



## Comparison of different physico-chemical methods for the removal of toxicants from landfill leachate

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### ABSTRACT

Our work was focused on investigation of different treatment procedures for the removal of toxic fractions from a landfill leachate, because sometimes the existing treatment in biological sequencing batch reactor (SBR) is not efficient enough, leading to a hazardous environmental impact of the present persistent and toxic compounds. The efficiency of the procedures used was monitored by chemical analyses and two toxicity tests (activated sludge and *Vibrio fischeri*). The existing SBR (HRT = 1.9 days) removed 46–78% of COD and 96–73% of  $\text{NH}_4^+\text{-N}$ . Experiments were conducted with three landfill leachate samples expressing significant difference in concentrations of pollutants and with low  $\text{BOD}_5/\text{COD}$  ratio (0.06/0.01/0.03). The applied methods were air stripping, adsorption to activated carbon and zeolite clinoptilolite and Fenton oxidation. Air stripping at pH 11 was a viable treatment option for the removal of ammonia nitrogen (up to 94%) and reduction of toxicity to microorganisms. In the adsorption experiments in batch system with different concentration of PAC the most effective was the highest addition ( $50.0 \text{ g L}^{-1}$ ) where 63–92% of COD was removed followed by significant reduction in toxicity to *V. fischeri*. In the column experiments with clinoptilolite 45/93/100% of  $\text{NH}_4^+\text{-N}$  as well as 25/32/39% of COD removal was attained. The removal efficiency for metals followed the sequence  $\text{Cr} > \text{Zn} > \text{Cd} > \text{Ni}$ . The procedure with zeolite was the second most efficient one regarding reduction of toxicity to both organisms. Fenton oxidation at molar ratio  $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1.0:10.0$  assured 70–85% removal of COD but it only slightly reduced the toxicity.

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### 1. Introduction

The deposition of wastes to a landfill is currently the most widely used method for municipal solid waste disposal. Leachate emissions from landfill sites are of concern, primarily due to their toxic impact when released untreated into the environment [1]. The impact of landfills is also long-term, due to the potential of landfills to generate leachates and emit biogas for many years after closure. At the same time, its quantity and quality varies with time, because deposited wastes are comprised of a wide range of inorganic, organic and/or xenobiotic compounds, which affects the composition and environmental potential of formed leachate. Its composition is therefore site and time specific, based on the characteristics of deposited wastes, physico-chemical conditions, rainfall regime that regulates the moisture level and landfill age [2,3]. In particular, the composition of landfill leachate varies generally depending on the age of the landfill. Even within a single landfill site variability is frequently evident. Significant components of leachate are heavy metals and degradable organics at the

beginning of landfill operation, while persistent organic pollutants usually appear later as a result of biotic and abiotic processes in the system [4]. Among these substances there are several compounds classified as potentially hazardous: bioaccumulative, toxic, genotoxic, and they could have an endocrine disruptive effect [5]. The leachate composition from different sanitary landfills, as reported in literature [3], shows a wide variation. COD values could vary from 100 to 70,900  $\text{mg L}^{-1}$ , resulting in severe toxicity in many cases. The  $\text{BOD}_5/\text{COD}$  ratio (from 0.70 to 0.04) could decrease rapidly with the ageing of the landfill [6] showing low biotreatability. With a few exceptions, the pH of leachates lies in the range of 5.8–8.5, which is due to the biological activity inside the body of the landfill. It is also important to notice that the majority of TKN (total Kjeldahl nitrogen) is ammonia, which can range from 0.2 to 13,000  $\text{mg L}^{-1}$ . As a result of intensive pollution of the leachate, biological treatment is usually not effective enough and must be accomplished by other pre-treatment methods (physico-chemical processes). One of the viable biological methods for treatment of heavily polluted leachate is SBR (sequencing batch reactor). This system is ideally suited to nitrification–denitrification processes since it provides an operation regime compatible with concurrent organic carbon oxidation and nitrification [7,8], resulting in a wide application for landfill leachates. Many authors have reported COD removals up to 75%.

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99% of ammonia nitrogen removal has been also observed by Lo [9] during the aerobic treatment of municipal leachates in SBR with a 20–40 days residence time. The greater process flexibility of SBR is particularly important when considering landfill leachates, which have a high degree of variability in quality and quantity [10].

Physico-chemical procedures for the treatment of landfill leachate are used as addition in the treatment line (pre-treatment or final polishing) or they are aimed for the treatment of a specific pollutant (like air stripping for ammonia). The mainly used methods are adsorption, air stripping and oxidation [11–13].

For the adsorption of pollutants, activated carbon or other naturally occurring materials are mainly used. Activated carbon in powder form [14,15] provides better reduction in COD levels than chemical methods, whatever the initial organic matter concentration. Its main drawback is a high consumption of powdered activated carbon (PAC). However, non-biodegradable organics, inert COD and the colour may be reduced to acceptable levels [16]. In some cases the use of zeolites is more favourable option. They are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations possessing an infinite, open three-dimensional structure [17,18]. The micro porous crystalline structure of zeolites is able to adsorb species that have diameters that fit through surface entry channels, while larger species are excluded, giving rise to molecular sieving properties.

Nowadays, the most common method for eliminating high concentrations of  $\text{NH}_4\text{-N}$  present in landfill leachates is air stripping, obtaining up to 93% ammonia removal in the case of the leachates with high initial ammonia concentration ( $0.5\text{--}0.7\text{ N g L}^{-1}$ ) [19]. High levels of ammonium nitrogen are usually found in younger landfill leachates, increasing their toxicity [5]. At higher concentrations (up to  $150\text{ mg L}^{-1}$  of  $\text{NH}_4\text{-N}$ ) ammonia stripping is a first-order reaction, however, which means that the mass transfer rate from liquid to gas phase depends on the initial concentration of ammonia [20]. Thus, the ammonia stripping rate is expected to be somewhat lower with low strength leachates than with concentrated ones. If this method is to be efficient, high pH values (11 and above) must be used.

