

Nitrification, denitrification, and dephosphatation capability of activated sludge during co-treatment of intermediate-age landfill leachates with municipal wastewater

S. Fudala-Ksiazek^a, E. Kulbat^b and A. Luczkiewicz^b

^aFaculty of Civil and Environmental Engineering, Department of Sanitary Engineering, Gdansk University of Technology, Gdansk, Poland;

^bFaculty of Civil and Environmental Engineering, Department of Water and Wastewater Technology, Gdansk University of Technology, Gdansk, Poland

ABSTRACT

This study focuses on the possible use and efficacy of the co-treatment of landfill leachate (intermediate-age) with municipal wastewater. The nitrification, denitrification, and dephosphatation capability of activated sludge acclimated with a mixture of raw municipal wastewater (RWW) with gradually increasing amounts of raw landfill leachate (RLL) (from 0.5 to 5% v/v) were tested. Biochemical tests were conducted simultaneously in batch reactors (BRs). According to the obtained data, the ammonia utilization rate (AUR) was 3.68 g N/(kg volatile suspended solids (VSS)-h) for RWW, and it increased to 5.78 g N/(kg VSS-h) with the addition of 5% RLL. The nitrate utilization rate under anoxic conditions (NUR_{AX}) remained at a comparable level of 1.55–1.98 g N/(kg VSS-h). During the anoxic phase, both nitrate utilization and phosphorus uptake occurred, suggesting that denitrifying phosphorus-accumulating organisms (DPAOs) utilized $N-NO_3$. With the addition of RLL, the rates of anoxic and aerobic phosphate uptake (PUR_{AX} and PUR_{AE}) and phosphate release rate (PRR) decreased. The PRR was likely negatively influenced by high $N-NO_3$ concentrations but not completely inhibited due to the availability of a biodegradable fraction of chemical oxygen demand (COD). Thus, monitoring the NH_4-N load in wastewater treatment plant influent before co-treatment is more informative than that using hydraulic-based criteria.

Abbreviations: σ – standard deviation; AUR – ammonia utilization rate; DPAO – denitrifying phosphorus-accumulating organisms; MLVSS – mixed liquor volatile suspended solids content; MSW – municipal solid waste; NUR_{AE} – nitrate production rate under aerobic conditions; NUR_{AX} – nitrate utilization rate under anoxic conditions; PAO – phosphorus-accumulating organisms; PRR – phosphate release rate under anaerobic conditions; PUR_{AX} – phosphate uptake rate under anoxic conditions; PUR_{AE} – phosphate uptake rate under aerobic conditions; RLL – raw landfill leachates; RM0.5 – raw mixture of RWW with 0.5% (vol.) of RLL; RM3 – raw mixture of RWW with 3% (vol.) of RLL; RM5 – raw mixture of RWW with 5% (vol.) of RLL; RWW – wastewater; VFA – volatile fatty acids; WWTP – wastewater treatment plant

KEYWORDS Intermediate-age landfill leachates; municipal wastewater; co-treatment; kinetics of biochemical processes; nitrification–denitrification–dephosphatation

1. Introduction

The European landfill directive (99/31/EC) was created to minimize the environmental impact of solid waste management and connects the promotion of waste-prevention-oriented technologies with the introduction of strict landfill management criteria. In addition to mandating procedures for waste recovery and disposal, this directive requires that landfill sites are managed for a period of at least 30 years after they close. However, this management period can be shortened or extended by the permitting authority. Monitoring the nearby groundwater composition, and the volume and

composition of the landfill gas and leachate is generally necessary. Landfill gas and leachate collection must be followed by treatment/utilization. Landfill leachate treatment is particularly expensive; thus, reducing costs in this area is challenging but necessary.

Landfill leachates are characterized by high chemical oxygen demand (COD), high ammonia, nitrogen, salt (especially chlorides and sulphates), and heavy metal concentrations as well as a strong colour and odour [1]. Additionally, the quality and quantity of landfill leachates vary with time, depend on the waste composition, climate, and solid waste disposal technique, and are primarily a function of landfill age and degree of waste

stabilization [2–4]. According to the latter factors, leachates can be classified into three categories: young, intermediate, and mature (old) [4], and various treatment approaches based on biological, chemical, or physical processes have been used.

Biological treatment is considered appropriate for leachates obtained from young prisms, which are rich in readily biodegradable organic matter. However, as the prism matures with time, the refractory organic fraction, including fulvic and humic-like compounds, increases. Decreases in the biodegradability of organic matter (biochemical oxygen demand (BOD_5)/COD < 0.3) generally correspond to elevated ammonia nitrogen ($NH_4-N > 400 \text{ mg/dm}^3$) and dissolved salt (e.g. chlorides, carbonates, and sulphates) concentrations, making the use of biological methods questionable [5]. Thus, for old leachates, reverse osmosis (RO) is often suggested as the most appropriate method. However, the RO process separates only pollutants and simultaneously generates both permeate and concentrate. The latter contains condensed pollutants and must be treated or discarded. In Poland, the concentrate is typically pumped back into the landfill prism, leading to an adverse feedback loop in which monovalent ions are barely retained or not retained in the landfill prism; with time, their reconcentration in leachate is observed. These important drawbacks and high operating costs force landfill operators to seek other technological solutions. Considering the above observations, this study evaluates the combined treatment of intermediate landfill leachates and municipal wastewater in a biological wastewater treatment plant (WWTP). This solution is justified by the effective share of landfill leachates in the municipal wastewater stream, which is typically negligible and does not exceed 0.4% (v/v) [6], and by the common possibility of discharging the landfill leachates directly into the municipal wastewater system.

To date, the co-treatment of landfill leachate with municipal wastewater has not been examined in detail; thus, WWTP exploiters may reluctantly agree to such an option. Therefore, this study aims to determine the efficacy of municipal wastewater co-treatment with increasing amounts of intermediate landfill leachate. Particular attention has been given to the nitrification, denitrification, and dephosphatation capabilities of activated sludge before acclimation to the laboratory-scale multiphase system, in which anaerobic/anoxic/oxic (A2/O) is continuously supplied to wastewater with increasing addition of landfill leachates (from 0.5 to 5% v/v). The biochemical processes that occur during such co-treatment (the ammonia utilization rate (AUR), the nitrate production rate under aerobic conditions (NUR_{AE}), the nitrate utilization rate under anoxic conditions (NUR_{AX}),

phosphate release rate (PRR), and the rates of anoxic and aerobic phosphate uptake (PUR_{AX} and PUR_{AE} , respectively) were determined in three-phase batch tests.

