IOŚ-PIB
Environmental Protection and Natural Resources
Ochrona Środowiska i Zasobów Naturalnych
sciendo
Vol. 31 No 3(85): 27-34
DOI 10.2478/oszn-2020-0012

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Nitrate removal from wastewater generated in wet Flue Gas Desulphurisation Systems (FGD) in coal-fired power generation using the heterotrophic denitrification method

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Keywords:
Denitrification, flue gas desulphurisation, industrial wastewater, nitrate, nitrogen

Abstract

The article presents an assessment of the possibilities of using the heterotrophic denitrification process to remove nitrates from wastewater produced in wet flue gas desulphurisation (FGD) installations and also its optimization in the scope of basic technological parameters. This kind of wastewater is characterized by high salinity (even up to 40,000 g/m^3), high temperature (up to 50°C) and low biodegradability, which is expressed by the biochemical oxygen demand (BOD5). The experimental rig consisted of a storage tank and a bioreactor in the form of a bed with an apparatus for measuring basic parameters (temperature, pH, nitrate nitrogen). After an initial adaptation period, a high degree of nitrate nitrogen removal from wastewater (exceeding 95% reduction) was obtained with a reaction time of 180 minutes during the denitrification rate test (NUR). It was also determined that the optimal loading range of the active surface of the bed of 300 m2/m3 should be between 1.5–2.5 gN-NO$_3$/m^2·d. The results of the study show that when the required conditions for the development of microorganisms are provided, it is possible to fully adapt the denitrification biomass to the adverse composition of wastewater from wet FGD unit.

1. INTRODUCTION

The most commonly used method of flue gas desulphurization (FGD) in power plants and cogeneration (CHP) plants in Poland is the wet lime based technology, which has been described by the European Union as one of the best available technology (BAT) [Brinkmann et al. 2017]. The flue gas desulphurisation installations basically generate large amounts of wastewater with particular characteristics, that is, very high salinity (even up to 40,000 g/m^3 of chlorides and sulphates in total) and high temperature up to 50°C [Vredenbreght et al. 1997]. This wastewater also contains a whole array of heavy metals [Huang et al. 2013]. It often has relatively high chemical oxygen demand (COD) (above 300 gO$_2$/m^3), with a very low proportion of readily biodegradable fraction expressed as biochemical oxygen demand (BOD$_5$). The essential aspect, from the point of view of this paper, is that such wastewater has a significant content of nitrogen compounds in all forms, with a predominance of nitrates, which usually constitute 70% of the total nitrogen content. There are also cases of very high ammonium nitrogen levels of 600 gN-NH$_4$/m^3 and nitrate nitrogen up to 200 gN-NO$_3$/m^3. Before further management or disposing to a reservoir, it is purified in physico-chemical processes in one- or two-stage systems that ensure reaching normative values, such as pH value, temperature, concentration of suspended solids, most of heavy metals and, to a partial extent, of compounds expressed as COD and total organic carbon (TOC); however, they are not adapted for removing nitrogen forms [Litwinowicz 2014]. From the point of view of efficiency of the heterotrophic denitrification process, especially in industrial wastewater, the supply of easily digestible substrate is necessary [Hirata, Nakamura 2001]. Alternatively, some studies are being conducted on autotrophic denitrification that has aroused the interest of many researchers [Park, Yoo 2009]. An attempt to remove nitrates from industrial wastewater of particular characteristics was undertaken by, among other Gabaldón [Gabaldón et al. 2007]. He received for wastewater from metalworking industry (high salinity and low BOD$_5$ concentration) the nitrate removal efficiency exceeding 90%.