Studies of leachate treatment by conventional Fenton, photo-Fenton and electro-Fenton processes have indicated that these methods can effectively reduce concentrations of organic contaminants and colour [21]. In addition, the process can increase the biodegradable fraction of organic constituents in the leachate, particularly in mature, thus more recalcitrant one. Oxidation and coagulation both play important roles in the removal of organics during the Fenton procedure. Initial pH, dosages of Fenton reagents, aeration, final pH, reagent addition mode, temperature, and UV irradiation may influence final treatment efficiency.

The efficiency of the pre-treatment procedure could be reliably assessed by bioassays, which in contrast to chemical analysis can be used to characterize the toxicity of landfill leachate integrating the complex impact of all of its constituents. Thus, factors like bioavailability, synergistic, antagonistic, or additive effects can be assessed directly without the need for assumptions and extrapolations made from chemical analysis. A significant role in toxicity determination of influents is played by the test for inhibition of oxygen consumption by activated sludge, where the impact of wastewater constituents to carbonaceous (oxidation of organics) and ammonium oxidation (nitrification) is simultaneously studied. It gives an overview of possible biological treatment efficiency in activated sludge systems [22–24].

The aim of our work was to investigate different physico-chemical procedures (adsorption, air stripping, Fenton oxidation) as pre-treatment methods for the removal of particular pollution from leachate generated in a local landfill, followed by the existing SBR treatment, because sometimes concentrations of monitored compounds in the effluent of the SBR do not meet the

discharge limits and this poses an additional problem for the management.

## 2. Materials and methods

The aim of our work was to compare different possible pre-treatment methods in order to improve the efficiency of the existing biological wastewater treatment plant (SBR) for treatment of leachates from a regional municipal landfill.

### 2.1. Site description

The investigated landfill is divided in two parts. The first one covers  $10,800\text{ m}^2$  and it was closed in 2006. Afterwards, wastes have been deposited to a new part of the landfill, which is estimated to contain  $160,000\text{ m}^3$  of wastes by 2013, when the landfill is going to be closed. All deposited wastes are collected separately and represent only non-recyclable and non-biodegradable wastes. Leachates from both parts of the landfill are mixed before treatment in an equalization basin; the mixing ratio is 36 vol.% of the mature leachate and 64 vol.% of the fresh leachate. Mixed leachate is currently treated in a sequencing batch reactor (SBR). In the secondary, biological phase metals are only removed from liquid to solid phase by adsorption, so they can accumulate in waste sludge and treatment efficiency is often reduced below an acceptable level and has to be followed by complete replacement of the activated sludge. After treatment in the SBR reactor, leachate goes to sand filtration, which is used for the removal of the remaining biomass prior to the activated carbon filter, used for the final removal of metals. Sometimes concentrations of toxic compounds in the effluent of the treatment plant do not meet discharge limits and this poses an additional problem for the management. This was the main reason for running additional experiments, where air stripping, adsorption on activated carbon and natural zeolite clinoptilolite, as well as Fenton oxidation was studied.

### 2.2. Sample preparation

Landfill leachates were sampled three times (March 2008, May 2008 and March 2009) to assess the impact of changes of the quality of the leachate to the SBR treatment performance. Each time samples of the non-treated leachate (raw leachate, RL) as well as in SBR treated leachate (treated leachate, TL) were taken. They were collected in high density polyethylene containers (3 L) from an equalization basin before drainage pipes leading to pumps for SBR. The samples were immediately transported on ice and processed without any delay to assess the baseline toxicity and frozen at  $-20 \pm 2\text{ }^\circ\text{C}$  for chemical analyses and treatment studies. To determine the effects that different treatment procedures have on the toxicity of leachates, chemical analyses and toxicity tests were performed prior and after every treatment procedure.

### 2.3. Investigated treatment procedures

#### 2.3.1. Air stripping

1 L of the sample was aerated by compressed outdoor air in two glass containers. The air flow was set to  $120\text{ L h}^{-1}$  and the systems were mixed (200 rpm). Before conducting the experiments, the pH of the raw sample in the first container was set to 11.0 using 1 M NaOH, while in the second one, pH of the sample was left non-modified. The aeration took place for 24 h and samples for different analyses were redrawn periodically. Neutralised final samples were used for toxicity determination. During the experiment, oxygen saturation, temperature and pH were checked frequently to assure steady conditions (WTWpH/OXI340, Germany 2005).

### 2.3.2. Adsorption on PAC

Experiments were performed in batch mode. Granulated activated carbon was used for this treatment procedure (GAC, DARCO, 20–40 mesh). We tried to determine the impact of different quantities of GAC to effectively remove organics from the investigated raw leachate. It was mixed in a 1-L glass container with different amounts of activated carbon added (0.0, 5.0, 10.0 and 50.0 g L<sup>-1</sup>). Experiments were conducted with constant mixing (200 rpm) for 5 h at a constant temperature of 25 ± 1 °C. We have left the mixture to settle down afterwards, it was filtered through black ribbon and chemical analyses and toxicity tests were performed. COD measurements after the addition of activated carbon to raw leachate (samples RL2 and RL3) were also used for the calculation of Freundlich isotherm equation (Eq. (1)):

$$\log q_e = \log K + \left(\frac{1}{n}\right) \cdot \log C_e \quad (1)$$

$q_e$  (mg g<sup>-1</sup>) represents the quantity of the adsorbate per unit of adsorbent, in our case expressed as COD.  $C_e$  (mg L<sup>-1</sup>) stands for equilibrium concentration of adsorbate in solution,  $K$  ((mg g<sup>-1</sup>) (L mg<sup>-1</sup>)<sup>1/n</sup>) is Freundlich adsorption coefficient, while  $n$  is empirical coefficient [25].