2. Materials and methods

2.1. Materials

The biochemical tests were performed in two bioreactors (BRs) supplied with raw municipal wastewater (RWW) and increasing amounts of raw landfill leachates (RLL). The RWW originated from the largest WWTP located on the Baltic Sea, Gdansk-Wschod (Northern Poland). This WWTP serves a population equivalent to 700,000 PE and has a daily flow of approximately $Q_{av.} = 96,000 \text{ m}^3/\text{d}$. More than 6.5% of the total inflow is discharged from industries (mainly the food industry, one shipyard and the chemical industry). The WWTP is operated as part of the modified University of Cape Town (mUCT) system. Wastewater was collected from December 2009 to July 2010. The activated sludge used in this study for inoculation of the laboratory-scale A2/O system was obtained from the sludge external recirculation of the WWTP.

The RLLs were obtained from the municipal solid waste (MSW) plant ‘*Eko Dolina Lezyce*’, which is located in northern Poland and serves the metropolitan area of Gdynia and its surroundings (approximately 460,000 people). The RLLs were collected from March to July 2010 from a prism that began operating in 2003. Each year, approximately 200,000 tonnes of waste was deposited in the prism, and approximately $27,000 \text{ m}^3$ of leachate was collected by its drainage system. The leachates were initially directed to the sewage system, but since 2004, they have been pre-treated on site using a reverse osmosis unit. The permeate was discharged to the municipal wastewater system while the concentrate was pumped back to the prism.

In the study, the collected RWW and RLL were transported to the laboratory and stored in a cold room at 4°C to minimize the occurrence of biological and chemical reactions prior to their use in experiments.

2.2. Acclimatization of activated sludge

The biomass was acclimatized in a laboratory-scale continuous-flow multiphase system known as A2/O (anaerobic/anoxic/oxic). The A2/O system is shown in Figure 1 and consists of three chambers: anaerobic (4 dm^3), anoxic (9 dm^3) and aerobic (14 dm^3), with a secondary clarifier (5.5 dm^3) at the end of the system. The flow rate was 27 dm^3 per day. The effluent from the aerobic



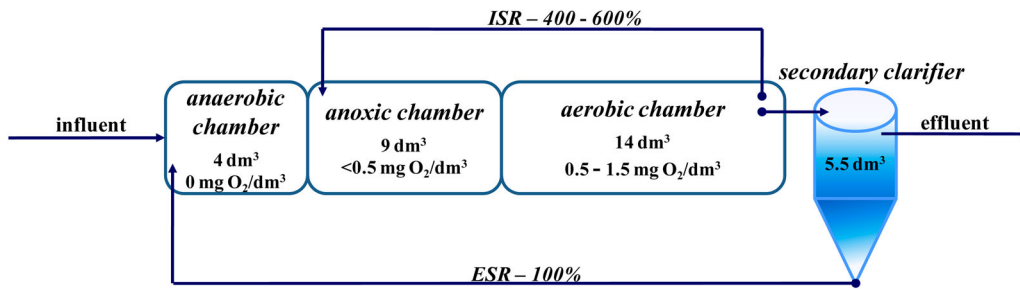


Figure 1. Schematic of the continuous-flow A2/O system. ISR – internal sewage recirculation; ESR – external sewage recirculation.

chamber was recirculated (internal sludge recirculation, ISR) into the anoxic chamber to support the denitrification processes. The ISR ratio varied from 400% to 600% of the flow rate depending on the efficiency of the co-treatment. Additionally, the sludge from the secondary clarifier was recirculated to the anaerobic chamber (external sludge recirculation, ESR) at a ratio equal to 100% of the flow rate. The dissolved oxygen (DO) concentration in the aerobic chamber was set at $1 \pm 0.5 \text{ mg O}_2/\text{dm}^3$, and the pH and temperature were controlled using online sensors. The concentration of activated sludge was maintained at $3.5 \text{ g dry mass}/\text{dm}^3$. Additionally, the efficiency of the A2/O treatment was checked twice weekly. To accomplish this, the basic physicochemical parameters of the A2/O inflow and outflow were tested (Figure 2).

During the first eight weeks of the study, the activated sludge was acclimated to the RWW. The biomass was then fed RWW mixed with increasing amounts of RLL (RM0.5, RM1, RM3, and RM5). For each landfill leachate addition, the acclimation of activated sludge lasted approximately six weeks.

2.3. Experimental setup

The effectiveness of the biochemical processes (AUR, NUR_{AE} , NUR_{AX} , PRR, PUR_{AX} , and PUR_{AE}) was tested in two BRs (maximal volume 4.2 dm^3 each), each of which was equipped with a mechanical stirrer, an aquarium air diffuser and electrodes for monitoring online pH, oxidation-reduction potential (ORP), temperature and DO (Photo 1). Eight 12-h experiments that were divided into anaerobic (2 h), anoxic (4 h), and aerobic (6 h) phases were conducted. During the control experiment, the two BRs were fed with RWW; in the three other tests, the two BRs were fed with mixtures of RWW and RLL (RM0.5, RM3, and RM5).

In each experiment, two BRs were inoculated with activated sludge, which was in parallel acclimated with the corresponding treatment mixture (RM0.5, RM3, or RM5) in a laboratory-scale A2/O system (see Section

2.2). Because the dry mass of activated sludge in each reactor was $2.5 \text{ g}/\text{dm}^3$, activated sludge from the external recirculation of the A2/O system was used. The temperature in the BRs was 20°C . The experiment began with an anaerobic phase at a DO concentration of less than $0.5 \text{ mg O}_2/\text{dm}^3$. After 120 min, potassium nitrate was added to increase the initial N-NO_3 concentration by $20 \text{ mg N-NO}_3/\text{dm}^3$. After 240 min of the anoxic phase, the aquarium air diffuser was used to deliver a DO concentration of $6.0 \text{ mg O}_2/\text{dm}^3$ for the next 360 min. During the experiments, samples ($V = 50 \text{ cm}^3$) were collected from each BR every 60 min and filtered under vacuum through Whatman GF/C glass fibre filters; the filtrate was analysed for COD, nitrate nitrogen (N-NO_3), nitrite nitrogen (N-NO_2), ammonia nitrogen (N-NH_4), and phosphate phosphorus (P-PO_4). The AUR, NUR_{AX} , NUR_{AE} , PRR, PUR_{AX} , and PUR_{AE} were determined as follows:

ammonia utilization rate (AUR)

$$= \frac{\Delta N_{\text{N-NH}_4}}{\text{VSS} \cdot \Delta t} \text{ (g N/kg VSS} \cdot \text{h)}, \quad (1)$$

nitrate utilization rate under anoxic conditions (NUR_{AX})

$$= \frac{\Delta N_{\text{AX}}}{\text{VSS} \cdot \Delta t} \text{ (g N/kg VSS} \cdot \text{h)}, \quad (2)$$

nitrate production rate under aerobic conditions (NUR_{AE})

$$= \frac{\Delta N_{\text{AE}}}{\text{VSS} \cdot \Delta t} \text{ (g N/kg VSS} \cdot \text{h)}, \quad (3)$$

phosphate release rate under anaerobic conditions (PRR)

$$= \frac{\Delta P_{\text{R}}}{\text{VSS} \cdot \Delta t} \text{ (g P/kg VSS} \cdot \text{h)}, \quad (4)$$

phosphate uptake rate under anoxic conditions (PUR_{AX})

$$= \frac{\Delta P_{\text{AX}}}{\text{VSS} \cdot \Delta t} \text{ (g P/kg VSS} \cdot \text{h)}, \quad (5)$$

