Bae, D.A. Scherson, J. Electroanal. Chem. 293 (1990) 179.
- [40].G.E. Badea, T. Badea, Rev. Roum. Chim. 48 (2003) 843.
- [41].G.E.Badea, T.Badea, Rev.Roum.Chim., 48(11), pg.843-848, **2003.**
- [42]. M.Wasberg, G. Horanyi, Electrochim. Acta 40 (1995) 615.
- [43]. M.Wasberg, G. Horanyi, Electrochim. Acta 42 (1997) 261.
- [44].G.E. Badea, T. Badea, U.P.B. Sci. Ser. B: Chem. Mater. Sci. 65 (2003) 11.
- [45].K. Shimizu, R. Goto, S. Piao, R. Kayama, K. Nakata, Y. Yoshinga, J. Electroanal.
- [46]. Chem. 601 (2007) 161.