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Optimal pre-treatment of moderately old landfill leachate at the pilot-scale treatment plant using the combined aerobic biochemical and reagent method

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ABSTRACT

Landfill leachates contain highly concentrated pollutants, and their uncontrolled discharge poses significant risks to the public health and environment. This study validated a pilot-scale two-stage aerobic biochemical and reagent method for the pre-treatment of moderately old landfill leachate at a pilot-scale treatment plant with a capacity of 400 L per day. The kinetic curves of key pollutants were described using two-factor dimensionless exponential equations, allowing for predicting maximally achievable treatment effects during the first aerobic biochemical stage. The optimal duration of aerobic biochemical pre-treatment was determined based on the concept of limiting pollutant content and minimizing operating costs for the two-stage process. Reagent-based leachate pre-treatment using the modified Fenton method was verified in a batch reactor. Optimal concentrations and dosages of reagent solutions, including polyacrylamide, aluminium sulphate, ferrous sulphate, and hydrogen peroxide, were found to comply with Ukrainian regulations for wastewater discharge into sewerage networks. Key pollution indicators of pre-treated leachate, such as NH_4^+–N (13.4–15.5 mg × L^{-1}), TKN (25.7–30.2 mg × L^{-1}), BOD_{tot} (71.8–76.9 mg × L^{-1}), and COD (390–459 mg × L^{-1}), meet the required standards.

1. Introduction

Uncontrolled hydrosphere pollution [1,2] and the lack of effective monitoring system of these pollutants, industrial pollution of the earth's surface [3] and household waste [4], municipal wastewater treatment waste [5,6], atmosphere pollution [7,8] and other anthropogenic threats to the environment are the most significant hazards to sustainable development. Among them, there are threats related to the lack of an effective solid waste management system.

Situation with the collection, processing and disposal of waste in general, including municipal solid waste (MSW), as for 2022, remains very problematic in Ukraine and needs to be solved urgently. More than 54 mln m^3, corresponding to about 10 mln t, of municipal waste was generated in Ukraine in 2020, and about 94% of this quantity were disposed on about 6,000 landfills and dumps with the total area of almost 9,000 ha. The number of overloaded MSW landfills was 261 (4.4%), and 868 (14.5%) did not meet

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environmental safety standards. Out of the 424 landfills requiring rehabilitation, only 24 had been recultivated [9].

Based on total area of MSW landfills and dumps, and assuming the average annual rainfall depth of 500–600 mm × yr^{-1} and runoff coeficient 0.05−0.1, total volume of leachates which are formed annually on landfills and dumps in Ukraine, is in the range from 2.25 to 5.4 mln m^3. Leachates from MSW dumps often have concentrations of key pollutants that are 5–50 times higher than the limit values, depending on the extent of dilution by atmospheric water [10]. The absence of waterproof lining, drainage, and leachate treatment in many landfill sites leads to the direct discharge of highly toxic leachates into soil, surface water, and groundwater. The problem of untreated leachates is important to society due to the significant risk it poses to public health, the environmental degradation it causes, and the potential for the spread of pollutants beyond the immediate area, emphasizing the need for effective leachate treatment to safeguard health, and protect the environment.

Despite the large number of studies on the leachate treatment and the variety of developed treatment technologies [11–13], the universal leachate treatment method suitable for all situations can not exist [14], because in each case chemical composition of leachate and the required degree of leachate pre-treatment are very different [15]. The choice of the leachate treatment method also depends on the method of disposal of concentrated contaminants resulting from treatment, the timing of commissioning and treatment plant performance [16,17]. In different countries, based on specific conditions, different strategies for leachate treatment are used, combining the pre-treatment and final treatment methods.

The following methods of leachate treatment are the most used in the world: aerobic biological treatment, which consists in the microbiological oxidation of pollutants under aeration conditions [11,18], anaerobic biological treatment resulting in leachate treatment and biogas output [12], reverse osmosis, which is implemented in membrane installations of osmotic treatment [13], physicochemical reagent treatment with a wide range of reagents, used in different studies [16,17], hydrodynamic cavitation by different types of cavitators [19]. Adsorption treatment methods [18,20], electroplasma methods [21] and others are less commonly used. These methods are seldom used alone; most often they are combined in different complex schemes.

