

Removal of organic and nitrogen compounds from landfill leachates by coagulation, Fenton, and adsorption coupling processes

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ABSTRACT

This paper aims at assessing organic matter and nitrogen compounds removal as well as identifying the organic compounds present in the leachate treated by an integrated physico-chemical system (coagulation–Fenton oxidation (FO)–adsorption). The raw and treated leachate were analyzed for the followings parameters: chemical oxygen demand (COD), biochemical oxygen demand (BOD₅), and ammonium nitrogen (N–NH₄⁺). The adsorption treatment was based on powdered zeolite 4 Å (PZ) and the commercially powdered activated carbon (PAC). The identification of organic compounds using gas chromatography coupled to the mass spectrometry (GC-MS). The raw leachate is characterized by high concentrations of organic load expressed in COD (16,200–26,200 mg O₂ L⁻¹) and a high ammonium nitrogen load (1,623–2,120 mg L⁻¹). The removal of leachate treatment was defined for raw and treated leachate. PZ adsorption removed the highest nitrogen pollutants then PAC adsorption. In the coagulation–FO–PZ adsorption, the removal efficiency reached 93% for N–NH₄⁺, 97% for COD, and 92% for BOD₅ and during coagulation–FO–PAC adsorption, the removal efficiency was equal to 59% for N–NH₄⁺, 98% for COD, and 95% for BOD₅. GC-MS analysis showed that both integrated systems studied promoted a high reduction of organic compounds from leachate (99%).

Keywords: Adsorption; Coagulation; Fenton; Landfill leachate; GC-MS

1. Introduction

Leachate generated from landfill sites is categorized as complex wastewater. The composition of landfill leachate depends on many factors such as type of the wastes, age of the dump, degradation phase, compaction level of the wastes, and the seasonal rainfall variations. Landfill leachate may contain high contents of salts, heavy metals, ammoniacal-nitrogen, organic, and inorganic compounds.

The disposal of landfill leachate into the environment without any kind of treatment may cause contamination of surface groundwater and water wells [1]. For these reasons,

the application of an adequate treatment process can provide an effective treatment of pollutants in order to fulfill the strict environmental rule and reduce the effect on the environment [2].

Many organic compounds with low and medium polarity have been identified in landfill leachate like alcohol, phthalates, carboxylic acids, aromatic, and polyaromatic hydrocarbons and PAHs [3–6]. In the leachate, organic compounds may derive from the landfill waste and the biological degradation products. The occurrence of the identified compounds can contaminate the receiving water due to their high toxicity and carcinogenic effect [7]. In this case, the

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identification and quantification of organic compounds in leachate is a priority owing to their toxicity.

Leachate generated from an old landfill site is more complex as compared to that generated from a new landfill site as it is practically impossible to be effectively treated via biological processes [8]. Various methods, such as precipitation, adsorption, oxidation, evaporation, reverse osmosis, and ion exchange have been exercised to remove diverse pollutants that originated from old landfill leachate [9].

Biological treatment can be applied successfully to younger leachate with high BOD₅/COD (biochemical oxygen demand/chemical oxygen demand) ratio, high C/N ratio. Thus, poor biodegradability and high ammonia concentration can reduce the performance of biological treatment. It was showed that inhibition might take place in the range of 1,500–7,000 mg L⁻¹ of total ammonia nitrogen [10].

Consequently, the treatment of landfill leachate by biological treatment may be costly and complicated. At present time, there are various techniques available for the treatment of landfill leachates by conventional treatment technologies including chemical oxidation, advanced oxidation, coagulation, and adsorption processes but they cannot be effectively used individually. Thus, the application of various physico-chemical combinations could be a good alternative for the treatment of landfill leachate [11]. Combination of these processes reduces the drawbacks of each single process.

It is well-known that coagulation–flocculation process is the most used treatment in the landfill leachate treatment plants in controlled discharges of Tunisia. Coagulation–flocculation process is simple and inexpensive technology with low environmental impact [12]. Coagulation–flocculation process has been used successfully for the treatment of wastewater. It was effective in the elimination of pollutant charges and the improvement of biodegradability of effluent [13]. Coagulation–flocculation was successful for COD and color removals from stabilized leachate. However, it could not treat NH₃–N effectively [14].

According to literature, advanced oxidation processes (AOP) (such as electrochemical oxidation, Fenton oxidation, photocatalysis, etc.) have been proved highly capable and efficient in reducing refractory organic substance and color as well as in oxidizing ammonia from raw and pretreated landfill leachate [9,15].