### 2.3.3. Adsorption on zeolite

For the preparation of the column for trough flow studies well characterized natural zeolite clinoptilolite was used. The applied zeolite was structurally studied using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), energy disperse X-ray analyses (EDMS) and X-ray photoelectron spectroscopy (XPS) [26]. 30 g of zeolite was added to 60 mL of high-purity water. Zeolite particles were approximately the same size to insure efficient ion exchange while preventing channelling (e.g. effluent not contacting the zeolite during flow through the column) or excessive resistance to flow. Removal of extremely large or small particles was accomplished by screening the zeolite with sieves or mesh screens. The zeolite slurry was poured into the column and three bed volumes of dilution water were passed through it. Next 200 mL of leachate was passed through the column at a rate of 2 mL min<sup>-1</sup> [27]. The dilution water, remaining in the column afterwards, was flushed out by the leachate, and the post column effluent was collected and measured for chemical analyses and toxicity tests.

### 2.3.4. Fenton oxidation

Experiments were performed using non-diluted samples. Leachates were filtered through black ribbon to remove solids and pH was adjusted to 4.0 (±0.2) before addition of reagents. 250 mL of the sample was placed into 500 mL Erlenmeyer flask, which was submerged in a temperature controlled water bath to attain the desired constant temperature (40 °C). FeSO<sub>4</sub>, p.a. was added to attain the selected Fe<sup>2+</sup> concentrations (0.3/1.0 M). Finally, Fenton reaction was started with addition of H<sub>2</sub>O<sub>2</sub> (30%, w/v, p.a.) to achieve concentrations of 1.0/3.0 M. The aqueous solution of Fenton reagent and the sample was stirred during the reaction period up to 35 min. Samples were redrawn at 5, 10, 20 and 30 min and COD was determined immediately. Prior to COD analysis 1 M NaOH was added to stop the oxidation at pH 12 (±0.2). To eliminate the excess H<sub>2</sub>O<sub>2</sub>, the sample was boiled for 10 min and then allowed to cool to room temperature. It was filtered through black ribbon paper to remove the formed ferric hydroxide and COD was determined. For other analyses, samples were also frozen (-28 ± 2 °C).

### 2.4. Chemical analyses

Analytical control of leachates characterization and monitoring of treatment efficiency included pH, BOD<sub>5</sub> (biochemical oxygen demand), COD (chemical oxygen demand), DOC (dissolved organic

**Table 1**

The operating parameters of SBR.

Process parameter	Unit	Value
Maximal influent flow	m <sup>3</sup> day <sup>-1</sup>	25
Max. deep; Hmax	m	4
Min deep; Hmin	m	2
Max. volume SBR; Vmax	m <sup>3</sup>	48
Min. volume SBR; Vmin	m <sup>3</sup>	24
Hydraulic retention time; HRT	day	1.9

carbon) (Shimadzu TOC 5000A Analyzer, 1998) and nitrogen as Kjeldahl nitrogen and ammonium. Phosphate, nitrite nitrate and chloride were determined by chemically suppressed ion chromatography (DIONEX 4000) in the filtered samples using a 0.2 μm filter. The concentrations of metals in samples were determined by ICP MS (inductively coupled plasma/mass spectrometry). All used methods were according to standard procedures [28].

### 2.5. Toxicity testing

To determine the toxicity of raw landfill leachates (samples RL1, RL2 and RL3) and their toxicity after investigated treatment procedures, two acute toxicity tests were performed: (i) measurement of inhibition of bioluminescence with freeze-dried luminescent bacteria *Vibrio fischeri* (Dr. Lange LUMiStox, 2001; ISO 11348-1, 1998) [29] and (ii) measurement of inhibition of oxygen consumption by activated sludge for carbonaceous and ammonium oxidation (ISO 8192, 2007) [30]. All tests were run in duplicates. For the second toxicity test activated sludge from a laboratory municipal wastewater treatment plant (1500 mg<sub>MLVSS</sub> L<sup>-1</sup>) was used. It consumes oxygen due to the presence of an easily biodegradable substance – peptone. Addition of a toxic substance – wastewater results in a decrease of the oxygen consumption rate, measured as mg<sub>O<sub>2</sub></sub> L<sup>-1</sup> min<sup>-1</sup> by oxygen electrode. The inhibition in terms of EC (effective concentration) values was estimated by comparison of the rate in the test mixture with the rate in the control mixture containing no test material. Because experiments were conducted twice, with and without N-allylthiourea (ATU, a specific inhibitor of the oxidation of ammonium to nitrite nitrogen) added, the inhibitory effect on oxygen uptake by all sludge microorganisms (without ATU added) as well as to heterotrophic microorganisms (with 11.4 mg L<sup>-1</sup> of ATU) could be measured. The difference between these two measurements is due to the nitrification and thus the inhibitory effect to nitrifying microorganisms could also be calculated. We also determined any oxygen consumption due to the abiotic processes in the systems with wastewater and synthetic medium but without inoculum. The tests were accomplished with 25 vol.% for all of the samples. Oxygen consumption rates were measured repeatedly after 30 and after 180 min. Consistency of activated sludge was assessed in a preliminary test with 3,5-dichlorophenol.

## 3. Results and discussion

### 3.1. Characterization of the landfill leachate

Biological treatment in SBR is ideally suited for nitrification–denitrification processes since it provides an operational regime compatible with concurrent organic carbon oxidation and nitrification thus it was selected as a treatment options also in this particular case. The operating parameters of the existing SBR are in Table 1.

