Treatment of Leachate from the Technical Landfill Centre Ain Defla (Algeria) by Oxidation and Biosorption Process

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Abstract
The aim of this study was the treatment of leachate from the Technical Landfill Centre Ain Defla in Algeria, which presents a serious threat to the environment. Elimination of organic matter (expressed as chemical oxygen demand (COD) and biological oxygen demand (BOD₅)), suspended matter (SM), mineral matter (phosphates and ammoniacal nitrogen), and heavy metals (zinc and iron) were experimentally studied using the coupling of oxidation (OP) and biosorption processes (BS). The analysis results showed that the leachate studied at pH 8.8 was very loaded in organic matter (turbidity of 553 NTU, SM = 820 mg l⁻¹, COD = 9669 mg O₂ l⁻¹, and BOD₅ = 8875 mg O₂ l⁻¹), in salts (EC = 19.4 mS cm⁻¹), in ammoniacal nitrogen (2027 mg l⁻¹), in phosphates (22.9 mg l⁻¹), and in sulphates (750 mg l⁻¹). It also contained significant amounts of heavy metals, notably zinc (4.21 mg l⁻¹) and iron (47.5 mg l⁻¹). The evolution of the physicochemical parameters during the treatment showed that, under the optimal conditions (T = 45 °C, [H₂O₂] = 1.6 mol l⁻¹, volume fraction φ(H₂O₂) = 5 %, and [Fe³⁺] = 0.5 mmol l⁻¹), the reduction in COD was about 99 %, the reduction in BOD₅ was 100 %, the elimination of colloidal particles (SM) could reach 95 %, reduction in phosphates was 78 %, reduction in ammonium was 98 %, reduction in sulphates was 96 %, reduction in zinc was 92 %, and the reduction in iron was 98 %.

Keywords
Leachate, landfill, oxidation process, biosorption

1 Introduction
Technical landfills present a prime solution for waste storage. However, this option creates different problems, among which is the production of leachate, an effluent with a high polluting potential (high organic matter content and salinity), which poses a serious threat to the environment and human health.¹,²

Their structure differs from one landfill to another based on the nature of the waste, age of the traps, age of the leachate, climatic circumstances, and site topography.³,⁴

The literature recognises three kinds of leachate: youthful leachates defined by the elevated and relatively biodegradable organic burden; intermediate leachates with reduced organic burden, and stable leachates consisting mainly of humic substances immune to biodegradation. Because of their variable structure over time, they must undergo varying procedures before being discharged into the recipient setting.⁵

The Technical Landfill Centre (TLC) Ain Defla was commissioned in 2013. Approximately 41 Mt per year of household waste was entering the TLC Ain Defla and the major-
they can possibly be applied. These methods of treatment can be categorised by the technique used:1

- **thermal** – by evaporation, incineration,
- **physicochemical** – by filtration/ultrafiltration, ozonation, and coagulation,
- **biological** – by anaerobic and aerobic treatment.7

However, when it comes to treating the (mature) leachate with a high proportion of bio-refractory compounds, these technologies face some limitations.8 To overcome this problem, in order to increase the efficiency of purification, biofiltration (BF) can be coupled with other non-biological systems.9 In recent studies, many combinations have been tested, including BF and chemical coagulation,10,11 BF membrane technologies,12,13 bio-process (BP) and advanced oxidising processes,14,15 BF and electrochemical processes, etc.16 Among these combinations, the homogeneous advanced oxidation process (HAOP) could be an interesting approach to support a biological system in a treatment process.17,18

The concept of HAOP comprises the generation of free radicals, very unstable species of oxidising substances that can degrade chemical compounds found in effluents.19,20 In chemicals that are hard to degrade, the Fenton-reaction has shown excellent outcomes. In this response, the following sequence of Fenton reactions was suggested, where hydrogen peroxide (H₂O₂) is used effectively in place of ferrous salts for leachate:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{HO}^- \quad (1) \\
\text{HO}^\bullet + \text{H}_2\text{O}_2 & \rightarrow \text{HOO}^\bullet + \text{H}_2\text{O} \quad (2) \\
\text{Fe}^{3+} + \text{HOO}^\bullet & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad (3) \\
\text{Fe}^{2+} + \text{HOO}^\bullet & \rightarrow \text{Fe}^{3+} + \text{HOO}^- \quad (4)
\end{align*}
\]