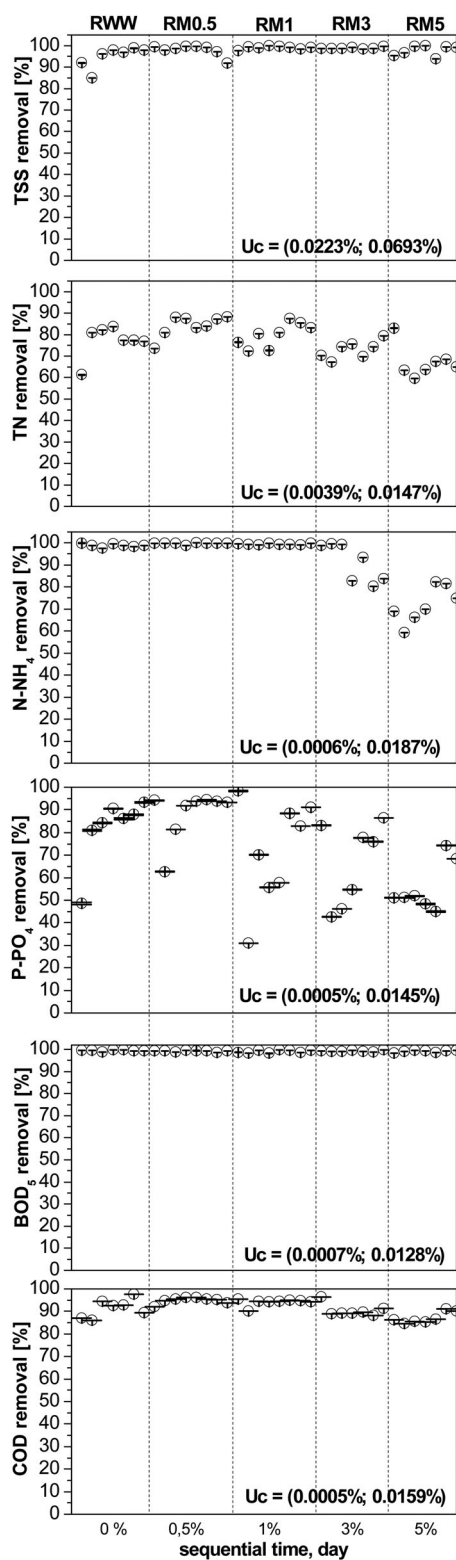


Figure 2. Removal of the main wastewater components by the co-treatment process in the A2/O system during the acclimation of the system to RWW containing activated sludge after the addition of RLL at volume percentages of 0.5–5% (RM0.5, RM1, RM3, and RM5). The dotted lines indicate the volume percentage of RLL, which ranges from 0.5 to 5%. The reported uncertainty (U) is an expanded uncertainty calculated using a coverage factor of $k = 1.65$, which gives a confidence level of approximately 95%.

phosphate uptake rate under aerobic conditions (PUR_{AE})

$$= \frac{\Delta P_{AE}}{VSS \cdot \Delta t} \text{ (g P/kg VSS} \cdot \text{h)}, \quad (6)$$

where Δt is the time during which the uptake/release/production of $N-NH_4$, $N-NO_3$, or $P-PO_4$ occurred (h), and VSS is the concentration of volatile suspended solids ($kg \text{ VSS}/m^3$).

2.4. Analytical methods

The COD, $N-NO_3$, $N-NO_2$, $N-NH_4$, total nitrogen (TN), $P-PO_4$, and total phosphorus (TP) concentrations were determined using colorimetric methods and a Hach Lange Xion 500 spectrophotometer (Dr Lange, GmbH, German). The total suspended solids (TSS) and VSS analyses were performed according to European Standard EN 872:2005 [7]. During the experiments, four variables were monitored online using the following electrodes: CelloX 325-3, (DO concentration and temperature), SenTix 41-3 (pH), and SenTix ORP (redox potential) (WTW, Germany).

2.5. Data analysis

The standard uncertainties of the concentrations and removal efficiencies of TN, $N-NH_4$, $N-NO_3$, $N-NO_2$, TP, $P-PO_4$, COD, BOD_5 , Cl^- , SO_4^{2-} , and TSS, as well as the pH and conductivity were calculated assuming a rectangular distribution. The reported uncertainty was an expanded uncertainty that was calculated using a coverage factor of $k = 1.65$, which resulted in a confidence level of approximately 95%. For AUR , NUR_{AX} , PRR , PUR_{AX} , and PUR_{AE} , the standard uncertainty was calculated assuming a Gaussian distribution. For these parameters, the reported uncertainty was an expanded uncertainty that was calculated using a coverage factor of $k = 2$, yielding a confidence level of approximately 95%. The median and standard deviation were used to indicate the central tendency and the spread of the data. Statistical analyses were conducted using MS Excel 2007 and Origin Pro 9.0 software.

3. Results and discussion

3.1. Characteristics of the raw leachates, raw wastewater, and leachate and wastewater mixtures

Generally, the RWW composition was similar to those of other municipal wastewaters [8,9] and was characterized by $N-NH_4$ concentrations of $52\text{--}59 \text{ mg } N-NH_4/dm^3$,





Photo 1. Experimental setup. 1 – batch reactors; 2 – units for the continuous measurement of oxygen uptake rate (OUR); 3 – peristaltic pumps; 4 – cooling/heating system; 5 – mechanical stirrers; 6 – control box; and 7 – computer control and data acquisition system.

CODs of 440–632 mg O₂/dm³, and Cl⁻ concentrations of 77–184 mg Cl⁻/dm³. The average BOD₅:COD ratio was 0.69, indicating that the RWW had a biodegradable COD greater than 50%. In addition, the TSS content varied from 154 to 166 mg/dm³.

High variability in RLL quality and quantity (Table 1) was observed during the studied period, and with the exception of TSS, the parameters were generally higher than those observed in the RWW, likely due to filtration of the leachate by the prism drainage system. In addition to high concentrations of COD and ammonia, which together constituted 96% of the total nitrogen (on average 2540 mg N-NH₄/dm³), the expected low BOD₅:COD ratio (approximately 0.19) was obtained. The total phosphorus concentration ranged from 17 to 20 mg P/dm³. Additionally, the RLL contained relatively high chloride concentrations (on average 2822 mg Cl⁻/dm³), potentially due to the discharge of reverse osmosis by-products (concentrate) into the studied landfill prism (see Section 2.1). In general, the obtained results are similar to the reported results for other mature leachates [1,3,4].

