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Hazardous waste landfill leachate treatment by combined chemical and biological techniques

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ABSTRACT

The efficacies of coagulation, ozonation, Fenton treatment, activated sludge process, Fenton treatment–activated sludge process (CHEM-BIO) and activated sludge process–Fenton treatment (BIO-CHEM) to treat hazardous waste landfill leachate were investigated and compared. The results of the biodegradability test revealed a high content of readily biodegradable organic matter in semicoke landfill leachate, and thus, aerobic biological oxidation was found to be a more reasonable and cost-effective technique for leachate treatment than direct chemical processes (ozonation, Fenton treatment). However, in terms of treatment efficacy, both chemical and biological processes resulted in a high residual organic load, indicating an insufficient leachate quality improvement. The treatment performance of the combined schemes (BIO-CHEM and CHEM-BIO) proved more effective and ensured the removal efficacy percentage met that required by EU legislation as well as the specific target discharge limits of the measured parameters. Accounting for the treatment cost-effectiveness, BIO-CHEM proved to be a more feasible option and could be suggested as the most efficient and practicable technological scheme for hazardous waste landfill leachate treatment.

Keywords: Fenton process; Activated sludge process; Oil shale semicoke; Leachate treatment; Multistage technological scheme

1. Introduction

Conventional municipal wastewater treatment, which usually includes stages such as primary settling, combined biological aerobic and anaerobic treatment, and secondary settling has proven to be a practicable and efficient technology, especially when operating under uniform conditions. However, biological methods, which typically use activated sludge treatment, are not always effective for complex industrial effluents mainly because of the toxic and bio-refractory compounds present in the matrix, hydraulic surges and high variability in organic loads [1]. As a result, a wide range of persistent pollutants remain in the effluent from the wastewater treatment

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plant (WWTP) and accumulate in receiving water bodies and bottom sediments, causing severe environmental problems. A promising solution to this problem could be combining biological treatment with other physicochemical techniques to improve the degradation of recalcitrant organics and the overall efficacy of wastewater treatment, reducing the total environmental pollution load. Furthermore, the obvious economic benefit, both in terms of capital investment and operating costs, of biological treatment over other wastewater treatment processes makes it a reasonable and essential part of an integrated treatment scheme to reduce the overall cost of wastewater treatment [2].

Various combinations of physicochemical processes, biological processes and membrane processes have been considered to provide an efficient treatment for industrial wastewater and landfill leachate [3–5]. Among other proposed combinations, the integration of advanced oxidation processes (AOPs) and aerobic biological systems has proven to be particularly effective [6–9] and promising for large-scale application in the treatment of different wastewaters. The strength of AOPs relies on the generation of highly reactive hydroxyl radicals that react quickly and non-selectively with the majority of organic contaminants. A hydroxyl radical can be generated by the combination of ozone and/or hydrogen peroxide with activators, including transition metals, semiconductors and ultraviolet and ultrasonic irradiation. The Fenton treatment is the most promising, both in terms of performance and cost, and widely studied AOP for wastewater and landfill leachate purification, beneficially combining the treatment potential of two processes, oxidation by hydroxyl radicals and coagulation with ferric sludge, followed by ozonation [9–14].

In this study, the efficacy of physicochemical and aerobic biological treatment technologies separately as well as in combinations was evaluated and compared. The following treatment processes/combined schemes were studied: coagulation, ozonation, Fenton treatment, activated sludge process, Fenton treatment–activated sludge process (CHEM-BIO), and activated sludge process–Fenton treatment (BIO-CHEM). An oil shale semicoke landfill leachate was used as a model hazardous waste-containing wastewater sample to assess and compare the performance of separate as well as combined treatment processes. Semicoke is a solid waste material that remains after oil shale retorting in the oil shale chemical industry; EU regulations consider semicoke to be a hazardous waste. Semicoke landfilling is accompanied with the generation of leachate, which contains residual organics from semicoke, including phenols, polycyclic aromatic hydrocarbons (PAHs) and oil products, which are potential pollutants with harmful environmental effects [15].

The novelty of the present study is the elaboration of new technological schemes for hazardous waste landfill leachate treatment by physicochemical processes combined with aerobic biological oxidation. The most applicable treatment scheme is established by taking into account both the treatment performance and cost minimization. There are no previously published studies evaluating the potential of combined treatment schemes for hazardous waste landfill leachate treatment. In general, the available literature regarding such types of leachate treatment is very limited.

2. Materials and methods

2.1. Materials and leachate samples

Hydrogen peroxide (PERDROGEN™, ≥30%) and ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, ≥99%) were purchased from Sigma-Aldrich Co. (USA). All other chemicals were of analytical grade and used without further purification. Stock solutions were prepared in ultrapure water (Millipore Simplicity® UV System, Merck, Germany). Sodium hydroxide and sulphuric acid aqueous solutions were used to adjust the pH.

