

THE EFFECT OF KALDNES BIO FILTER MEDIA PACKING VOLUME ON THE EFFICIENCY OF MUNICIPAL LANDFILL LEACHATE TREATMENT

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Abstract The purpose of study was to determine the effect of Kaldnes filtration media packing volume on the efficiency of ammonium removal in SBRs fed with municipal landfill leachate. The leachate was obtained from municipal landfill operated for over 10 years, and was characterized by COD of 4125.6 mg L^{-1} , BOD_5 – 490 mg L^{-1} , total nitrogen – 750 mg L^{-1} and ammonia nitrogen 580 mg L^{-1} . Increase of filtration media's packing volume, has reduced the rate of ammonia nitrogen removal calculated per activated sludge units, while rate of reaction calculated per reactor volume has been comparable, regardless of media volume, with COD removal efficiency at the level of 17% to 28% and ammonia nitrogen 43% to 47%.

Key words: landfill leachate, Kaldnes media, ammonium removal, simultaneous nitrification and denitrification (SND), sequencing batch reactor (SBR)

1. INTRODUCTION

The leachate composition and quantity may vary, depending on landfill age, climate, amount of precipitation, construction and operational conditions of the landfill and finally the technology of collection, retention and treatment. Also, the processes taking place in the landfill bed, as organic matter decomposition, gas generation or settling efficiency have significant impact (Guo et al., 2010; Afsharnia et al., 2012; Shima et al., 2012).

The leachate from young, newly established landfill in acidogenic phase, is characterized by low pH, moderate concentration of ammonia nitrogen ($500 - 2000 \text{ mg L}^{-1}$) and high organic matter content, expressed as both biochemical oxygen demand (BOD_5 from 4000 to $13,000 \text{ mg L}^{-1}$) and chemical oxygen demand (COD from 30,000 to $60,000 \text{ mg L}^{-1}$). This resulting in high BOD/COD ratio within the range of 0.4 to 0.7. In the methanogenic phase volatile fatty acids (VFA) degrade and sparingly decomposed organic matter forms the leachate which pH increases to approx. 7. As scientific data indicates (Foo & Hameed, 2009; Ahmed & Lan, 2012) with the passage of waste disposal time, the prevalence of anaerobic processes within the landfill bed is observed, hence the leachate is characterized by

higher concentration of ammonium nitrogen ($3000 - 5000 \text{ mg L}^{-1}$), and reduced value of COD $5000 - 20,000 \text{ mg L}^{-1}$, resulting in unfavourable BOD/COD proportion, often lower than 0.1 (Table 1).

Table 1. Classification and composition of landfill leachate with the time of operation.

Parameter	Young	Intermediate	Stabilized
Age (years)	< 5	5 – 10	> 10
pH	< 6.5	6.5 – 7.5	> 7.5
COD [mg L^{-1}]	> 10,000	4,000 – 10,000	< 4,000
BOD/COD	0.5 – 1.0	0.1 – 0.5	< 0.1
Organic compounds	80% (VFA)	5 – 30% VFA + humic and fulvic acids	Humic and fulvic acid
N-NH_4^+ [mg L^{-1}]	< 400	N.A.	> 400
TOC/COD	< 0.3	0.3 – 0.5	> 0.5
Heavy metals [mg L^{-1}]	Low to medium	Low	Low
Biodegradability	High	Medium	Low

Unconventional biological treatment methods, which require both limited aeration and demand for organic carbon, have been proposed in the recent years for treatment of landfill leachate with low COD/N ratio. Although, less efficient in organic carbon