The need to maintain allowable nitrogen concentrations in treated wastewater is regulated by the Act of Minister of Marine Economy and Inland Navigation of 12 July 2019 on substances that are particularly harmful to the aquatic environment and the conditions to be met when disposing wastewater into waters or into the ground, as well as when disposing rainwater or snowmelt into waters or into water facilities [J. of L. 2019, item 1311]. The limit for total nitrogen has been set at 30 gN/m^3, which for the energy sector plants is determined individually on the basis of integrated permits, however, often at the level of several hundred gN/m^3. According to the authors of this publication, the legal solution to the problem of wastewater disposal containing large amounts of nitrogen into the aquatic environment is insufficient, and over time, it may pose a significant contribution to the inland water quality deterioration and the Baltic Sea consequently. The previously mentioned document [Lecomte et al. 2017] and BREF summary for waste water and waste gas treatment and management in the chemical sector [Brinkmann et al. 2016] indicate that it is required to look for opportunities to improve the situation, with particular regard to streams with a higher concentration, charge, potential threat and impact on the water reservoir, to which it is disposed. According to available information, the global technology providers for FGD systems have no technological solutions in their offers allowing to reduce the wastewater nitrate concentration to the required level. This creates a well-grounded basis for seeking methods to intensify the nitrogen removal for wastewater from the wet FGD units. One of such methods is the use of heterotrophic denitrification, which involves the reduction of nitrates through nitrites to gaseous products under anoxic conditions with a respectively available amount of readily biodegradable organic compounds [Zhu et al. 2008]. Table 1 presents the methods used for wastewater treatment from wet FGD systems given their major advantages and disadvantages. The methods for which the nitrate removal is possible are additionally highlighted.

2. EXPERIMENTAL COMPONENT

2.1. Purpose and subject of the studies

The aim of this study was to evaluate the possibilities for the application of heterotrophic denitrification process in the nitrates removal from wastewater from wet flue gas desulphurization installations and optimization of the process in the scope of basic technological parameters. The object of the studies was particular wastewater from wet FGD installations where the flue gas desulphurisation process is carried out with the wet lime method.

2.2. Experimental rig

The pilot experimental installation consisted of one technological line, and its diagram is presented in Fig. 1. Before the wastewater was disposed into a reactor in the form of a biological bed, it had been collected in a balancing tank (ZŚ) with a capacity of 1 m^3. The tank was equipped with an *online meter* for pH value, nitrate concentration (NO_3) and temperature (T). The pH value was corrected with hydrochloric acid or sodium base if needed. Then, the wastewater was directed with a peristaltic pump to a denitrification bed (ZD) with a permanent submerged filling being the base for biofilm formation of denitrification biomass. The plastic carriers used in the reactor were BCP 750-1.2 with a specific surface area of 700 m^2/m^3, which equalled the active surface of approximately 7.42 m^2. The reactor was provided with a source of organic carbon ($C_{org.}$) and phosphate nourishment (PO_4). The wastewater after the denitrification process was directed to the final tank (ZO), part of which was directed back to the reactor through a recirculation stream (α). The final tank is also equipped with a nitrate concentration measurement (NO_3).

2.3. Experimental material

The material was the wastewater from one of the country wet FGD installations after physicochemical treatment. Table 2 provides detailed characteristics of the material from the studies. Nitrate concentrations varied, and they changed within quite a wide range from 53 to 185 gN-NO_3/m^3, constituting a significant part of total nitrogen. It was also found that the experimental material had a very low concentration of phosphorus in absorbable form and BOD_5 and high concentration of dissolved compounds and suspended solids. This wastewater differs radically from typical municipal wastewater, being simultaneously an unfavourable material for conducting biological processes. Fig. 2 presents the changes in the wet FGD wastewater composition (wastewater from an actual energy facility). These data indicate that the wastewater composition has changed quite significantly. The nitrate nitrogen concentrations reached the highest value in first days and in the 120th day of the studies. In periods when its concentration was relatively low, before being transferred to the model reactor, it would be increased to approx. 100 gN-NO_3/m^3 by dosing the sodium nitrate solution. The COD mean value was 222 gO_2/m^3, however, it was a substratum inassimilable for microorganisms leading the denitrification process. The value of BOD_5 determining the amount of easily biodegradable organic compounds did not exceed 5% of the COD value. There were also no assimilable forms of phosphorus recorded. The experimental bacteria inoculum was taken from the activated sludge system from a municipal wastewater treatment plant. The composition bacteria biomass was not tested.

