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Pre-treatment of landfill leachate using potassium ferrate(VI)

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ABSTRACT

Potassium ferrate was used in the decontamination of leachate from the landfill in Janczyce, which is part of the Municipal Waste Treatment Plant in Janczyce and has been operating since 2003. The aim of the research is to assess the effectiveness of pre-treatment of landfill leachate with the use of potassium ferrate(VI) (K_2FeO_4). The potassium ferrate(VI) (K_2FeO_4) used acts as an oxidant and coagulant. The effects of the K_2FeO_4 dose, the duration of the oxidation process and pH were modelled. Analysis of the test results indicates a high elimination efficiency for colour and UVA_{254}. The elimination of pollutants measured by the chemical oxygen demand (COD) index is slightly worse. Based on the results obtained, a mathematical model was developed for the oxidation process of landfill leachate with K_2FeO_4 as oxidant and coagulant. The best COD elimination results (45%) were obtained for a potassium ferrate(VI) dose equal to 2.0 $g \cdot L^{-1}$, pH = 4.5 and after 90 min of landfill leachate oxidation. The best leachate pre-treatment effects were achieved in terms of colour elimination, where managed to reduce the colour by 97% and UV absorbance by approx. 60% at a potassium ferrate(VI) dose equal to 4.5 $g \cdot L^{-1}$ and, pH = 5.01 and landfill leachate oxidation duration of 60 min.

Keywords: Landfill leachate; Pre-treatment landfill leachate; Potassium ferrate(VI); Oxidation; Coagulation

1. Introduction

In 2018, 27 European Union countries collected $2{,}168 \cdot 10^6$ Mg of waste, of which almost 40% ($834 \cdot 10^6$ Mg) was landfilled (D1 – storage in the ground or above ground, for example, landfills, D5 – placing in sealed separate chambers, covered and insulated from each other and from the environment, etc., D12 – permanent storage, for example, placing containers in mines, etc.) [1,2]. The long-term objective of EU policy in terms of waste management is reducing the amount of generated waste and manage the already generated. Despite the downward trend ($844 \cdot 10^6$ Mg in 2016 and $897 \cdot 10^6$ Mg in 2014), still a considerable percentage of waste is landfilled, which constitutes a potential loss of resources in the form of materials and energy [1,2]. Please note that waste disposal entails huge environmental consequences – it takes up space, and can lead to air, water and soil pollution [1,2]. Up to 10% of organic substances decomposed through microbiological methods is evacuated in the form of landfill leachates [3]. Leachates may appear immediately after disposing of waste at a landfill, but usually, large amounts of leachates are generated within 1–2 y of waste deposition, even after heavy rainfall. Leachates are also generated at the post-operating stage [2–4]. Leachate composition depends on numerous factors, the most important of which include the composition of deposited waste, landfill age, applied landfill construction technology and its operation method, season, precipitation, etc. The considerable number of factors impacting the landfill leachate generation process results in leachates characterized by a very complex and diverse composition. Their main ingredients are organic substances, ammonia nitrogen, heavy metals and inorganic salts (Table 1) [2,5,6].

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Besides the most frequently mentioned contaminants, leachates also contain newly occurring ones, such as synthetic and natural chemical substances, which are not subject to large-scale monitoring (among others, toxins, hormones, pharmaceuticals, plasticizers, drugs, nanomaterials and personal care products) [7–11]. Therefore, evaluating the leachate quantity and quality, followed by management and treatment constitute major issues worldwide [12,13]. Landfill leachates may be treated through mechanical, physico-chemical, chemical, biological and wetland methods, as well as a combination of the former [6,13]. A comparison of landfill leachate treatment methods, taking into account landfill age, as well as system and operating costs can be found in Table 2 [14,15]. Leachate recirculation onto the landfill heap can be applied in order to pre-treat leachates and reduce their volume. Most usually, leachates (due to low disposal cost) are transported in septic tanks to wastewater treatment plants and subjected to traditional treatment process with municipal waste therein.

Selecting an optimal leachate treatment method or a combination of methods must take into account a number of factors, among others, variability of composition and volume, requirements in terms of treated leachates, as well as economic capabilities of the administrator. The effectiveness of biological processes significantly reduces with landfill age, due to the appearance of refractive compounds in the leachates. This is why physico-chemical methods (oxidation, advanced oxidation, adsorption, membrane-based) are optimal. The very high variability in terms of leachate quantity and quality within the studied facilities indicates that it is advisable and justified to search for modern methods of their neutralization.

