Environment Protection Engineering

Vol. 37 2011 No. 3

MAGDALENA GAJEWSKA*

FLUCTUATION OF NITROGEN FRACTION DURING WASTEWATER TREATMENT IN A MULTISTAGE TREATMENT WETLAND

Factors influencing COD and removal and transformation of N fractions have been investigated in the conditions of horizontal (SSHF) and vertical (SSVF) flow reed beds. Multistage treatment wetland in Wiklino ensured a stable and very effective removal of all the analysed pollutants. Based on the resultsof investigation, it could be assumed that the working conditions of SSHF beds play an important role in the transformation of particulate fractions to colloidal ones and colloidal to dissolved fractions of COD and Org-N while the SSVF bed was very effective in the removal of dissolved fractions.

1. INTRODUCTION

At present, evaluation of the effectiveness of a wastewater treatment plant (WWTP) is based upon determination of organic matter content expressed by BOD and COD as well as the removal of nutrients (N and P). Although the size of pollutants discharged to a WWTP plays an important and often underestimated role in characterizing treat ability and hence the degree of contaminant removal of wastewater. According to Tiehm [1], the size of the suspended solids has a considerable impact on separation processes such as sedimentation, flocculation and filtration. Many authors confirm that the biological degradation rate in terms of COD reduction is influenced by particulate size distribution [1–3].

In order to obtain efficient nitrogen removal in the denitrification process, sufficient amounts of bioavailable carbon source should be ensured. In the case of treatment wetlands (TWs), the preferred approach is to use an internal carbon source already present in wastewater. According to Tanner [4], nitrogen removal in many TWs occurred concurrently with organic matter removal due to limited carbon sources. In

---

*Faculty of Civil and Environmental Engineering, Gdansk University of Technology, ul. Narutowicza 11/12, 80-233 Gdańsk, Poland, e-mail: mgaj@pg.gda.pl

biofilter systems such as TWs, particulates from the wastewater are naturally trapped by filtration, causing headloss due to the clogging of the filter layer. Although accumulation of organic matter is a typical feature of both natural and treatment wetlands, the over net inputs of external organic matter present in wastewater and outputs from decomposition potentially contribute to clogging in the pore space in sub-surface flow TWs [5–9].

Most of the initial total nitrogen (TN) can be successfully removed by nitrification and denitrification in a wastewater treatment plant. In contrast, the portion of dissolved organic nitrogen (DON) which has not been converted into inorganic N forms is very difficult to remove from wastewater [10]. Recently it has been found out that wastewater treatment leads to the formation of dissolved and colloidal organic compounds resistant to biochemical degradation, similar to humic acids [11].

So far very few studies have been conducted on organic matter and N speciation and the available data focus mainly on investigation in a conventional WWTP. Since data on nitrogen speciation during wastewater treatment in TWs is rather limited, the goal of the study was to investigate both organic matter (COD) and N speciation during wastewater treatment in a multistage treatment wetland (MTW). The investigations carried out bring information about factors and conditions influencing (limiting) COD and N fractions removal and transformation in the changing condition of SSVF and SSHF beds.

2. STUDY FACILITY AND METHODS

2.1. CHARACTERISTICS OF THE TW STUDIED

The studies were carried out in a full scale multistage treatment wetland (MTW) situated in Wiklino, a village in northern Poland near Słupsk. Wastewater after mechanical treatment in a three chamber settlement tank (with two day retention time) was pumped into the wetland responsible for biological treatment. This system consisted of a subsurface horizontal flow bed (SSHF I) followed by two subsurface vertical flow beds (SSVF) working with intermittent lodgings and the second SSHF II bed.

Table 1

Characteristics of Wiklino MTW

WWTP	Flow [m^3·day^{-1}] (pe)	Configuration	Effective grain size [mm]	HRT [day]	Area [m^2]	Depth [m]	Hydraulic load [mm·day^{-1}]	Unit area [m^2·pe^{-1}]
Wiklino	20.5 (220)	SSHF I	2–6	12.3	1050	0.6	19.5	4.7
		SSVF		–	312	0.4	65.7	1.4
		SSHF II		6.3	540	0.6	38.0	2.4
					Total 1902			Total 8.5

The basic characteristic of the applied solution is presented in Table 1. The MTW is covered in 95% by *Phragmites australis* with the plant density of 200–300 m^{-2}, and by a few other species (*Typha latifolia*) and grasses, e.g. *Carex.* sp. The matrix medium was coarse sand with the porosity of 0.4 and with the permeability coefficient $k = 110$ m·day^{-1}. The coefficient of graining non-uniformity $U = d_{60}/d_{10}$ equalled 0.35.