removal, the biological treatment of leachates is still an economically viable solution as far as nitrogen removal is concerned. It is usually carried out as the nitrification and denitrification process occurring in separate tanks (Lan et al., 2011). In the nitrification process, aerobic autotrophic nitrifiers oxidize the ammonium nitrogen to nitrites, then to nitrates, whereas denitrification consists in reduction of nitrates to gaseous nitrogen by heterotrophic bacteria in anoxic conditions (Schmidt et al., 2003; Wan et al., 2009; Guo et al., 2013). As it follows from the available literature, nitrification and denitrification can occur in a single reactor in aerobic conditions which is commonly known as the process of simultaneous nitrification and denitrification (SND) (Munch et al., 1996; Guo et al., 2013, Wang et al., 2013). Apart from improved wastewater treatment economy, SND offers higher nitrogen removal efficiency at low C/N ratios, because more carbon is available for heterotrophic bacteria (Hocaoglu et al., 2011). It is estimated that the carbon demand during SND process is lower by 22–40% and about 30% less of sludge is generated compared to conventional nitrogen removal methods (Seifi & Fazaelipoor, 2012; Wang et al., 2013). There are many factors affecting the efficiency of SND process, e.g. C/N ratio (Chiu et al., 2007), sludge retention time (Wu et al., 2011), concentration of dissolved oxygen (DO) (Hocaoglu et al., 2011) or temperature (Ilies & Mavinic, 2001).

The process may be carried out by microbial cultures in a single bioreactor or by microflora forming a biofilm, where the efficiency depends on concentration of dissolved oxygen and biofilm thickness. High biomass concentration and extended age of activated sludge in the biological reactor allow to increase the effectiveness of municipal landfill leachate treatment.

Fluidized beds and reactors with suspended biomass have been used to increase the biomass concentration and microorganism's age. The tests consisting on the improvement of nitrification efficiency have been conducted using combined methods - activated sludge with biofilm on medium (moving or fixed). Different biomass carriers are currently available, such as: Kaldnes (polyethylene media), Liapor (ceramic media), Linpor (plastic media with high porosity), foam cubes (mainly polyurethane) (Lim et al., 2011) or BioBall (polypropylene media) (Masłoń & Tomaszek, 2015). Lim et al., (2012) report that suspended biomass plays an important role in ammonia nitrogen oxidation, when the biomass, which colonizing inner surfaces of polyurethane foam media, is used as a carbon source in the denitrification process.

In 1997 Welander et al., reported that use of biomass media in reactors allows to maintain

nitrification at temperatures below 5°C. Karapinar & Kargi (1996) used a sponges as an FBBR packing, achieving a biomass concentration in the reactor at level of 55 gL⁻¹ thus allowing to maintain aerobic-anaerobic conditions. The ratio of suspended biomass to biomass on media was 42%. The use of sponge packing allowed for increase the biomass content to 90%. Wang et al., (2005) report that increase of the amount of filter media in the reactor, leads to the biofilm abrasion and thinning. A large amount of filter media contributes to removal of microorganisms from the biofilm and elution from the reactor, which results in the decrease in biomass concentration (Zhang et al., 2014).

It is assumed, that introduction of the mixing phase and various volumes of movable bio-carriers, while maintaining correct concentration and age of activated sludge, will contribute to increase the efficiency of process. The purpose of the study was to assess the effect of packing volume (as the ratio to the reactor active volume) on the efficiency of landfill leachate treatment.

2. MATERIALS AND METHODS

The leachate used in the tests has been sampled from municipal landfill in Kozodrza (near Rzeszów, south-eastern Poland, Subcarpathian Province) operating since 1998 and receives municipal and non-hazardous waste in an average quantity of 20 Mg/day. The leachate, collected from retention pond, had an organic matter concentration expressed as COD – 4125.6 ± 150mgL⁻¹, BOD₅ – 490 ± 20mgL⁻¹ and total nitrogen (TN) – 750 ± 20 mgL⁻¹, including ammonium nitrogen – 580 ± 18mgL⁻¹.

Leachate treatment has been carried out with an activated sludge method, in sequence batch reactors (SBRs) of 2L active volume, and operating in a 24h cycle that consists of: filling (0.1 h), mixing (3 h), aeration (20 h), sedimentation (0.7 h) and decantation (0.2 h) (Fig. 1). Dissolved oxygen concentration (DO) in the reactors during the aeration phase has been maintained at <1±0.1mgL⁻¹. Kaldnes filter media (diameter 11 mm, height 7 mm, specific surface area >845 m²m⁻³) have been used as a reactor packing. The packing bulk volume was fixed at 5% (SBR1), 10% (SBR2) and 20% (SBR3) of the active volume of the reactor and hydraulic retention time (HRT) was set at 2 days.