Two leachate samples were collected from a semicoke (hazardous waste rich in phenols such as phenol, p-cresol, dimethylphenols, resorcinol, 5-methylresorcinol and 2,5-dimethylresorcinol) landfill area of an oil-shale thermal treatment plant. The chemical composition of these samples differs significantly, but generally, semicoke landfill leachate can be characterized by high concentrations of organic material, medium biodegradability and a low concentration of nitrogen. The collected leachate samples were stored at 4°C. The main properties of the wastewater samples are presented in Table 1.

2.2. Chemical treatment

The coagulation with ferric sulphate (KEMIRA PIX-322, Fe_{total} 12.5 ± 0.3%) was performed in a jar test apparatus (Kemira, Finland). The wastewater volume in each jar was 0.6 L. The coagulant doses (Fe_{total}) varied within the range of 100–1,000 mg/L. The operating conditions were as follows: 1 min of fast mixing at 400 rpm ($G = 956$ 1/s), 30 min of slow mixing at 40 rpm ($G = 30$ 1/s) and 24 h of sedimentation. Afterward, the supernatant was collected for further analysis.

Table 1
Chemical composition and main properties of leachate samples

Parameter	Unit	Leachate 1 (L1, March 2013)	Leachate 2 (L2, September 2014)
COD	mg/L	2,040 ± 75	851 ± 47
BOD_7	mg/L	500 ± 48	330 ± 30
BOD_7/COD		0.25	0.39
TOC	mg/L	505 ± 49	367 ± 37
DOC	mg/L	463 ± 8	243 ± 5
DN	mg/L	16 ± 0.7	10 ± 0.3
NH_4-N	mg/L	n/a	3.5
Conductivity	μS/cm	9,000	6,050
pH	–	7.9	9.3
TS (105˚C)	mg/L	8,650 ± 10	4,537 ± 1
TFS (600˚C)	mg/L	7,639 ± 17	4,030 ± 30
TSS (105˚C)	mg/L	21 ± 7	24 ± 5
F^-	mg/L	1	0.8
Cl^-	mg/L	615	943
PO_4^{3-}	mg/L	42	40
SO_4^{2-}	mg/L	1,510	794
TPh	mg/L	6	18
D. magna acute toxicity EC_{50}	%	19.5 ± 2.9	n/a

All of the Fenton-based process trials were performed in batch mode and in non-buffered solutions. Half-litre wastewater samples were treated in a 1 L cylindrical glass reactor with a permanent agitation speed for a period of 24 h. The activator ($FeSO_4·7H_2O$) was added, and after its complete dissolution, the reaction was initiated by adding H_2O_2. The pH of the wastewater samples was not adjusted in the subsequent treatment unless specified otherwise. The weight ratio of H_2O_2/Fe^{2+} was maintained at 5/1, which is optimal [16]. The oxidation was stopped by the addition of NaOH (10 M) to adjust the pH to approximately 9. This process was followed by a ferric hydroxycomplex settling period of 24 h (for the effective thickening of the iron sludge). Finally, the supernatant was collected for further analysis. The experiments on wastewater oxidation with non-activated hydrogen peroxide were conducted in an identical reactor under the same treatment conditions as for the respective Fenton treatment trials.

The ozonation experiments on 0.6 L leachate samples were performed in a 2.6 L semi-continuous reactor equipped with a foam catching vessel for a period of 4 h. The pH of the leachate samples was not adjusted or adjusted to 11. Ozone was produced from compressed air in a Trailigaz LABO LO ozone generator, delivering 1.0 L/min feed gas with a 30 mg/L ozone concentration. An Anseros GM 6000-PRO ozone analyser was used to measure the ozone concentration in the gaseous phase. The stripping trials of the leachate samples at the initial pH value were carried out in identical reactors and under the same treatment conditions for the respective ozonation trials.

All experiments were performed in duplicate, and the data of the initial parameters of the wastewater samples were verified with at least three replicates. The results of the analysis are presented as the mean with a standard deviation below 5% in all cases. The experiments were performed at ambient room temperature (21 ± 1˚C).

2.3. Biological treatment

The activated sludge used in all of the biological tests and analyses was obtained from a municipal WWTP in Kohtla-Järve (Estonia), which receives effluents from a semicoke thermal processing area and semicoke landfill. Consequently, the sludge from this WWTP was proposed to be largely adapted to higher concentrations of hazardous substances. The aerobic biological pre-treatment experiments were performed in batch mode, simulating a typical activated sludge process. The leachate was treated with pre-adapted activated sludge in an 8 L tank, with a HRT of 3 d, on average, and a F/M loading of 0.02 $gBOD_7$/gMLSS d. The aerobic biological post-treatment (BIO) experiments were carried out with pre-adapted activated sludge as well in a 1 L tank, with a HRT of 1–2 d and F/M loading of 0.055–0.06 $gBOD_7$/gMLSS d. The pH value in both biological systems was regulated to 7.3 ± 0.2, ensuring the bacterial activity in the activated sludge. During the treatment periods, MLSS in the aeration basin and COD in the effluent were measured on a daily basis. The effluent was stored in a refrigerator at 4°C to avoid further decomposition.