2.2. SAMPLING PROGRAM AND LABORATORY ANALYSES

Samples were collected every two or three weeks during the period from June 2008 to October 2009 (29 sampling events). The composite samples of influent and effluent as well as those after subsequent stages of treatment were collected for nitrogen and organic matter characterization.

At this stage of the investigation, standard analyses of chemical properties (COD, BOD, TN, NH_4^+-N, NO_3^--N, NO_2^--N, TKN, TSS and VSS) were carried out in accordance with the Polish Standard Methods and the procedures adopted by Hach Chemical Company which are in accordance with APHA 2005 [12, 13]. Additionally, COD_f was also analysed after filtration in aqueous phase through a millipore nitrocellulose filter with the pore size of 0.45 μm. Furthermore, the content of volatile suspended solids in the total suspended solids was determined as loss on ignition.

The quantification (dissolved, colloidal, and particulate) of organic matter and N was based on the filtration of the influent and subsequent stage effluents through a series of filters (0.1, and 1.2 μm pore size millipore nitrocellulose filters). The dissolved fraction was obtained by filtration of a wastewater sample through a 0.1 μm pore size filter. The filtration of the wastewater sample through a 1.2 μm pore size filter enabled obtaining a non-dissolved fraction (particulate) and the sum of the colloidal and dissolved ones. Having the value of the dissolved fraction, it was possible to calculate the colloidal one. Then the filtrates were analysed for COD, NH_4^+-N, and TKN. Organic nitrogen concentration was estimated based on the difference between TN and the summation of NH_4^+-N, NO_3^--N and NO_2^--N concentrations. The temperatures of wastewater and air as well as dissolved oxygen and redox potential were measured directly in sampling points by Multi 340i/SET by WTW. Organic nitrogen concentration was estimated based on the difference between TN and the summation of NH_4^+-N, NO_3^--N, NO_2^--N concentrations.

3. RESULTS AND DISCUSSION

3.1. POLLUTANT CONCENTRATIONS AND EFFICIENCY REMOVAL

The characteristics of pollutants, in the influent and effluent and after the subsequent stages of treatment in MTW, with the range as well as mean values with standard deviation, are presented in Table 2. As is seen, the mean and median values did not vary significantly. Additionally, the standard deviation was lower than 30% of mean values, which suggests that the data were normally distributed. Thus, the mean values were taken under further consideration.