The method of aerobic biochemical leachate pre-treatment in aerated lagoons is especially promising for implementation at Ukrainian MSW landfills. This method was successfully tested in the UK, Norway, Sweden and other countries [11,22]. Number of studies [11,23] confirmed that microbial communities of wastewater treatment plants (WWTP) are well adapted to the destruction of complex organic compounds in various liquid waste flows, including landfill leachates. An appropriate aerobic biocenosis develops in leachate treatment structure after some period of aeration, which is able to efficiently destruct complex organic compounds of highly concentrated leachate [18].

Reagent methods of leachate treatment, in particular coagulation and flocculation, are widely used for pre-treatment or complete leachate treatment in the UK, Germany, and other European countries. These methods allow the removal of non-oxidizing humic and fulvic acids from the leachates, as well as other specific persistent contaminants, including heavy metal ions, organochlorine compounds, etc. [24,25]. Fenton method and its modifications is one of the most effective methods of reagent treatment of landfill leachates. The systematic studies on the possibilities of application of the Fenton process and its variations, such as photo-Fenton process, electro-Fenton process, were done in last two decades [17,26,27]. Effectiveness of leachate treatment from the persistent organic contaminants using a simple or modified Fenton process depends on the type of leachate, reagent dosage, methods of input and mixing the reagents, initial and final pH values, temperature and aeration intensity [28,29].

Leachate pre-treatment at the landfill site followed by complete treatment at WWTP [18,30] or at bio-plateau [4,31] is of particular interest from the economical point of view. Despite the high concentrations of pollutants in landfill leachate, preliminary treatment of leachate at the landfill to the threshold limit values (TLV) for discharge into the sewerage network, followed by complete treatment in a mixture with domestic and industrial wastewater at municipal wastewater treatment plants (WWTP), remains a relevant tactic for minimizing threats to the environment from leachate. Such an approach to the disposal of leachates is especially relevant in countries with a low share of landfills and dumps with treatment facilities for complete leachate treatment, in particular, this also applies to Ukraine. It should also be noted that such an approach requires a certain justified compromise, which is expressed in compliance with the TLV for the pre-treated leachate only for the main, determining indicators of pollution, which can potentially have a negative toxic effect on the performance of biological treatment facilities of WWTP, even at sufficiently significant ratios of leachate dilution by the city wastewater. In practice, such indicators of pollution for most WWTP are ammonium nitrogen (NH_4^+–N), Total Kjeldahl nitrogen (TKN), chemical oxygen demand (COD), biological oxygen demand (BOD) and pH [18].

Pilot-scale studies of the biological treatment of a mixture of Lviv city wastewater with untreated leachate of the Hrybovychi MSW landfill indicated the safety of such an approach, although only for high dilutions of 500:1 and above [18]. In order to reduce the dilution ratio and to increase the degree of reliability of the WWTP performance, lechate should be pre-treated mainly by ammonium nitrogen, TKN, COD and pH. Previous lab-scale studies proved the effectiveness of the combined aerobic-reagent method for the pre-treatment of different age leachates of MSW landfills [10,29]. The main gap, crucial for the implementation of this combined method, is the lack of data on scaling-up this technology, and this is especially relevant for the modified Fenton method.

The purpose of this study was to validate at the pilot-scale level the efficiency of the combined aerobic biochemical and reagent method for leachate pre-treatment, and to specify the optimal parameters of such treatment. The scientific novelty of the study is that the experimental results regarding the optimal implementation conditions and efficiency of the two-stage technology of aerobic biochemical and reagent leachate pre-treatment using the modified Fenton method have been validated in a relevant environment.