Increasing the volume of RLL added to RWW from 0.5% to 5% increased the ammonia nitrogen concentration in the studied mixtures RM0.5, RM3, and RM5 (Table 1). The ΔTN:ΔCOD ratio increased from 0.134 in

the RWW to 0.212 in RM5 (Table 2). This result indicates that the biodegradability of the mixture decreased when RLL was added to RWW, which can supposedly influence the biochemical processes that occur in activated sludge.

The nitrification, denitrification, and dephosphatation capabilities of activated sludge that was acclimatized to RWW supplemented with increasing amounts of RLL (RM0.5, RM3, and RM5) were tested in this study. Because limited data are available that describe the effectiveness of the biological processes (AUR, NUR_{AX}, PRR, PUR_{AX}, and PUR_{AE}) that occur during the co-treatment of wastewater and landfill leachates, the obtained results were compared with the results of biochemical tests conducted for activated sludge acclimatized to municipal wastewater. The results obtained in three-phase batch tests are given in Table 2. Selected results are presented in Figures 3–6; the remaining results are presented as supplementary figures (Figures S1–S64).

3.2. Anaerobic phase

Activated-sludge processes following anaerobic-aerobic stages favour enhanced biological phosphorus removal (EBPR) from wastewater. Generally, EBPR is regarded as the most economical and sustainable process for



Table 1. Characteristics of the raw landfill leachates (RLLs), raw wastewater (RWW), and obtained mixtures of RWW with the addition of 0.5% (RM0.5), 3% (RM3), and 5% (RM5) RLL.

Parameter	RLL	RWW	RM0.5	RM3	RM5
	mean \pm U min \div max	mean \pm U min \div max	mean \pm U min \div max	mean \pm U min \div max	mean \pm U min \div max
	Σ	σ	σ	σ	σ
TN [mg N/dm ³]	<u>2649 \pm 0.5</u> 2167 \div 3131 682	<u>71 \pm 0.05</u> 64 \div 78 10	<u>122 \pm 0.05</u> 115 \div 129 10	<u>185 \pm 0.05</u> 168 \div 203 25	<u>215 \pm 0.05</u> 197 \div 233 25
N-NH ₄ [mg N-NH ₄ /dm ³]	<u>2540 \pm 0.5</u> 2040 \div 3040 707	<u>56 \pm 0.05</u> 52 \div 59 5	<u>92 \pm 0.05</u> 89 \div 96 5	<u>164 \pm 0.05</u> 146 \div 182 25	<u>193 \pm 0.05</u> 174 \div 212 27
N-NO ₃ [mg N-NO ₃ /dm ³]	<u>16 \pm 0.5</u> 14 \div 17 3	<u>0.49 \pm 0.05</u> 0.41 \div 0.57 0.12	<u>1.07 \pm 0.05</u> 0.95 \div 1.18 0.16	<u>0.87 \pm 0.05</u> 0.79 \div 0.96 0.13	<u>1.37 \pm 0.05</u> 1.32 \div 1.42 0.07
N-NO ₂ [mg N-NO ₂ /dm ³]	<u>0.32 \pm 0.5</u> 0.074 \div 0.65 1.7	<u>0.21 \pm 0.05</u> 0.21 \div 0.21 0.004	<u>0.32 \pm 0.05</u> 0.23 \div 0.40 0.12	<u>0.24 \pm 0.05</u> 0.22 \div 0.26 0.02	<u>0.09 \pm 0.05</u> 0.072 \div 0.111 0.03
TP [mg P/dm ³]	<u>19 \pm 0.05</u> 17 \div 20 3	<u>11 \pm 0.05</u> 10 \div 12 1.2	<u>12 \pm 0.05</u> 11 \div 12 0.9	<u>10 \pm 0.05</u> 9.5 \div 10 0.6	<u>12 \pm 0.05</u> 10 \div 14 3
P-PO ₄ [mg P-PO ₄ /dm ³]	<u>11 \pm 0.05</u> 9 \div 14 3	<u>8 \pm 0.05</u> 7.5 \div 8.1 0.41	<u>10 \pm 0.05</u> 9 \div 10 0.2	<u>8 \pm 0.05</u> 7 \div 8 1	<u>9 \pm 0.05</u> 6 \div 11 4
BOD ₅ [mg O ₂ /dm ³]	<u>418 \pm 0.05</u> 355 \div 480 88	<u>412 \pm 0.05</u> 149 \div 608 123	ND ND	ND ND	ND ND
COD [mg O ₂ /dm ³]	<u>3256 \pm 0.5</u> 2869 \div 3642 547	<u>536 \pm 0.5</u> 440 \div 632 136	<u>949 \pm 0.5</u> 880 \div 1017 97	<u>769 \pm 0.5</u> 709 \div 829 85	<u>1026 \pm 0.5</u> 921 \div 1130 148
TSS [mg/dm ³]	<u>38 \pm 0.165</u> 28 \div 47 13	<u>160 \pm 0.165</u> 154 \div 166 8	<u>268 \pm 0.165</u> 242 \div 294 37	<u>258 \pm 0.165</u> 244 \div 272 20	<u>535 \pm 0.165</u> 499 \div 570 50
pH	<u>7.8 \pm 0.5</u> 7.8 \div 7.9 0.1	<u>7.1 \pm 0.5</u> 6.69 \div 7.35 0.15	ND ND ND	ND ND ND	ND ND ND
Conductivity [mS/cm]	<u>29 \pm 0.5</u> 26 \div 32 4	<u>1.44 \pm 0.5</u> 0.94 \div 1.66 0.14	ND ND ND	ND ND ND	ND ND ND
Cl ⁻ [mg Cl ⁻ /dm ³]	<u>2822 \pm 0.185</u> 2354 \div 3829 487	<u>130 \pm 0.185</u> 77 \div 184 27	ND ND ND	ND ND ND	ND ND ND
SO ₄ ²⁻ [mg SO ₄ ²⁻ /dm ³]	<u>387 \pm 0.5</u> 130 \div 665 199	<u>96 \pm 0.5</u> 51 \div 209 37	ND ND ND	ND ND ND	ND ND ND
BOD ₅ /COD	<u>0.19 \pm 0.002</u> 0.11 \div 0.24 0.05	<u>0.69 \pm 0.001</u> 0.59 \div 0.84 0.07	ND ND ND	ND ND ND	ND ND ND

Note: ND – not determined; Mean \pm standard uncertainty (U), level of confidence is 95%; σ – standard deviation; min – minimum value; max – maximum value.