Table 2

Characteristics of wastewater in the Wiklino MTW

Parameter	Influent				After SSHF I			
	Mean	SD	Median	Min–Max	Mean	SD	Median	Min–Max
Flow, $m^3\cdot day^{-1}$	20.5	0.7	20.3	19.9–22.1	19.3	0.8	19.5	18.7–20.8
pH	6.9	0.06	7.0	6.9–7.1	7.05	0.2	7.1	6.9–7.4
TSS, $mg\cdot dm^{-3}$	392.9	259.8	348.4	162.1–922.4	80.0	48.6	84.6	24.6–132.6
VSS, $mg\cdot dm^{-3}$	269.5	188.7	195.5	125.6–644.3	43.3	33.8	28.5	10.2–96.1
TN, $mg\cdot dm^{-3}$	130.5	8.1	129.1	119.9–146.7	72.1	18.1	68.3	44.2–92.5
NH_4^+-N, $mg\cdot dm^{-3}$	86.2	17.5	95.1	57.1–105.4	50.8	16.9	54.7	26.1–70.3
Org-N, $mg\cdot dm^{-3}$	43.5	15.87	49.9	23.3–66.2	19.1	10.3	18.9	6.6–33.7
NO_3^- -N, $mg\cdot dm^{-3}$	0.9	0.5	0.7	0.1–1.8	1.1	0.6	1.3	0.2–2.2
COD, $mg\cdot dm^{-3}$	660.3	212.6	604.8	382.1–965.3	234.1	126.6	167.2	110.4–425.7
COD_f, $mg\cdot dm^{-3}$	283.6	69.1	280.4	184.4–00.6	56.4	19.7	62.2	22.3–78.6
BOD, $mg\cdot dm^{-3}$	323.8	126.2	280.6	194.8–500.7	33.5	24.6	30.3	10.5–73.5
T_s, °C	12.7	5.7	12.5	8.1–17.5	11,7	5,6	12.0	8.0–16.2
O_2, $mg\cdot dm^{-3}$	0.5	0.2	0.4	0.0–0.9	1,8	1,0	1.5	0.6–2.1
Redox, mV	–242.7	21.8	–240	–301.5—140.5	–87,3	14,2	–85	–146.5—25.5
	After SSVF				Effluent (after SSHF II)			
Flow, $m^3\cdot day^{-1}$	18.1	1.0	18.3	17.1–19.4	16.9	1.1	17.3	15.9–18.1
pH, $mg\cdot dm^{-3}$	7.1	0.23	7.1	6.7–7.4	6.9	0.3	6.9	6.6–7.2
TSS, $mg\cdot dm^{-3}$	64.5	24.9	67.8	22.4–96.4	25.1	11.1	28.3	6.5–40.1
VSS, $mg\cdot dm^{-3}$	23.6	7.6	25.0	14.2–36.9	9.7	6.7	6.6	1.2–29.7
TN, $mg\cdot dm^{-3}$	49.0	18.3	47.8	14.7–73.5	22.8	6.3	20.9	15.9–34.5
NH_4^+-N, $mg\cdot dm^{-3}$	33.7	16.6	33.5	7.6–53.5	10.5	4.9	10.1	0.7–15.3
Org-N, $mg\cdot dm^{-3}$	7.9	3.4	8.9	4.2–14.1	4.2	3.6	4.0	2.4–9.1
NO_3^- -N, $mg\cdot dm^{-3}$	9.1	5.4	9.1	4.2–19.8	8.2	5.3	6.8	1.9–15.6
COD, $mg\cdot dm^{-3}$	75.4	31.3	76.8	35.6–115.5	59.6	29.8	45.7	30.4–104.3
COD_f, $mg\cdot dm^{-3}$	47.0	23.3	46.4	10.0–78.6	26.6	14.8	24.1	3.8–54.5
BOD, $mg\cdot dm^{-3}$	14.7	6.6	15.6	5.7–23.5	6.7	3.8	4.7	3.6–12.4
T_s, °C	9.9	5.6	10.0	8.5–11.7	11.1	5.6	10.5	8.2–11.1
O_2, $mg\cdot dm^{-3}$	3.9	1.1	3.8	2.8–4.9	2.1	1.1	2.0	1.1–3.2
Redox, mV	210.5	24.5	212.0	105–320	32.6	5.2	31.5	–10–60.5

The concentrations of pollutants were much higher than those for domestic wastewater discharged to TWs [14–16]. Vymazal [15] reported BOD_5 concentration in the influent almost fourfold lower and that of TSS over sixfold lower. Only in France, where raw wastewater is treated in two stage vertical flow TWs, the concentrations of

BOD and TSS in the influent were similar to the concentrations observed in this investigation [17]. The concentration of TN in the influent was two- to even threefold higher than that reported in the literature [14–17]. The reasons for higher pollutant concentrations could be lower water consumption by the person equivalent (ca. 100 $dm^3 \cdot day^{-1}$), lack of rain water infiltration to the sewer system, and what is undoubted, incorrect operation of the septic tank (too high concentration of TSS discharged to the MTW). Nitrogen in the influent was present mainly in the form of NH_4^+-N (ca. 65%) and Org-N (over 34%), which confirms that in the septic tank the conditions were favourable for the ammonification process. The hydraulic and pollutant loads discharged to the first stage of treatment (SSHF) in the MTW investigated are consistent with the range values reported elsewhere [4, 14–17] under conditions protecting the facility against clogging.

The COD/BOD and BOD/N ratios bring information about biodegradability for microbiological transformations. Additionally in this study, COD_f/BOD is presented as an indicator of easy degradable dissolved organic matter [18]. The wastewater studied was characterized by a typical COD/BOD ratio – ca. 2.0, and BOD/N – ca. 2.5. Furthermore, the COD_f/BOD ratio was less than 0.9, which suggests that organic matter is mostly present in an easy biodegradable dissolved fraction, and comparing with the high content of VSS in TSS, the rest was probably present in easy decomposable suspended organic matter [18].