2.4. Analytical methods

The chemical oxygen demand (COD) was determined using a closed reflux colorimetric method [17]. The correction for the hydrogen peroxide interference on the COD test was performed by the correlation equation, as described previously [11]. The total suspended solids (TSS), total solids (TS), total fixed solids (TFS) and 7 d biochemical oxygen demand (BOD_7) were determined according to APHA [17]. The biodegradability of raw semicoke leachate samples was determined using a Zahn-Wellens test [18]. The test results were also used for assessing three different COD fractions: easily biodegradable (7 d of test period), slowly biodegradable (7–28 d of test period) and recalcitrant fractions (COD value after 28 d of the test). Tests for the inhibition of oxygen consumption and the nitrification rate by activated sludge were performed according to ISO 8192 [19] and ISO 9509 [20], respectively. The acute toxicity of the initial and treated samples to *Daphnia magna* (*Cladocera*, *Crustacea*) was assessed with DAPHTOXKIT F™ MAGNA (MicroBioTest Inc, Belgium) by a 24 h toxicity test according to ISO 6341 [21].

The pH was measured using a digital pH/ion metre (Mettler Toledo S220, Switzerland), and the electrical conductivity was measured using a digital EC metre (HANNA Instruments HI9032, USA). The total and ferrous iron concentrations in the solution were measured by the phenanthroline method [17]. The initial hydrogen peroxide concentration in the stock solutions was measured spectrophotometrically at $\lambda = 254$ nm; the residual hydrogen peroxide concentration in the treated samples was measured as described in [11] by a Heλios-β UV/vis spectrophotometer (Thermo Electron Corporation, USA). The concentrations of F^-, Cl^-, PO_4^{3-}, and SO_4^{2-} ions were measured by ion chromatography with chemical suppression of the eluent conductivity (761 Compact IC, Metrohm Ltd., Switzerland). NH_4-N was determined by a spectrophotometric method with a Nessler reagent adapted from [17]. The concentration of the total phenols (TPh, sum of mono- and diphenols) was measured by the 4-aminoantipyrine method using the HACH-Lange cuvette test [17]. The dissolved organic carbon (DOC) and dissolved nitrogen (DN) were measured in filtered (Puradisc Aqua, 0.45 μm, CA, Whatman®, GE Healthcare, UK) wastewater samples by a TOC analyser multi N/C® 3100 (Analytik Jena, Germany). The total organic carbon (TOC) was measured in unfiltered samples by the HACH-Lange cuvette test according to EN 1484 [22].

3. Results and discussion

3.1. Chemical treatment

3.1.1. Coagulation

In the present study, coagulation was utilized to remove suspended organic and inorganic compounds from semicoke leachate (sample L1), providing a pre-treatment step before subsequent chemical oxidation for potential reduction in the oxidant dosage. A commercial formulation, PIX-322, containing ferric sulphate was applied as a common coagulant for the treatment of wastewater samples. Based on the TSS of the wastewater samples (Table 1), employing a coagulation process was expected to result in the low treatment efficacy for semicoke leachate samples. Accordingly, the highest observed COD and DOC reductions of 10 and 2%, respectively, were achieved only at elevated coagulant dosages (≥1,000 mg/L of Fe_{total}), suggesting that coagulation processes are ineffective pre-treatment techniques.

3.1.2. Ozonation

Sample L1 was treated by ozonation at initial and alkaline pH values. The results of the ozonation experiments, presented in Fig. 1, indicated a higher efficacy of direct ozone oxidation in terms of COD and DOC removal compared to indirect oxidation via hydroxyl radical attack at an alkaline pH of 11. Accordingly, ozonation without pH adjustment allowed for the removal of 58 and 35% of COD and DOC, respectively,

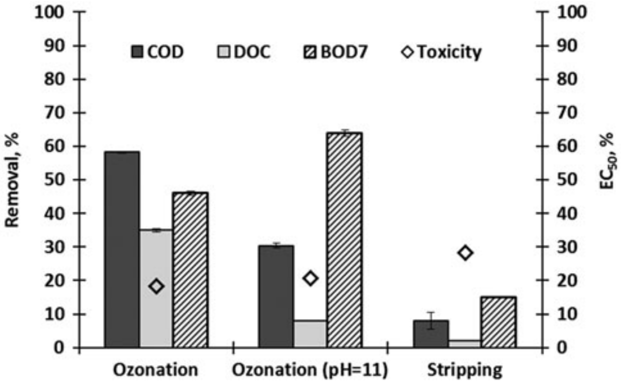

Fig. 1. COD, DOC and BOD_7 removal and the EC_{50} value by ozonation and air stripping of the semicoke leachate (sample L1).

in contrast to 30 and 8%, respectively, for alkaline ozonation. In the case of BOD_7 and toxicity reduction, the adjustment of pH prior to ozonation proved to be more favourable.