phosphorus removal [8,9]; thus, EBPR is essential for WWTP efficiency. In the anaerobic phase of this process, nearly all of the readily biodegradable and available COD, which is typically in the form of volatile fatty acids (VFAs), is used by phosphorus-accumulating organisms (PAOs), which take up VFAs and store them as poly- β -hydroxyalkanoates (PHAs) while simultaneously releasing orthophosphates [8,9]. The same group of bacteria (PAOs) in the aerobic phase uses only oxygen as an electron acceptor for the stored PHAs, which are used as an energy source to take up P from the bulk solutions and to synthesize poly-P in the new cells [9,8]. In this study, phosphorus was released (PRR) during the anaerobic phase at concentrations of 1.94–5.28 g P/(kg VSS-h) for RWW, 4.18–6.17 g P/(kg VSS-h) for RM0.5, 1.92–2.15 g P/(kg VSS-h) for RM3 and 3.08–4.26 g P/(kg VSS-h) for

RM5. The Δ TN: Δ COD ratio increased, and the PRR decreased as the amount of RLL added to the RWW increased (Table 2). For comparison, the PRR reported in the literature for municipal wastewater from the WWTP in Gdynia (Poland) was higher, ranging from 12.8 to 21.1 g P/(kg VSS-h) at temperatures from 18.1 to 20.3°C [10], whereas Sorm et al. [11] reported a lower range of 9.9–12 g P/(kg VSS-h) for a full-scale A2O system (T = 20.3°C). The lower PRR noted during the anaerobic phase of the current study could be explained by the high initial N-NO₃ concentration (approximately 20 mg N/dm³). This N-NO₃ concentration in the anaerobic phase was introduced into the BRs with the acclimated activated sludge that was taken from the internal recirculation of the A2/O system (see Figure 1). The elevated amount of N-NO₃ resulted from the

Table 2. Rates of biochemical processes measured during three-phase (12-h) batch tests.

Treated mixture (% RLL addition to RWW)	Process temperature	Rates of biochemical processes (this study)					
		AUR	NUR _{AX}	PRR	PUR _{AX}	PUR _{AE}	ΔTN:ΔCOD
		$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$	$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$	$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$	$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$	$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$	$\frac{\text{mean} \pm U}{\text{min} \div \text{max}}$
		Σ	σ	σ	σ	σ	σ
%	°C	g N/(kg VSS-h)		g P/(kg VSS-h)			g N/g COD
0 (RWW)	20	3.68 ± 0.72	1.55 ± 0.65	3.55 ± 0.97	1.82 ± 0.63	2.34 ± 0.66	0.134 ± 0.00012
		$3.42 \div 3.86$	$1.24 \div 1.83$	$1.94 \div 5.28$	$1.46 \div 2.19$	$1.92 \div 2.84$	$0.122 \div 0.146$
		0.22	0.26	1.84	0.39	0.46	0.017
0.5 (RM0.5)	20	3.69 ± 0.85	1.84 ± 0.54	5.15 ± 0.94	1.09 ± 0.78	1.51 ± 0.63	0.129 ± 0.000076
		$3.21 \div 4.43$	$1.45 \div 2.20$	$4.18 \div 6.17$	$0.82 \div 1.42$	$1.09 \div 1.89$	$0.127 \div 0.131$
		0.54	0.40	1.09	0.29	0.42	0.003
3 (RM3)	20	3.89 ± 0.74	1.03 ± 0.68	2.05 ± 0.92	0.42 ± 0.59	0.48 ± 0.53	0.240 ± 0.000095
		$3.25 \div 4.52$	$0.89 \div 1.20$	$1.92 \div 2.15$	$0.38 \div 0.47$	$0.45 \div 0.51$	$0.236 \div 0.244$
		0.66	0.16	0.12	0.04	0.03	0.006
5 (RM5)	20	5.78 ± 0.91	1.98 ± 0.73	3.69 ± 0.97	0.56 ± 0.68	0.62 ± 0.51	0.212 ± 0.000072
		$5.62 \div 6.19$	$1.29 \div 2.48$	$3.08 \div 4.26$	$0.28 \div 0.85$	$0.34 \div 0.96$	$0.211 \div 0.214$
		0.28	0.56	0.57	0.32	0.32	0.002
Other studies							
Treated medium	Literature	AUR	NUR _{AX} g N/(kg VSS-h)	PRR	PUR _{AX} g P/(kg VSS-h)	PUR _{AE}	Remarks
RWW	[10]	–	–	12.8 ÷ 21.1	–	–	batch test
RWW	[11]	–	–	4.4 ÷ 7.0	1.9 ÷ 2.8	15.1 ÷ 30.0	A/O system
RWW	[11]	–	–	9.9 ÷ 12.0	12.4 ÷ 13.0	16.1 ÷ 17.9	A2/O system
RWW	[12]	–	–	9.6 ÷ 20.9	0 ÷ 5.9	6.2 ÷ 19.2	three-phase batch tests
RWW	[13]	–	–	5 ÷ 9	1.2 ÷ 1.6	4 ÷ 6	UCT system
RWW	[14]	–	–	–	6	–	UCT system
RWW	[15]	–	1.6 ÷ 2.7	–	–	–	batch test
RWW	[16]	–	2.0 ÷ 3.4	–	–	–	conventional NUR batch test
RWW	[17]	–	–	–	2	–	batch test
co-treatment of RWW and RLL	[18]	2 ÷ 4.7	–	–	–	–	batch and continuous-flow reactors; RLL addition to RWW ranged from 6.7% to 20%
synthetic LL	[19]	0.02	–	–	–	–	batch reactor system for nitrification
RLL	[20]	5	–	–	–	–	SBR with limited oxygen concentration
RWW	[21]	4.2 ÷ 5.6	–	–	–	–	SBR system
RWW	[22]	2.48 ÷ 4.91	–	12.8 ÷ 21.8	2.05 ÷ 3.09	5.83 ÷ 8.90	BARDENPHO

Note: Mean ± standard uncertainty (U), level of confidence is 95%; σ – standard deviation; min – minimum value; max – maximum value; VFAs – volatile fatty acids.

intensive nitrification that occurred during the treatment of RM3 and RM5 in A2/O. However, phosphate did occur (Figure 5), despite the notion that phosphate release should be inhibited under these conditions [8,9,23]. Similar results regarding phosphate release in the presence of nitrate were obtained by Yuan and Oleszkiewicz [24].

