

Characterization of the Leachate from the Municipal Landfill of Akouédo (Abidjan, Côte d'Ivoire)

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Abstract

Municipal solid waste in developing countries especially in Africa are commonly managed by discharging in uncontrolled landfill. This leads to the generation of huge amounts of leachate that are rejected in the nature without any treatment. This study consisted in characterizing the leachate from the Landfill of Akouédo in the District of Abidjan (Côte d'Ivoire) despite the completion of filling operations in 2019. The physico-chemical composition of raw leachate suggested a stabilized landfill, with alkaline pH (i.e. $\sim 8.85 \pm 0.03$). However, the concentrations of nutrients and organics such as NH_4^+ ($212.5 \pm 0.31 \text{ mg.L}^{-1}$), NO_2^- ($257.5 \pm 0.42 \text{ mg.L}^{-1}$), NO_3^- ($301.85 \pm 0.16 \text{ mg.L}^{-1}$), BOD_5 ($1015 \pm 0.12 \text{ mg O}_2 \text{ L}^{-1}$) et COD ($9640 \pm 0.4 \text{ mg O}_2 \text{ L}^{-1}$) obtained in Landfill of Akouédo were slightly weak, compared to the FEPA's standard (1991). This could confirm the stabilization of the leachate, with a $\text{BOD}_5 / \text{COD}$ ratio of around 0.1 ± 0.05 . In addition, most of the metallic trace element contents (i.e. Iron, Copper, Nickel, Zinc and Lead) were below FEPA's standard (1991). To further investigate, humic acid (HA), fulvic acid (FA) and humin were extracted from the humic substance of this leachate. Thus, about 91 % and 9 % were obtained for humic acid and fulvic acid + humin, respectively. For better understanding, synthetic humic acid (SHA) was used as the reference material. The DRIFT analysis helped determine some difference between the LHAs of the leachate and SHA. However, the characteristics of the functional groups of the LHA and SHA molecules were essentially similar. The data on the characteristics of the HS shown in the results of the landfill leachate can be used in several related research areas, such as the optimization of leachate treatment processes and the remediation of groundwater contaminated with leachate.

Keywords: Municipal solid waste, Landfill, Leachate, humic substance, humic and fulvic acid.

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1. Introduction

The population growth causes an intensification of socio-economic activities (trade, industry, agriculture, etc.). This leads to an increase in solid waste generation. Thus, municipalities have to deal with huge amounts of solid waste. As an alternative, urban municipalities are developing waste recycling and waste to energy initiatives to reduce waste amounts and add value to waste management systems. However, in developing countries, the preferred way of solid waste management is disposing of in uncontrolled landfills (Zalaghi *et al.*, 2014). The major and unavoidable concern with an uncontrolled landfill is the mismanagement of leachate that causes serious environmental issues (Baccini *et al.*, 1987). Their rejection in the nature without any treatment results in pollution of soil, water and wildlife, greenhouse gas emissions, health impacts, etc. (Kouame *et al.*, 2006; Sang *et al.*, 2010; Zhao *et al.*, 2012).

In Côte d'Ivoire, in the District of Abidjan, the uncontrolled landfill of Akouédo is among the perfect examples of bad waste management and their by-products such as leachate and biogas. There is no network of collection, storage and treatment leachate and biogas indeed. Yet the landfill of Akouédo generates a significant amount of leachate in the range of $474 \text{ m}^3/\text{d}$ that flows into the Ebrié Lagoon downstream (Adjiri *et al.*, 2008). This situation has continued for the commissioning of the landfill Akouédo and leads to degradation of the water quality of the lagoon and the loss of ecosystem services. Given all these problems of contamination due to leachate, it is imperative to find out suitable and cost-effective treatment techniques of raw leachates from urban landfills.

However, before developing a treatment technique or technology a good knowledge of the content of leachate in terms of inorganic and organic matter is required.

Indeed, characterization studies conducted yet on the leachate from the landfill of Akouédo focused on the content of inorganic materials and organic matter determined as Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) (Kouame *et al.*, 2006; Adjiri *et al.*, 2008; Kouassi *et al.*, 2014). So far, there is no scientific reference to the chemical nature of the organic matter contained in the leachate of the landfill of Akouédo.