Many authors have reported COD removal during biological treatment of the leachate up to 75%, while our monitoring data (Table 2) indicated, that COD was removed from 46% (the first sampling) to 78/72% (the second and the third sampling). 99% NH<sub>4</sub><sup>+</sup>-N

**Table 2**  
Physico-chemical analysis of the landfill leachates.

	Sample					
	RL1 sampled in Mach 2008	RL2 sampled in May 2008	RL3 sampled in March 2009	TL1 sampled in Mach 2008	TL2 sampled in May 2008	TL3 sampled in March 2009
pH	8.41 ± 0.1	8.23 ± 0.1	8.10 ± 0.1	8.41 ± 0.1	8.23 ± 0.1	7.83 ± 0.1
COD (mg L <sup>-1</sup> )	2455 ± 50	1396 ± 70	5025 ± 155	1130 ± 15	300 ± 35	1407 ± 20
BOD <sub>5</sub> (mg L <sup>-1</sup> )	150 ± 60	19 ± 5	136 ± 16	43 ± 7	5 ± 3	49 ± 8
BOD <sub>5</sub> /COD <sup>a</sup>	0.06	0.01	0.03	0.04	0.02	0.03
DOC (mg L <sup>-1</sup> )	336 ± 7	276 ± 6	637 ± 2	40.4 ± 2.1	145 ± 7	376 ± 3
IC (mg L <sup>-1</sup> )	796 ± 16	519 ± 11	510 ± 10	519 ± 30	515 ± 36	501 ± 22
PO <sub>4</sub> <sup>3-</sup> -P (mg L <sup>-1</sup> )	21.5 ± 1.9	10.1 ± 1.2	14.3 ± 0.8	13.1 ± 0.8	3.08 ± 0.33	3.91 ± 0.68
NH <sub>4</sub> <sup>+</sup> -N (mg L <sup>-1</sup> )	597 ± 40	388 ± 35	1445 ± 96	160 ± 15	13.2 ± 4.0	410 ± 37
N <sub>Kjel</sub> (mg L <sup>-1</sup> )	651 ± 33	410 ± 2	1676 ± 123	169 ± 22	15.7 ± 4.0	475 ± 27
Norg (mg L <sup>-1</sup> ) <sup>a</sup>	54.1	18.4	231	9.0	2.5	65.0
NO <sub>2</sub> <sup>-</sup> -N (mg L <sup>-1</sup> )	62.2 ± 17.5	55.9 ± 12.6	18.7 ± 2.1	8.40 ± 1.20	13.2 ± 2.3	10.2 ± 1.5
NO <sub>3</sub> <sup>-</sup> -N (mg L <sup>-1</sup> )	38.8 ± 5.1	23.0 ± 2.1	28.9 ± 3.6	60.2 ± 4.1	22.1 ± 1.2	36.1 ± 2.8
Cl <sup>-</sup> (mg L <sup>-1</sup> )	1388 ± 190	839 ± 10	2000 ± 220	708 ± 70	313 ± 25	675 ± 45
Al (μg L <sup>-1</sup> )	586 ± 81	420 ± 55	1320 ± 60	112 ± 15	142 ± 28	332 ± 45
Cr (μg L <sup>-1</sup> )	513 ± 65	489 ± 46	586 ± 55	53.0 ± 6.8	86.5 ± 13.7	113 ± 25
Cu (μg L <sup>-1</sup> )	<10	<10	38.4 ± 7.8	<10	<10	<10
Fe (μg L <sup>-1</sup> )	3440 ± 350	3360 ± 250	4460 ± 350	1350 ± 125	870 ± 86	2470 ± 220
Zn (μg L <sup>-1</sup> )	188 ± 18	231 ± 28	583 ± 65	56.8 ± 8.2	66.8 ± 10.1	154 ± 23
Ni (μg L <sup>-1</sup> )	132 ± 13	111 ± 11	57.3 ± 7.5	48.9 ± 9.3	63.4 ± 15.8	33.9 ± 5.8
Mn (μg L <sup>-1</sup> )	344 ± 21	328 ± 31	564 ± 81	164 ± 11	78.2 ± 16.3	81.8 ± 11.8

RL, raw leachate; TL, treated leachate.

<sup>a</sup> Calculated values.

removal during the aerobic treatment of leachate in SBR has been observed by Lo [9], but the applied HRT of 20–40 days was too long, because HRTs from 0.5 to 3.2 days are usually applied in the performance of SBR. In the investigated existing SBR, HRT was 1.9 days (Table 1) and it was possible to remove 96% NH<sub>4</sub><sup>+</sup>-N (the second sampling) and 73/71% (the first and the third sampling). Considering the fact, that treatment efficiency is often reduced below an acceptable level (internal monitoring data), the activated sludge in SBR has to be replaced completely every few months. It has been estimated, that the influent is toxic to microorganisms of activated sludge, and that adsorption or bioaccumulation of hazardous pollutants can take place.

Physico-chemical analyses of three samples of the influent to SBR (raw leachate 1 (RL1); raw leachate 2 (RL2); raw leachate 3 (RL3) and three samples of the SBR effluent (treated leachate 1 (TL1); treated leachate 2 (TL2) and treated leachate 3 (TL3) are presented in Table 2. Experiments were conducted with three samples of leachate, sampled during the year. Raw samples RL1, RL2 and RL3 were used for adsorption experiments, air stripping and Fenton oxidation, while the comparison of raw and treated leachates enables determination of SBR treatment efficiency. If all influents are compared, we can notice a significant difference between COD, DOC, BOD<sub>5</sub>, organic nitrogen, NH<sub>4</sub><sup>+</sup>-N and chloride (Table 2). Higher values were obtained in March 2008 and March 2009 (RL1, RL3), probably as a consequence of the rainy season, resulting in higher leaching of the components from the waste and faster degradation processes in the body of the landfill.