2.4. Experimental methods

Before the wastewater was disposed into the model reactor, it was subjected to preliminary treatment by raising its temperature to approx. 35°C, pH value correction to 8.3 and, according to needs, correction of nitrate concentration to the value of approx. 100 gN-NO_3/m^3. The wastewater was disposed to the process reactor by peristaltic pumps dosing in the amount resulting from the studies stage. A separate stream provided a source of

Table 1. The summary of methods used for wet FGD wastewater treatment

Item.	Method name	Major advantages	Major disadvantages	Nitrate removal
1	*2*	*3*	*4*	*5*
1	Simplified methods	• Operation does not require qualified service • Resilience to changes in the FGD technology	• Large area required for use of lagoons for wastewater /sediment disposal	No
2	Chemical methods	• Small installation volume (short time chemical reaction) • Technology with a wide range of both customization and control strategy options	• High demand for chemical reagents	No
Biological methods				
3	Treatment reactors	• Lower maintenance costs compared to chemical methods • Consuming less chemical reagents	• Operation requires qualified staff • Small resilience to changes in wastewater composition	Yes
4	Hydrophyte wastewater treatment plants	• Possibility of achieving parameters similar to those for treatment reactors	• Large area required • Significant reduction in the efficiency of wastewater treatment at low temperatures	Yes
Physical methods				
5	Evaporative methods	• A significant reduction in the amount of generated wastewater	• High maintenance costs of concentrating wastewater on evaporators	No
6	Membrane methods	• Lower maintenance costs compared to evaporative methods	• The need for frequent flushing of membranes • High risk of precipitation of mineral salts on the surface of membranes (fouling) • High investment costs	Yes[1]
7	Ion exchange methods	• In the case of an existing ion exchange installation at the facility, the extension will take lower investment costs	• Need for frequent ionites regeneration • Higher efficiency of sulphate ion exchange than nitrate ion	Yes

Source: own elaboration based on (EPA 2013; EPA 2015; Hedayati, Sargolzaei 2013; Tchobanoglous et al. 2003)

organic carbon and phosphorus in the amount of 130% of stoichiometric consumption in the denitrification process. In order to increase the degree of even spread of the specific surface loading rate on the denitrification bed, recirculation of treated wastewater in the amount of 200% of the inflow value was used. The operational control of the denitrification bed included daily sampling of treated wastewater and determination of the most important parameters from the point of view of the denitrification process – COD, N_{total}, N-NO_3, P-PO_4. An additional tool for controlling the outflow quality was the use of an optical probe monitoring the nitrate nitrogen concentration *on-line*. In the initial period of the studies, a mixture of municipal wastewater (after mechanical treatment) and wastewater from wet FGD installations were delivered into the reactor. Along with the progressing development of the denitrification bed, the share of wet FGD wastewater inflow to the reactor was increased until the share of municipal wastewater in the reactor inflow to completely switched off.

2.5. Results and discussion

The effects of the biological bed performance are shown in Figure 3. In the initial period of the studies involving the adaptation of biomass to the composition of wastewater

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1 when using ultrafiltration or reverse osmosis