2. Materials and methods

2.1. Raw leachate parameters

The object of the study was the leachate of Hrybovychi MSW landfill, located in Lviv region, Ukraine (49.90 N; 24.04E). Hrybovychi MSW landfill in 1958–2016 served as the main landfill of the city of Lviv, and it is under the technical remediation since 2020. Previous studies found out that untreated Hrybovychi leachate causes severe water pollution by phosphates, exceeding the threshold limit values (TLV) for surface water bodies in Ukraine in 81.2 times, ammonium nitrogen (48.4 times), Pb (27.8 times), Ni (12.4 times), Mn (89.3 times), Cr (47.2 times), Co (10.3 times) [32]. In addition, the ponds of acid tars, hazard industrial waste of the Lviv Oil Refinery, are located at the Hrybovychi MSW landfill. These oil products penetrate into the soil porous environment [33,34], the oil content in ground water in the area of impact of the landfill exceeds the TLV up to 77.1 times. This TLV exceedance, in samples taken from observation wells due to biodegradation of petroleum products, was slightly lower and was 16.8 times [35,36]. As for the end of 2021, there was about 50,000 m^3 of leachate accumulated in storage ponds at Hrybovychi MSW landfill.

The content of suspended solids, as well as BOD5 and COD of raw and pre-treated leachate were found using Standard methods for the examination of water and wastewater [37]. The concentrations of ammonium nitrogen and TKN were measured using Nessler's reagent and photoelectric colorimeter KFK-2-IHL4.2, value of pH was measured by a Checker 1 HI98103 pH meter.

The main physico-chemical parameters of leachate, which were controlled during the pilot-scale treatment process, are shown in Table 1. The values of the controlled parameters were checked for compliance with the discharge limits defined by the relevant Ukrainian regulation [38] to ensure environmental safety in the areas of MSW landfills location. Considering that C_{NH4-N} is above 400 $mg \times L^{-1}$ and $BOD_{tot}/COD = 0.120$, the tested Hrybovychi landfill leachate can be classified as moderately old leachate [39,40], and its content is a typical one for most Ukrainian landfills and dumps.

2.2. Pilot-scale treatment plant

Landfill leachate pre-treatment technology, tested in this study, consists of two successive stages: 1) aerobic biochemical treatment; 2) reagent physico-chemical treatment by a modified Fenton method. The main criterion of effectiveness of the tested technology was the achieving in the treated leachate of main pollution indicators that meet Ukrainian regulations [38]. This enables the discharge of the pre-treated leachate in the mixture with domestic and industrial wastewater for full treatment at municipal WWTP. A pilot-scale leachate treatment plant with a capacity of 400 $L \times day^{-1}$ was installed at the territory of the Hrybovychi MSW landfill site, which is operated by Lviv Communal Enterprise "Green City".

Aerobic pre-treatment of leachate by saturating it with air using a jet type aerator was done in a biochemical treatment unit 1 (Fig. 1). Both the duration of the initial start-up period, realized in the batch reactor mode, and the optimal intensity and periodicity of aeration were specified. The duration of the initial start-up period corresponds to the decreasing of main pollution indicators at values close to stationary ones. According to previous laboratory study, the optimal duration of the initial start-up process of aerobic biochemical treatment is about 7–15 days. The biochemical treatment unit after the initial start-up period operated in a continuous reactor mode, which included daily removal of 400 $L \times day^{-1}$ of the biochemically pre-treated leachate in the reagent treatment unit 2, and the same volume of raw leachate was pumped in the biochemical treatment plant 1. In this mode, the biochemical treatment plant operated until the end of field research cycle.

In the reagent treatment unit 2 (Fig. 1) the second treatment stage was tested using the mixtures of four working solutions, namely polyacrylamide (PAA), aluminum sulphate, ferrous sulphate and hydrogen peroxide. Circulating mixing of leachate with reagent solutions using portable submersible sewage pumps 7 was used to intensify the reagent treatment process. Reagent treatment unit 2 was operated in periodic mode. After the adding of reagent working solutions, the resulting mixture was precipitated for 1.5−2 h, after which the sediment from the lower part of the reagent treatment unit 2 was removed, and pre-treated leachate that met the requirements of [38], was pumped into the city sewerage network.

2.3. Parameters of leachate reagent treatment using the modified Fenton's method

Leachate was fed in portions of 100 L for one cycle to the reagent treatment unit 2 (Fig. 1). Working solutions of PAA, aluminum sulphate, ferrous sulphate and hydrogen peroxide were sequentially fed by pumps 6 into the reagent treatment unit 2. Preparation of

Table 1
Parameters of the Hrybovychi landfill leachate in November 2021, comparing the Ukrainian threshold limit values (TLV) for discharge into the sewerage networks.