Blank trials on semicoke leachate (L1) air stripping at the initial pH value resulted in less than a 10% leachate quality improvement in terms of COD and DOC removal. Nevertheless, almost 1.5-fold toxicity reduction was observed during air stripping of L1, proposing that those removed volatile compounds are mainly responsible for the observed toxicity reduction effect.

3.1.3. Fenton/Fenton-based treatment

The results of a semicoke leachate treatment by Fenton/Fenton-based treatment are presented in Figs. 2 and 3. The leachate samples were treated with (Fenton process) and without (Fenton-based process) adjusting the pH to acidic ~3 values, as required in the classical Fenton reaction [23]. However, at the beginning of the oxidation without pH adjustment, a fast decrease in the pH of the reaction mixture was observed in systems with higher reagent doses ($COD/H_2O_2/Fe^{2+}$ w/w/w ≥1/1/0.2 and 1/2/0.4 for samples L1 and L2, respectively), resulting in a final treatment efficacy similar to that of the Fenton treatment. This decrease was primarily due to the acidity of the added ferrous iron salt and hydrogen peroxide as well as the formation of acidic transformation products. On the other hand, the adjustment of the pH to ~3 prior to the addition of the reagents in the Fenton treatment of L2 at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/1/0.2 resulted in additional COD, DOC and BOD_7 removal of 29, 28 and 29%, respectively (Figs. 2 and 3).

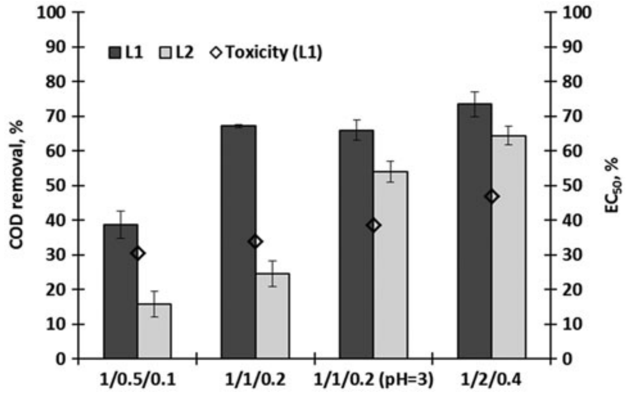

Fig. 2. COD removal and the EC_{50} value as a function of the $COD/H_2O_2/Fe^{2+}$ weight ratio in the Fenton/Fenton-based treatment of semicoke leachate samples (L1 and L2).

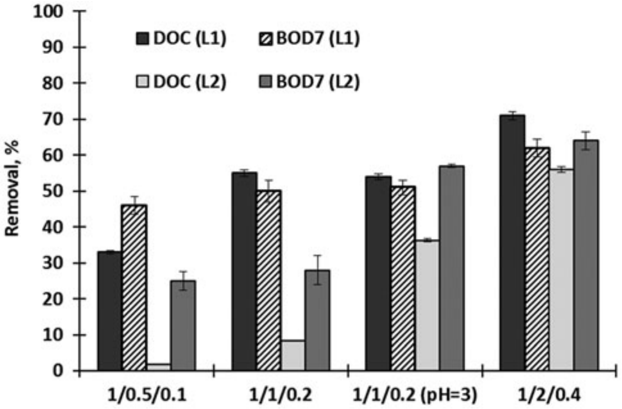

Fig. 3. DOC and BOD_7 removal as a function of the $COD/H_2O_2/Fe^{2+}$ weight ratio in the Fenton/Fenton-based treatment of semicoke leachate samples (L1 and L2).

The oxidative potential of non-catalysed hydrogen peroxide was studied as well. For both samples, hydrogen peroxide oxidation at a COD/H_2O_2 w/w of 1/1 resulted in approximately 10% COD and negligible DOC removal and more than 85% of unused H_2O_2 after 24 h of treatment, indicating that the main treatment effect of the Fenton/Fenton-based system is due to the oxidative action of the hydroxyl radicals generated during the ferrous ion-activated decomposition of hydrogen peroxide.