The MTW investigated ensured a stable and very effective removal of all the analysed pollutants. Consequently, the concentration of the pollutants in the effluent did not exceed Polish permissible values [12]. The total removal efficiency of BOD_5 and COD was equal to 97.9% and 90.6% respectively. Among the N species, Org-N was removed with the highest effectiveness – 90.3%, the removal effectiveness of NH_4^+-N was 87.8%, and that of TN was only 82.5%. An unexpectedly high efficiency of N species was observed in the first stage of treatment (SSHF). The removal efficiency of TKN was over 46% and was accomplished with very high BOD removal, ca. 80.5%, which suggests potential heterotrophic competition for oxygen, whose supply in this stage of treatment is strongly limited. The SSVF bed, which is usually used for nitrification, showed the lowest efficiency of NH_4^+-N removal, equal to 31.1%, although the Org-N removal was the highest – 58.6%. Both BOD and COD_f were present in each stage of the treatment, which indicates the availability of organic carbon. Thus, denitrification was not limited by this factor. Neither the fluctuation of alkalinity nor pH confirmed the sequential of conventional nitrification and denitrification.

3.2. FLUCTUATION OF COD AND N FRACTIONS

Table 3 presents a detailed fractionation of organic matter (COD) and total organic nitrogen (TON) including the dissolved (< 0.1μm), colloidal (0.1 –1.2 μm) and particulate (> 1.2 μm) ones. The analysis of the organic matter (COD) and Org-N fractions showed the highest contribution of particulate forms of both COD (65.2%) and TON (67.2%) in the influent. The contributions of the colloidal fractions were almost similar for COD (25.4%) and Org-N (26.4%), while the contributions of the dissolved fractions were the lowest and equalled 9.4% for DCOD and 6.0% for DON.

Table 3

COD and Org-N fractions in the analysed MCW Wiklino [%]

Stage of treatment	Organic matter (COD)			Organic nitrogen (ON)		
	Dissolved (DCOD)	Colloidal (CCOD)	Particulate (PCOD)	Dissolved (DON)	Colloidal (CON)	Particulate (PON)
Influent	9.4	25.4	65.2	6.0	26.8	67.2
After SSHF I	16.3	35.4	48.3	12.5	26.4	61.1
After SSVF	32.7	27.2	40.1	18.8	28.1	53.1
Effluent (after SSHF II)	41.5	37.1	21.4	31.2	20.6	48.2

The particulate fractions of COD and Org-N were removed in all the stages of treatment with the highest efficiency removal, 98.5 and 94.2% respectively (Table 4, and Fig. 1). Both the COD and Org-N fractions were effectively removed and/or transformed into other fractions in the first stage of treatment. Long retention time in SSHF I with limited oxygen conditions (0.5 $mgO_2 \cdot dm^{-3}$) and redox potential equal to – 240 mV create favourable conditions for a very effective transformation of the colloidal fraction into the dissolved one (Tables 2 and 3, Fig. 1).

Table 4

Removal efficiency of COD and Org-N fraction in subsequent stages of treatment in the MTW Wiklino [%]

Stage of treatment	Removal efficiency of COD fractions			Removal efficiency of Org-N fractions		
	Dissolved (DCOD)	Colloidal (CCOD)	Particulate (PCOD)	Dissolved (DON)	Colloidal (CON)	Particulate (PON)
After SSHF I	38.5	50.6	73.7	7.6	56.4	59.9
After SSVF	35.3	75.1	73.3	37.5	56.9	64.1
After SSHF II	49.8	46.1	78.8	26.7	65.9	59.5
Total	80	93.4	98.5	57.7	93.6	94.2

The removal of the dissolved Org-N was 7.6%, being the lowest one in SSHF I, which could be explained by very high concentrations of 95.1 $mg \cdot dm^{-3}$ NH_4^+-N in the wastewater influent (Table 2), which is the most preferable form of nitrogen for plants and microorganisms [19]. The second stage of treatment in SSVF with oxygen conditions (3.8 mg $O_2 \cdot dm^{-3}$) and redox potential equal to 212 mV enhanced the removal of the dissolved Org-N and colloidal COD (Tables 2 and 4).