The initial response is the overall Fenton reaction. In order to obtain the important quantities of radical HO•, the cycle must be optimised. Ferric ion (Fe³⁺) and a range of oxidising species (HO•, HOO•, HOO⁻, and H₂O₂) will be available. Furthermore, the ferric ions (Fe³⁺) will interact with the hydroperoxide radicals (HOO•) and will be reduced to Fe²⁺. However, Fe²⁺ will react with extra HOO• to generate Fe³⁺.21,22

As seen during the Fenton reaction, the hydrated ferrous oxide will eventually be formed. For the Fenton reaction to be effective, the pH must be adjusted between 2 and 4. The primary benefits of HAOP are small sludge output contrary to the chemical products.19,20

A BF method can be used to achieve the extra suppression of contaminants following the advanced oxide treatment. The frequently used absorber is active carbon (AC), whose effectiveness is high (20%). However, the impact from palm oil and empty fruits on extraction of phenol has been explored under various production circumstances for active carbon. These parameters include temperature, ignition moment, and speed of CO₂ stream.19,20

Activated charcoal is made from various fresh products, such as coconut marrow activated with ZnCl₂, pecan and caps tile nuts shells, jackfruit bark, oak bowl pulp, H₃PO₄ acid treatment, and palm seeds shell. Coffee grounds and sawdust have been used as adsorbents because of their structure and characteristics.19–30

The main objective of this study was to optimise the conditions for the elimination of organic and nitrogenous matter by coupling the oxidation process (OP) with biosorption (BS). The experiments were carried out on the leachate from the TLC Aïn Defla. After characterisation of the leachate, treatment trials made it possible to determine the optimal treatment doses. Finally, a process coupling performance analysis was conducted.

2 Materials and methods

2.1 Sampling and characterisation of leachate

Samples of coarse leachate were acquired from TLC Ain Defla, Algeria. The leachate was collected and analysed between 1/9/2018 and 1/3/2019, and stored at 4 °C until its use within 48 h or as a note that the climate in this area is semi-arid.

The multi-parameter water analyser model HI19629 (HANNA Instruments, USA) was used to measure the electrical conductivity (EC), dissolved solids (DS), pH, and temperature in situ. A PP OmniTop® A6 thermostat was
used to measure BOD. The COD was evaluated using a H1839800 reactor model (HANNA Instruments, USA) with sulphochromic oxidation. Atomic absorption spectrometer (AAS) 700 was used to determine the heavy metals Al, Ca, Cd, Cu, Pb, Fe, K, and Mn. Turbidity was measured by the turbidity meter model H188703 (HANNA Instruments, USA) for nephelometric turbidity units (NTU).

These leachate samples were forwarded in iceboxes to the Environment and Cleanliness Laboratory, Khemis Miliana Ain Defla, Sustainable Development Laboratory of the Region, University of Djillali Bounaama Khemis Miliana, Microbiology Laboratory and the Materials Laboratory of Yahia Farès, University of Médéa, with respect to the circumstances of conservation needed by the norms in order to slow down the biological, chemical, and physical processes.

2.2 Oxidation of the leachate

2.2.1 Determination of the optimal oxidation temperature

To ensure the complete homogenisation of the reactionary milieu, leachate was poured into volumetric glaze and shaken by a magnetic agitator for 30 min. The reactor thermostat was started and the set-up temperature was adjusted to the desired value. The reactor temperature was set to the following temperatures: 40, 45, 50, 55, and 60 °C. The pH of leachate was raised to 2.6 with a few drops of 10 % H2SO4 (for the homogeneous Fenton response the optimum pH is around this level). After stabilisation of reactor temperature, the first sample was drawn at time zero with the addition of hydrogen peroxide to start a method for oxidation. To monitor turbidity reduction, regular samples were taken. About 3 ml of fluid samples were taken during specified periods (after 15, 30, 45, 60, 75, 90, 115, and 120 min) during 2 h of oxidation.