Table 1
Landfill leachate characteristics [6]

Parameter	Landfill age (y)	
	Young (0–5)	Intermediate (5–10)
pH (–)	<6.5	6.5–7.5
COD ($mg{\cdot}L^{-1}$)	>10,000	5,000–10,000
BOD5/COD	0.5–1.0	0.1–0.5
Heavy metals	Medium to low	Low
Biodegradability	High	Medium

Table 2
Comparison of wastewater treatment methods [14,15]

Method	Landfill leachate type			Costs (system + process)
	Young (<5 y)	Moderate (5–10 y)	Old (>10 y)	
Biological				
Activated sludge	+	+/–	–	High
SBR	+	+/–	–	Average
Oxygen filters	+	+/–	+/–	High
Physico-chemical				
Coagulation/ flocculation	–	+/–	+/–	Average
Adsorption	–	+/–	+	Average
Chemical oxidation	–	+/–	+/–	High
Membrane processes				
Microfiltration	–	–	–	High
Nanofiltration	+	+	+	High
Reverse osmosis	+	+	+	High

Key: "+" good, "–" low, "+/–" satisfactory.

Based on the results obtained by Thomas et al. [16], it can be concluded that potassium ferrate(VI) is a promising and effective oxidant, used for decolourization. The application of potassium ferrate(VI) as an oxidant for the Acid Red 27 (AR27) and Reactive Black 5 (RB5) dyes provides satisfactory outcomes (noticeable decolourization) at pH 7.0, K_2FeO_4 concentration of 180 and 240 $mg{\cdot}L^{-1}$ over a process time of 10 min. Chemical oxygen demand (COD) reduction relative to the initial value amounted to 83.7% (AR27) and 81.4 (RB5). Unfortunately, weaker effects were obtained in the case of Acid Green 16 (AG16). Thomas et al. [17] used K_2FeO_4 also for treating landfill leachates (pH 7.9, colour 550 $mgPt{\cdot}L^{-1}$, COD 1,880 $mgO_2{\cdot}L^{-1}$, total organic carbon (TOC) 620 $mg{\cdot}L^{-1}$, total phosphorous 6 $mg{\cdot}L^{-1}$). Under optimal process conditions (pH 3.5, K_2FeO_4 dose of 2.0 $g{\cdot}L^{-1}$, time 45 min, temperature 30°C, pressure 1 MPa), the colours value was reduced by 97%, COD by 92%, TOC by 91% and total phosphorous by 48%. For comparison, under conditions of atmospheric pressure (1,013 hPa) and a temperature of 19°C, colour value was reduced by 99%, COD by 83%, TOC by 79% and total phosphorous by 19%. Research by Lan et al. [18] and Yang et al. [19] also confirms that potassium ferrate(VI) effectively pre-treats all kinds of landfill leachates, but it requires selecting optimal process conditions due to the variable leachate composition in each case.

Compared to conventional landfill leachate treatment coagulants (COD 770 $mgO_2{\cdot}L^{-1}$, TOC 230 $mg{\cdot}L^{-1}$, total nitrogen 120 $mg{\cdot}L^{-1}$, total phosphorous 12 $mg{\cdot}L^{-1}$, total coliform counts 6.8 $logCFU{\cdot}mL^{-1}$) the application of K_2FeO_4 under the same process conditions (pH 2.3, time 25 min, K_2FeO_4 dose 0.39 $g{\cdot}L^{-1}$, $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ calculated as iron amount equivalent) provides much better contamination removal effects (Table 3) [20].

The aim of the research is to assess the effectiveness of pre-treatment of landfill leachate with the use of potassium

Table 3
Comparison of K_2FeO_4 pre-treatment efficiency with other reagents [20]

Parameter	Reduced initial value in landfill leachates after application (%)		
	K_2FeO_4	$FeSO_4{\cdot}7H_2O$	$FeCl_3{\cdot}6H_2O$
COD	76.2	38.1	41.6
TOC	82.6	37.0	45.7
Total nitrogen	68.3	20.8	29.2
Total phosphorus	91.6	95.8	95.8
Total coliform counts	99.0	94.4	92.1

ferrate(VI) (K_2FeO_4). The potassium ferrate(VI) (K_2FeO_4) used acts as an oxidant and coagulant.

2. Material and methods

Collecting leachate samples, as well as their storage and testing the chemical composition was conducted in accordance with the applicable PN-ISO 5667-10:2021-11 standard. Leachate samples (pH 7.975, COD 1,742 $mgO_2·L^{-1}$, colour 2,442 $mgPt·L^{-1}$, UV_{254} 3.435) were collected at the landfill in Janczyce, which is part of the Municipal Waste Treatment Plant in Janczyce and has been operating since 2003. The facility covers approximately 150,000 residents, and almost 300 kg waste per capita per year is generated within the region. Waste after the mechanical treatment of mixed communal waste, sorting residues and other waste unsuitable for recovery are stored within the landfill area (3.64 ha). More than 6,600 m^3 of leachates is generated on average per year in association with landfill operation.