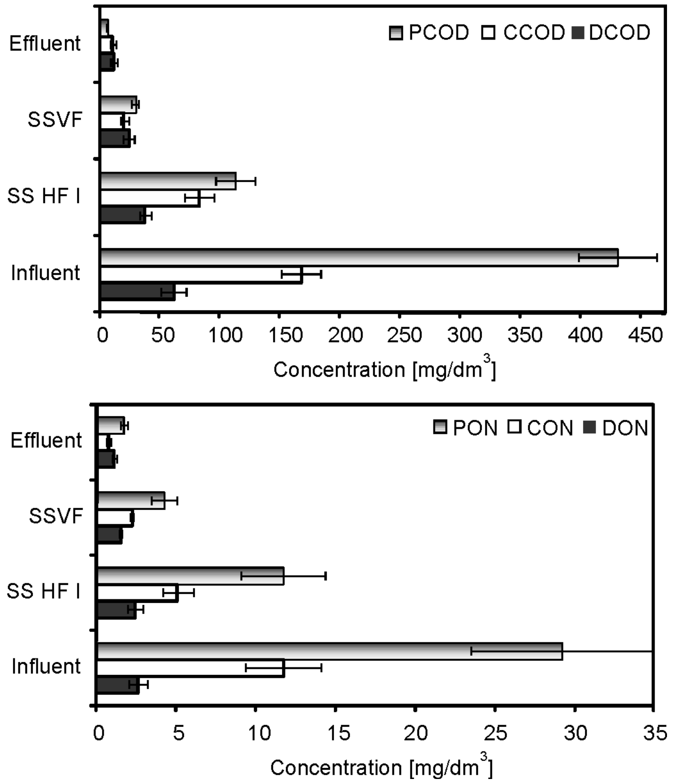

Fig. 1. The fluctuation of organic matter (upper) and org-N fraction (lower) in the MTW Wiklino

The particulate and colloidal fractions of both COD and Org-N transformed in the SSHF I stage into adequate dissolved Org-N and colloidal COD, were rapidly removed from the wastewater during treatment in SSVF. Thus, the working condition of the SSVF bed and its role can be compared with those of an oxygen biological reactor in a conventional WWTP (but with much shorter retention time).

In the case of the MTW Wiklino, well aerated wastewater was entered into the last stage of treatment (SSHF II), where favourable conditions existed for further transformation of the particulate form into colloidal one, and the colloidal form into the dissolved one. This stage of treatment was designated for the polishing of the treated wastewater and denitrification process, which can confirm the results obtained in this stage of treatment. The most effective removal of dissolved organic compounds (49.8%), and both the colloidal and dissolved Org-N fractions accomplished with a very high efficiency of TN (56.2%) and organic matter (49.0%) removal proved the importance of this stage of treatment (Tables 2 and 4, Fig. 1).

During the subsequent treatment stages at MTW, the forms changed significantly, and finally COD and Org-N were present in the effluent, mainly in the dissolved and colloidal fractions, except particulate Org-N (PON), which still consisted of 48.2% of total Org-N (TON) (Table 3). Both the dissolved and colloidal fractions could be products of the treatment processes as in the case of organic matter produced during cell decay, previously recognized as a soluble microbial product (including cell debris), and could be potentially hardly degradable [20, 21]. Such refractory compounds are similar to humic acids (fluvic and humin acids), and according to Nguyen [6] are the predominant stable organic matter fraction accounting for 63–96% of deposit in subsurface TWs. According to Pagilla [2], TON in the effluent from a conventional WWTP in the USA consists of 10% CON and 85% of DON. Such results may suggest that DON and CON as well as CCOD and DCOD can originate from the microbiological decomposition of raw wastewater, and can be both humic acids and microorganisms. The same authors assumed that the concentrations of PON ranged from 20% to 42% of TON in the treated wastewater, which is in accordance with the value achieved in this investigation. Similar results for wastewater treated with extensive methods and natural methods (TWs) could suggest that part of particulate Org-N and COD is recalcitrant, thus resistant to any treatment processes applied. Such compounds resistant to biochemical degradation, similar to humic acids can modified the properties of the recipient and could be responsible for trace metals transport and increase of their bioavailability in the ecosystem [11, 22].

4. CONCLUSIONS

The investigated MTW in Wiklino ensured a stable and very effective removal of all the analysed pollutants. Consequently, the concentration of pollutants in the effluent did not exceed Polish permissible values (Dz.U.nr 137 item 984). The efficiency removal of BOD5 and COD were equal to 97.9% and 90.6%, respectively. Among N species, Org-N was removed with the highest effectiveness – 90.3%, whereas the effectiveness of NH_4^+-N removal was 87.8% and that of TN was only 82.5%. The analysis of the organic matter (COD) and Org-N fractions showed the highest contribution of particulate forms of both COD (65.2%) and TON (67.2%) in the influent. The share of colloidal fractions were almost similar for COD (25.4%) and Org-N (26.4%), while the contribution of the dissolved fractions was the lowest and equalled 9.4% for DCOD and 6.0% for DON in the influent. During the subsequent treatment stages at MTW, the forms changed significantly, and finally COD and Org-N were present in the effluent, mainly in the dissolved and colloidal fractions. Based on the achieved results it could be assumed that the working condition of SSHF beds play an important role in the transformation of particulate to colloidal and colloidal do dissolved fractions of organic matter and Org-N. The SSVF bed was very effective in the removal of the dissolved fraction, which can suggest that very effective microbiological processes take place in it.