2.2.2 Determination of the optimal concentration of H2O2

In this part, the pH of liquid was decreased to 2.6 and the temperature was set at 45 °C because this temperature gave a reduction of 50 %. In this process, the amount of oxidising agent of varying degrees was used (0.8, 1.6, 2.4, and 3.2 mol l⁻¹). A sample was taken every 15 min for 2 h.

2.2.3 Determination of the optimal volume fractions of H2O2

The following processes are quite comparable to the past two. The reactor contained the same concentration of H2O2, which was equivalent to 1.6 mol l⁻¹. The investigated hydrogen peroxide volume fractions (φ) were 1, 2.5, 5, and 10 %.

2.2.4 Effect of soluble catalyst on treatment

The strong catalytic agent to study was Fe(III). Therefore, under the current working conditions, it was planned to examine the impact of metal oxide – FeCl3 · 6H2O (99 %) which is the source of Fe(III).

The experiment was carried out under optimal conditions, at 45 °C and pH 2.6, with a volume fraction of 5 % of H2O2 at concentration of 1.6 mol l⁻¹.

2.2.5 Effect of the ratio R = [H2O2]/[Fe3+] on processing

In the attempt to optimise the operating circumstances of leachate oxidation, the proportions between the oxidising agent and the catalyst were investigated. These proportions were R = 10 to R = 60. The operating conditions were T = 45 °C, [H2O2] = 1.6 mol l⁻¹, pH = 2.6, and [Fe3+] = 0.5 mmol l⁻¹.

2.3 Treatment of leachate with biomaterials

Sand or activated carbon filtration or filter media are water filtration systems used to solve many problems in the treatment of liquid effluents. Each filter medium has a specific function in the liquid effluents treatment:

- Sand filters for the sediments.
- Coffee grounds and sawdust transformed into activated carbon to absorb chlorine and organic matter.

2.3.1 Preparation of the constituents for biosorption column

A – Sand: The sand was screened after drying in an oven at 150 °C for 24 h. The diameter of the used particle ranged from 0.040 to 0.500 mm.

B – Sawdust: Sawdust or chips are scraps of material after wood is cut or formed. It was crushed and sieved after washing the scrub thoroughly with distilled water, and put in an oven at a temperature of 105 °C for 24 h. There were two kinds of particle magnitude chosen. The first one was between 0.2 and 1 cm in diameter. The second diameter was between 0.040 and 0.025 cm. The resulting particles were cured in free air at 300 °C for 4 h, and then treated for 1 h in sodium hydroxide (3 mol l⁻¹) baths, thoroughly washed out with distilled water, and dried for 2 h at 105 °C.

C – Coffee grounds: After washing the coffee grounds of any impurities, they were baked at 300 °C for 4 h in open air. They were then washed in sodium hydroxide (3 mol l⁻¹) baths, washed to a neutral pH with distilled water, and dried for 2 h at 105 °C.

D – Peat: Peat is a mix between the Ain Defla landfill pot soil and the water retrieved from the lagoon floor.

2.3.2 Biosorption column

The column was made of PVC, 150 cm high and 10 cm in diameter. The packing of the column was mainly composed of sawdust, sand, coffee grounds, and peat. These four components were arranged in five layers (Fig. 2). The
column was formed from top to bottom as soot: a vacuum of 20% was maintained to ensure the atmospheric pressure on the leachate, and then a first course upper layer composed only of sawdust with a diameter between 0.2 and 1 cm, which had the role of facilitating the passage of liquid and limiting clogging. The second layer was made up of 5% sand, 35% sawdust of diameter 0.04 to 0.25 mm, 35% coffee grounds, 20% peat, and 5% calcite by volume percentage. Calcite (CaCO₃) added to these layers made it possible both to stabilise the pH of the effluent thanks to the buffering capacity of carbonates, and to optimise nitrification with the availability of a mineral carbon source for the autotrophic bacteria responsible for the nitrification. To facilitate the percolation of the liquid in the filter medium, another 20-cm layer of 50% sand and 50% wood chips with a diameter of 0.2 to 0.1 cm was placed between the second and fourth layer. The fourth layer was 50 cm high and composed of 50% sawdust with a diameter of 0.04 to 0.25 mm, 40% peat, 5% sand, and 5% calcite. The fifth layer was placed on 5-cm high coffee grounds, and finished with a 5-cm layer of green beads to allow the filtrate to drain.