Laboratory tests of landfill leachate pre-treatment were conducted with the use of potassium ferrate(VI) (K_2FeO_4) by Angene (Compound ID: AG00793B, 198.4 $g·mol^{-1}$) and 0.10 L samples (sample volume selected so that it was possible to analyse all determined parameters). The design of experiment (DOE) module of the Statistica 12 software by StatSoft Inc. was used for this purpose. An advantage of such an approach is reducing workload and the time required to obtain reliable results. A central composition plan with 5 input values ($-\alpha$, -1, 0, 1, α) was selected. The choice of this plan was imposed by the lack of knowledge in terms of the impact of input values on output values, which prompts the inclusion of a non-linear model in further considerations. However, bear in mind that the range of appropriate input values and their discretization always remain a compromise between ensuring a correct test object operation and experiment planning requirements. Used 0.20 L Erlenmayer flask and weighed appropriate (in accordance with Table 4) doses of potassium ferrate(VI) and added 0.1 L of leachate (20°C ± 1°C), followed by mixing in a shaker, with a min. speed of 150 rpm^{-1} over a specified time. The pH value was adjusted using concentrated H_2SO_4 (98%, pure for analysis). The samples were neutralized with 10% NaOH to the pH of approx. 7.0. Contact time according to Table 4 was assumed. Next, the samples were filtered. COD, colour, UV_{254} (dissolved organic compounds) and heavy metals were determined in pre- and post-treatment samples.

Table 4
Experiment plan

Lp.	pH (–)	Dose K_2FeO_4 ($g·L^{-1}$)	Time (min)
1	3.75	4.50	60
2	3.00	7.00	90
3	4.50	7.00	90
4	3.75	8.70	60
5	2.49	4.50	60
6	3.75	4.50	60
7	4.50	7.00	30
8	3.75	4.50	110
9	3.75	4.50	10
10	5.01	4.50	60
11	3.00	2.00	30
12	4.50	2.00	30
13	3.00	2.00	90
14	3.00	7.00	30
15	3.75	0.30	60
16	4.50	2.00	90

Heavy metal content in the prepared samples was determined using the ICP-OES Optima 8000 spectrophotometer, in accordance with ISO 9001:2000. Aqua regia mineralization was conducted in compliance with the PN-EN ISO 15587-1:2005 standard, with the following parameters adopted:

- a 25 cm^3 leachate sample was supplemented with: 7.5 cm^3 HCl p.a. grade (1.19 $g·cm^{-3}$, 38%) and 2.5 cm^3 HNO_3 p.a. grade (1.40 $g·cm^{-3}$, 65%),
- the sample was heated for approx. 30 min under a watch glass,
- next, the contents were evaporated almost dry, the residue was flooded with 20 cm^3 p.a. grade HNO_3 with a concentration of 5%,
- the cooled solution was quantitatively transferred to a 50 cm^3 volumetric flask and supplemented with 50 cm^3 of redistilled water

Chemical oxygen demand was determined with the Spectroquant photometric method – determination through cuvette testing using a Spectroquant Nova 60 spectrophotometer by MERCK, after prior heating in a TR 320 thermo-reactor by MERCK (120 min at 148°C). The determination limit for the selected method was 300–3,500 $mg·L^{-1}$ (Standard Deviation of Procedure ± 13.9 $mg·L^{-1}$).

Colour was determined with the spectrophotometric method using a UV/VIS spectrophotometer, in accordance with PN-EN ISO 7887:2012, and dissolved organic compounds were determined through UV spectrophotometry (wavelength – 254 nm) as per the PN-C 04572:1984 standard. Both parameters were tested using the Genesis 150 UV-VIS spectrophotometer by ThermoScientific.

The pH was determined with a potentiometric method using a CX-505 Multifunction Meter, pursuant to PN-EN ISO 10523:2012.

3. Results and discussion

Test results obtained in the course of the experiment are presented in Table 5. Samples were arranged according to the sequence presented in the experiment plan (Table 4). An analysis of the test results from Table 5 indicates high efficiency of colour and UVA_{254} elimination. The issue of eliminating pollutants measured with the COD index looks slightly worse in this respect. Based on the obtained results, developed a mathematical model for the oxidation process of landfill leachates originating from Janczyce, with the use of K_2FeO_4 as an oxidant and coagulant.

The best remediation outcomes were obtained when eliminating colour in sample no. 10. At a potassium ferrate(VI) dose equal to 4.5 $g·L^{-1}$ and pH = 5.01, and after 60 min of