All three investigated raw samples exhibited low BOD<sub>5</sub>/COD ratio (0.06/0.01/0.03) indicating a poor biodegradability potential. Regarding low BOD<sub>5</sub>/COD ratios and not a very high amount of organics, expressed as COD (<3500 mg L<sup>-1</sup>), the investigated leachate showed characteristics for characterization as a mature one (more than 10 years old) [2,31]. Samples RL1, RL2 and RL3 were also not intensively polluted with metals. However, only the amount of total Cr in the samples RL1 and RL3 exceeded the required limit of 0.5 mg L<sup>-1</sup>. Low values of heavy metals in the leachate were also measured by other authors and they are explained as a consequence of adsorption, precipitation and complexation in the landfill [2,33].

According to Slovenian effluent limits [32], leachate from a non-hazardous landfill could be released into surface waters if maximal

COD is below 300 mg L<sup>-1</sup>; BOD<sub>5</sub> must not exceed 30 mg L<sup>-1</sup>, while ammonium and nitrate N must be less than 50. However, after the treatment of the more polluted RL1 and RL3 in the SBR system, effluent limits were still not met [32], while RL2 was treated enough to meet the limit values. The investigated leachate samples could clearly not be released directly into surface waters. Prior to entering surface waters also some additional parameters, such as other heavy metals, AOX, BTX and toxicity to daphnids must be met. It was concluded that the major presence of refractory compounds tends to limit process effectiveness, as already confirmed by many other authors [1,8,23] dealing with similar leachates. As could be seen from Table 2, samples RL1, RL2 and RL3 were not intensively polluted with metals. However, only the amount of total Cr in the samples RL1 and RL3 exceeded the required limit of 0.5 mg L<sup>-1</sup>. Low values of heavy metals in the leachate were also measured by other authors and they are explained as a consequence of adsorption, precipitation and complexation in the landfill [2,33].

Both raw leachates, sampled in the year 2008, expressed only slight toxicity to *V. fischeri*; the more polluted sample RL1 caused 64.2% inhibition, the less polluted sample RL2 caused 57.7% inhibition. On the other hand, the third sample, sampled in the year 2009 (RL3) with higher concentrations of organic substances and ammonium nitrogen was more toxic. Its 30 min EC<sub>50</sub> was 22.5 vol.%. Results of toxicity of leachates to organisms of activated sludge are presented in Table 3. The most toxic one was sample RL3, which also contains the highest amount of pollution (Table 2), which was comparable to the results of the *V. fischeri* toxicity test. Raw leachates were more toxic to nitrifying microorganisms than to heterotrophic ones, confirming poor performance of the nitrification process in the existing SBR, assessed on the basis of high ammonium nitrogen and IC concentrations in the treated leachates. Toxicity of the raw samples to nitrifying microorganisms even increased with time of incubation (30/180 min, Table 3).

### 3.2. Pre-treatment methods

#### 3.2.1. Air stripping

The effect of pH at constant temperature and air flow rate on ammonia removal in air stripping studies was determined with all three raw leachates (Fig. 1). During a 24-h test the highest ammonia removal obtained was 96% at pH 11 for sample RL1. The final

**Table 3**

Toxicity of the samples RL1, RL2 and RL3 to total, nitrifying and heterotrophic microorganisms of activated sludge (30 and 180 min of incubation).

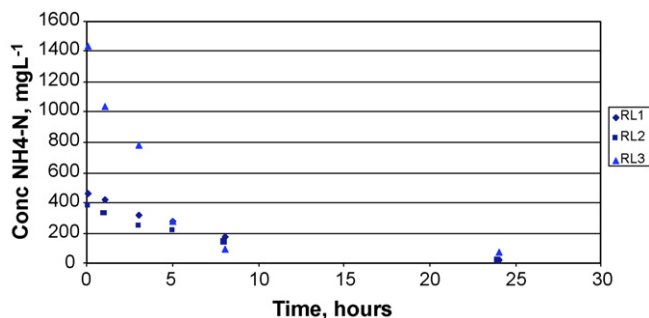
Time of incubation (min)	Inhibition (%)		
	Total microorganisms	Heterotrophic microorganisms	Nitrifying microorganisms
25 vol.% of sample RL1			
<i>t</i> = 30 min	55	12	100
<i>t</i> = 180 min	53	<1	100
25 vol.% of sample RL2			
<i>t</i> = 30 min	16	<1	41
<i>t</i> = 180 min	38	1	58
25 vol.% of sample RL3			
<i>t</i> = 30 min	64	10	18
<i>t</i> = 180 min	62	19	100

RL, raw leachate; TL, treated leachate.

values of removal were 95% for samples RL3 and RL2 were 95% and 96%, respectively. This is comparable to RL1. At higher concentrations of  $\text{NH}_4\text{-N}$  (up to  $150 \text{ mg L}^{-1}$ ) process followed a first-order kinetics model. When concentration dropped below  $150 \text{ mg L}^{-1}$  the kinetics changed. For the first-order kinetics model we calculated the reaction rate for sample RL1 as  $0.155 \text{ h}^{-1}$  ( $R^2 = 0.791$ ), for sample RL2 it was  $0.124 \text{ h}^{-1}$  ( $R^2 = 0.987$ ) and for sample RL3 it reached  $0.318 \text{ h}^{-1}$  ( $R^2 = 0.9725$ ). Obtained values are in accordance with the data reported in literature [34]. As expected, ammonia removal was significantly higher at pH 11 than at a lower pH (Fig. 1) because the proportion of volatile  $\text{NH}_3$  of total ammonia nitrogen ( $\text{NH}_4^+\text{-N}$ ) is a function of pH and temperature. In the 24 h of the experiment without pH regulation, it changed from the initial level of 8.2–9.2, probably due to stripping of carbon dioxide before equilibrium conditions were reached. COD removals during air stripping reached 4–11%, regardless of pH and initial concentration of COD (data not shown), indicating that leachates contained poorly volatile organic compounds. In addition to stripping, some of the COD adhered to the walls of reactors.