**Table 1** – Average values of the physicochemical parameters of the leachate from TLC Ain Defla

| Parameter          | Unit  | Value |
|--------------------|-------|-------|
| pH                 | –     | 8.8   |
| total dissolved solids (TDS) | mg l⁻¹ | 10    |
| EC                 | mS cm⁻¹ | 19.4  |
| turbidity          | NTU   | 533   |
| SM                 | mg l⁻¹ | 820   |
| O₂ dissolved       | mg l⁻¹ | 3.12  |
| BOD₅               | mg O₂ l⁻¹ | 8875 |
| COD                | mg O₂ l⁻¹ | 9669 |
| BOD₅/COD           | –     | 0.91  |
| NH₄⁺               | mg l⁻¹ | 2027  |
| NO₂⁻               | mg l⁻¹ | 2.73  |
| NO₃⁻               | mg l⁻¹ | 5021  |
| PO₄³⁻              | mg l⁻¹ | 22.9  |
| SO₄²⁻              | mg l⁻¹ | 750   |
| Ca²⁺               | mg l⁻¹ | 12.80 |
| Mg²⁺               | mg l⁻¹ | 350   |
| K⁺                 | mg l⁻¹ | 2.85  |
| Na⁺                | mg l⁻¹ | 2.5   |
| As                 | mg l⁻¹ | 0.19  |
| Cd                 | mg l⁻¹ | 1.25  |
| Cr                 | mg l⁻¹ | 2.0   |
| Cu                 | mg l⁻¹ | 1.45  |
| Fe                 | mg l⁻¹ | 47.5  |
| Mn                 | mg l⁻¹ | 1.10  |
| Ni                 | mg l⁻¹ | 3.43  |
| Pb                 | mg l⁻¹ | 0.9   |
| Zn                 | mg l⁻¹ | 4.21  |

Presuming that the release or juices of leachate can be compared to the complicated manufacturing releases comprising both organic and inorganic contaminants, the previously found sand results of physicochemical parameters of Ain Defla landfill coarse leachate with a faecaloid odour release are presented in Table 1.

Aïn Defla landfill leachate is essential. The mean pH-value registered is 8.8. The characteristic of acidic conditions in the initial aerobic waste degradation phase is generally increased in order to solubilize chemical elements (hydrox-
ide acids and carbonate species) and to decrease the waste sorption capacities. However, the pH is essential in this situation, probably because of the recycling system between the lagoons and lockers.

The analysis of the results showed that the leachate was rich in natural material and that elevated BOD₃ and COD numbers (8875 mg O₂ l⁻¹, 9669 mg O₂ l⁻¹, respectively) were true. COD in the leachate exceeded appropriate values. On average, it was more than 80 times higher than the prescribed level of Algerian industrial discharges, which is about 120 mg O₂ l⁻¹, with regard to the BOD₃ detected in the various leachate samples after 5 days of incubation, thus exceeding the approved norm by approximately 35 mg O₂ l⁻¹. However, the real level of BOD₃ continued to be superior to the actual figures since the substrate was packed with toxic materials. Furthermore, the BOD₃/COD proportion is the indication of organic matter biodegradation and leachate maturation. Therefore, for young rejects from which the biological activity corresponds to the acid phase of anaerobic degradation, this ratio reaches the value of 0.83. It was down to 0.05 for ancient sites, where the final phase of methanogenesis fermentation was achieved. The decreases in COD and specifically in BOD₃ characterise this formation phase in our situation. The TLC Ain Defla leachate appeared to be in the acidic phase (BOD₃/COD = 0.91).