Table 5
Results of testing landfill leachate oxidation using K_2FeO_4

Sample		COD	UV_{254}	Color	Cd	Cu	Cr	Ni	Pb	Zn	Co
		(mg·L^{-1})	–	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})
1	Mean	1,060	1.49	166	0.0001	0.0755	1.6136	0.0996	0.0110	0.3500	0.0085
	Standard deviation	39	0.03	7	0.0001	0.0009	0.0323	0.0033	0.0002	0.0105	0.0003
2	Mean	1,076	1.80	195	0.0001	0.0858	2.2955	0.1913	0.0033	0.2730	0.0021
	Standard deviation	36	0.04	8	0.0001	0.0020	0.0643	0.0061	0.0001	0.0082	0.0001
3	Mean	1,152	2.10	276	0.0001	0.0791	2.4018	0.0967	0.0098	0.2916	0.0037
	Standard deviation	36	0.05	11	0.0001	0.0015	0.0600	0.0063	0.0002	0.0085	0.0001
4	Mean	1,612	2.02	285	0.0001	0.0676	2.6330	0.0933	0.0039	0.2826	0.0003
	Standard deviation	49	0.05	11	0.0001	0.0011	0.0685	0.0061	0.0001	0.0081	0.0001
5	Mean	1,012	1.67	149	0.0001	0.0931	1.4574	0.0945	0.0058	0.2629	0.0039
	Standard deviation	35	0,05	6	0.0001	0.0019	0.0349	0.0060	0.0001	0.0075	0.0001
6	Mean	1,004	1.59	162	0.0001	0.0747	1.2833	0.1121	0.0084	0.3383	0.0083
	Standard deviation	35	0.04	6	0.0001	0.0016	0.0269	0.0059	0.0002	0.0101	0.0002
7	Mean	1,452	2.04	276	0.0001	0.0687	1.7868	0.0492	0.0059	0.3240	0.0001
	Standard deviation	46	0.05	11	0.0001	0.0011	0.0447	0.0033	0.0001	0.0097	0.0001
8	Mean	1,040	2.60	437	0.0001	0.0926	1.6043	0.0986	0.0201	0.4327	0.0021
	Standard deviation	36	0.07	17	0.0001	0.0017	0.0417	0.0068	0.0004	0.0129	0.0001
9	Mean	1,024	2.47	318	0.0001	0.0672	1.8682	0.0406	0.0128	0.2820	0.0001
	Standard deviation	36	0.06	13	0.0001	0.0009	0.0523	0.0039	0.0003	0.0085	0.0001
10	Mean	964	1.40	69	0.0001	0.0864	0.0529	0.2559	0.0077	0.3339	0.0064
	Standard deviation	31	0.04	3	0.0001	0.0016	0.0014	0.0087	0.00002	0.0101	0.0002
11	Mean	1,060	2.79	509	0.0001	0.1155	0.7214	0.1050	0.0117	0.2985	0.0039
	Standard deviation	33	0.07	19	0.0001	0.0013	0.0180	0.0032	0.0002	0.0089	0.0001
12	Mean	1,056	2.79	525	0.0001	0.0880	0.8267	0.0670	0.0134	0.3151	0.0012
	Standard deviation	37	0.07	22	0.0001	0.0014	0.0190	0.0020	0.0003	0.0094	0.0001
13	Mean	1,060	2.69	521	0.0057	0.1277	0.5616	0.2114	0.0979	0.3111	0.0080
	Standard deviation	36	0.06	21	0.0001	0.0028	0.0123	0.0068	0.0019	0.0090	0.0003
14	Mean	1,032	1.92	274	0.0001	0.0691	2.7632	0.1088	0.0021	0.3248	0.0001
	Standard deviation	36	0.05	9	0.0001	0.0012	0.0773	0.0033	0.0001	0.0096	0.0001
15	Mean	1,224	3.40	1116	0.0001	0.1104	0.1938	0.1049	0.0992	0.4410	0.0064
	Standard deviation	43	0.08	41	0.0001	0.0014	0.0052	0.0037	0.0019	0.0100	0.0002
16	Mean	960	2.14	306	0.0001	0.0922	0.4591	0.1604	0.0096	0.3227	0.0015
	Standard deviation	33	0.06	11	0.0001	0.0020	0.0124	0.0058	0.0002	0.0085	0.0001
Raw landfill leachate	Mean	1,742	3.44	2442	0.0087	0.1269	0.0780	0.0549	0.0607	0.3006	0.0062
	Standard deviation	63	0.09	85	0.0001	0.0027	0.0023	0.0021	0.0012	0.0090	0.0001

landfill leachate oxidation, it was possible to reduce to initial value equal to 2,442 mg·L^{-1} down to 68.6 mg·L^{-1}. This means that as much as 97.2% solution colour was removed during the process. The highest effectiveness in terms of removing UVA_{254} absorbing substances from leachates was also achieved for sample no. 10. UV absorbance for this sample amounted to 1.396, which corresponds to eliminating almost 60% of this index. Evaluating COD content in the samples after the oxidation process is average. The best results of COD elimination were obtained for sample no. 16. At a potassium ferrate(VI) dose equal to 2.0 g·L^{-1}, pH = 4.5 and after 90 min of landfill leachate oxidation, it was possible to reduce COD from the initial value equal to L^{-1} down to 960 mg·L^{-1}. This means that the process removed only 45% of COD. On the other hand, the issue associated with heavy metal elimination during the landfill leachate pre-treatment process looks interesting. In general, it can be seen that metal concentrations in raw leachates are relatively low. In this regard, the pre-treatment process causes certain changes, and so it was possible almost the entire cadmium content from the leachates. When averaging metal content within this experiment, one can indicate that leachate composition was improved in the case of cadmium, copper, lead and cobalt. A slight deterioration of effluent quality was recorded for zinc. Whereas in terms of nickel and, particularly, chromium content, the researchers recorded a significant deterioration in leachate composition. It is especially evident for nickel in sample no. 10 and chromium in sample no. 7. Fig. 1 shows the relationship between potassium ferrate(VI) dose and chromium content in post-treatment leachates.