The reactors have been inoculated with mix of an activated sludge from II^o nitrification chamber of municipal wastewater treatment plant (PE≈200k) and 20% vol. addition of sludge from laboratory reactor supplied with leachate and operating in oxy-anoxic conditions. The reactor temperature was

maintained at $35\pm1^\circ\text{C}$ and experiment was carried out for 90 days.

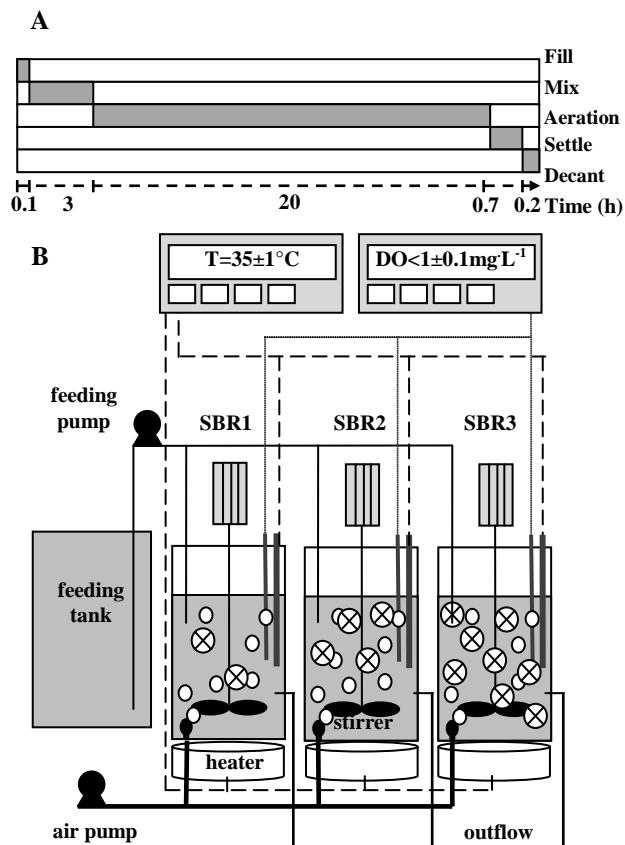


Figure 1. Operation cycle of each sequencing batch reactors (A) and the experiment setup (B) with three reactors of different biomass carriers volume.

To determine the influence of packing volume on treatment efficiency, the average values of BOD_5 (DIN EN 1899-1/EN 1899-2 Respirometric method), COD (PN-ISO 6060:2006 Colorimetric Method), N-NH_4^+ (PN-ISO 5664:2002 Colorimetric Method), N-NO_2^- (PN-ISO 26777:1999 Spectrophotometric Method) and N-NO_3^- (PN-82/C-04576/08 Spectrophotometric Method) were analyzed after the stabilization of concentration in runoffs. Concentration of the dissolved oxygen and volatile suspended solids (VSS) were controlled both in a suspended sludge and on the carriers (fixed and volatile solids incinerated at 550°C , Weight Method).

3. RESULTS AND DISCUSSION

3.1. Organic substances removal

A key factor affecting the efficiency of nitrogen removal from carbon deficient leachate is a concentration of available organic matter. In tested leachate, value of COD in the influent was $4125.6\pm150\text{mgL}^{-1}$, and BOD_5 was $490\pm20\text{mgL}^{-1}$ thus BOD_5/COD ratio of 0.12 was unfavourable from the

point of view of biological treatment process. The outflows have stabilized after 35 days of the experiment. The highest reduction of COD in leachate has been observed in the reactor operating with the lowest volume of Kaldnes filter media (SBR1) – $28\pm0.5\%$, while the lowest reduction in SBR 2 – $17\pm0.4\%$ (Fig. 2).