In fact, the average EC was 19.4 mS cm⁻¹, indicating strong mineralisation of TLC Ain Defla leachate. This mineralisation was mainly attributable to the following parameters: ammonium (2027 mg l⁻¹), phosphate (22.9 mg l⁻¹), sulphate (750 mg l⁻¹), potassium (2.85 mg l⁻¹), and sodium (2.5 mg l⁻¹). Dissolved solids (DS = 10 mg l⁻¹) refer to all the minerals, salts, metals, cations or anions dissolved in the water. This includes anything present in the water other than H₂O molecules, including suspended solids. Turbidity of leachate was significant. This was because the sun had not penetrated the algae that show biological imbalance, confirmed by the elevated level of suspended material (SM).

For nitrites (Table 1), it was noticed that, on several occasions, the quantity passed the obtained level. The existence of nitrites showed the identification of our samples as comparable to industrial discharges.

The most responsible ingredients of leachate smell are sulphates, and in this model, they were concentrated at 750 mg l⁻¹. The sulphates were then reduced to sulphides in the form of H₂S, the gas responsible for bad smells emanating from the landfill.

The evolution of the levels of salt, potassium, calcium, and magnesium in leachate, like most metallic components (Table 1), is linked to the quantity of organic matter dissolved. Indeed, the high concentrations of the magnesium element is due to the fact that, during the dry period, the organic matter responsible for the complexity of these elements is very low.

Table 1 shows the heavy metal composition of the leachate. The metal load in these percolates was significant. Iron was the metal in larger amounts with concentration levels of 47.5 mg l⁻¹, which is compatible with the bibliographic data. The metal products of the waste dump are primarily composed of iron. Toxic metals were present in relatively low concentrations (nickel – 3.43 mg l⁻¹, cadmium – 1.25 mg l⁻¹, copper – 1.45 mg l⁻¹), and they were lower than leachate generated by other landfills. The household waste treatment scheme positioned before the container was responsible for these values, but most heavy metals were stuck in the waste. The following rates were classified: Fe > Zn > Ni > Cu and Mn > Cd > Cr > Pb > As in increasing orders. Therefore, in these leachates, there was an obstruction of microbial development and interference with the competitive BOD₃ outcomes by the existence of heavy metals.

3.2 Study of the oxidation process

The oxidation study revealed that the sophisticated oxidation method under consideration was dependent on the HAOP. What treatment of this leachate was needed to prevent any type of environmental pollution?

3.2.1 Temperature effects

The turbidity evolution of crude leachate alone (witness 1) with oxidising agent (witness 2), and with oxidising agent plus pH = 2.6 adjustment (sample) was monitored during 120 min corresponding to the standard reaction time (Fig. 3).

The results showed that H₂O₉ hardly decreased leachate during the reaction time at 20 °C (less than 3 % transformation within 120 min). Fig. 4 shows that turbidity had decreased with time at various temperature conditions (T from 40 to 60 °C).
At the start of responses, turbidity usually amounted to about 460 NTU and above, and the study was carried out within a 120-min period. Following the increase in temperature (40, 45, 50, 55, and 60 °C), it was noted that the impact of $\text{H}_2\text{O}_2$ in acidic environment (pH = 2.6) became more efficient than the findings in the neuter environment (pH = 7).

The leachate turbidity from the TLC Aïn Defla had a value of 465 ± 5 NTU. After studying the influence of temperature on the turbidity, it was found that the value of 235 NTU was reached with a yield of 50%. Once the temperature rises, it starts to demineralise because of the degradation of hydrogen peroxide at high temperature.

### 3.2.2 Determination of the optimal volume fraction of $\text{H}_2\text{O}_2$

According to Eq. 2, at high concentrations, the hydroxyl radicals preferentially react with the hydrogen peroxides of the leachate.

### 3.2.3 Determination of the optimal concentration of $\text{H}_2\text{O}_2$

According to the obvious first-order kinetics, when a leachate solution is subjected to HAOP, original turbidity reduces linearly with a moment. After 2 h of treatment, a decrease frequency for an $\text{H}_2\text{O}_2$ level was more than 61%, equivalent to 1.6 mol l$^{-1}$ (Fig. 5). Fig. 6 also demonstrates the turbidity image. Therefore, low concentration of $\text{H}_2\text{O}_2$ (0.8 mol l$^{-1}$) led to a reduction in reaction rate.