The value of the correlation coefficient $R = 0.8842$ may prove that the source of chromium in the tested samples are contaminants contained in potassium ferrate(VI).

Based on the obtained test results and using the Statistica 12 software by StatSoft Inc., develop correlation models using the variance analysis method. The COD of leachates after remediation using K_2FeO_4 is impacted by input values shown in Fig. 2. However, the Pareto test demonstrated lack of a statistically significant influence of the time variable and its linear combination with pH and K_2FeO_4 concentration on standardized estimation results. In the light of the above, further considerations were conducted after eliminating the impact of these factors. The conducted variance analysis showed a considerable impact of the K_2FeO_4 dose, as well as its product with pH on the COD of post-remediation leachates, with an assumed probability of a type I error equal to 0.05. Variance analysis results for COD are shown in Table 6. The equation for the COD model as a function of pH and K_2FeO_4 concentration is as follows:

$$\left[\text{COD}\right] = 1276.477 - 205.531\left[K_2FeO_4\right] + 21.897\left[K_2FeO_4\right]^2 + 11.854\left[K_2FeO_4\right]\text{Ph} \quad (1)$$

A graph of COD as a function of pH and K_2FeO_4 concentration is shown in Fig. 3. Best effects were obtained for pH < 4.2 and a potassium ferrate(VI) dose of $2.0\ g\cdot L^{-1} < D < 6\ g\cdot L^{-1}$. An already significant improvement of leachate composition was recorded within this range of input value variance.

Consistency of COD predictions relative to experimental data is shown in Fig. 3.

The adaptation of the COD model to the results obtained during the experiment is average. The absence of a time variable and its combination with pH, and, especially, with K_2FeO_4, does not have a positive effect on predictor precision (Fig. 4).

The variance analysis method (Tables 7 and 8) was also applied to evaluate the impact of input values on UVA_{254} and colour of leachates treated using K_2FeO_4. Similarly to developing the COD = *f*(pH, dose, time) model, employed the regressor reduction method (Table 6) when constructing this model, which enables utilizing only these factors that are statistically significant with the assumed $p = 0.05$.

Analysis results are shown in Figs. 5–9. Mathematical models were expressed through Eqs. (2) and (3). Oxidant dose and process duration also significantly impact UVA_{254} values. The best results were obtained at potassium ferrate(VI) doses within the range of $5\ g\cdot L^{-1} < D < 6.5\ g\cdot L^{-1}$ and a duration below 50 min. Slightly better results were obtained with respect to eliminating leachate colour, where

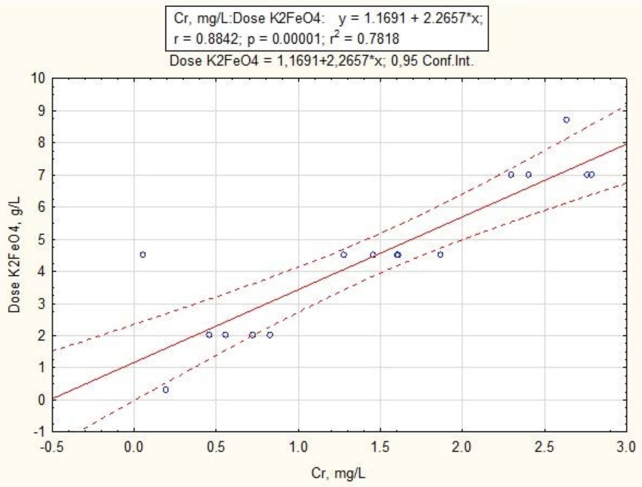

Fig. 1. Relationship between potassium ferrate(VI) dose and chromium content in post-treatment leachates.

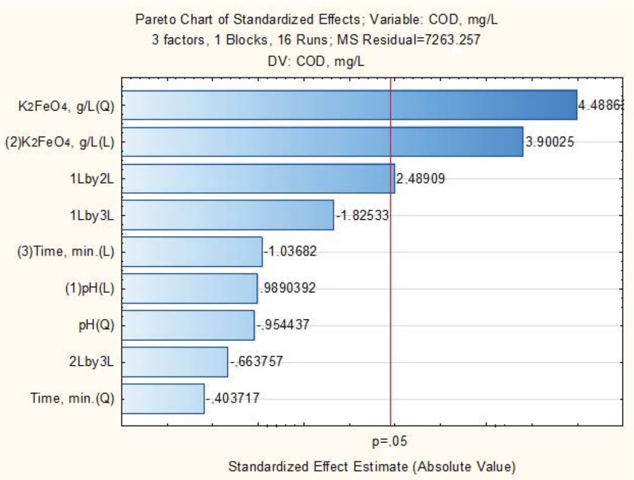

Fig. 2. Standardized COD estimation effects obtained with the variance analysis method.