The tendency of organic load removal as a function of the added reagent dose was similar for both studied leachate samples as well as for different parameters (Figs. 2 and 3). Accordingly, an increase in the amount of oxidant added led to an improvement in the organic load removal (COD, DOC, BOD_7) and biodegradability (BOD_7/COD) of the treated leachate samples. Irrespective of the applied $COD/H_2O_2/Fe^{2+}$ ratio, the mineralization was lower than the COD removal. The highest organic load removal was achieved at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/2/0.4 for both studied leachate samples and resulted in 73/64, 71/56 and 62/64% of COD, DOC and BOD_7 removal for L1/L2, respectively. A further increase in the reagent dose to a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/4/0.8 led to a subsequent improvement in organic load removal but also doubled the treatment cost, rendering it not economically viable. Notably, no traces of residual hydrogen peroxide were detected in the treated leachate samples, indicating the complete utilization of H_2O_2 under the treatment conditions.

In the case of sample L1, an acute toxicity to *D. magna* was also measured; similar to other parameter reductions, a higher oxidant dose ratio provided a somewhat higher detoxification effect. Thus, at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/2/0.4, a more than

2.4-fold increase in EC_{50} was observed. The removal of TPh by the Fenton treatment was only studied for sample L2. The efficacy of the TPh reduction was noticeably improved from 39 to 98% by an increase in the $COD/H_2O_2/Fe^{2+}$ weight ratio from 1/0.5/0.1 to 1/2/0.4, respectively. The Fenton-based treatment at a $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/1/0.2 without pre-adjusted pH removed 50% of TPh, whereas at a regulated pH, the removal was 79%.

The treatment performance was also compared with Estonian legislation, which is in compliance with EU regulations [24] for effluents originating from chemical industries, including semicoke landfill leachate, and states discharge limits for COD and BOD_7 of 250 mg/L (≥75% removal) and 15 mg/L (≥80% removal), respectively. Accordingly, the Fenton-based treatment ($COD/H_2O_2/Fe^{2+}$ w/w/w of 1/2/0.4.) was found to be the most efficient of the studied chemical treatment methods in terms of both organic load removal and other parameter reductions. At the same time, high residual concentrations of COD (542/303 mg/L) and BOD_7 (190/120 mg/L) in effluents L1/L2, respectively, make the Fenton process alone an inefficient treatment option for semicoke leachate.

3.2. *Biological treatment*

To assess the leachate inhibitory effect on activated sludge microorganisms and its treatability with an activated sludge process, wastewater inhibition of oxygen uptake and the nitrification rate were analysed. The test for the inhibition of the oxygen uptake rate (Fig. 4) showed that the leachate samples had a mildly negative effect on activated sludge. Only sample L1, with its higher concentration, demonstrated inhibitory characteristics, with 10% of the sample in an activated sludge mixture causing a 10% decrease in oxygen consumption. On the other hand, the tests indicated the inhibitory effect to be more noticeable on the nitrification process (Fig. 5). Approximately 16% of sample L1 caused a 50% decrease in the nitrification rate. Nevertheless, the aerobic biological treatment of semicoke leachate is expected to be technologically feasible without inhibition problems emerging. Furthermore, the results presented in Figs. 4 and 5 show that sample L1 (March 2013) was more inhibitory than sample L2 (September 2014), suggesting a gradual decrease in leachate toxicity over a couple of years, which can be explained with an on-going landfill closure.

With regard to semicoke leachate biodegradability, Zahn-Wellens test results (Fig. 6) show that sample L2 is easily bio-treatable. Rapid degradation during the first three days indicates a high percentage of a readily biodegradable organic fraction in leachate; therefore, biodegradability over 3 d achieved a level of 74%. Less than 11% of COD degraded in the remaining test period, giving 85% biodegradability in 28 d. The percentage of recalcitrant COD in semicoke leachate is estimated as 15% of the leachate's initial COD, with a concentration of 120 mg/L.

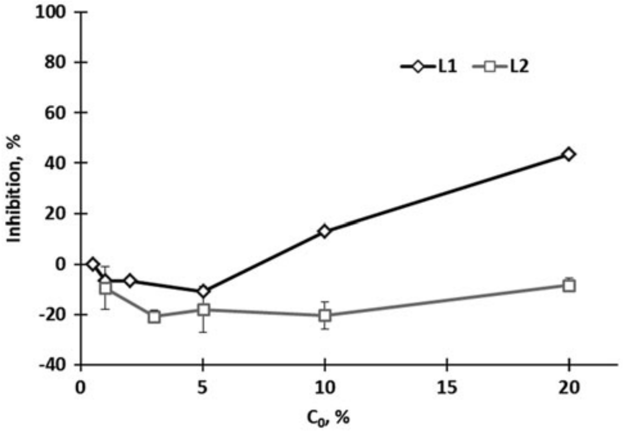

Fig. 4. Inhibition of the activated sludge oxygen uptake rate as a function of the concentration (C_0) of raw leachate samples (L1 and L2).