Among AOPs, heterogeneous photocatalysis have proven to be of interest due to their efficiency in degrading recalcitrant organic compounds. Nowadays, several semiconductors (TiO₂, ZnO, Fe₂O₃, CdS, and ZnS) can act as photocatalysts. TiO₂ has been most commonly studied due to its ability to break down organic pollutants and even achieve complete mineralization [16]. It was reported that a rational combination of graphitic carbon nitride (g-C₃N₄) with boron nitride quantum dots (BNQDs) improved photocatalytic activity for molecular oxygen activation, and provided a novel metal-free and highly efficient photocatalyst for environmental remediation and energy conversion [17]. Nevertheless, advanced oxidation techniques result in high treatment cost and are generally used to obtain high purity grade water.

Chemical oxidation using the Fenton process has represented a suitable technology for the treatment of landfill leachate. This process is easy, clean, and effective.

This system used hydrogen peroxide (H₂O₂) for the treatment of a wide range of recalcitrant compounds.

The activation of H₂O₂ by ferrous salts promotes the formation of the high hydroxyl radical (*OH). It is able to oxidize different organic substances and mineralize them in CO₂, H₂O, and inorganic ions or transform them into simple biodegradable organic substances [7].

Adsorption is an effective method used successfully for the post-treatment of landfill leachate. Adsorption is applied to remove large amounts of organic and inorganic pollutants. The limitations of this technology are the eco-friendly disposal of spent adsorbents, excessive maintenance costs, and pretreatment of wastewater to reduce the SS under acceptable range before it is fed into the adsorption column [18].

It is well-known that activated carbons are the most effective adsorbents for the removal of organic pollutants from the aqueous or gaseous phase. However, its application is very expensive. Recently, the use of hydrophobic zeolites in the adsorption process is an attractive method to remove ammonia, COD, and other inorganic pollutants from leachate or other wastewaters. Zeolites are characterized by their high thermal stability and resistance to humidity and their non-flammability [19].

Generally, physicochemical treatment processes alone are not preferred, despite their effectiveness, due to the high costs involved [18]. Therefore, the application of combined treatment processes can be a suitable solution for the efficient removal of pollutants.

To the best of our knowledge, we found no papers assessing the removal of organic compounds identified through gas chromatography coupled to the mass spectrometry (GC-MS) of landfill leachate through coagulation combined with FO and adsorption. Due to the complex and variable composition of leachates and the shortage of studies concerning their treatment using coagulation combined with FO and adsorption. This paper aims at assessing organic matter and nitrogen compounds removal as well as identifying the organic compounds present in the leachate from the sanitary landfill of Tunisia (Bizerte), through GC-MS, before and after its treatment with coagulation, FO, and adsorption.

2. Materials and methods

2.1. Physical chemical characteristic of landfill leachate

Leachate used for research derived from the sanitary landfill leachate, located in Bizerte, in the northeastern part of Tunisia (37°16'N; 9°52'E). The landfill has been used for the deposition of waste since 2008. The landfill site received an average of 3,000 tons of wastes per day. Nowadays, the leachates are collected and stored in special storage tanks. The location is characterized by a warm and temperate climate. In winter, there is much more rainfall in Bizerte than in summer. The Köppen–Geiger climate classification is Csa. The average annual temperature is 18.0°C in Bizerte. The average annual rainfall is 527 mm. The relative humidity of the area is relatively high, with a maximum in December (80.6%) and a minimum in July (66.5%).

The sample of leachate were collected from the storage tank and stored in 40 L polyethylene carboys. They

were transported, stocked at 4°C, and analyzed within 2 d. The landfill leachate was analyzed in accordance with French standard NF XPT 90-210 [20] for the concentration of NTK, N-NH_4^+ , COD, BOD_5 , SS, turbidity and pH. Parameters were achieved in three replicates for raw and treated leachate. The composition of raw landfill leachate is indicating in Table 2.

Raw and treated leachate were analyzed with an Agilent series 6890 gas chromatograph coupled to a mass-selective detector. Samples were separated on a 30 m \times 250 μm \times 0.5 μm fused silica capillary column (JW Scientific DB-5MS). Samples (1 μL) were injected at an injector temperature of 250°C with a rate of flow of 1.07 mL min^{-1} . Identification of organic compounds was carried out from mass spectra, by comparison with library data; retention data was used for confirmation when literature data or standard compounds were available. The determination of COD was performed using a Thermo Scientific Shimadzu U 1000 spectrophotometer. A 2020 turbidimeter (LaMotte) was used for the indication of the turbidity. The determination of NTK and N-NH_4^+ was performed using an automated apparatus (Buchi, Switzerland). The value of pH was carried out by pH meter (INOLAB WTW720). The determination of SS was assessed by drying at 105°C.