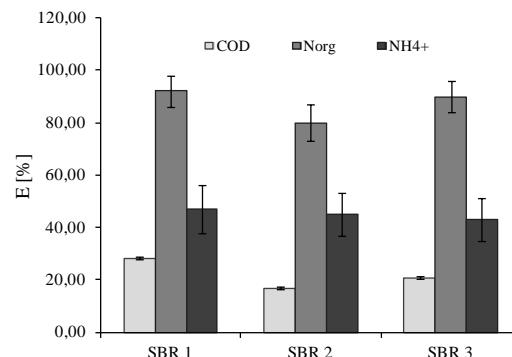


Figure 2. Leachate treatment efficiency in SBRs

Based on the analysis of concentration of easily decomposing organic matter, regardless of packing volume, the efficiency of BOD_5 removal was over $90\pm1\%$.

The process mainly removes biodegradable substances from the leachate. Similar results have been obtained by Xu et al. (2010) in SBR working in 12 h cycle, with alternate mixing and aeration phase, and BOD_5/COD ratio 0.14 ($\text{COD} = 3876\text{mgL}^{-1}$, $\text{BOD}_5 = 458\text{mgL}^{-1}$). They achieved efficiency of COD removal below $6.7\pm0.08\%$ (average 5.1%), whereas BOD_5 removal efficiency reached $82.95\pm9\%$. Whereas, Loukidou & Zoudoulis (2001) conducted studies on treatment of leachate characterized by concentration of organic matter $\text{COD} = 5000\text{mgL}^{-1}$ in SBR filled with polyurethane cubes, and they obtained 65% reduction.

3.2. Nitrogen removal

In raw leachate, used as the inflow to the reactors, total nitrogen concentration was approx. $750\pm20\text{mgL}^{-1}$, while ammonium nitrogen accounted for $77\pm2\%$ ($580\pm18\text{mgL}^{-1}$) with low N/COD ratio (0.18). 18mgL^{-1} The stabilization of ammonium nitrogen removal process was achieved at 50th day of the experiment. Mean values in the outflows after stabilization were used to determine the efficiency of treatment, as in the case of COD.

The efficiency of organic nitrogen removal from the leachate, as well as COD was the lowest in the reactor with 10% packing volume ($80\pm8\%$). In case of a lower or higher packing volume, the efficiency of organic nitrogen removal was higher, $92\pm9\%$ and $90\pm8\%$ for SBR1 and SBR3,

respectively. The efficiency of ammonia nitrogen removal is comparable for all reactors and was $43 \pm 6\%$ to $47 \pm 7\%$ (Fig. 1). Both in raw and treated leachate, no other nitrogen forms, i.e. nitrates and nitrites have been observed.

Mixing phase lasted 3 hours, and 20 h of aeration seemed to be not sufficient to completely remove the ammonium from the leachate. Loukidou & Zoudoulis (2001) have obtained 60% reduction of ammonia nitrogen using 18 h aeration phase. As reported by Kulikowska et al., (2010) the efficiency of leachate treatment in reactors with packing is related with packing volume and its specific surface area. Due to the fact that the packing is a carrier of biofilm, increase in packing volume may improve nitrification efficiency. It is also confirmed by Wang et al., (2005) who defined the effect of packing volume (PVC filter media) on the efficiency of ammonium nitrogen removal from synthetic sewage. They proved that the increase in reactor packing volume from 10% to 75% have increased the nitrification efficiency from 20% to 50%. Based on literature, the packing may constitute up to 70% reactor volume. This was not confirmed by our tests, where the efficiency of the ammonium nitrogen removal was the highest in the reactor operating with the lowest packing volume (SBR1 – $47 \pm 4\%$) and has been reduced with the increase in the packing volume (SBR 2 – $45 \pm 2\%$, SBR3 – $43 \pm 3\%$).