### 3.2.4 Effect of soluble catalyst ($\text{Fe}^{3+}$) on the treatment

For removing leachate turbidity, Fig. 7 shows the initial $\text{Fe}^{3+}$ level at varying concentrations.

According to Eq. 2, at high concentrations, the hydroxyl radicals preferentially react with the hydrogen peroxides of the leachate.
Table 2 – Performance of leachate treatment with OP. Conditions: $T = 45 \, ^\circ\mathrm{C}$, $[\text{H}_2\text{O}_2] = 1.6 \, \text{mol}\,	ext{l}^{-1}$, $[\text{Fe}^{3+}] = 0.5 \, \text{mmol}\,	ext{l}^{-1}$, $R = 40$.

| Characteristics of leachate | pH | BOD$_{5}$ | COD | EC | Turbidity | SM | NH$_4^+$ | NO$_2^-$ | NO$_3^-$ | PO$_4^{3-}$ | Ca$^{2+}$ | Mg$^{2+}$ | Fe |
|----------------------------|----|-----------|-----|----|-----------|----|---------|---------|---------|-----------|--------|--------|-----|
| unit before treatment      | 8.8| 8875      | 9669| 19.4| 0.024     | 533| 2027    | 2.73    | 5021    | 22.9      | 12.80  | 350    | 47.5 |
| after treatment            | 6.39| 0        | 1933.8| 0.024| 53.3  | 235| 1479    | 1.52    | 1300    | 5.04      | 1.64   | 27.94  | 3.25 |
| output/%                   | 100| 80       | 99.99| 90 | 71      | 24  | 44      | 74      | 78      | 87.18     | 92     | 93     |     |

3.2.5 Influence of the ratio $R = [\text{H}_2\text{O}_2]/[\text{Fe}^{3+}]$

An experiment was carried out in order to determine the effect of the ratio $R = [\text{H}_2\text{O}_2]/[\text{Fe}^{3+}]$ on leachate mineralisation as a function of time. Fig. 8 shows the results obtained by the Fenton process.

![Graph showing turbidity vs. time](image)

Fig. 8 – Assessment of turbidity during leachate mineralisation as a function of time for variable $R$ values for $[\text{Fe}^{3+}] = 0.5 \, \text{mmol}\,	ext{l}^{-1}$

Thus, when treated leachate by the Fenton process, $R = 40$ was selected as the ideal value for the initial $\text{Fe}^{3+}$ concentration ($0.5 \, \text{mmol}\,	ext{l}^{-1}$).

3.2.6 OP performance on the leachate treatment of Ain Defla landfill

Table 2 summarises the efficient removal of pollutants under the best operating conditions by the oxidation process ($45 \, ^\circ\mathrm{C}$, $[\text{H}_2\text{O}_2] = 1.6 \, \text{mol}\,	ext{l}^{-1}$, $[\text{Fe}^{3+}] = 0.5 \, \text{mmol}\,	ext{l}^{-1}$, $R = 40$). It should be noted that the values in this table are the average values obtained through analyses of leachate treated for feeding the biosorption unit under the optimum conditions. It can be seen that ammonia and siltation were insignificant. It was anticipated that OP would have poor ammonia suppression effectiveness. Other studies have also reported low ammonia removal in such landfill leachate treatment processes. After treatment, turbidity, colour, and metals had been efficiently removed. Ninety percent of the turbidity was withdrawn, likely because of the humic acid removal. In fact, despite the low proportion of humic acids in the waste leachate of landfills, it had a high colouring capacity. Metals, zinc, and iron, among others, have been effectively removed (87 % Zn and 93 % Fe removed).

The good removal of metals by the OP could be attributed to the precipitation and co-precipitation. The total phosphorus concentration was reduced by 78 %. Finally, in terms of BOD$_{5}$, the biodegradable organic matter was eliminated 100 % with a COD efficiency of 80 % for the non-biodegradable organic matter. This is explained by the existence of non-oxidising compounds by OP, since it is hard to degrade carboxylic acids that were produced as intermediate. Some carboxylic acids, especially polyacids, form stable complexes with iron, which, in the absence of UV/Vis irradiation, inhibit the reaction by immobilising the metal in an inactive form (Eq. (8)):

$$\text{Fe}^{3+} + n\text{L} \rightarrow [\text{FeL}_n]^{3+}$$

where L are the mono- and dicarboxylic acids.