2.2. Experimental procedure

The treatment of wastewater was performed in two integrated systems, which were a combination of physical chemical processes; coagulation–FO–PAC adsorption and coagulation–FO–PZ adsorption.

The first stage of experiment consisted of the treatment of raw leachate by the coagulation process. The coagulation process was conducted by jar test equipment with six beakers with a capacity of 1 L. The experimental process was controlled by the time and intensity of mixing. The experiment process consisted of a rapid mixing step for 5 min at 200 rpm, the following slow mixing stage for 60 min at 60 rpm. The coagulant used for the experiment was the commercially alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, Merk). The coagulant is well-known for its ability for the neutralization and destabilization of colloids contained in the wastewaters. For the conduct of tests, a dose range of 0.2–1 g L^{-1} from a solution of alumina sulfate of 100 g L^{-1} was used. The optimum dose was 0.6 g AL^{3+} L^{-1} . After 2 h settling period, the supernatant was withdrawn from the beakers and was used for analysis.

In the second stage of the experiment, the leachate was cleaned by the Fenton oxidation (FO) process. The tests were performed in 1 L beakers in an orbital shaker at 10 rpm. The sample was treated with iron sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, Fe = 20%) and hydrogen peroxide (H_2O_2 , 30%). The FO was conducted at acidic pH 3. The optimum dose was equal to 1.2 g L^{-1} of Fe^{2+} and 2.8 g L^{-1} of H_2O_2 .

The last stage of research, the treated leachate by coagulation and FO were submitted to the adsorption process. The experiments were conducted with an appropriate amount of powdered zeolite PZ (zeolite 4A, aluminosilicate, $[\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})] \cdot 27\text{H}_2\text{O}$) and powdered activated carbon (PAC) (Kanto Chemical Co., Inc., Cica reagent).

The mixture was stirred at 150 rpm for 1 h. The stirring temperature was adjusted to 20°C. The optimum dose was

30 g L^{-1} for PZ and 20 g L^{-1} for PAC. The supernatant was recovered for further analysis. The optimum conditions used in this study were determined according to the result of the highest removal of COD obtained from the preliminary tests obtained in previous work [21]. After each treatment was applied, the efficiency of the removal process was evaluated via COD, BOD_5 , N-NH_4^+ , and organic compounds identified using GC-MS. The main characteristic of the adsorbents used in this research are presented in Table 1.

3. Results and discussions

3.1. Characterization of landfill leachate

The results of physicochemical characterization regarding the raw leachate samples are shown in Table 2. The leachate is shown to contain a high inorganic and organic charge. The leachate samples were alkaline with a pH range of 7.74–8.11. The leachate is characterized by high concentrations of organic load expressed in COD (16,200–26,200 mg O_2 L^{-1}). A high ammonium nitrogen load (1,623–2,120 mg L^{-1}). The dark brown color of the liquid is due to the presence of humic substances, phenolic, heterocyclic, aromatic hydrocarbons, carboxylic acids, and carbohydrates. Likewise, the high value of electrical conductivity of 16.8–19.6 mS cm^{-1} suggested the presence of high loads of dissolved inorganic materials in the leachate [22]. This may be attributed to the decrease in the concentration of free volatile acids due to anaerobic composition, as fatty acids can be partially ionized and contribute to higher pH values. The TSS represents the totality of the insoluble mineral and organic particles, floating, or suspended, that are contained in leachate. They are largely biodegradable. The average TSS content ranged from 250 to 491 mg L^{-1} [23]. The ratio of biodegradability varied between 0.15 and 0.19 revealed that the leachate from the landfill of Bizerte presents a high concentration of non-biodegradable organic matter in relation to the biodegradable ones. The metallic pollutants are distinguishable from the other chemical pollutants by a weak biodegradability and an important ability of bioaccumulation along the tropical chain, which could be harmful to the population as well as to the fauna and flora [24]. The concentrations of pollutants characteristic of the raw landfill leachate exceed the standardized indices and this interdicts their discharge into natural receivers and sewers. Results indicate the need to have treatment for this effluent.