The investigation proved that a part of particulate organic matter and Org-N present in raw wastewater is resistant to treatment.

ACKNOWLEDGEMENTS

The investigations were carried out within the project N 207 073 31/3481 *Conversion of nitrogen compounds during wastewater treatment in a hybrid constructed wetland* funded by the Ministry of Higher Education and Science. The authors especially thank the managing body of the facility for assistance during the investigations.

REFERENCES

[1] Tiehm A., Herwig V., Neis U., Wat. Sci. Tech., 1999, 39 (8), 99.
[2] Pagilla K.R., Czerwinka K., Urguj-Demirtas M., Makinia J., Water Sci. Technol., 2008, 57 (10), 1511.
[3] Templeton D.M., Ariese F., Cornelis R., Danielsson L.G., Muntau H., Van Leeuwen H.P., Łobiński R., Pure Appl. Chem., 2000, 72 (8), 1453.
[4] Tanner Ch.C., Kadlec H.R., Gibbs M.M., Sukias J.P.S., Nguyen M.L., Ecol. Eng. 2002, 18, 499.
[5] Kadlec R.H., Knight R.L., *Treatment wetlands*, Boca Raton, FL, USA, Lewis CRC Press, 1996.
[6] Nguyen L.M., Ecol. Eng., 2000, 16, 199.
[7] Kayser K., Kunst S., Fehr G., Voermanek H., *Nitrification in reed beds-capacity and potential control methods*, World Water Congress, publ. IWA, Berlin, Germany, October 2001, 126.
[8] Gajewska M., Tuszyńska A., Obarska-Pempkowiak H., Polish J. Environ. Studies, 2004, 13, 149.
[9] Langergraber G., Prandtstetten C., Pressl A., Rohrhofer R., Harbel R., *Removal efficiency of subsurface vertical flow constructed wetland for different organic loads*, [In:] Proc. 10th International Conference on Wetland Systems for Water Pollution Control, Lisbon, Portugal, 2006, 1, 587.
[10] Pagilla K.R., Urgun-Demirtas M., Ramani R., Water Sci. Technol., 2006, 53 (3), 165.
[11] Pempkowiak J., Obarska-Pempkowiak H., Gajewska M., Wojciechowska E., Polish J. Environ. Studies, 2009, 3, 27.
[12] Environment Ministry Regulation according limits for discharged sewage and environmental protection from 24 July 2006 (Dz.U. No. 137, item 984).
[13] *APHA 2005 Standard Methods fir Examination of Water and Wastewater*, 21st Ed., American Public Health Association, Washington, D.C.
[14] Puigagut J., Villaseñor J., Salas J.J., Becares E., Garcia J., Ecol. Eng. 2007, 30, 312.
[15] Vymazal J., Ecol. Eng. 2005, 25, 478.
[16] Kuschk P., Wießner A., Kappelmeyer U., Weißbrodt E., Kästner M., Stottmeister U., Water Res., 2003, 37 (17), 4236.
[17] Dong Z., Sun T., 2007, Ecol. Eng., 2007 31, 69.

[18] PAGILLA K.R., CZERWIONKA K., URGUJ-DEMIRTAS M., MAKINIA J., *Nitrogen Speciation In Wastewater Treatment Plant Influent and Effluent – the US and Polish Case Studies*, Proc. 10th IWA Specialised Conference, Design, Operation and Economics of Large Wastewater Treatment Plants, Viena, Austria, 2007, 1, 113.

[19] KADLEC R.H., 2008, Ecol. Eng., 2008, 33, 126.

[20] AQUINO S.F., STUCKEY D.C., J. Envir. Eng., 2003, 129 (11), 1007.

[21] RAMESH A., LEE D.J., HONG S.G., 2006, Appl. Microbiol. Biotechnol., 2006, 73 (1), 219.

[22] PAWŁOWSKI L., Environ. Prot. Eng., 2011, 1, 105.