It should however be noted that it is well known that humic substances (SH) and volatile fatty acids are the main organic material in the landfill leachate (Tahiri *et al.*, 2016). These organic substances are composed mainly of humic and fulvic acid which are refractory to biodegradation. The studies of Lagier (2000) and Labanowski (2004) found out that 80% of the dissolved organic carbon was comprised of type humic macromolecules to said

leachate stabilized. This means that humic substances (HS) may be the major organic matter in landfill leachate.

Therefore, the overall goal of this study was to determine the relative content of humic and make a complete characterization of the leachate. More specifically, the study aimed at (i) to determining the physico-chemical characteristics of leachate from the landfill of Akouédo, (ii) to extract the crude humic substance and determine its composition in humic acid, fulvic acid and humin, and (iii) to compare the obtained humic acid in the leachate with humic acid purchased from Sigma Aldrich.

2. Materials and methods

2.1. Location of the study area

The District of Abidjan, has an estimated population of around 4,7 million, representing almost 21 % of Côte d'Ivoire's national population (RGPH, 2014). The city of Abidjan is located at an average height of 10 m above the sea level and is surrounded by the Ebrié Lagoon. Spatially, this city covers an area of 2,119 km² (i.e. 0.66 % of country) (Yao-Kouassi, 2010) and experiences a mainly tropical climate with an annual rainfall estimated between 1,250 and 1,922 mm (Kouassi *et al.*, 2018). The study area is the former main municipal landfill of the District of Abidjan, named Landfill of Akouédo which was built since 1965 and has an area of 153 ha. The Landfill of Akouédo which is uncontrolled is located at about 15 km from the center of Abidjan City. According to ANASUR, only 35 ha of the site received continuously waste from populations throughout the District of Abidjan since 1965 and reached saturation in 2004. Despite that, the waste continued to be piled up at the landfill until 2019 (Gevalor, 2015). It received domestic, industrial and institutional waste collected and transported by public and private waste management operators. Waste were then discharged in the Landfill of Akouédo without following any standard until the saturation of the site. As waste were piled up, 2 natural drains at the downstream of the landfill collected leachate that flowed from the landfill into a central pond, from which the leachate were discharged without any treatment into the Ebrié Lagoon (Figure 1).



Figure 1: Mapping of the Landfill of Akouédo and the leachate stream.

2.2. Chemicals

Synthetic humic acid, sulfuric acid (H₂SO₄), Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were purchased from Sigma-Aldrich® in France. All chemicals used were of pro-analytical quality or better.

2.3. Leachate sampling and analyses

Leachate sampling was carried out at the leachate stream outlet. To avoid dilution effects, leachate sampling was performed during dry season, and the leachate samples were collected in well-labeled polyethylen bottles. Analytical methods were compliant with "AFNOR Standard water and wastewater analysis methods" (AFNOR, 1990). One duplicate was acidified to pH 2 by addition of 100 mL of 10 M HCl solution to each 100 mL sample and used for determination of metals, nitrogen (ammonia, nitrite and nitrate) and phosphorous (as phosphate). The

second duplicate was kept at its natural pH and used for determination of conductivity and organic matter (Chemical Oxygen Demand, COD, and Biochemical Oxygen Demand, BOD). Conductivity and pH were measured *in situ* using Electrochemical probe method according to NFT 90-008 and NFT 90-031 standards, respectively, whereas Suspended Solids (SS) were determined with NFT 90-105 standard. The results are expressed in mg L⁻¹. Temperature was also determined using a Cobra 4 Mobile-Link thermometer. Molecular absorption spectrometry methods were used to analyze nitrite (NO₂⁻), nitrate (NO₃⁻), ammonium (NH₄⁺) and phosphates (PO₄³⁻) according to NFT 90-13, NFT 90-45, NFT 90-15 standards respectively. An Atomic Absorption Spectrophotometer was used for metal (i.e. Copper (Cu), Nickel (Ni), Lead (Pb), Iron (Fe) and Zinc (Zn)) analysis after sample acid digestion. In fact, these metals are most commonly found in household leachate. The BOD₅ was measured using the Oxitop method (Reuschenbach *et al.*, 2003), while COD was determined by the dichromate reduction method (APHA, 1989 ; ISO, 1989) employing Hach[®] COD digestion vials (Hach, 2015).