3.2.7 Biosorption

The biosorption unit was supplied with oxidised leachate or mineralised leachate previously acquired after adaptation to activate the microorganisms.
3.2.7.1 Elimination of organic matter

The performance of biological treatment with regard to the removal of COD is shown in Fig. 9. Compared to the total removal of COD (99.87%), BOD₃ was fully removed after treatment with OP. Following biological treatment, this value was maintained. The overall suppression of COD can be clarified by the presence of organic refractory content in leachate that had been adsorbed by the biosorption components and even biodegraded.

![Fig. 9 – Assessment of organic matter before and after biosorption of mineralised leachate](#)

Biosorption used to treat leachate from landfills, that were pre-treated under oxidation process, reported similar findings. After biosorption treatment of landfill leachate, a good rate of removal of the Hyl fraction and an insignificant rate of removal of humic substances (humic acid – HA and fulvic acid – FA) was observed.

3.2.7.2 Removal of ammonia

As stated in Table 5, at 27% of the initial load during OP, the removal of ammonia was low. Therefore, the primary task of treatment was the effective treatment of ammonia pollution. Average inlet flux of 500 ml d⁻¹ was provided for the biosorption column. During the biological treatment, nitrogen variations were formed, as shown in Fig. 10. After biosorption, ammonia was almost entirely removed. The average outlet ammonia concentration was 0.68 mg l⁻¹, i.e., well below the Algerian standard norms. Nitrate (NO₃⁻) and nitrite (NO₂⁻) levels were also monitored during the biosorption. The results were 99.57% and 99.96% elimination effectiveness. These results showed that nitrification was the principal mechanism for removing the ammonia from biosorption.

However, other biological and physicochemical events, such as NH₄⁺-removal, assimilation, denitrification, and adsorption could also occur in a biosorption column.

Despite the small phosphorus level and significant quantity of remaining SS acquired after OP treatment, the nitrification method was very efficient. Taking into account the sensitivity of nitrifying bacteria, inhibition of toxicity was a problem. These critical parameters cause the nitrification method. With respect to phosphorus, the suitable item, the amount needed for microorganisms is a contentious topic.

The traditional proportion of C/N/P : 100/5/1 is usually recognised for suitable biosorption treatment. However, amid phosphorus deficiency, several researchers recorded excellent nitrogen extraction rates, describing the small phosphorus demand by the feasible biofilm recycling of phosphorus, arising from biomass decomposition. No negative effects on the nitrifying bacteria were found with respect to the effect of residual SM. This was in contradiction with some studies that argued that the ions present in OP’s remaining SM had an adverse effect on the biological treatment. In fact, metal ions can create dormant bonds and associations with certain bacterial enzymes and cause inhibition of their biological functions.

Moreover, it has been stated that microorganisms are more susceptible to the toxicity of metals when they are in the shape of bare ions. On the other hand, metals’ toxicity decreases when they are chelated by certain organic ligands in the shape of bare ions. On the other hand, metals’ toxicity decreases when they are chelated by certain organic ligands such as humic substances. This may clarify the negligible effect of ions on the method of nitrification, according to this research using Ain Defla landfill leachate.

3.2.8 Biosorption performance on mineralised leachate

Table 3 summarises the efficacy of mineralised and oxidised leachate biosorption treatment. The very low BOD₃ and COD concentrations of organic matter at the outlet indicated that all biodegradable organic matter had been removed. The pH adjustment was associated with the use of inorganic carbon during the nitrification phase by nitrifying autotrophic bacteria.