3.3. Anoxic phase

During the anoxic phase of the experiments, the NUR_{AX} varied within the following ranges: 1.24–1.83 g N/(kg VSS-h) for RWW, 1.45–2.20 g N/(kg VSS-h) for RM0.5, 0.89–1.20 g N/(kg VSS-h) for RM3, and 1.29–2.48 g N/(kg VSS-h) for RM5 (Table 2). The parallel phosphorus uptake (PUR_{AX}) of RWW measured in the anoxic phase ranged from 1.46 to 2.19 g P/(kg VSS-h). The addition of leachate to wastewater decreased the average observed PUR_{AX} values, which were 1.09 g P/

(kg VSS-h), 0.42 g P/(kg VSS-h), and 0.56 g P/(kg VSS-h) for RM0.5, RM3, and RM5, respectively. The obtained NUR_{AX} results were similar to those reported in the literature, where NUR_{AX} was determined for nitrate utilization rates during anoxic phosphorus uptake processes (NUR_{AX} = 1.6–1.7 g N/(kg VSS-h) in the winter, NUR_{AX} = 2.4–2.7 g N/(kg VSS-h) in the spring, and NUR_{AX} = 2.0–2.1 g N/(kg VSS-h) in the summer [15]. Furthermore, the NUR_{AX} data, which ranged from 2.0 to 3.4 g N/(kg VSS-h), were similar to the data obtained by Swinarski et al. [16]. In contrast, for conventional nitrate use, reported NUR_{AX} values are higher than those obtained in this study and range from 3.27 to 5.65 g N/(kg VSS-h) [25]. It should be noted, however, that the conventional method for the determination of nitrate utilization rates is performed as a one-step procedure; thus, denitrifying bacteria can utilize the readily biodegradable substrate. In our study, the anoxic phase was preceded by the anaerobic phase, during which

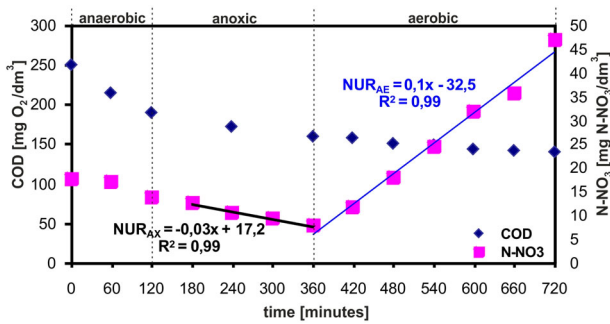


Figure 3. Examples of the nitrate utilization rate under anoxic conditions (NUR_{AX}) and the nitrate production rate under aerobic conditions (NUR_{AE}) measured for RM3 (RWW with 3% addition of RLL; $T = 20^\circ\text{C}$, $MLVSS = 2.16 \text{ kg/m}^3$).

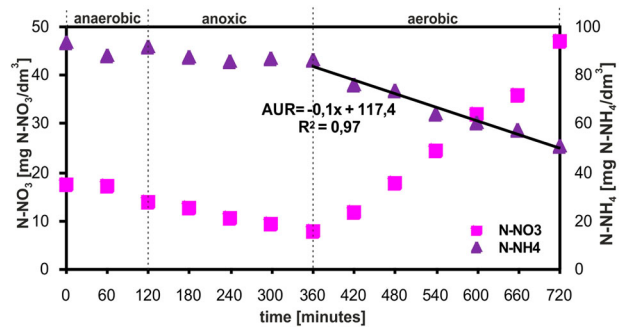


Figure 5. Examples of AUR measured for RM3 (RWW with the addition of 3% RLL; $T = 20^\circ\text{C}$, $MLVSS = 2.16 \text{ kg/m}^3$).

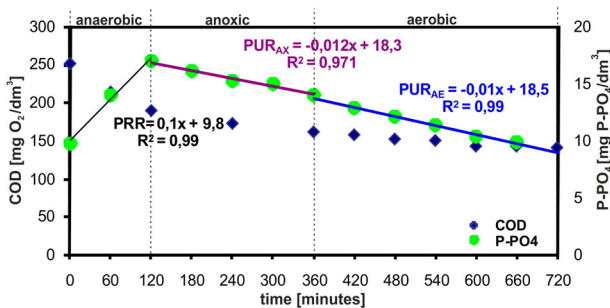


Figure 4. Examples of the phosphate release rate (PRR) under anaerobic conditions, the phosphate uptake rate under anoxic conditions (PUR_{AX}), and the phosphate uptake rate under aerobic conditions (PUR_{AE}) measured for RM3 (RWW with the addition of 3% RLL; $T = 20^\circ\text{C}$, $MLVSS = 2.16 \text{ kg/m}^3$).

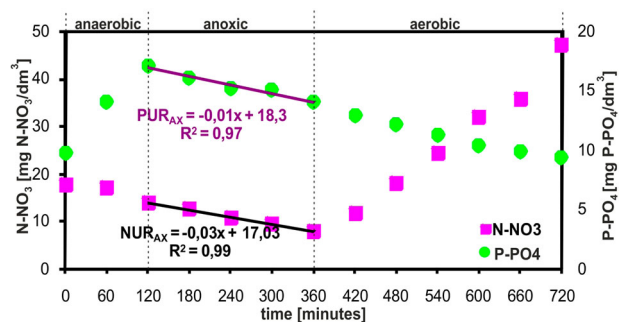


Figure 6. Examples of the phosphate uptake rate (PUR_{AX}) and the nitrate utilization rate under anoxic conditions (NUR_{AX}) measured for RM3 (RWW with the addition of 3% RLL; $T = 20^\circ\text{C}$, $MLVSS = 2.16 \text{ kg/m}^3$).

phosphate release depends on the utilization of readily biodegradable substrate. Thus, during the subsequent anoxic phase, denitrifying bacteria can use only the remaining COD fraction (mainly consisting of slowly biodegradable substrate). This could have influenced the obtained NUR_{AX} values.

In this study, the obtained PUR_{AX} values for RWW and RM0.5 were comparable to the values reported by Sorm et al. [11] (from 1.9 to 2.8 g P/(kg VSS-h) in an A/O system; $T = 20^\circ\text{C}$) and by Drewnowski and Makinia [17] (an average value of 2.0 g P/(kg VSS-h) but lower than those reported by Kuba et al. [14] (an average value of 6.0 g P/(kg VSS-h); $T = 20^\circ\text{C}$). However, the PUR_{AX} values for RM3 and RM5 were lower than those reported in the literature [11,14,17].

The lower PUR_{AX} values for RM3 and RM5 resulted from the high initial COD (Table 1). When a high COD was maintained in the anoxic phase, phosphate was released until the biodegradable COD was exhausted rather than taken up as expected. A similar result was observed in the experiments conducted by Hou et al. [26] and Jabari et al. [27], who used a pilot scale A2/O system and an SBR laboratory system, respectively.

The parallel processes of nitrate utilization and phosphorus uptake under anoxic conditions may indicate the presence of specific denitrifying PAOs (DPAOs) that can oxidize intracellular PHA using nitrate and/or nitrite (instead of free oxygen) as the terminal electron acceptor, thereby providing energy for phosphorus uptake [28]. Thus, the carbon taken up by PAOs in the anaerobic phase may be used advantageously for both denitrification and phosphorus removal when the wastewater contains relatively low levels of organic carbon [25]. An additional benefit of P- PO_4 uptake in the anoxic phase is that the aeration energy demand in the subsequent aerobic phase is lower [28].