Indicator of pollution	Raw leachate C_{en}	TLV (Rules, 2017)	C_{en}/TLV
NH_4^+–N ($mg \times L^{-1}$)	554.1	30	18.5
TKN ($mg \times L^{-1}$)	889.3	50	17.8
BOD_5 ($mg \times L^{-1}$)	192.0	–	N/A
BOD_{tot} ($mg \times L^{-1}$)	610.3	350	1.74
COD ($mg \times L^{-1}$)	5082	500	10.2
pH	9.09	6.5–9.0	N/A

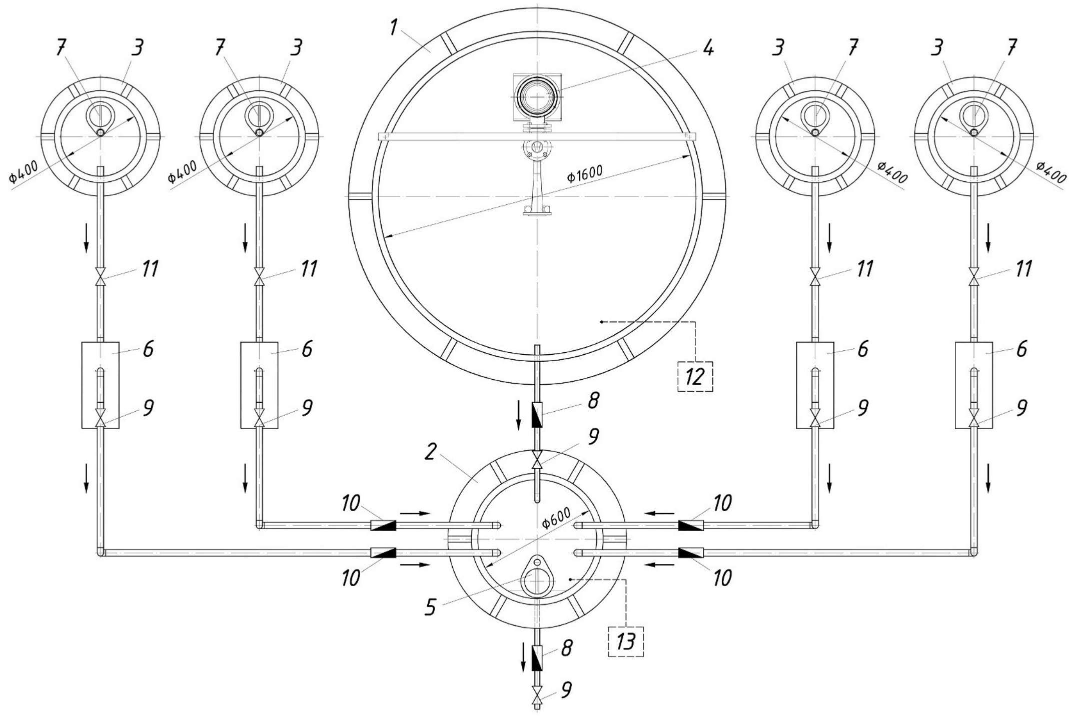

Fig. 1. Experimental pilot-scale leachate treatment plant with a capacity of 400 L × day^{-1}: 1 – biochemical treatment unit ($D = 1.6$ m, $H = 1.8$ m); 2 – reagent treatment unit ($D = 0.6$ m, $H = 0.8$ m); 3 – tanks with working reagent solutions ($D = 0.4$ m, $H = 0.5$ m); 4 – jet type aerator ($P = 2.2$ kW); 5 – submersible sewage pump; 6 –pumps for reagent solutions; 7 – mixing pumps; 8 – flowmeters DN25; 9 – valves DN25; 10 – flowmeters DN15; 11 –valves DN32; 12 – oximeter AZ-86021; 13 – laboratory device Ezodo PL-700PCS.

PAA, aluminum sulphate and ferrous sulphate solutions was performed once a day, and preparation of hydrogen peroxide solution – immediately before its addition into the reagent treatment unit at each cycle.