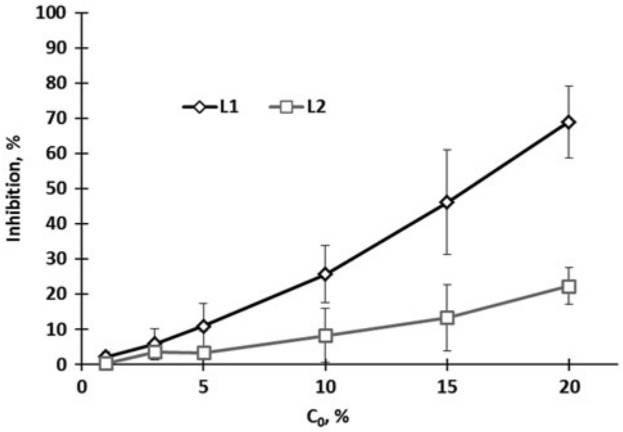

Fig. 5. Inhibition of the activated sludge nitrification rate as a function of the concentration (C_0) of raw leachate samples (L1 and L2).

Consequently, due to the high biodegradability of the leachate and its low inhibitory effect on activated sludge, it is reasonable to employ biological pre-treatment for the leachate. In this study, aerobic biological oxidation of sample L2 was carried out. The results of L2 biological treatment in an activated sludge system are shown in Table 2. Generally, the semicoke leachate bio-treatment efficacy was reasonably high, resulting in 67% COD, 94% BOD_7 and 69% DOC removal. The TPh concentration also substantially decreased (81%),

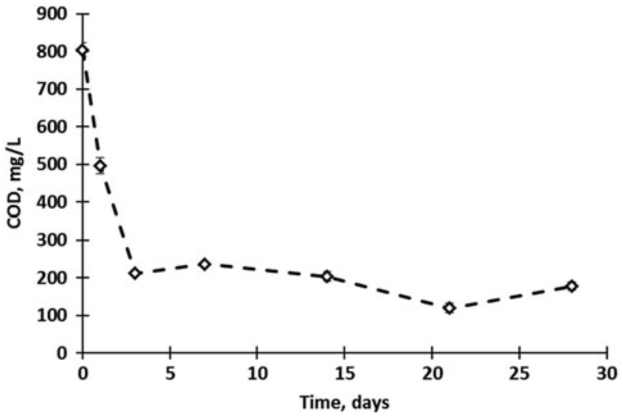

Fig. 6. Degradation of semicoke leachate (sample L2) in terms of COD in a 28 d biodegradability test.

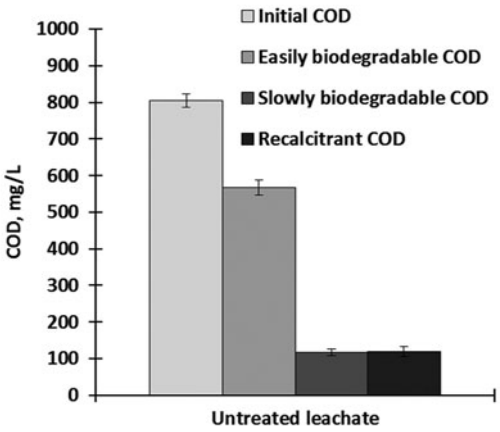

Fig. 7. COD fractions of raw semicoke leachate (sample L2) based on the biodegradability test.

from 18 to 3.4 mg/L. However, the residual concentrations of COD (278 mg/L) and TOC (151 mg/L) were still high, indicating the presence of recalcitrant pollutants in the leachate. The remaining COD in the effluent reflects mainly slowly biodegradable and recalcitrant COD fractions, as determined by the prior biodegradability test (Fig. 7).

At the preliminary stage, biological treatment can be effective, primarily for removing easily biodegradable organics, but the leachate still needs further treatment, preferably chemical post-treatment.

3.3. *BIO-CHEM*

The main economic benefit of the BIO-CHEM scheme is that the biological oxidation stage (BIO) helps decrease the consumption (cost) of reagents in the subsequent Fenton treatment step (CHEM) by the elimination of biodegradable COD. On the other hand, the application of the Fenton treatment as a powerful polishing step could substantially improve the overall treatment efficacy of the combined technological scheme. The results of combined biological pre-treatment and Fenton post-treatment are presented in Table 2 and Fig. 8.

The BIO-CHEM scheme applied on semicoke leachate resulted in a higher than 35 and 75% reduction of biologically pre-treated and initial COD, respectively, and a residual COD value lower that 250 mg/L for all of the ratios studied, except the lowest one ($COD/H_2O_2/Fe^{2+}$ w/w/w of 1/0.5/0.1). The reduction of BOD_7 was even more notable and comprised more than 20 and 96% of supplementary and total removal, respectively, which corresponds to a residual value ≥15 mg/L for all of the studied systems.