The performances of DPAOs that use nitrate or nitrite as an electron acceptor in activated sludge biomass systems have been extensively studied. However, identification of other parameters that affect the denitrifying behaviour of DPAOs and their influence on biological nutrient removal process is required. For example, Carvalho et al. [29] and Jabari et al. [27] observed a correlation between the denitrification ability of DPAOs and the type of carbon source provided. However, state-of-the-art DPAO technology has been developed, they are

not commonly used to better detect the presence of DPAOs and understand their metabolic activities. To obtain a more comprehensive picture of DPAOs, simultaneous analysis of both PUR_{AX} and PUR_{AE} is required.

3.4. Aerobic phase

In this study, the phosphate uptake rates under aerobic conditions (PUR_{AE}) ranged from 1.92 to 2.84 g P/(kg VSS·h) for RWW and decreased with increasing addition of landfill leachates to the RWW. For RM0.5, RM3, and RM5, the PUR_{AE} values ranged from 1.09 to 1.89 g P/(kg VSS·h), 0.45 to 0.51 g P/(kg VSS·h), and 0.34 to 0.96 g P/(kg VSS·h), respectively. These values indicate that the PUR_{AE} was higher than the PUR_{AX} , a finding that was also reported by Merzouki et al. [30] and Hou et al. [26].

In addition to PRR, PUR_{AX} , and PUR_{AE} , another important parameter that describes the efficiency of the co-treatment of landfill leachate and wastewater is the AUR. The ammonia concentration in RLL is very high. In this study, the average initial ammonia concentration in the RWW was 56 mg N-NH₄/dm³, whereas during the treatment of RM5, it reached 193 mg N-NH₄/dm³. According to the obtained results, increasing the addition of landfill leachates to wastewater did not inhibit nitrification. The AURs in the RWW varied from 3.42 to 3.86 g N/(kg VSS·h), whereas the highest rate of landfill leachate addition (RM5) increased the AUR by up to approximately 6 g N/(kg VSS·h) (Table 2). As in this study, Çeçen and Aktas [18] observed that the AUR increased from 2 to 4.7 g N/(kg VSS·h) during the co-treatment of wastewater and landfill leachates as the landfill leachate content increased from 6.7% to 20%. Considerably lower AUR values of only 0.02 g N/(kg VSS·h) were obtained by Yusof et al. [19] during landfill leachate treatment (at an N-NH₄ concentration of 1452 mg/dm³) in a biofilm airlift system. On the other hand, studies of the rate of removal of ammonia from landfill leachates in SBRs in the presence of limited oxygen concentrations (0.7 mg O₂/dm³) conducted by Kulikowska and Bernat [20] showed AUR values of approximately 5 g N/(kg VSS·h). Notably, limited data are available for the co-treatment of wastewater and landfill leachates and RLLs. As a comparison, the AURs reported in the literature for municipal wastewater (initial amount of ammonia between 16.3 and 19.8 mg/dm³) range from 4.2 to 5.6 g N/(kg VSS·h) [21]. Furthermore, the AURs measured during this study are also comparable to those reported by Makinia [22] for settled wastewater from WWTPs in Gdynia and Gdansk (the average initial amount of ammonia was 48 mg N-NH₄/dm³ in both cases), which varied within the ranges of

2.48–4.91 g N/(kg VSS·h) and 3.20–.75 g N/(kg VSS·h), respectively.

Notably, during the treatment of RM3 (Figure 4) and RM5 in this study, the maintained 6-h aerobic phase was not sufficient for achieving full nitrification when the initial concentration of N-NH₄ was greater than 160 mg N-NH₄/dm³ (Table 1). Extension of the duration of the aerobic phase could increase the AURs and the effectiveness of this process. However, the oxidation of large amounts of ammonia results in a high nitrate concentration, and this nitrate is directed to the anaerobic phase during the recirculation of activated sludge. As a consequence, elevated nitrate concentrations may decrease the effectiveness and stability of both EBPR and denitrification processes [9,23].

According to the data obtained in this study, the quality of tested matured landfill leachates and, to a minor extent, those of raw wastewater vary with time. Thus, during the co-treatment of municipal wastewater and landfill leachate, it seems reasonable to use the N-NH₄ concentration in the WWTP influent as a border condition instead of following the hydraulic approach (volume-to-volume addition). This information can also be useful for calculating the additional costs of co-treatment. Increased levels of N-NH₄ in the WWTP inflow significantly affect the aeration requirements and influence the WWTP operating costs. The addition of 0.5% RLL to RWW increased the TN concentration by approximately 51 mg N/dm³ and the aeration costs by approximately 1007 euros per day (assuming 85% removal of the nitrogen load and a price of 1 kWh = 0.12 euro). Thus, under these conditions, the entire WWTP exploitation costs, including sewage sludge treatment, may increase by approximately 3097 euros per day. Nonetheless, co-treatment of landfill leachate and municipal wastewater can be considered an alternative treatment option because physical methods, such as reverse osmosis, in addition to their high cost, only separate permeate (high-quality effluent) from the condensed pollutants, which must then be treated or disposed of.

4. Conclusion

The results reported in this study confirm the feasibility of the co-treatment of landfill leachate and wastewater. Even the addition of the largest amount of landfill leachates (5%) influenced but did not inhibit the biological treatment processes. Increasing the addition of landfill leachates from 0.5 to 5% increased the AURs, but denitrification remained nearly the same regardless of the experimental conditions. In the case of dephosphatation, the obtained data indicated that the efficiencies of the PUR_{AX} and PUR_{AE} and the PRR decreased with the



addition of landfill leachates. During the anoxic phase, the release of phosphate was observed until the readily biodegradable COD was exhausted, in contrast to the expected uptake of phosphate. However, additional extensive studies are needed to increase our knowledge of simultaneous nitrate utilization and phosphorus uptake. In addition to the co-treatment efficiency, the amount of nitrogen in the WWTP influent is particularly important in calculating the operational costs of a WWTP. Thus, instead of using the hydraulic approach, which considers the volumetric addition of landfill leachate to raw wastewater, use of the boundary ammonia concentration by WWTP exploiters is suggested. This approach is more reliable since ammonia concentration can be controlled online in the WWTP influent and used to determine the current landfill leachate volumetric addition to wastewater.

Funding

This research was co-financed by the following projects: The Polish Ministry of Science and Higher Education (Warsaw, Poland) [grant no. N N523 557538] and 'The Centre for Advanced Studies – the development of interdisciplinary doctoral studies at the Gdansk University of Technology in the key areas of the Europe 2020 Strategy' [POKL04.03.00-00-238/12].