Technical characteristics of the reagents were as follows: polyacrylamide-co-diallyldimethyl-ammonium chloride (PAA) produced by ALDRICH Chemistry Co was used in the form of 10 wt% water solution, hydrogen peroxide 35 wt%, technical aluminum sulphate with the mass content of $Al_2(SO_4)_3 \times n\ H_2O$ equal to 99.7%, and technical ferrous sulphate with the mass content of $FeSO_4 \times 7H_2O$ at least 97%. Dosages and concentration of reagent solutions which were tested are given in Table 2. Active substance concentrations are presented, and the mass fractions of aluminum sulphate and ferrous sulphate solutions are given in terms of technical products, crystallic hydrates. Aluminum sulphate and ferrous sulphate molar concentrations are given for aluminum ions and iron (II) ions, respectively.

3. Results and discussion

3.1. Simple and modified first order models of aerobic pre-treatment

An important technological issue of scaling-up the two-stage method of leachate pre-treatment is the determination of the optimal

Table 2
Dosages and concentrations of reagent solutions in the field study of the Hrybovychi landfill leachate reagent treatment (per leachate volume 100 L).

No of mixture	PAA (0.1 wt%)		$Al_2(SO_4)_3 \times 18H_2O$ (10 wt%)		$FeSO_4 \times 7H_2O$ (10 wt%)		Hydrogen peroxide (2 wt%)	
	dosage (L)	C (mg × L^{-1})	dosage (L)	C_M (mmol × L^{-1})	dosage (L)	C_M (mmol × L^{-1})	dosage (L)	C_M (mmol × L^{-1})
1	5	50	5	15.0	10	36.0	6	35.3
2	5	50	4	12.0	8	28.8	5	29.4
3	4	40	5	15.0	8	28.8	5	29.4
4	4	40	4	12.0	6	21.6	5	29.4
5	4	40	3	9.0	8	28.8	4	23.5
6	3	30	4	12.0	8	28.8	4	23.5
7	3	30	5	15.0	6	21.6	3	17.7
8	3	30	4	12.0	6	21.6	3	17.7

hydraulic retention time (HRT) of the leachate in the aerobic biochemical treatment unit in order to achieve the maximum technical and economic efficiency of the two-stage pre-treatment as a whole. In practice, the optimal ratio of the first and second stages of pre-treatment should correspond to the minimum costs for the implementation of two-stage process under the meeting of TLV for discharge into the city sewer [38].

The kinetics of aerobic biochemical treatment of old and medium-aged leachates for most basic pollution indicators (e.g. ammonium nitrogen, TKN, COD), as shown in Ref. [29], can be well described by a two-parameter first-order reaction equation (1) that takes into account the lower limiting concentration C_{lim}, which corresponds to the share of non-biodegradable compounds:

$$dC / dt = - k(C - C_{lim}) \tag{1}$$

k – rate constant of biochemical reactions, day^{-1}; C_{lim} – the lower limit value of the pollution indicator in the process of aerobic biochemical pre-treatment, mg·L^{-1}.

The solution of equation (1) is a two-parameter exponent

$$C = C_{lim} + (C_0 - C_{lim}) \times \exp(-kt) \tag{2}$$

C_0 – initial concentration at $t = 0$.

To compare the kinetics of leachate treatment by the different indicators of pollution, it is convenient to present (Eq. (2)) in a dimensionless form:

$$C' = C'_{lim} + (1 - C'_{lim}) \times \exp(-kt) \tag{3}$$

$C' = C(t)/C_0$ – dimensionless current concentration; $C'_{lim} = C_{lim}/C_0$ – dimensionless limiting concentration.

3.2. Results of aerobic biochemical pre-treatment

The generalized results of the aerobic biochemical pre-treatment of Hrybovychi landfill leachate at the pilot-scale treatment plant by the main pollution indicators, expressed in dimensionless variables, are presented in Fig. 2 and Fig. 3.

Applying the least squares method to the experimental results of the change of NH_4^+–N and TKN (Fig. 2), the dimensionless trend lines in the form of two-parameter exponent (Eq. (3)) were obtained, respectively:

$$C'_{NH4-N} = 0.07 + (1–0.07) \times \exp(-0.0861\ t) \tag{4}$$

$$C'_{TKN} = 0.285 + (1–0.285) \times \exp(-0.0986\ t) \tag{5}$$

During the batch mode, realized for HRT = 15 days, the concentration of ammonium nitrogen decreased from 554.1 mg × L^{-1} to 178 mg × L^{-1}, which corresponds to exit dimensionless concentration of 0.321 or treatment effect E_1 of 67.9%. Limiting dimensionless content of NH_4^+–N is found to be equal to 0.07 (Eq. (4)) or 38 mg × L^{-1} which almost satisfies the corresponding TLV = 30 mg × L^{-1}.