As for specific pollutant removal, the TPh concentration of 3.4 mg/L in the semicoke leachate sample after biological treatment was supplementary reduced by 68–89% with the Fenton post-treatment at $COD/H_2O_2/Fe^{2+}$ w/w/w ratios of 1/0.5/0.1—1/4/0.8, respectively.

Considering the removal efficiencies and discharge limits, the Fenton post-treatment, at a $COD/H_2O_2/Fe^{2+}$ w/w/w ≥1/1/0.2 of biologically pre-treated

Table 2
The results of the biological and BIO-CHEM treatment of semicoke leachate (sample L2)

	Biological treatment		BIO-CHEM (1/1/0.2)		BIO-CHEM (1/2/0.4)	
Parameter	Value (mg/L)	Removal (%)	Value (mg/L)	Removal (%)	Value (mg/L)	Removal (%)
COD	278 ± 7	67	191 ± 18	78	183 ± 11	79
BOD_7	19 ± 3	94	14 ± 2	96	14 ± 1	96
DOC	74.4 ± 2	69	54.5 ± 2	78	50.2 ± 1.75	79
BOD_7/COD	0.07		0.09		0.07	
NH_4-N	< l.d[a]	>99	< l.d[a]	>99	< l.d[a]	>99
TPh	3.4 ± 0.05	81	1.06	94	0.71	96

[a] Below the limit of detection.

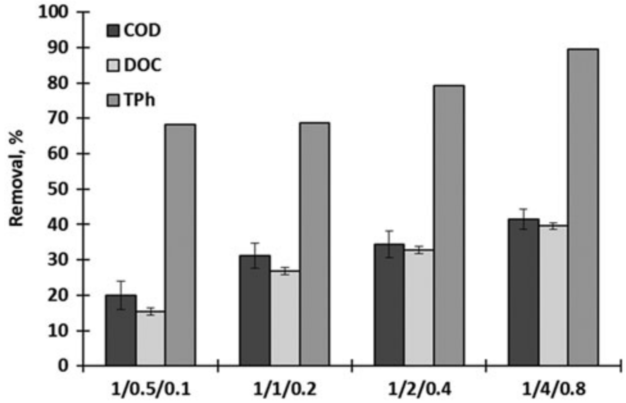

Fig. 8. COD, DOC and TPh removal as a function of the $COD/H_2O_2/Fe^{2+}$ weight ratio in the Fenton treatment of biologically pre-treated semicoke leachate (sample L2).

semicoke leachate, proved sufficient to meet all legislative requirements.

3.4. CHEM-BIO

The results of combined Fenton treatment (CHEM) and BIO are presented in Table 3. CHEM experiments were performed at lower reagent ratios of 1/0.5/0.1 and 1/1/0.2 ($COD/H_2O_2/Fe^{2+}$, w/w/w) to keep the chemical consumption as low as possible.

CHEM (1/1/0.2)—BIO proved to be a more reasonable treatment option than the combined scheme with lower reagent dosages. Thus, the total COD removal with the CHEM (1/1/0.2)—BIO scheme was 79%, which is 17% higher than in the CHEM (1/0.5/0.1)—BIO system, and resulted in a residual COD value of 178 mg/L. Similarly, the application of the CHEM-BIO treatment at a higher reagent dose was more efficient in terms of BOD_7 removal, and 13 mg/L of residual BOD_7 in the effluent was achieved. Therefore, according to the residual values of COD and BOD_7 in the effluent as well as the total removal efficiencies, the treatment performance required by Estonian legislation was attained.

3.5. Operational costs of treatment processes/schemes

To assess the economic feasibility of different treatment schemes for semicoke leachate treatment, the operational costs were calculated. The cost estimation and methodology were based on the calculations made by Dulov et al. [11].

The data obtained from the laboratory experiments allowed for approximate calculations of the operating costs comprising the energy required for ozonation and biological oxidation and chemicals for the Fenton process. Doses of ozone and H_2O_2 injected into the studied samples were used in calculations without the presumption of re-circulation of non-consumed chemicals or ferric sludge reuse. All of the calculations were performed in units per m^3 of treated semicoke leachate.

In the Fenton process, the costs of H_2O_2 (50%) and $FeSO_4{\cdot}7H_2O$ was estimated as 1 and 0.35 €/kg, respectively. Energy consumption in the Fenton process was not taken into consideration, as it would be small and highly dependent on the exact equipment used.