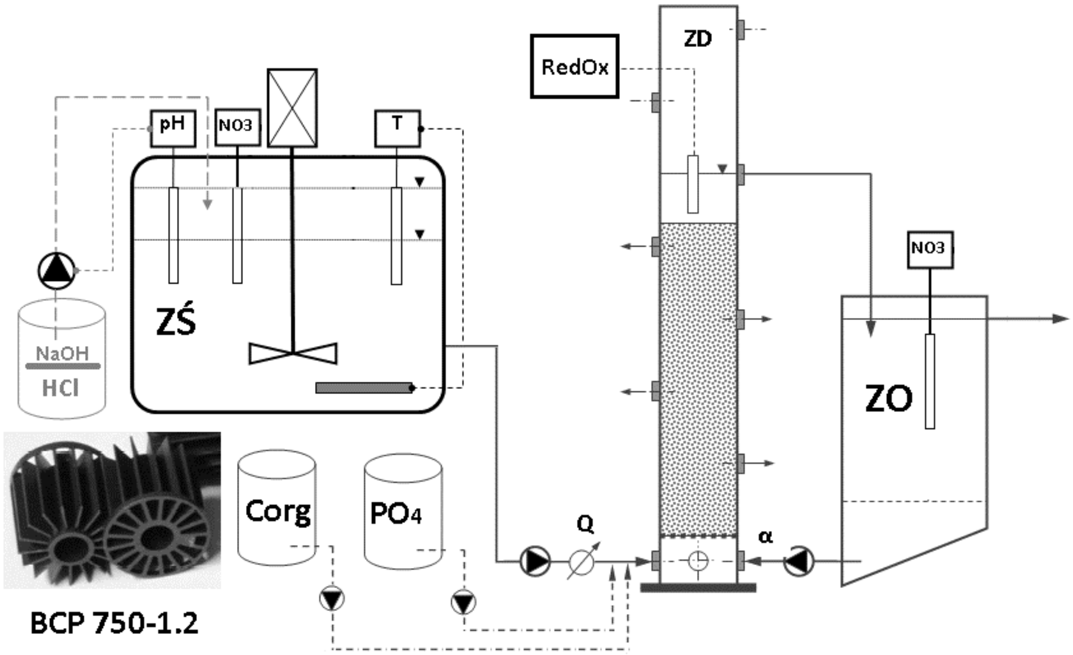

Figure 1. Diagram of the installation for conducting the denitrification process: ZŚ - raw wastewater tank, ZO - treated wastewater tank, ZD - denitrification bed, Q - wastewater flow measurement, α - denitrified effluent recirculation pump, pH - pH measurement, NO_3 - nitrate measurement, T - temperature measurement, RedOx - measurement of oxidoreductive potential

Table 2. The wet FGD wastewater characteristics during the studies

Item.	Feature/indicator tested	Unit	Wastewater batch no.				Mean
			I	II	III	IV	
1	pH value	-	8.84	8.87	8.57	7.47	-
2	BOD_5	gO_2/m^3	0.73	0.87	1.11	1.39	1.0
3	COD	gO_2/m^3	209	213	246	222	222.5
4	Total nitrogen (N_{total})	gN/m^3	233	68.2	87.7	101.9	122.7
5	Kjeldahl nitrogen (TKN)	gN/m^3	43.2	21.9	35.9	0.97	25.5
6	Ammonium nitrogen ($N-NH_4$)	gN/m^3	30.5	14.9	19.6	0.62	16.4
7	Nitrate nitrogen ($N-NO_3$)	gN/m^3	185.2	53	58	100.9	99.3
8	Nitrite nitrogen ($N-NO_2$)	gN/m^3	4.61	0,84	1.1	0.03	1.6
9	Total phosphorus (P)	gP/m^3	7.5	5.73	1.7	-	5.0
10	Orthophosphates ($P-PO_4$)	gP/m^3	0.043	0.18	0.07	0.03	0.1
11	Total suspended solids (TSS)	g/m^3	422	392	212	69	273.8
12	Chlorides (Cl^-)	g/m^3	35400	19200	18500	16000	22275.0
13	Sulphates (SO_4^{2-})	g/m^3	1186	1100	1227	-	1171.0