The leachate became transparent with a minimum turbidity value of 0.7 NTU, likely due to the double effect of biosorption: the adsorption and the nitrification of pollutants. The oxidation of the SM gave the yield of 71%. This value improved with biosorption and reached the yield of 95.6%. There was a slight increase in EC, which could be explained by the salt ion adsorption (NaCl) present in the physiological water used to wash the biosorption. The column was washed in abundance with physiological and demineralized water to remove all the salts and metals.
present in the components of the biomaterials. This technique has demonstrated an efficiency or no increase in the concentration of metals justified in other works by leaching the sludge used.\textsuperscript{16,34} Iron and other metals were also removed either by adsorption into pores of sawdust and activated coffee grounds or by the use of the bacterial sludge.

4 Conclusion

Relating to the characterization and treatment of the leachate from the TLC Ain Defla, it can be concluded that these effluents are at neutral pH 8.8 and have high content of organic matter (COD of 9669 mg O\textsubscript{2} l\textsuperscript{-1}, BOD\textsubscript{5} of 8875 mg O\textsubscript{2} l\textsuperscript{-1}) and suspended matter of 820 mg l\textsuperscript{-1}. These contents greatly exceed the permitted chemical element contents of industrial effluents according to the Algerian standard. Analysis of the mineral fraction of the leachate showed a dominance of magnesium. The treatment of leachate by coupling oxidation and biosorption under optimal conditions (45 °C, pH 2.6, with H\textsubscript{2}O\textsubscript{2} volume fraction of 5 %, H\textsubscript{2}O\textsubscript{2} concentration of 1.6 mol l\textsuperscript{-1}, Fe\textsuperscript{3+} concentration of 0.5 mmol l\textsuperscript{-1}, and the ratio [H\textsubscript{2}O\textsubscript{2}]/[Fe\textsuperscript{3+}] is 40) is an efficient treatment process with BOD\textsubscript{5} reduction of 100 % and COD reduction of 99 %. Removal of colloidal particles (SM) was up to 95.6 %. Reductions of phosphates, ammonium, sulphates, zinc, and iron were 78, 98, 96, 92, and 98.2 %, respectively. This methodology could be transposed to other national and international landfill sites with the same intrinsic and extrinsic characteristics.

Conflict of interests

The corresponding author states that there is no conflict of interest.

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**SAŽETAK**

Obrada procjednih voda iz odlagališta otpada Aïn Defla (Alžir)

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Tema ovog istraživanja je obrada procjednih voda odlagališta otpada Aïn Defla u Alžiru, koje predstavljaju ozbiljnu prijetnju po okoliš. Ispitivano je uklanjanje organskih tvari (izraženo preko kemijske potrošnje kisika (KPK) i biološke potrošnje kisika (BPK₅)), suspendiranih čestica (SC), mineralnih tvari (fosfati i amonjačni dušik) i teških metala (cink i željezno) iz procjednih voda kombiniranjem procesa oksidacije i biosorpcije. Rezultati analiza pokazali su da je pH-vrijednost procjedne vode iznosila 8,8 te da je bila izrazito opterećena organskom tvari (zamućenje = 553 NTU, SC = 820 mg l⁻¹; KPK = 9669 mg O₂ l⁻¹, te BPK₅ = 8875 mg O₂ l⁻¹), u solima (EC = 19,4 mS cm⁻¹), amonjačnim dušikom (2027 mg l⁻¹), fosfatima (22,9 mg l⁻¹) i sulfatima (750 mg l⁻¹). Također sa-državala je i značajne količine teških metala, osobito cinka (4,21 mg l⁻¹) i željeza (47,5 mg l⁻¹). Iz fizikalno-kemijskih parametara praćenih tijekom obrade vidljivo je, pri optimalnim uvjetima (45 °C, [H₂O₂] = 1,6 mol l⁻¹), volumni udio φ (H₂O₂) = 5 % i [Fe³⁺] = 0,5 mmol l⁻¹), smanjenje KPK vrijednosti od 99 %, BPK₅ vrijednosti od 100 %, smanjenje fosfata, amonijaka, sulfata, cinka i željeza za 78 %, 98 %, 96 %, 92 %, odnosno 98 %. Također, 95,6 % suspendiranih čestica uklo-njeno je tijekom obrade procjedne vode.

**Ključne riječi**

Procjedne vode, odlagalište, proces oksidacije, biosorpcija

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