TKN content in the batch mode decreased from 889.3 mg × L^{-1} to 385 mg × L^{-1}, or to the dimensionless concentration of 0.433 or treatment effect E_1 = 56.7%. Dimensionless limiting value for TKN 0.285 is obtained (Eq. (5)), corresponding to exit concentration of 253 mg × L^{-1} which is 5.1 times higher than the corresponding TLV.

Comparing the kinetics of aerobic leachate pre-treatment of NH_4^+–N and TKN indicates close values of rate constants in both cases (0.0861 day^{-1} and 0.0986 day^{-1} respectively), but reveal the low biodegradability of organic nitrogen in Hrybovychi leachate, which is expressed in a significantly higher value of the dimensionless limiting concentration for TKN comparing NH_4^+–N (0.285 vs 0.07, respectively).

A significant difference in the kinetics of leachate aerobic treatment by BOD and COD was obtained (Fig. 3) which can be explained

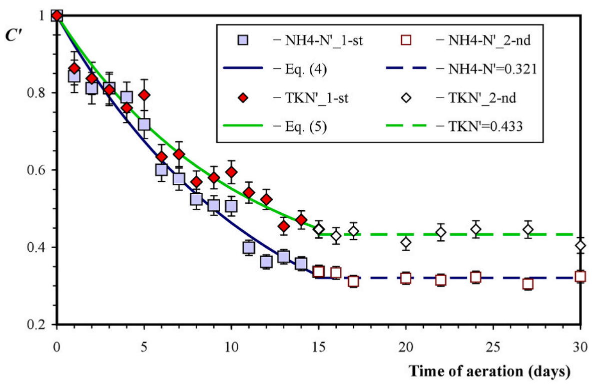

Fig. 2. Dimensionless content of ammonium nitrogen and TKN in Hrybovychi landfill leachate in aerobic biochemical treatment unit for the 1st stage (batch reactor mode) and for the 2nd stage (semi-continuous mode); error bars ±5% are specified.

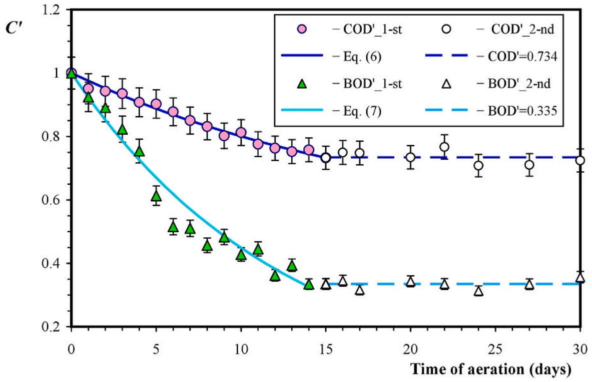

Fig. 3. Dimensionless content of BOD_{tot} and COD in Hrybovychi landfill leachate in aerobic biochemical treatment unit for the 1st stage (batch reactor mode) and for the 2nd stage (semi-continuous mode); error bars ±5% are specified.

by the age category of Hrybovychi leachate. Rate constant for COD is obtained equal to 0.051 day^{-1} which is the less value from all four controlled parameters, and dimensionless limiting concentration is as high as $C'_{lim} = 0.50$ (Eq. (6)).

$$C'_{COD} = 0.50 + (1\text{–}0.50) \times \exp(-0.051\ t) \quad (6)$$

According to the obtained limit parameters, the effect of leachate pre-treatment by COD of 45% can be achieved in as much as 45 days. Treatment effect of 49.5% is achievable in 90 days. Such low efficiency of COD removal is quite typical for old leachates with high content of persistant organic substances [41].