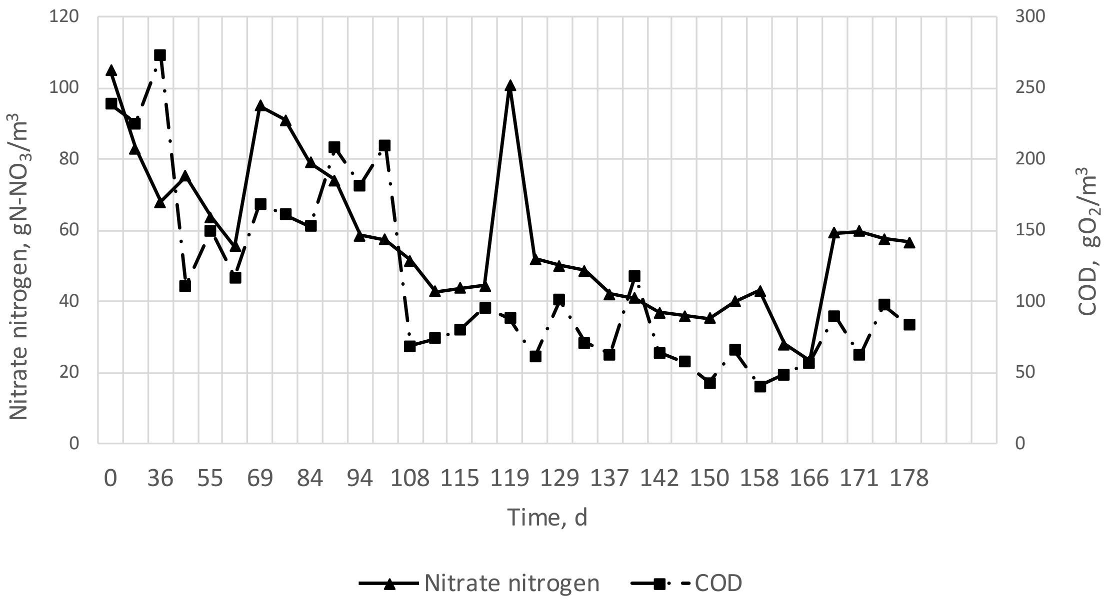

Figure 2. Changes in nitrate and COD concentration in wastewater from wet FGD unit

from wet FGD, quite big fluctuations of obtained results were observed. Drastic decreases in efficiency were observed especially in periods corresponding to the increase in the share of wet FGD wastewater inflow to the reactor. However, the most important element during this period was not obtaining a satisfactory wastewater quality but avoiding permanent inhibition of the biological bed biomass caused by the unfavourable for the microorganisms composition of the wet FGD wastewater. Therefore, the reactor was operated at a low nitrates loading rate. After about 3 months of developing the reactor, the municipal wastewater supply was turned off and a systematic increase of nitrate loading rate began. Not counting periodic performance decreases, a very high process efficiency was observed over the next three months. The nitrate nitrogen removal rate was above 95% and considering its initial concentration at the level of approx. 100 g/m^3, it was found that the target effluent quality was successfully achieved, that is, below 30 gN/m^3 at the wastewater reaction time being 180 minutes during the denitrification rate test (NUR). It was also determined that the optimal loading range of the active surface of the bed about 300 m^2/m^3 should be within 1.5–2.5 gN-NO$_3$/m^2·d, which is illustrated by the results presented in Figure 4. During the period of optimal work of the reactor, a test was also carried out to determine the loading rate limits and resistance of organisms to the abrupt changes in loading rate. To this end, the inflow loading rate was reduced to approx. 5 gN-NO$_3$/d, followed by a sudden increase to value approx. 10 gN-NO$_3$/d, which corresponded to the loading rate on the active surface of the bed being 3 gN-NO$_3$/m^2·d. The basis for this experiment was the fact of large irregularities on the inflow and in the composition of the wastewater from wet FGD. The sudden change in the bed loading rate inhibited the efficiency of nitrate reduction, which fell from 99 to barely 20%. However, this continued for a fairly short time, because in the next days of the experiment, the reactor operation was improving, namely, the denitrification biomass worked with increasing efficiency, eventually reaching the nitrate reduction level of 93–97% after approx. 17 days. This experiment has shown that the biological system does not tolerate rapid changes conditions of its operation. It has been defined that the work regime changes should be introduced gradually, and they must not exceed 10–15% per day in relation to the initial values.