References

- [1] Lema JM, Mendez R, Blazquez R. Characteristics of landfill leachates and alternatives for their treatment: a review. *Water Air Soil Poll.* 1988;40(3):223–250. doi:10.1007/BF00163730
- [2] Černila Zajc N, Glancem M, Grömping M, et al. Laboratory scale and pilot study of the treatment of municipal landfill leachate. *Chem Biochem Eng Q.* 2004;18(1):77–84.
- [3] Kulikowska D, Klimiuk E. The effect of landfill age on municipal leachate composition. *Bioresource Technol.* 2008;99(13):5981–5985.
- [4] Renou S, Givaudan JG, Poulain S, et al. Landfill leachate treatment: review and opportunity. *J Hazard Mater.* 2008;150(3):468–493. doi:10.1016/j.jhazmat.2007.09.077
- [5] Rodríguez J, Castrillón L, Marañón E, et al. Removal of non-biodegradable organic matter from landfill leachates by adsorption. *Water Res.* 2004;38(14–15):3297–3303. doi:10.1016/j.watres.2004.04.032
- [6] Fudala-Ksiazek S, Luczkiewicz A, Fitobor K, et al. Nitrogen removal via the nitrite pathway during wastewater co-treatment with ammonia-rich landfill leachates in a sequencing batch reactor. *Environ Sci Pollut R.* 2014;21(12):7307–7318.
- [7] British Standards Institution. Water quality – determination of suspended solids – method by filtration through glass fiber filters. Standard No. EN 872:2005.
- [8] Henze M, van Loosdrecht MCM, Ekama G, et al., editors. Biological wastewater treatment. Principles, modelling and design. London: IWA Publishing; 2008.
- [9] Tchobanoglous G, Burton FL, Stensel HD. Wastewater engineering: treatment and reuse. 4th ed. New York (NY): McGraw-Hill; 2003.
- [10] Makinia J, Dobiegała E, Swinarski M. The Polish perspective on adopting EU standards for nitrogen removal at large WWTP's – case studies. *Water Sci Technol.* 2004;50(7):27–34.
- [11] Sorm R, Bortone G, Wanner J, et al. Behaviour of activated sludge from a system with anoxic phosphate uptake. *Water Sci Technol.* 1998;37(4–5):563–566.
- [12] Lopez-Vazquez CM, Hooijmans CM, Brdjanovic D, et al. Factors affecting the microbial populations at full-scale-enhanced biological phosphorus removal (EBPR) wastewater treatment plants in the Netherlands. *Water Res.* 2008;42:2349–2360. doi:10.1016/j.watres.2008.01.001
- [13] Kuba T, van Loosdrecht MCM, Brandse FA, et al. Occurrence of denitrifying phosphorus removing bacteria in modified UCT-type wastewater treatment plants. *Water Res.* 1997a;31:777–786.
- [14] Kuba T, van Loosdrecht MCM, Heijnen JJ. Biological dephosphatation by activated sludge under denitrifying conditions: pH influence and occurrence of denitrifying dephosphatation in a full-scale waste water treatment plant. *Water Sci Technol.* 1997b;36(12):75–82. doi:10.1016/S0273-1223(97)00713-0
- [15] Drownowski J, Makinia J. The role of colloidal and particulate organic compounds in denitrification and EBPR occurring in a full-scale activated sludge system. *Water Sci Technol.* 2011;63(2):318–324.
- [16] Swinarski M, Makinia J, Czerwionka K, et al. Comparison of the effects of conventional and alternative external carbon sources on enhancing the denitrification process. *Water Environ Res.* 2009;81(9):896–906.
- [17] Drownowski J, Makinia J. The role of biodegradable particulate and colloidal organic compounds in biological nutrient removal activated sludge systems. *Int J Environ Sci Te.* 2014;11(7):1973–1988.
- [18] Çeçen F, Aktas Ö. Effect of PAC addition in combined treatment of landfill leachate and domestic wastewater in semi-continuously fed batch and continuous-flow reactors. *Water SA.* 2001;27(2):177–188.
- [19] Yusof N, Hassan MA, Phang LY, et al. Nitrification of ammonium-rich sanitary landfill leachate. *Waste Manage.* 2010;30:100–109. doi:10.1016/j.wasman.2009.08.018
- [20] Kulikowska D, Bernat K. Nitritation-denitritation in landfill leachate with glycerine as a carbon source. *Bioresource Technol.* 2013;142:297–303. doi:10.1016/j.biortech.2013.04.119
- [21] Kim H, Hao OJ, McAvoy TJ. SBR system for phosphorus removal: ASM2 and simplified linear model. *J Environ Eng.* 2001;127(2):98–104.
- [22] Makinia J. Performance prediction of full-scale biological nutrient removal systems using complex activated sludge models. Hanover: Publications of Institute for Sanitary Engineering and Waste Management of Leibniz University of Hanover; 2006.
- [23] Kuba T, Wachtmeister A, van Loosdrecht MCM, et al. Effect of nitrate on phosphorus release in biological phosphorus removal systems. *Water Sci Technol.* 1994;30(6):263–269.
- [24] Yuan Q, Oleszkiewicz J. Interaction between denitrification and phosphorus removal in a nutrient removing



SBR system. Proceedings of the 81st Annual WEF Technical Exhibition and Conference WEFTEC; 2008 Oct 15-16; Chicago (IL).

- [25] Naidoo V, Urbain V, Buckley C. Characterization of wastewater and activated sludge from European municipal wastewater treatment plants using the NUR test. *Water Sci Technol.* 1998;38(1):303–310. doi:10.1016/S0273-1223(98)00415-6
- [26] Hou H, Wang S, Peng Y, et al. Anoxic phosphorus removal in a pilot scale anaerobic-anoxic oxidation ditch process. *Front Environ Sci En.* 2009;3(1):106–111.
- [27] Jabari P, Munz G, Oleszkiewicz JA. Selection of denitrifying phosphorous accumulating organisms in IFAS systems: comparison of nitrite with nitrate as an electron acceptor. *Chemosphere.* 2014;109:20–27. doi:10.1016/j.chemosphere.2014.03.002
- [28] Zeng RJ, Saunders AM, Yuan Z, et al. Identification and comparison of aerobic and denitrifying polyphosphate-accumulating organisms. *Biotechnol Bioeng.* 2003;83(2):140–149.
- [29] Carvalho G, Lemos PC, Oehmen A, et al. Denitrifying phosphorus removal: linking the process performance with the microbial community structure. *Water Res.* 2007;41(19):4383–4396.
- [30] Merzouki M, Delgenes JP, Bernet N, et al. Polyphosphate-accumulating and denitrifying bacteria isolated from anaerobic-anoxic and anaerobic-aerobic sequencing batch reactors. *Curr Microbiol.* 1999;38(1):9–17.