3.2. Landfill leachate treatment

Table 3 presents the removal of Ammonium nitrogen, turbidity, BOD, and COD after each treatment. In the coagulation treatment, pH plays an important role since the coagulation takes place within a specific pH range for each coagulant. In the present study, a wide range of pH between 2 and 8 was selected. The pH of the leachate after the coagulation process decreased to 5.5. The results corroborate with the results of other studies. It was reported that the use of alum as a coagulant affected the pH of landfill leachate, it decreased to 5.3 and 6.4, respectively [25]. Li et al. [1] showed that removal efficiency is better at acidic than the basic condition. The equilibrium concentration

Table 1
Characteristic of adsorbents used in leachates treatment

Adsorbent	BET surface area (m ² g ⁻¹)	Cation-exchange capacity, CEC (meq g ⁻¹)	Application
Zeolite 4A	725	5.47	Adsorption, ion exchange, catalysis
Activated carbon	1,031	2.42	Adsorption, catalysis, purification

Table 2
Physicochemical characterization of raw leachates

Indicator	Unit	Raw municipal landfill leachates	Indices of sewage pollution which is carried away to the sewers (NT 106.02)	Indices of sewage pollution which is carried away to the natural receiver
pH	–	7.74–8.11	6.5–9	6.5–8.5
Turbidity	(NTU)	390–422	ns	ns
Electrical conductivity	(mS cm ⁻¹)	16.8–19.6	ns	ns
Salinity	(g L ⁻¹)	14.28–16.66	ns	ns
COD	(mg O ₂ L ⁻¹)	16,200–26,200	1,000	90
BOD ₅	(mg O ₂ L ⁻¹)	2,430–5,200	400	30
BOD ₅ /COD	–	0.15–0.19	ns	ns
Nitrogen	(mg L ⁻¹)	1,770–2,350	100	ns
Ammonium	(mg L ⁻¹)	1,623–2,120	ns	ns
phosphorus	(mg L ⁻¹)	13.64–14.80	10	0.002
Total suspended solids	(mg L ⁻¹)	250–491	400	30
Dry matter	(g L ⁻¹)	16.15–19.20	ns	ns
Mn	(mg L ⁻¹)	0.15–0.18	1	0.5
Cu	(mg L ⁻¹)	0.087–0.089	–	0.5
Fe	(mg L ⁻¹)	6.87–7.90	5	1
Al	(mg L ⁻¹)	1.73–1.80	10	5
Cr	(mg L ⁻¹)	1.64–1.69	2	0.5

ns: not standardized.

Table 3
Removal of ammonium nitrogen, turbidity, BOD, and COD after each treatment process

	Leachate after treatment with						Removal (%)			
	Raw leachate	Coag.	FO	PACAd	PZAd	Limit	Coag.	FO	PACAd	PZAd
pH	7.74 ± 0.4	5.5 ± 0.3	3 ± 0.11	8.6 ± 0.3	6.5 ± 0.22	6.5–9	–	–	–	–
COD (mg L ⁻¹)	26,200 ± 130	12,058 ± 75	4,990 ± 45	398 ± 12	620 ± 22	1,000	53	81	98	97
BOD (mg L ⁻¹)	5,200 ± 65	4,341 ± 55	1,982 ± 23	220 ± 9	391.3 ± 12	400	16	61	95	92
BOD/COD	0.19	0.36	0.4	0.55	0.63	–	–	–	–	–
Ammonium nitrogen (mg L ⁻¹)	1,623 ± 21	1,406 ± 19	931 ± 25	660 ± 22	107.3 ± 27	100	13	42	59	93
Turbidity (NTU)	422 ± 15	48 ± 4.20	27 ± 1.7	0.61 ± 0.02	9 ± 0.7	–	88	93	99	97

Coag: coagulation; FO: Fenton oxidation; PAC Ad: PAC adsorption; PZ Ad: PZ adsorption; Limit: The indices of sewage pollution which is carried away to the sewers (NT 106.02).

was controlled by $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$ concentration at alkaline medium ($\text{pH} > 7.2$) and $\text{Al}(\text{OH})_3$ and $\text{Al}_{13}(\text{OH})_{34}^{7+}$ concentration in the pH range 7.2 to 5.6 [26]. Amor et al. [27] indicated that the highest removal of COD occurs at pH 6. At this pH, the process occurs probably due to adsorption and charge neutralization and enmeshment in sweep flocculation.

The pH value decreased to three after the FO process. The decrease of pH after FO was reported by other research. It showed a decrease of pH from 8.3 to 3.9 after FO [7].