Thus, for mature Hrybovychi leachate, COD and TKN are critical indicators of pollution, which confirms the conclusions drawn in particular by Refs. [29,42], and influence on the duration of aerobic biochemical treatment and fixes the requirements for the efficiency of the second, reagent stage of pre-treatment. Taking into account that the operating costs of aerobic treatment at fixed values of capacity and of aeration intensity are proportional to the square of time, and using the obtained TKN and COD kinetic curves (Eq. (5) and (6)), it was found that it is economically unefficient to aerate old Hrybovychi leachate for more than 15 days.

In contrast to COD, very positive kinetics of leachate pre-treatment by BOD is obtained. Dimension limiting BOD_{tot} value is obtained to be equal zero, and two-parameter exponent turns in this case into a simple exponent (Eq. (7)).

$$C'_{BOD} = \exp(-0.080\ t) \quad (7)$$

Constant rate by BOD_{tot} is obtained equal to 0.08 day^{-1} which is only 7% less, comparing $k_{NH4\text{–}N} = 0.0861$ day^{-1} and 12% less, comparing $k_{TKN} = 0.0986$ day^{-1}. Dimensionless BOD_{tot} of 0.335, obtained after 15 days of batch mode and maintained in semi-continuous mode, is equal to 205 mg × L^{-1} which is 59% from the corresponding TLV 350 mg × L^{-1}. Obtained efficiency of BOD_{tot} decreasing equal to 66.5%, corresponds reasonably well with the relevant efficiency of 74.6%, obtained by Ref. [23] for the moderate age leachate with BOD_5/COD ratio of 0.36.

Table 3
Main pollutant indicators of aerobically pre-treated leachate before and after the reagent treatment unit.

Indicator of pollution and unit	Values before (en) and after (ex) reagent treatment for differnet reagent mixtures							
	No 1 (en)	No 1 (ex)	No 2 (en)	No 2 (ex)	No 3 (en)	No 3 (ex)	No 4 (en)	No 4 (ex)
pH	9.71	6.26	9.79	6.63	9.73	6.54	9.76	6.78
NH_4^+–N (mg × L^{-1})	186.6	14	184.9	16.3	172.7	17.4	177.2	15.5
TKN (mg × L^{-1})	397.2	27.3	382	30.1	392.9	32.4	367.3	30.2
BOD_5 (mg × L^{-1})	70.4	15.8	56.9	17.1	49.3	17.9	68.1	20.4
BOD_{tot} (mg × L^{-1})	204.4	62.7	210.8	59.6	193.1	57.5	209.7	71.8
COD (mg × L^{-1})	3724	371	3809	405	3801	387	3732	390
Suspended solids (mg × L^{-1})	219	82.5	224.8	97	223.8	103.2	224.9	106.9
Indicator of pollution and unit	Values before (en) and after (ex) reagent treatment for differnet reagent mixtures							
	No 5 (en)	No 5 (ex)	No 6 (en)	No 6 (ex)	No 7 (en)	No 7 (ex)	No 8 (en)	No 8 (ex)
pH	9.8	6.67	9.71	6.57	9.72	6.7	9.72	6.81
NH_4^+–N (mg × L^{-1})	174.4	13.4	178.5	22	168.8	24.9	179.6	32.5
TKN (mg × L^{-1})	390.2	25.7	397.1	39.4	396.7	45.8	359.8	56.2
BOD_5 (mg × L^{-1})	53.5	26.5	53.1	25.2	51.7	23.7	55.3	28.8
BOD_{tot} (mg × L^{-1})	204.4	76.9	191.3	95.1	204.1	72.1	217.6	87.9
COD (mg × L^{-1})	3897	459	3599	520	3610	631	3681	615

3.3. Reagent treatment stage using the modified Fenton's method

Main pollution indicators after adding to the aerobically pre-treated leachate of the appropriate reagent compositions and settling of the resulting mixtures are given in Table 3. The maximum achieved treatment effect for ammonium nitrogen was equal to 92.5%, for TKN – 93.4%, for COD – 90.0%, and 71.7% for BOD_5. There is a tendency of increasing of the content of ammonium nitrogen, BOD and COD in the treated leachate with decreasing of dosages of reagent working solutions, which limits the minimum allowable dosages of working solutions at the level of those used. On the other hand, increasing the dosages of working solutions causes a decrease in the pH value below the minimum limit for discharge into the sewerage ($pH_{min} = 6.5$), which requires subsequent alkalinization of treated leachate.