In all reactors, irrespective of the packing volume, ammonium nitrogen was removed from the leachate in accordance with the first-order reaction (Eq. 1):

$$r_1 = \frac{dC_N}{dt} = -k_1 \cdot (C_{0,NH_4} - C_{e,NH_4}) \quad (1)$$

where the relation between the concentration and time is expressed as (Eq. 2):

$$C_N = (C_{0,NH_4} - C_{e,NH_4}) \cdot e^{-k_1 t} + C_{e,NH_4} \quad (2)$$

The rate of ammonia nitrogen removal expressed in activated sludge units ($r_{1,N}$) has been calculated from the following formula (Eq. 3):

$$r_{1,N} = \frac{dC_N}{dt} = \frac{-k_1 \cdot (C_{0,NH_4} - C_{e,NH_4})}{C_{v,s.s.}} \quad (3)$$

where C_N is the ammonium nitrogen concentration ($\text{mg}\cdot\text{L}^{-1}$), $C_{0,N}$ is the ammonium nitrogen concentration at the start of SBR run ($\text{mg}\cdot\text{L}^{-1}$), $C_{e,N}$ is the ammonia nitrogen concentration at the end of SBR run ($\text{mg}\cdot\text{L}^{-1}$), $C_{v,s.s.}$ is the organic suspension in SBR ($\text{g}_{v,s.s.}\cdot\text{L}^{-1}$), k_1 is the constant rate of reaction (h^{-1}), r_1 is the reaction rate ($\text{mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$), $r_{1,N}$ is the reaction rate expressed in activated sludge units ($\text{mg}\cdot\text{g}_{v,s.s.}^{-1}\cdot\text{h}^{-1}$) and t is the time (h).

Based on the analysis of ammonium nitrogen concentration in the reactor operating cycle, process of stabilization was observed after 4 hours of operation. Figure 3 shows the concentration profiles of ammonium nitrogen during treatment cycle, and constant rate of reaction (k_1).

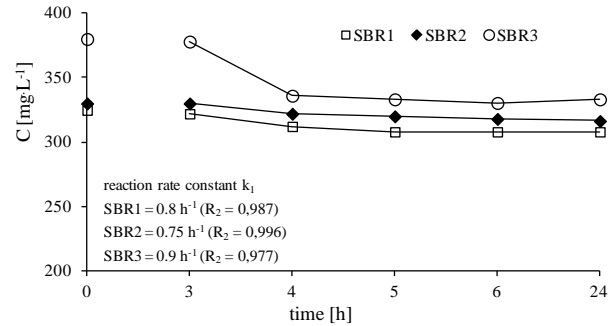


Figure 3. The concentration profiles of ammonium nitrogen in SBR operating cycle, and constant rate of reaction (k_1)

Removal of ammonium nitrogen occurred with similar rate, irrespective of the packing volume ($22.5 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ in SBR1 and SBR2; $25.2 \text{ mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$ in SBR3) (Table 2).

Table 2. Kinetic parameters obtained for the analyzed technological conditions

	SBR 1	SBR 2	SBR 3
$C_0 [\text{mg}\cdot\text{L}^{-1}]$	306	316	327
$C_e [\text{mg}\cdot\text{L}^{-1}]$	24	15	47
$r_1 [\text{mg}\cdot\text{L}^{-1}\cdot\text{h}^{-1}]$	22.5	22.5	25.2
$r_{1,N} [\text{mg}\cdot\text{g}_{v,s.s.}^{-1}\cdot\text{h}^{-1}]$	28.3	8.7	8.5
$C_{v,s.s.} [\text{g}_{v,s.s.}\cdot\text{L}^{-1}]$	0.8	2.59	2.94