Results indicated that in the FO process pH in the acidic range strongly favors oxidation. A pH below optimal conditions can inhibit oxidation for three reasons. First, the cleaning effect of H^+ on $\cdot\text{OH}$ becomes more efficient at lower pH. Second, at low pH, the $[\text{Fe}(\text{OH})]^{2+}$ formed reacts slowly with H_2O_2 producing less $\cdot\text{OH}$. Third, acidic pH can inhibit the reaction between Fe^{3+} and H_2O_2 . A pH above optimal can prohibit Fenton oxidation. Several reasons for this inhibition have been proposed. First, the oxidation potential of $\cdot\text{OH}$ radical decreases with increasing pH. Second, the ferrous catalyst is deactivated with the formation of ferric oxyhydroxide at pH above 5. Finally, the lack of H^+ can inhibit the decomposition of H_2O_2 to minimize the production of $\cdot\text{OH}$ [28].

During PAC adsorption process, the value of pH increased to 6.5 and during PZ adsorption, it increased to 8.6. According to the Polish legalization, the value of pH did not exceed the permissible values of 6.5–9.0 in the treated wastewater collected to the sewers [28].

The value of COD decreased after coagulation to 12,058 $\text{mg O}_2 \text{ L}^{-1}$ with a percentage of 53%. The effectiveness of the use of alum in the removal of the initial COD could reach 53% [1] 60% [22], respectively. Gandhimathi et al. [29] reported that alum has better COD removal efficiency than that of FeCl_3 . At optimum conditions, 75% COD removal was achieved using alum and 59% in case of treatment with FeCl_3 . This is due to difference in hydrolysis of these coagulants.

Composite polyaluminum silicate chloride (PASiC) was used in non-organic matter (NOM) removal from raw surface water. The results demonstrate that PASiC coagulant was capable of removing TOC, COD, UV, and turbidity from raw water by 93.77%, 93.5%, 63%, and 95%, respectively [30]. The results demonstrated the significant advantage of PASiC compared to Alum coagulant in the removal of COD and turbidity.

Leachate quality in terms of organic content can be greatly improved following Fenton treatment. Most important, the Fenton process can significantly remove recalcitrant and toxic organic compounds, and increase the biodegradability of organic compounds [31]. In our study, the COD removal efficiency during FO was equal to 59%, the overall removal of COD was 81%. These results are similar to another research. The treatment of textile wastewater by combined chemical coagulation (using poly aluminum chloride (PAC) as coagulant), electrocoagulation (using aluminum electrodes), and adsorption process (using pistachio nut shell ash) led to removal of both organic and inorganic compounds from textile wastewater. The results showed that COD, BOD_5 , and dye removals of 98%, 94.2%, and

99.9% were achieved by overall combined process (chemical coagulation, electrocoagulation, and adsorption processes) [32]. Other studies reported COD removal efficiencies range from 45% [33] to 81% [31].

It was reported that final BOD_5/COD ratio can be increased from less than 0.10 initially to values ranging from 0.14 to more than 0.60 [34], depending on leachate characteristics and dosages of Fenton reagents.

The combined process enhanced the biodegradability of leachates from 0.19 to 0.55 (with PAC) and 0.63 (with PZ). The results suggested the effectiveness of two systems studied. The results corroborate with another study. Amirhossein et al. [35] indicated that integrated sonocatalysis-biological systems improved biodegradability of landfill leachate. BOD_5/COD increased from 0.35 to 0.786 (with TiO_2) and 0.783 (with Zn O).

The final concentration of COD after adsorption was equal to 398 $\text{mg O}_2 \text{ L}^{-1}$ with PAC adsorption. The use of PZ in current study was less efficient. The final concentration of COD after PZ adsorption was equal to 620 $\text{mg O}_2/\text{L}$. The final COD did not exceed the permissible values of 1,000 $\text{mg O}_2 \text{ L}^{-1}$ in the treated wastewater collected to the sewers [28]. The reason for this efficiency may be that the effluent from Fenton leachate treatment contains a high fraction of low molecular organics, which may be efficiently removed by adsorption.

Activated carbon is an extremely powerful adsorbent for the removal of organic and inorganic pollutants from both gaseous and aqueous mixtures [36]. The surface of carbon is hydrophobic with higher pore sizes which make it appropriate for the adsorption of organic substances. However, numerous side factors are responsible for the limited use of PAC adsorption techniques such as precursor cost for preparing activated carbon and the need for frequent regeneration of columns or equivalently high consumption of PAC.