Thus, COD is the most problematic indicator of pollution, in terms of ensuring the requirements for discharge of pre-treated leachate into the municipal sewerage systems (Table 3). In the same time, treatment effects by COD, obtained in this study using the modified Fenton method, are quite higher comparing the results for the traditional Fenton method, reported by Deng [26], Bae et al. [28] and Badawy et al. [17], equaul to 61%, 63% and 77–83%, respectively. Another encouraging result is the low specific discharge of hydrogen peroxide, which in optimal dosages was equal to 0.23−0.25 from the COD at the entry of the reagent stage, which is less than the ratio 4.4, obtained by Badawy et al. [17], and even more less than 6.8 in Ref. [26]. These positive results can be explained by the synergistic effect of additional coagulant ($Al_2(SO_4)_3 \times 18H_2O$) and of PAA flocculant on the reagent treatment process.

Formally, the Ukrainian requirements for discharge into sewer networks (Rules, 2017) are met by reagent treatment by mixtures No.2 − No. 5. Technical and economic considerations point out that mixtures No. 4 and No. 5 are optimal, and correspond to the minimum specific cost of reagents based on 1 cubic meter of pre-treated leachate, namely USD 17.4 and USD 16.5, respectively. The sludge obtained after reagent treatment is relatively safe for the environment, and can be either disposed at a landfill or used for other purposes, e.g., such as in Ref. [43].

4. Conclusions

Research on leachate treatment using new effective technologies is crucial for society as it is necessary for the reclamation of solid waste landfills and the mitigation of environmental hazards. The study successfully validated an innovative two-stage aerobic biochemical and reagent method for leachate pre-treatment at a pilot-scale treatment plant with a capacity of 400 L per day, using moderately old leachate from the Hrybovychi MSW landfill in the Lviv region of Ukraine.

Treatment effects for key pollution indicators (NH_4^+−N, TKN, BOD, COD, and pH), previously examined in lab-scale conditions, were verified and specified at the pilot-scale treatment plant to meet the local Ukrainian regulations for sewerage network discharge. Initial pollution indicators in the raw leachate were NH_4^+–N: 554.1 mg $\times$ L^{-1}, TKN: 889.3 mg $\times$ L^{-1}, BOD_{tot}: 610.3 mg $\times$ L^{-1}, and COD: 5082 mg $\times$ L^{-1}. The results confirmed the high efficiency of aerobic pre-treatment in reducing ammonium nitrogen and BOD content, potentially reaching the required TLV with sufficient duration of aeration process. However, the kinetic curves indicated lower achievable treatment effects for TKN and COD, with exit concentrations of 253 mg $\times$ L^{-1} and 2541 mg $\times$ L^{-1}, respectively, which exceeded the corresponding TLV by 5.1 times. Based on cost optimization, the estimated hydraulic retention time for batch-mode aerobic pre-treatment is approximately 15 days.

The modified Fenton method was applied as the reagent stage of leachate pre-treatment in batch mode, and optimal concentrations and dosages of PAA, aluminum sulphate, ferrous sulphate, and hydrogen peroxide solutions were determined. Technical and economic analysis revealed that mixtures No. 4 and No. 5 are the optimal choices, as they offer the lowest specific cost of reagents per cubic meter of pre-treated leachate while still meeting the TLV requirements for discharge into sewerage networks, namely NH_4^+−N: 13.4–15.5 mg $\times$ L^{-1}, TKN: 25.7–30.2 mg $\times$ L^{-1}, BOD_{tot}: 71.8–76.9 mg $\times$ L^{-1}, and COD: 390–459 mg $\times$ L^{-1}. Considering the variability and unique composition of leachates, it is recommended to implement the two-stage leachate pre-treatment method on a full-scale industrial level for other landfill sites, following the pilot treatment plant testing described in this article.

Author contribution statement

Myroslav Malovanyy: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Volodymyr Zhuk: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Ivan Tymchuk: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Bohdan Zavoyko: Contributed reagents, materials, analysis tools or data.

Ruslan Grechanik: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Vira Sliusar: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Nataliya Vronska: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Anastasiya Marakhovska; Andriy Sereda: Performed the experiments; Analyzed and interpreted the data.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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