The specific energy requirement for ozone production from air was estimated as 10 kWh/kgO_3 [25] with an expected unit energy cost of 0.0588 €/kWh. In the case of aerobic biological oxidation, the energy consumption for aeration to remove 1 kg of COD was estimated as 0.9 kWh [26]. The aeration usually composes approximately 53% of the total energy consumption in the activated sludge process [27,28], and thus, the overall energy consumed per 1 kg of COD removed in the aerobic biological oxidation was estimated to be 1.7 kWh. Treatment cost estimates in €/m^3 can be seen in Table 4.

The results indicate that combined treatment schemes proved to be more efficient both in terms of treatment efficacy and cost than solely biological or

Table 3
The results of semicoke leachate (sample L2) Fenton and CHEM-BIO treatment (for Fenton treatment with a $COD/H_2O_2/Fe^{2+}$ weight ratio and at pH 3)

	CHEM (1/0.5/0.1)		CHEM (1/1/0.2)		CHEM (1/0.5/0.1)–BIO		CHEM (1/1/0.2)–BIO	
Parameter	Value (mg/L)	Removal (%)	Value (mg/L)	Removal (%)	Value (mg/L)	Removal (%)	Value (mg/L)	Removal (%)
COD	555 ± 9	35	391 ± 11	54	324 ± 12	62	178 ± 19	79
BOD_7	128 ± 3	61	142 ± 10	57	29 ± 5	91	13 ± 1	96
TOC	265 ± 13	28	207 ± 10	44	163 ± 6	56	117 ± 21	68
BOD_7/COD	0.23		0.36		0.09		0.07	
TPh	6.57	64	3.84	79	n/a		n/a	

Table 4
Operational costs of different semicoke leachate treatment processes/schemes

Process	Sample	Energy consumption, kWh/m^3	H_2O_2 (50%), kg/m^3	$FeSO_4 \cdot 7H_2O$, kg/m^3	Effluent corresponding to legislation (removal %[a]/effluent concentrations[b])	Treatment cost, €/m^3
Ozonation (30 mgO_3/L)	L1	120			−/−	7.06
Fenton treatment (1/1/0.2, w/w/w)	L1	n/a	4.08	2.03	−/−	4.8
	L2	n/a	1.7	0.85	−/−	2
Fenton treatment (1/2/0.4, w/w/w)	L1		8.16	4.06	−/−	9.6
	L2		3.4	1.7	−/−	4
Biological oxidation	L2	0.98			−/−	0.06
BIO-CHEM (1/1/0.2, w/w/w)	L2	0.98	0.56	0.28	+/+	0.72
BIO-CHEM (1/2/0.4, w/w/w)	L2	0.98	1.12	0.56	+/+	1.38
CHEM-BIO (1/0.5/0.1, w/w/w)	L2	0.39	0.85	0.43	−/−	1.02
CHEM-BIO (1/1/0.2, w/w/w)	L2	0.36	1.7	0.85	+/+	2

[a] COD (≥ 75%), BOD_7 (≥ 80%), TN (≥ 75%), TPh (monophenols ≥ 75%, diphenols ≥ 70%) [24].
[b] COD (250 mg/L), BOD_7 (15 mg/L), TN (75 mg/L), TPh (monophenols 0.1 mg/L, diphenols 15 mg/L) [24].

chemical processes. Generally, the use of direct chemical treatment (Fenton treatment, ozonation) for semicoke leachate containing high amounts of readily biodegradable organic matter was expensive and not efficient enough for organic load removal. Biological treatment was found to be the cheapest of the studied options, but the quality of the effluent did not meet the target discharge limits. As for a comparison between the two combined schemes, both ensure the required removal percentage as well as the specific target discharge limits of the investigated parameters; however, in terms of treatment cost reduction, BIO-CHEM was the more feasible option. Thus, the application of the BIO-CHEM system led to an effluent that completely corresponded to the legislation, even at the $COD/H_2O_2/Fe^{2+}$ w/w/w of 1/1/0.2 used in the CHEM step. Moreover, the treatment cost of this scheme was 2.8 times lower than that of the Fenton treatment at the same reagent dose, with a cost of only 0.72 €/m^3.

4. Conclusions

As hazardous waste landfill leachate is a potential threat for the environment as well as for local WWTP, separate treatment is necessary for the leachate. The study included purification of the leachate with a combination of biological and chemical processes to make the water purification cost-efficient. The results indicate that combined treatment schemes proved more efficient both in terms of treatment performance and cost minimization than solely biological or chemical processes. The combined schemes (BIO-CHEM and CHEM-BIO) equally ensure the required removal efficacy percentage as well as the specific target discharge limits of the investigated parameters, but for treatment cost reduction, BIO-CHEM was the more feasible option. Therefore, the BIO-CHEM combination was found to be the most efficient and practicable technological scheme for hazardous waste landfill leachate treatments. The results of this study are unique and may provide important insight for further implementation in the treatment of hazardous waste landfill leachates and complex industrial wastewaters.

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