The coagulation–flocculation treatment removed approximately 13% of the initial ammonium nitrogen (1,406 $\text{mg NH}_4^+\text{L}^{-1}$). The ammonium–nitrogen removal efficiency during FO was equal to 42% (931 $\text{mg NH}_4^+\text{L}^{-1}$). It reached 59% (660 $\text{mg NH}_4^+\text{L}^{-1}$) after PAC adsorption and 93% (107.3 $\text{mg NH}_4^+\text{L}^{-1}$) after PZ adsorption. The use of PZ in the present study was more effective in the treatment of ammonium. These results were shown by other studies. Lim et al. [37] reported removal of ammoniacal nitrogen up to 96% by zeolite. These results could be attributed to the characteristic of the adsorbent. The surface of zeolite is hydrophilic with regular aligned molecular level pores and cationic exchange ability, which makes it a good adsorbent for metallic ions and catalysts. However, activated carbon does not have enough adsorption capacity for ammonia because it usually possesses a non-polar surface due to manufacturing conditions at high temperatures, which is a disadvantage for some applications because of poor interaction with some polar adsorbates.

Adsorbent's cost is one of the most crucial and important criteria to peer in to check the economic feasibility of the treatment process. For this reason, the application of natural and modified zeolite as ion exchange is one of the most effective technologies used to remove various contaminants due to their high ion exchange capacity, high specific

surface areas, and relatively low cost [31]. The results showed that the best efficiency of the treatment of landfill leachate was represented by an integrated system: coagulation–FO–PZ adsorption. The highest removal efficiency of 93% was obtained for ammonium nitrogen after PZ adsorption. There was also a high degree in the removal of BOD 92%, turbidity 97%, and COD 97%. The results showed a high removal of COD, turbidity, and BOD after coagulation–FO–PAC adsorption with a percentage of 97%, 97%, and 92%, respectively. However, a lower removal of $N-NH_4^+$ was observed (59%).

The obtained research results can lead to the conclusion that leachate treated by the process of PAC adsorption still did not meet the Polish standards of wastewater quality carried away to the sewer since the concentration of ammonium nitrogen was high.

3.3. Identification of organic compounds of the leachate by GC-MS

A total ion chromatogram of the organic compounds in landfill leachate is shown in Fig. 1, and this proved the good GC separation. Each peak was characterized by their retention times and mass spectra. Table 4 presents the predominant compounds identified through GC-MS in the leachate samples. The compounds with a probability of $\geq 95\%$ found through the Agilent serie 6890 mass spectral library and compared with the data from the literature were considered.

Twelve predominant compounds were identified in the raw leachate chromatogram. Among them, there were two phenolic compounds (4-2 bisphenol, 4-methyl phenyl), three aromatic hydrocarbons compounds (4-phenyl cyclohexane, 2,1-diphénylcyclobutane, 1,2-benzenedicarboxylic acid), an aliphatic hydrocarbon (2-bismethoxyethyl ester), four polyaromatic hydrocarbons (PAHs; butylphthalate, naphtalene, anthracene, 2 dicarboxylic acid monoester ethylexyl 1,2-benzene, and two alcohols (cholesterol, chlorocyclohexanol).

Among them phenolic compounds have been previously reported in the leachate of municipal and industrial landfills [38,39]. 4-2 bisphenol, 4-methyl phenyl may originate from different types of wastes. The origin of phenolic compounds in landfill leachate were considered to be incineration residues, solidified fly ash, and incombustibles. It was shown that the phenolic compounds are

present in plastics, resins, pesticides, medicinal drugs, disinfectants, and inwood preservative. These compounds are considered persistent in the environment, carcinogenic, mutagenic, and endocrine disruptors. Bisphenol A that had migrated from polycarbonate asks increased the rate of proliferation of human breast cancer cells MCF-7. Therefore, migration of bisphenol A form several kinds of plastic to foodstuffs is a significant problem [40].

Alcohols (cholesterol, chlorocyclohexanol) also have a significant fraction of raw leachate. Alcohols are mainly used as solvents in industrial degreasing; lacquering and coating application [38]. Alcohols are also derived from synthetic products of bacteria that contribute to the decomposition of organic matter in the landfill [41].

The hydrocarbons found in leachate may principally be biosynthesized on-site during degradation of organic matter. However, several of these compounds are also widely used and are persistent to biotransformation under the methanogenic conditions found in the landfill. A large group of compounds found in leachate originates from disposed wastes containing petroleum based solvent and/or naphhtelicoils [38].

The raw leachate revealed PAHs. PAH derived from the combustion of organic materials, including, for example, coal, petroleum products, woods, and waste products [42]. The origin of PAHs in the landfill can be from atmospheric deposition and via deposited material, such as tires, asphalt, used oil, and creosote treated wood. The presence of naphtalene in the leachate suggested a previous disposal of wastes containing low aromatic solvents [38]. Naphthalene is a substantial compound of creosote tar and asphalt material.