Removal of nitrate nitrogen from wastewater from wet FGD installation is a relatively new issue. This specific wastewater group is characterized by significantly high concentrations of chlorides and sulphates, the presence of heavy metals and suspensions (mainly gypsum) and significant content of forms of nitrogen compounds. So far, the main attention has been paid mainly to the removal of heavy metals, which are quite strictly limited in BAT conclusions established for large combustion plants (LCP). Depending on the type of metal, emission standards range from 0.2 µg/L for cadmium to 200 µg/L for zinc. Controlling these requirements implies the use of highly effective precipitation methods, often requiring several steps of its treatment. However, such treatment plants have a minor impact on the content of nitrogen compounds. This studies showed a great potential in removing nitrate nitrogen using denitrification bacteria. Cheng et al. [2011] considered that artificial ecosystem (wetlands) can be a cost-effective and low-energy method of removing biogenic pollutants. Biological reactors constructed in this way can remove and degrade nitrogen, phosphorus and some metals. In relation to nitrogen compounds, these

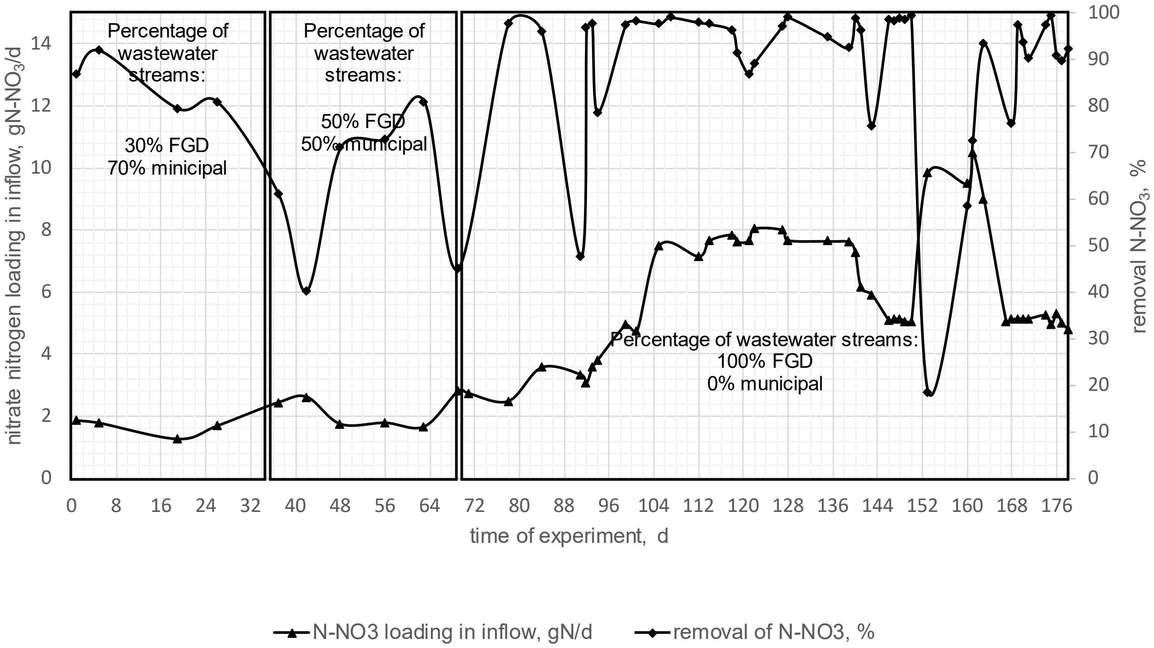

Figure 3. Nitrate nitrogen removal rate apposed its loading rate at the reactor inflow during the studies