### 3.2.2. Adsorption on PAC

Adsorption experiments were accomplished in a batch system with powdered activated carbon (0, 5, 10 and  $50 \text{ mg L}^{-1}$ ) conducted with RL1, RL2 and RL3. In Fig. 2, treatment efficiency according to COD removal at various amounts of added activated carbon is shown. The most effective removal of organic substances was achieved at the addition of  $50.0 \text{ g L}^{-1}$  of activated carbon; we were able to remove up to 92% of organics present. At the same concentration of activated carbon ( $50.0 \text{ g L}^{-1}$ ) 86% of initial COD has been removed from sample RL1 and 63% from sample RL3.  $\text{NH}_4^+\text{-N}$  removals in PAC adsorption experiments were 1–6% regardless of the amounts of activated carbon added and initial concentration of  $\text{NH}_4^+\text{-N}$  (data not shown). Freundlich isotherm equation, calculated for samples RL2 and RL3 using Eq. (1), also showed

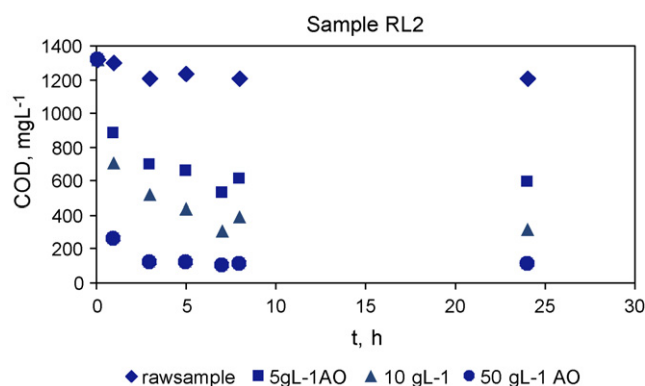
**Fig. 1.** Removal of ammonia nitrogen at pH 11 of the samples RL1, RL2 and RL3.

that adsorption for sample RL2 was much more efficient than for sample RL3 (RL2:  $K = 0.108 \text{ (mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$ ;  $n = 0.866$ ; RL3:  $K = 7.15 \times 10^{-4} \text{ (mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$ ;  $n = 0.66$ ), because of a higher  $K$  value.

At the addition of  $50.0 \text{ g L}^{-1}$  of activated carbon, the efficiency of the adsorbing system for the removal of metals from samples RL1 and RL2 was checked. The concentration of Cr in sample RL1 after PAC adsorption was below the detection limit of the analytical method ( $513 \mu\text{L}^{-1}$  in the non-treated RL1, Table 2), while in the sample RL2 it was  $211 \mu\text{L}^{-1}$  ( $418 \mu\text{L}^{-1}$  in the non-treated RL2, Table 2). Fe was removed the most efficiently: 97% from sample RL1 and 79% from sample RL2.

### 3.2.3. Adsorption on zeolite

In Table 4 the removal efficiencies of zeolite adsorption of samples RL1 and RL2 are presented. Clinoptilolite was addressed in literature as appropriate for removal of metals, especially Zn [26], so our research was focused towards studying its effectiveness for the removal of metals as one of the possible sources of leachate toxicity. The initial concentrations of metals were not very high except for Fe. The natural zeolite (clinoptilolite) is produced with the following sequence for the removal of metals:  $\text{Cu} > \text{Cr} > \text{Zn} > \text{Cd} > \text{Ni}$ , according to literature data [18]. Two factors appear as the most responsible for the retention sequences: the  $\text{H}^+$  exchange capacity of zeolites and the strength of the hydration shells of cations. The experimental results are in good agreement with theoretical expectations (Table 4). The concentration of Cu, which should be removed with the greatest affinity was below the detection limit even at the beginning. The highest removal efficiencies were obtained for Cr (49/32%) and for Zn (44/56%), while the lowest efficiency was observed in the case of Ni: 17% and 14%, respectively.

**Fig. 2.** Removal of COD at different concentration of PAC for sample RL2.

**Table 4**  
Removal of metals in samples RL1 and RL2 with zeolite adsorption.

Metal	Conc. in RL1 ( $\mu\text{g L}^{-1}$ )	Conc. after adsorption ( $\mu\text{g L}^{-1}$ )	Removal (%)	Conc. in RL2 ( $\mu\text{g L}^{-1}$ )	Conc. after adsorption ( $\mu\text{g L}^{-1}$ )	Removal (%)
Al	586	332	43	420	289	31
Cr	513	266	49	489	331	32
Cu	<10	<10	–	<10	<10	–
Fe	3440	2210	36	3360	1750	48
Zn	188	105	44	231	98	56
Ni	132	110	17	111	95	14
Mn	344	221	36	328	167	50

RL, raw leachate; (–) not possible to calculate.

**Table 5**  
Removal of COD and  $\text{NH}_4\text{-N}$  in samples RL1, RL2 and RL3 with zeolite adsorption.

	RL1		RL2		RL3	
	Conc. after adsorption ( $\text{mg L}^{-1}$ )	Removal (%)	Conc. after adsorption ( $\text{mg L}^{-1}$ )	Removal (%)	Conc. after adsorption ( $\text{mg L}^{-1}$ )	Removal (%)
COD	1530	38	951	32	3750	25
$\text{NH}_4\text{-N}$	39.1	93	1.40	100	800	45

RL, raw leachate.

In Table 5, treatment efficiency according to COD and  $\text{NH}_4^+\text{-N}$  removal in all of the three samples is shown. The column experiments have an advantage in comparison to the batch ones, because adsorbent material – zeolite could be regenerated. In sample RL1 39% of COD and 93% of  $\text{NH}_4^+\text{-N}$  were removed; in sample RL2 32% of COD and practically total ammonia nitrogen was removed, while in sample RL3, with the highest initial concentration of pollution, concentration of COD and  $\text{NH}_4^+\text{-N}$  was decreased for 25% and 45%, respectively. 130 mg of  $\text{NH}_4^+\text{-N}$  is the maximal removal capacity of the column.