Phthalic acid diesters (PAEs) are amply used in polyvinyl chloride (PVC) plastics and other resins such as polyvinyl acetates, cellulotics, and polyurethanes, also in paints, adhesives, cardboard, lubricants, fragrances roofing, cladding materials, and sealants [43].

With time, the diester products may be landfilled. Degradation of diesters may be abiotic or biotic. The abiotic degradation (hydrolysis) of diesters to monoesters ranges from a few dimethyl phtalate (DMP) to thousands (DEHP). Biotic degradation of diesters to monoesters is an unspecific ester cleavage and the diester degradation capacity should be abundantly present in the environment since diester-degrading strains were relatively easy to isolate

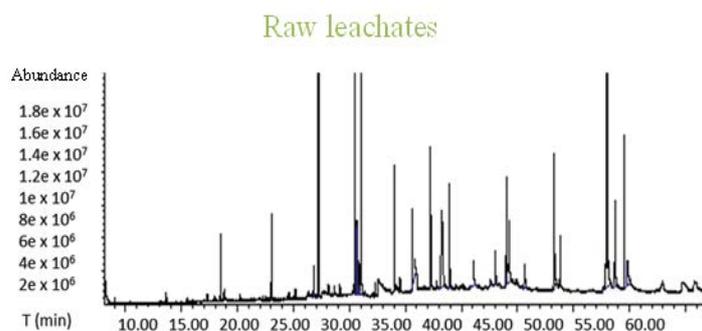


Fig. 1. Total chromatogram obtained by GC-MS with ethyl acetate from raw leachates, between retention times 10 and 60 min. The names of peak compounds are found in Table 4.

Table 4
Predominant compounds identified through GC-MS in the leachate samples

	Raw leachate	Leachate after treatment with				Removal (%) by			
		Coag.	Fent.	Ad PAC	Ad PZ	Coag.	Fent.	Ad PAC	Ad PZ
Naphtalene	13.4×10^6	11.4×10^6	8.9×10^6	NI	NI	14.86	33.44	100	100
Anthracene	15.8×10^6	13.1×10^6	6.9×10^6	NI	NI	17.18	56.38	100	100
4-2 Bisphenol	16.9×10^6	15.1×10^6	13.2×10^6	NI	NI	10.31	22.04	100	100
4-methylphenyl	12.1×10^6	9.8×10^6	4.3×10^6	NI	NI	18.26	63.88	100	100
4-Phenylcyclohexane	19.1×10^6	15.7×10^6	4.9×10^6	NI	NI	17.70	74.3	100	100
2,1-diphénylcyclobutane	10.4×10^6	7.9×10^6	3.12×10^6	NI	NI	23.95	70.04	100	100
2-Bis methoxyethyl ester	11.9×10^6	8.41×10^6	2.46×10^6	NI	NI	26.76	78.58	100	100
2-dicarboxylic acid monoester ethylhexyl 1,2 benzene	19.1×10^6	14×10^6	3.81×10^6	0.87×10^6	3.5×10^6	27.05	80.12	95.44	81.76
1,2-Benzenedicarboxylic acid	11.7×10^6	9×10^6	6.5×10^6	NI	NI	23.60	44.83	100	100
Butyl phthalate	21×10^6	17.52×10^6	7.20×10^6	NI	NI	16.93	65.85	100	100
Cholestenol	14×10^6	11.53×10^6	9.76×10^6	NI	NI	18.14	30.68	100	100
Chlorocyclohexanol	19.8×10^6	16×10^6	0.69×10^6	NI	NI	19.35	96.47	100	100
Total peak area	9.92×10^9	7.89×10^9	3.28×10^9	6.68×10^6	6.81×10^6	20.41	66.85	99.93	99.93

NI: not identified, Coag: coagulation, Fent: Fenton, Ad PAC: adsorption by powdered activated carbon, Ad PZ: adsorption by powdered zeolite.

[44]. Mono(2-ethylhexyl) ester 1,2-benzenedicarboxylic acid, which is a phthalate acid used in the manufacture of PVC and industrial additives, could impair the function of hormones in the human body, even at trace level. The phthalic acid was supposed to be responsible for the majority of estrogenic activity in the raw and treated leachate [45].

Aliphatic hydrocarbons have been identified in landfill gas as well as leachate at full scale landfills. Aliphatic hydrocarbon compounds are among the most commonly used solvents in industry and households and are expected to enter most landfills, either intentionally with industrial waste or as trace compounds in other waste types.