It was found that presence of the filling influences the organic biomass concentration in the reactors. Lim et al., (2011) observed decrease of the reaction rate (r) along with increased volume of media in the reactors - from $20 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ in SBR containing 20% of biomass carriers to $15.7 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$ in SBR filled in 40%. The decrease of r factor could be explained by decrease of specific external surface area (calculated on reactor volume). It seems that the main role in ammonia removal plays rather suspended biomass than this attached to carriers. In addition, higher number of carriers creates larger anoxic zone thus the space with conditions appropriate for AOB organisms decreases. The concentration of biomass in SBR filled with 5% of Kaldnes carriers amounted to $0.8 \text{ g}_{vss}\cdot\text{L}^{-1}$ and 10% increase of the fillings volume, resulted in over 3-fold increase of the biomass concentration. However, a further increase of the volume to 20% had no effect on the organic biomass

quantity. Considering total activated sludge in the reactor, both suspended and fixed inside the Kaldnes filter media, in the reactor with 5% packing volume (SBR1) rate of reaction was 3.2 times higher compared to reactor with higher packing volume (SBR2 and SBR3). The increase in packing volume compared to the active reactor volume reduces both effluent quality, and rate of reaction ($r_{1,N}$). Ammonium nitrogen load in the reactors was $0.29 \text{ kg m}^{-3} \text{ d}^{-1}$ and removed ammonium nitrogen load was $0.14 \text{ kg m}^{-3} \text{ d}^{-1}$ irrespective of packing volume. Liu et al., (2012) have treated synthetic sewage in 1.8 L reactor at $30 - 35^\circ\text{C}$, with retention time of $0.5 - 0.6 \text{ h}$ and ammonium nitrogen load $1.32 \text{ kg m}^{-3} \text{ d}^{-1}$, obtaining the removal of 91% of ammonium nitrogen.

The efficiency of nitrogen compounds removal is also affected by dissolved oxygen (DO) concentration. Podedworna & Żubrowska-Sudoł (2009) report, that DO concentration of $0.5 - 1.0 \text{ mg L}^{-1}$ and 7.5% packing volume in relation to active reactor volume is sufficient to remove ammonium nitrogen from the sewage. Low oxygen concentration in the reactor allows to form oxygen deficient zones inside the biofilm and flocks of activated sludge, where denitrification process could take place. Maintaining the oxygen concentration at $2 - 3 \text{ mg L}^{-1}$, makes the nitrification a prevalent process in the nitrogen conversion. Elimination of ammonium nitrogen in systems with activated sludge in anaerobic-aerobic conditions can be linked with the ability of *Nitrosomonas* genus bacteria to produce nitrogen oxides and molecular nitrogen (Remde & Conrad 1990; Stüven et al., 1992; Bock et al., 1995; de Graaf et al., 1997; Park et al., 2001; Yao et al., 2013). According to Park et al., (2001), in the course of ammonium nitrogen removing from municipal wastewater, N_2O was generated mainly in the beginning of aeration, when DO concentration did not exceed 1 mg L^{-1} . Yao et al., (2013) informed that bioactivity of *plantomycete*-like anammox bacteria could be enhanced by increasing the concentration of N_2H_4 , which is the intermediate product of anammox reaction, according to most possible metabolic pathway.

The tests have been carried out by maintaining DO concentration in the aeration phase below 1 mg L^{-1} . It has not been sufficient to completely remove ammonium nitrogen from leachate, and also no nitrification process has been observed. The thesis that the ammonia removal was a biological process could be supported by studies of Xu et al., (2010). These authors report that the dissolved oxygen concentration of $1.0 - 1.5 \text{ mg L}^{-1}$ favours simultaneous processes of partial nitrification, Anammox and heterotrophic denitrification processes.

4. CONCLUSIONS

The study covers the effect of Kaldnes media packing volume on effectiveness of ammonium nitrogen removal in process of landfill leachate biological treatment. The leachate has been obtained at regional landfill in the south-eastern Poland, operating for over 10 years. The lowest efficiency of organic matter COD removal has been obtained with SBR2, working with 10% packing, whilst both reduction and increase of packing volume improved the efficiency of treatment. Ammonium nitrogen was removed from the leachate in accordance with the first-order reaction. The volume of filtration media did not affect the efficiency of ammonia nitrogen removal from leachate, although it affected the removal rate of ammonia nitrogen. Considering total suspended activated sludge and sludge accumulated on the surface of media, the rate of reaction decreases with the increase of media volume.

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