### 3.2.4. Fenton oxidation

Different molar ratios of Fenton reagents ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) were studied to determine the optimal amount of reagents for maximal treatment efficiency. The first investigated molar ratio  $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1.0:1.0$  was not effective; no treatment concerning COD removal was detected, so in Fig. 3 only the more efficient molar ratio  $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1.0:10.0$  is presented. Oxidative treatment was the most efficient in the case of RL1 and RL2, where it reached 70–85% within the first 10 min of oxidation, while in the case of RL3 oxidation was much slower and it reached 45% after 40 min. If the experiment was prolonged, higher treatment efficiency could be expected, probably in the range of the first two samples. However, COD of the oxidised leachates was not below  $300 \text{ mg L}^{-1}$ , as required by the Slovenian legislation [32].

Treatment efficiency in oxidation experiments was also monitored by other physico-chemical parameters.  $\text{BOD}_5$  increased,

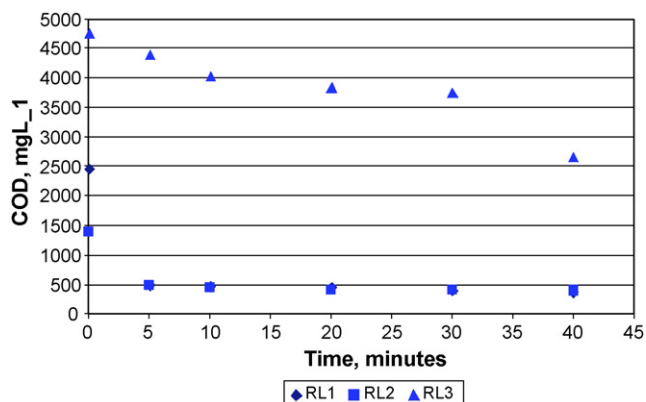


Fig. 3. Removal of COD with Fenton oxidation.

indicating formation of more easily biodegradable by-products during oxidation. After the treatment, the concentration of ammonia nitrogen was higher than allowed by the legislation ( $50 \text{ mg L}^{-1}$ ).

### 3.3. Changes of toxicity during the applied pre-treatment procedures

The changes in toxicity of leachates during different pre-treatment methods were followed by an acute toxicity test with *V. fischeri* and measurement of inhibition of oxygen consumption by activated sludge for carbonaceous and ammonium oxidation. The inhibition of raw leachates was compared with the inhibition of the same samples after air stripping at pH 11, adsorption on PAC at a concentration of  $\text{PAC } 50 \text{ g L}^{-1}$ , after adsorption on zeolite and after Fenton oxidation. The toxicity is presented in Tables 6 and 7.

#### 3.3.1. Air stripping

After a 24-h of air stripping, the highest ammonia removal obtained was 96% at pH 11 for sample RL1. The final values of removal were 95% for sample RL3 and 94%, for RL2, which was comparable to RL1. A lower ammonia removal rate was noticed with RL2, which has a lower initial concentration in comparison to the other two samples. The toxicity of treated samples RL1 and RL2 to *V. fischeri* was not significantly decreased due to residue organic pollution in the treated samples. *V. fischeri* bioluminescence inhibition test is well known by its sensitivity to organic toxicants [4,22,23]. On the contrary, as we can see from comparison of data from Tables 3 and 7, inhibition of air stripped samples to microorganisms of activated sludge significantly decreased. The most noticeable detoxification to nitrifying and heterotrophic microorganisms was observed in the case of sample RL3 after 30 min of incubation. Inhibition was a little higher with longer incubation

**Table 6**  
Relative effectiveness of treatment procedures for toxicity removal according to *Vibrio fischeri* (RL1 and RL2).

Treatment procedure	Inhibition (%)	
	RL1	RL2
Raw sample	64	58
Air stripping	65	60
Adsorption on PAC	33	7
Adsorption on zeolite	62	48
Fenton oxidation	66	63

RL, raw leachate.

**Table 7**  
Toxicity of the treated samples RL1, RL2 and RL3 to total, nitrifying and heterotrophic microorganisms of activated sludge (30 and 180 min of incubation).

Treatment procedure	Sample	Time (min)	Inhibition (%)		
			Total microorganisms	Heterotrophic microorganisms	Nitrifying microorganisms
Air stripping	RL1	30	17	<1	53
		180	19	<1	58
	RL2	30	10	<1	24
		180	7	<1	13
	RL3	30	23	4	44
		180	47	16	84
Adsorption on PAC	RL1	30	46	8	100
		180	43	19	75
	RL2	30	32	9	44
		180	30	13	41
	RL3	30	49	1	82
		180	42	16	61
Adsorption on zeolite	RL1	30	17	<1	23
		180	19	<1	58
	RL2	30	<1	<1	4
		180	<1	<1	2
	RL3	30	51	17	85
		180	45	15	100
Fenton oxidation	RL1	30	43	7	90
		180	40	22	68
	RL2	30	15	<1	35
		180	26	12	46
	RL3	30	46	27	100
		180	75	56	100

25 vol.% of sample RL.

period (30/180 min), but ammonium nitrogen could be definitively hold responsible for toxicity of the leachates to microorganisms of activated sludge.