Fig. 2 presents the organic compounds identified through GC-MS in the leachate submitted to coagulation–FO–PAC and coagulation–FO–PZ adsorption. We considered the compounds with a probability of $\geq 95\%$ found through the mass spectral library. Some of the identified compounds, in

the raw leachate were eliminated by the two integrated processes studied by a percentage of 99% (Table 4). There was a decrease which is greater than 95% in the total corrected area from the chromatograms of the adsorption effluents compared to the raw leachate chromatograms. Therefore, the reduction of organic matter was high. This is in accordance with the results obtained above for organic matter in term of COD and BOD. The two-treated water obtained achieved a percentage of COD and BOD greater than 90%.

The only compound persisted in the treated leachate was Mono(2-ethylhexyl) ester 1,2-benzenedicarboxylic acid, corresponds to phthalic acid, which can result from the degradation of di(2-ethylhexyl) phthalate (DEHP). DEHP is an oily, colorless, and odorless liquid. The esters are of synthetic origin. They are used as an additive in many PVC building materials; it also serves as a plasticizer in other types of polymer (cellulose esters, rubber). Chemically, DEHP has

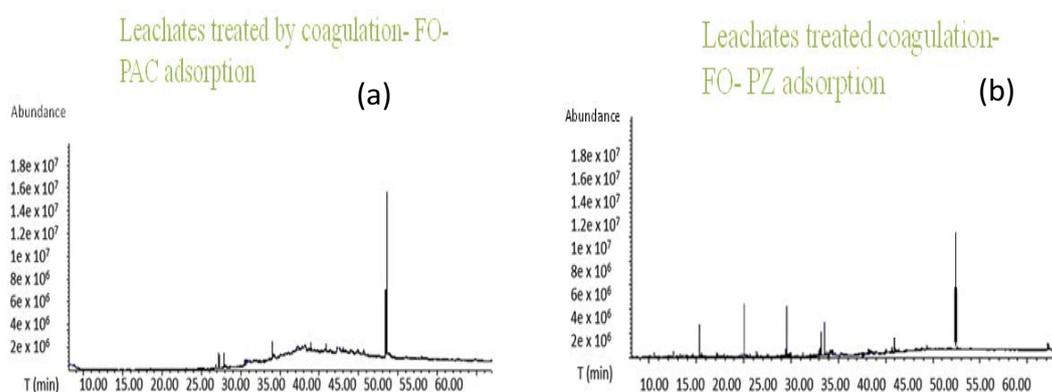


Fig. 2. Total chromatogram obtained by GC-MS with ethyl acetate from leachates treated by coagulation–FO–PAC adsorption (a), coagulation–FO–PZ adsorption (b), between retention times 10 and 60 min.

a lower risk of contamination due to its hydrophobicity, solubility, and the way it is incorporated into commercial products [46].

4. Conclusion

In this study, integrated physicochemical systems (coagulation–FO–PZ adsorption; coagulation–FO–PAC adsorption) were used for the removal of selected organic compounds from municipal landfill leachate. It can be concluded that coagulation process was not efficient in treating ammonia. In addition, Fenton oxidation was not adequate to treat ammonia. Thus, a further step is required to remove the residual amount of N-NH_4^+ . Using PZ as adsorbent resulted in a good quality removal COD as well as N-NH_4^+ .

The final removal efficiencies of selected parameters were higher for integrated coagulation–Fenton reagent–PZ adsorption system. The later exhibited the highest removal efficiency of ammonium nitrogen with percentage of 93%. The final effectiveness in the removal of COD and BOD_5 was 97% and 92%, respectively. The final removal efficiencies of integrated coagulation–FO–PAC adsorption system were equal to 59% for N-NH_4^+ , 98% for COD, and 95% for BOD_5 . Based on the results obtained above, coagulation–FO–PAC adsorption system still did not meet the polish standards quality carried away the sewers since the concentration of ammonium nitrogen is still too high.

The quali–quantitative analysis of a raw sanitary landfill leachate allowed to identify twelve organic compounds, including phenolic compounds, aromatic and PAHs compounds, aliphatic hydrocarbon, and alcohols, which can be considered responsible for the low biodegradability of the leachate. The combined physico-chemical process was able to totally eliminate 99% of those compounds. The process allowed the degradation of most recalcitrant high-molecular weight organic compounds, leading to an increase of leachate biodegradability by 70%. The two integrated process studied removed toxic and carcinogenic compounds present in raw leachate. Finally, it can be concluded that the combined process of coagulation, Fenton, and adsorption treatment has the potential to be utilized for the cost-effective removal of pollutants from landfill leachates.

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