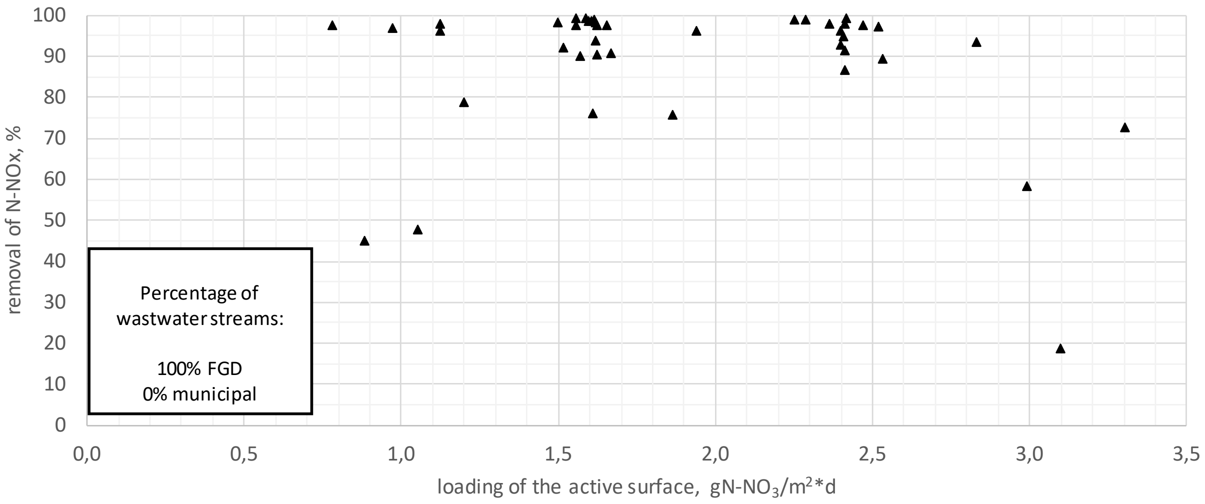

Figure 4. Effect of active surface loading rate on efficiency (% removal)

can be both nitrification and denitrification processes. In turn, Zhu and Liu [2017] believed that elevated levels of salinity in industrial wastewater can have a major impact on denitrification, but few studies have been done so far. To remove nitrates from such kind of wastewater, it is important to understand the effect of salinity on process kinetics, selection of carbon sources, periodic fluctuations in salinity and microorganism communities in process selection and engineering design.

The problem of the presence of nitrogen forms in wastewater from wet FGD installations has also been noticed by researchers from the Electric Power Research Institute (EPRI). In a report on pollution from the energy sector [EPRI, 2007], they suggested that the presence of nitrates may require additional purification steps due to high concentrations. As a possible way, they indicate the ABMet® system, which can effectively remove metal, metalloid, non-metal and inorganic compounds such as nitrates. The purification system consists of a series of connected chambers (in the form of fluidized beds), each of which contains specialized bacteria. Problem of nitrate nitrogen removal from high salinity wastewater was also taken up by Yang et al. [1995]. In their studies, they analysed the process of immobilizing microbial cells trapped in a mixed culture (EMCI) to remove nitrates from brine waste resulting from the regeneration of used ion exchange resins. With salinity up to 20 g/L, they achieved nitrate nitrogen concentration in the outflow of 0.1–0.2 g/m^3.

3. CONCLUSIONS AND SUMMARY

The wet FGF installations are provided with wastewater treatment plants, the technological level of which does not allow to meet all the legal requirements for the treated wastewater from the energy sector, which in particular relates to nitrogen compounds. In this context, the existing wastewater treatment plants can be considered as a two-stage physico-chemical pre-treatment plants providing correction of pH value, temperature, concentration of suspensions, COD and heavy metals. One of the promising methods for their efficiency improvement is the extension by a biological facility, enabling the removal of nitrogen compounds by the method of heterotrophic denitrification. The studies show that after providing right conditions for the development of microorganisms, it is possible to develop and adapt the denitrification biomass completely to the adverse composition of the wastewater from wet FGD installations. While maintaining the optimal bed loading rate in the range of 1.5–2.5 gN-NO$_3$/m^2·d, the over 90% reduction level of nitrate nitrogen has been repeatedly achieved. Considering that this parameter constituted for approx. 70% of total nitrogen in influent wastewater, it gives a strong chance of reduction to the level required by law. The developed technology has been submitted to the Patent Office of the Republic of Poland and currently pending at the application stage.

ACKNOWLEDGEMENTS

The study was carried out under IEP-NRI's statutory research framework co-financed by the Ministry of Science and Higher Education.

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