### 3.3.2. Adsorption on PAC

Adsorption experiments were accomplished with RL1, RL2 and RL3 in a batch system applying different concentrations of PAC. The changes in inhibitory effect of the treated samples in both toxicity tests depended upon the concentration of PAC added. The most effective removal of organic substances was achieved at addition of 50.0 g L<sup>-1</sup> of PAC, where up to 92% of organics present was removed. At the same concentration of activated carbon 86% of the initial COD from sample RL1 and 63% from sample RL3 was removed. Experiments with activated carbon confirmed that it is possible to remove organic pollution and metals completely from raw leachate and to significantly reduce the toxicity to *V. fischeri* and less to activated sludge. The inhibition of the PAC treated sample RL2 to *V. fischeri* was reduced to 7% (Table 7) from initial 58%. The correlation between content of organics (COD) and toxicity to *V. fischeri* has been clearly confirmed and reported also in other scientific papers [5,22]. On the other hand, the inhibition of samples treated with PAC to nitrifying and heterotrophic microorganisms was not reduced in comparison to the raw samples; it even increased in the case of sample RL2 (Tables 3 and 7).

### 3.3.3. Adsorption on zeolite

In the column adsorption experiments with zeolite, 39% of COD and 93% of NH<sub>4</sub><sup>+</sup>-N were removed from sample RL1; from sample RL2 32% of COD was removed and practically complete ammonia nitrogen removal was achieved, while in the case of sample RL3 containing the highest initial concentration of pollution, 25% of COD and 45% of NH<sub>4</sub><sup>+</sup>-N were treated. The highest removal efficiencies for the metals were obtained for Cr (49/32%) and for Zn (44/56%), while the lowest efficiency was observed in the case of Ni: 17% and 14%, respectively. Adsorption on zeolite was the second most effective treatment procedure after PAC adsorption, regarding the

decrease of toxicity to *V. fischeri*. Decrease of toxicity was significant for sample RL2 (58/48%). Sample RL2 was also non-toxic to nitrifying and heterotrophic microorganisms after zeolite treatment, while treated samples RL1 and RL3 still expressed some toxicity, especially towards nitrifying microorganisms of activated sludge, which even increased with longer incubation time (Table 7). The same pattern was also observed for the raw samples. The RL1 sample was also very successfully treated with zeolite. After treatment it contained lower amount of residual organic pollution, ammonia nitrogen and metals, and it caused 58% inhibition of nitrification (Table 7) in comparison to 100% inhibition of the raw sample (Table 3). It was concluded that the efficiency of toxicity removal in a column experiment with zeolite strongly depended upon the maximal removal capacity of the column.

### 3.3.4. Fenton oxidation

Different molar ratios of Fenton reagents (Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>) were studied in Fenton. The most efficient molar ratio was Fe<sup>2+</sup>:H<sub>2</sub>O<sub>2</sub> = 1.0:10.0 in the case of RL1 and RL2, where it reached 70–85% of COD removal within the first 10 min of oxidation, while in the case of RL3 oxidation was much slower and reached 45% after 40 min. After oxidative treatment BOD<sub>5</sub> increased due to the formation of more easily biodegradable by-products. After treatment, also the concentration of ammonia nitrogen remained high. Toxicity of the treated samples RL1 and RL2 to *V. fischeri* was not reduced (Table 6). Similar were the results of toxicity tests with nitrifying and heterotrophic microorganisms. Toxicity of all treated samples was practically the same as of raw samples, with only one insignificant exception sample RL1 after 180 min of incubation. For this particular sample the inhibition to total microorganisms decreased from 53% to 40%, for heterotrophic microorganisms from 46% to 22% and for nitrifying microorganisms from 100% to 68%. Fenton oxidation was not an appropriate method for the removal of toxicity according to both toxicity tests used, probably due to the formation of toxic by-products during oxidation and poor removal of ammonium nitrogen.

### 3.3.5. Comparison of pre-treatment methods

However, several authors [22,34] have shown that ammonium nitrogen and alkalinity were the most probable factors contributing to the observed toxicity from 27 landfill leachates and found that ammonia was the primary cause of acute toxicity of municipal landfill leachate. Thus, patterning and characterizing of the leachate toxicities depending on the types of waste in the landfills are necessary after obtaining more data with different types of landfills.

The potential of detecting toxicity and its source in leachate samples increases with batteries of bioassays from different trophic levels, as shown in the case of other complex environmental matrices, and it helps to improve the environmental impact evaluation of effluent discharge in aquatic ecosystems [34]. However, for an ecologically realistic evaluation of the hazard of landfills, the minimum battery of tests required has not yet been determined and different responses of tested organisms may make an adequate interpretation of the results difficult, since toxicity responses rely on the characteristics of the effluent, changing with the types of processes within the body of the landfill and the effects of which may be species-dependent and chemical-dependent.

## 4. Conclusions

Our work was focused on investigation of different treatment procedures for the removal of toxic pollution from a landfill leachate, followed by the existing SBR treatment, because sometimes the existing treatment procedure is not efficient enough, leading to a hazardous environmental impact. Air stripping at pH 11 was a viable treatment option for the removal of ammonia nitrogen and reduction of toxicity to microorganisms. At the highest addition PAC ( $50.0 \text{ g L}^{-1}$ ) where 63–92% of COD was removed followed by significant reduction in toxicity to *V. fischeri*. In the experiments with clinoptilolite 45/93/100% of  $\text{NH}_4^+\text{-N}$  as well as 25/32/39% of COD removal was attained. The procedure was the second most efficient one regarding reduction of toxicity. Fenton oxidation at molar ratio  $\text{Fe}^{2+}:\text{H}_2\text{O}_2 = 1.0:10.0$  assured 70–85% removal of COD but it only slightly reduced the toxicity.

When treating less biodegradable and toxic leachate the integrated chemical–physical–biological processes (whatever the order) ameliorates the drawback of individual processes contributing to a higher efficiency of the overall treatment. However, with the continuous hardening of the discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachates, conventional treatments are not sufficient anymore to reach the level of purification needed to fully reduce the negative impact of landfill leachate on the environment. It implies that new treatment alternatives must be proposed [3].

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