Table 6
COD variance analysis results

Factor	Effect estimates; Var.: COD, mg·L⁻¹; $R^2 = 0.80658$; Adj. 0.75823 (K_2FeO_4) 3 factors, 1 blocks, 16 run; MS residual = 7,709.102 DV:COD, mg·L⁻¹									
	Effect	Std. Err.	*T*(12)	*p*	–95, % Cnf. Limt.	+95, % Cnf. Limt.	Coeff.	Std. Err. Coeff.	–95, % Cnf. Limt.	+95, % Cnf. Limt.
Mean/Interc.	995.0396	30.62355	32.49263	0.000000	928.3167	1,061.763	995.0396	30.62355	928.3167	1,061.763
(2) K_2FeO_4, $g\cdot L^{-1}$; (L)	179.9719	47.53881	3.78579	0.002596	76.3937	283.550	89.9859	23.76940	38.1968	141.775
K_2FeO_4, $g\cdot L^{-1}$; (Q)	273.7110	50.07916	5.46557	0.000144	164.5978	382.824	136.8555	25.03958	82.2989	191.412
1L by 2L	150.0000	62.08503	2.41604	0.032552	14.7283	285.272	75.0000	31.04251	7.3642	142.636

already at values lower than 5 g of $K_2FeO_4 \cdot L^{-1}$, and particularly within the range of 3.5 $g \cdot L^{-1} < D < 7$ $g \cdot L^{-1}$, the experiments provided excellent remediation effects, the best in terms of indicators assessed within the study ($\eta > 95\%$). This is demonstrated in Fig. 8. However, please note that the pH independent variable did not exhibit any significant impact on the colour estimator. However, despite the above, it can be noted that there is a certain area of elevated colour elimination, respectively, for pH < 3.0, where K_2FeO_4 oxidation capacity increases and for pH > 4.5, where the coagulation process will be the basic discolouration mechanism. This dual nature of potassium ferrate(VI) is its advantage, which under optimal conditions can contribute to it providing landfill leachate treatment results that are competitive to classic oxidants.

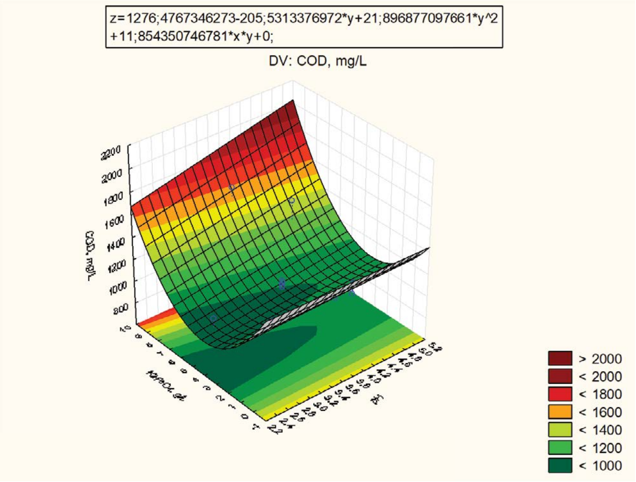

Fig. 3. Graph of COD as a function of pH and K_2FeO_4 concentration.

The equation for UV absorbance model as a function of K_2FeO_4 concentration is as follows:

$$\left[\mathrm{UVA}(254)\right] = 3.611824 - 0.684889\left[K_2FeO_4\right] + 0.060218\left[K_2FeO_4\right]^2 + 0.000012t^2 \tag{2}$$

The equation for the colour variability model as a function of K_2FeO_4 concentration is as follows:

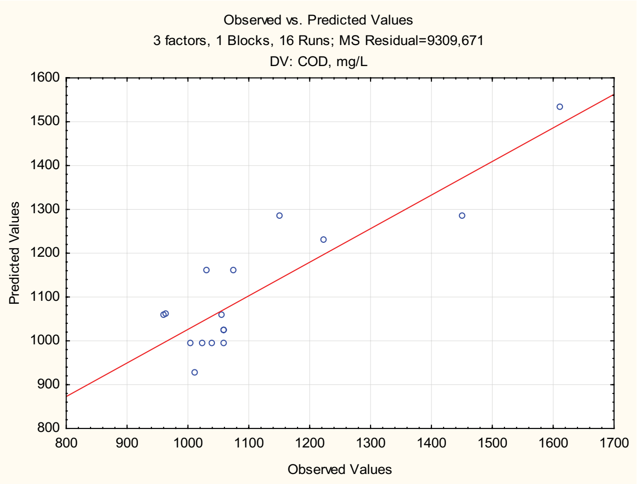

Fig. 4. COD prediction relative to experimental data.

Table 7
Variance analysis results for UVA_{254}

Factor	Effect estimates; Var.: UVA_{254}, $mg \cdot L^{-1}$; *R*-sqr. = 83,084; Adj. 78,855 (K_2FeO_4) 3 factors, 1 blocks, 16 run; MS residual = 0958718 DV:UVA_{254}									
	Effect	Std. Err.	*T*(12)	*p*	–95, % Cnf. Limt.	+95, % Cnf. Limt.	Coeff.	Std. Err. Coeff.	–95, % Cnf. Limt.	+95, % Cnf. Limt.
Mean/Interc.	1.315666	0.148917	8.83488	0.000001	0.99120	1.640128	1.315666	0.148917	0.991203	1.640128
(2) K_2FeO_4, $g \cdot L^{-1}$; (L)	–0.714617	0.167645	–4.26267	0.001102	–1.07988	–0.349348	–0.357308	0.083823	–0.539942	–0.174674
K_2FeO_4, $g \cdot L^{-1}$; (Q)	1.005999	0.184754	5.44507	0.000149	0.60345	1.408544	0.502999	0.092377	0.301727	0.704272
Time, min (Q)	0.897172	0.187426	4.78680	0.000443	0.48881	1.305538	0.448586	0.093713	0.244403	0.652769

Table 8
Colour variance analysis results

Factor	Effect estimates; Var.: UVA_{254}, $mg \cdot L^{-1}$; $R^2 = 0.83084$; Adj. 0.78855 (K_2FeO_4) 3 factors, 1 blocks, 16 run; MS residual = 0.0958718 DV:UVA_{254}									
	Effect	Std. Err.	*T*(12)	*p*	–95, % Cnf. Limt.	+95, % Cnf. Limt.	Coeff.	Std. Err. Coeff.	–95, % Cnf. Limt.	+95, % Cnf. Limt.
Mean/Interc.	205.159	43.29484	4.73865	0.000387	111.626	298.692	205.159	43.29484	111.626	298.69221
(2) K_2FeO_4, $g \cdot L^{-1}$; (L)	–327.635	67.20923	–4.87485	0.000303	–472.832	–182.439	–163.818	33.60462	–236.416	–91.2193
K_2FeO_4, $g \cdot L^{-1}$; (Q)	337.228	70.80072	4.76306	0.000371	184.272	490.183	168.614	35.40036	92.136	245.0917

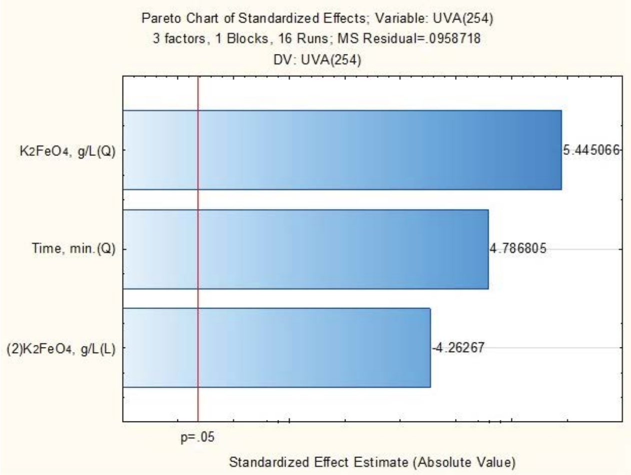

Fig. 5. Standardized UVA_{254} estimation effects obtained through the variance analysis method, after employing the regressor reduction method.

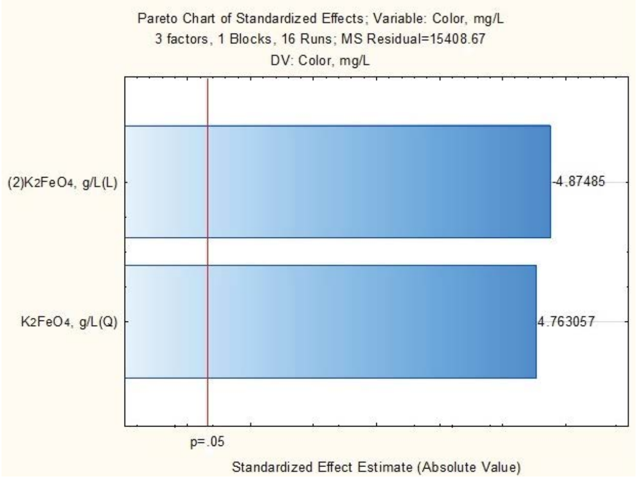

Fig. 7. Standardized colour estimation effects obtained using the variance analysis method, after employing the regressor reduction method.

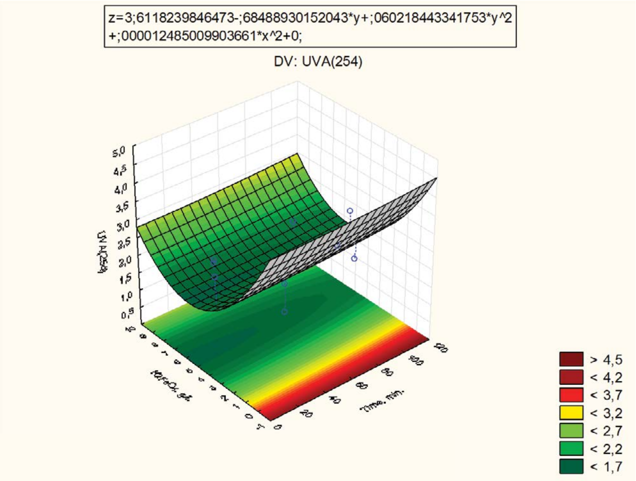

Fig. 6. Graph of UVA_{254} as a function of time and K_2FeO_4 concentration.

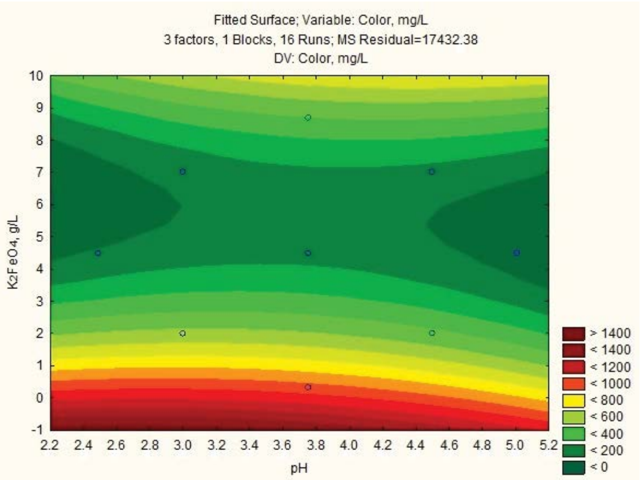

Fig. 8. Response surface for the colour = $f(\text{pH}, C_{K2FeO4})$ system.

$$[\text{Colour}] = 1046.340 - 308.331[K_2FeO_4] + 26.978[K_2FeO_4]^2 \tag{3}$$

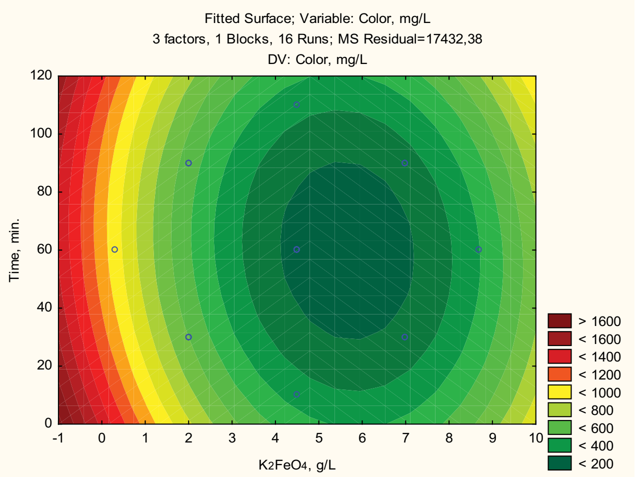

Fig. 9. Response surface for the colour = $f(C_{K2FeO4}, \text{time})$ system.

4. Conclusions

The results above confirm the effectiveness of employing potassium ferrate(VI) for the treatment of such a complex medium as landfill leachates. However, it requires further research with respect to different leachates, in order to select optimal process conditions. The best COD elimination results (COD – 45%) were obtained for a potassium ferrate(VI) dose equal to 2.0 g·L^{-1}, pH = 4.5 and after 90 min of landfill leachate oxidation. The best leachate pre-treatment effects were achieved in terms of colour elimination, where managed to reduce the colour by 97% and UV absorbance by approx. 60% at a potassium ferrate(VI) dose equal to 4.5 g·L^{-1} and, pH = 5.01 and landfill leachate oxidation duration of 60 min. However, this does not represent a significant improvement over the parameters that achieved the best color reduction and UV_{254} effects. Considering the above, the optimal parameters for the treatment of landfill leachate are dose equal to 4.5 $g \cdot L^{-1}$ and, pH = 5.01 and landfill leachate oxidation duration of 60 min. A change in heavy metal concentration was recorded in the course of the pre-treatment process. It was possible to remove almost the entire cadmium content from the leachates and significantly reduce copper, lead and cobalt contents. A slight deterioration of effluent quality was recorded for zinc. Whereas in terms of nickel and, particularly, chromium content, the researchers recorded a significant deterioration in leachate composition. Because compound reactivity grows with temperature, increasing the temperature gives hope for a real improvement of landfill leachate treatment effectiveness in terms of COD elimination when using potassium ferrate(VI), and such research will be conducted in the future. This dual nature of potassium ferrate(VI) is its advantage, which under optimal conditions can contribute to it providing landfill leachate treatment results that are competitive to classic oxidants. The potassium ferrate(VI) can partially replace traditional oxidants, such as ozone, sodium hypochlorite, potassium permanganate and others in the future.

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