2.3.1. Humic substance (HS) extraction

Extraction of HS from the leachates was performed by acid–base treatment method proposed by Thurman and Malcolm (1981) and modified by Tahiri *et al.* (2016). Briefly, 20 mL of leachate samples, previously filtered in order to retain the Suspended solids, was adjusted to pH between 10 and 11 by adding 1 N NaOH solution, which caused the metals and dissolved humic acid precipitation. After 3 h of stirring, the solution was centrifuged at 4000 rpm for 45 minutes. The supernatant leachate (i.e. humic substances), containing humic acid (HA), fulvic acid (FA) and humin was collected. The leachate samples were centrifuged and filtered through glass-fiber filter paper (i.e. 0.45 μm) to remove suspended materials that may react with HS. The extracted HS were separated into humic and fulvic acid fractions by acidifying (e.g. sulfuric acid, H₂SO₄) the HS solution to pH 1.0 and precipitating humic acid fraction. The resulting humic acid pellets were filter and dried and weighed to determine the humic acid mass corresponding to the volume of crude leachate used. Supernatant samples were used to determine the COD content, which represents the residual humic acid. COD of the supernatant was determined as above. All the experiments were carried out in triplicate.

2.3.2. Diffuse Reflectance InfraRed Fourier Transform Spectroscopy

Diffuse Reflectance InfraRed Fourier Transform (DRIFT) spectra were recorded between in the 400 and 4000 cm⁻¹ regions with a IS50 Nicolet spectrometer equipped with a KBr beam splitter and a TCD detector. A powdered sample is mixed with KBr powder. The DRIFT cell reflects radiation to the powder and collects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from material in a sampling cup or, alternatively, from material collected by using an abrasive sampling pad. DRIFT is particularly useful for sampling powders or fibres. The resolution of the single beam spectra was 4 cm⁻¹. The pellets of synthetic humic acid and that provided from leachate were used for DRIFT. For quantitative analysis, where spectral absorption is required to follow Beer's law, or where direct comparison with pressed KBr disc spectra is required, the nonlinear intensities can be partly corrected by application of the Kubelka-Munk function (1) (Hecht, 1980; Griffiths and Fuller, 1982). DRIFT spectra were then recorded immediately.

$$A(KM) = \frac{2R}{(1-R)^2} = \frac{a^\circ}{s} \quad (1)$$

Where:

- A(KM) is the required intensity in Kubelka-Munk (KM) units,
- R is the observed reflectivity, for infinite sample thickness, relative to a non-absorbing matrix, a is the absorptivity due to volume reflection, and
- s, is the scattering coefficient.

3. Results and discussion

3.1. Physico-chemical composition

Table 1 shows the Physico-chemical composition of the raw leachate of the Landfill of Akouédo. Indeed, alkaline leachate was observed, with pH value ~ 8.85 ± 0.03, thereby underscoring the Landfill of Akouédo is exploited for a long period (i.e. sample provide from aged wastes) (Talalaj, 1998). However, alkaline leachate was also obtained from several landfills such as the municipal solid waste landfill site in Ibadan, Nigeria (Aluko *et al.*, 2003). Although the characteristics of landfill leachate depend on several parameters (i.e. the type of wastes dumped, the solid waste stabilization degree, hydrology site, moisture content, seasonal weather variations, landfill age and stage of the decomposition in the landfill) (Wang *et al.*, 2003), the common characteristics of stabilized leachate are high resistance of NH₃-N (3,000 –5,000 mg.L⁻¹) and COD (5,000 –20,000 mg.L⁻¹), as well as a low ratio of BOD/COD (i.e. less than 0.1) (Li *et al.*, 2002). Unlike the literature, the values of NH₄⁺ (212.5 ± 0.31 mg.L⁻¹), NO₂⁻ (257.5 ± 0.42 mg.L⁻¹), NO₃⁻ (301.85 ± 0.16 mg.L⁻¹) et COD (9640 ± 0.4 mg O₂ L⁻¹) obtained within the Landfill of Akouédo were widely weak, despite the completion of filling operations. All these values exceeded the FEPA's standard (1991) (Table 1). The BOD₅ / COD ratio was approximately 0.1 ± 0.05, thus confirming the stabilization of leachate and its biodegradability (Kouassi *et al.*, 2014 ; Naveen *et al.*, 2017). Unlike the present

study, where the BOD₅/COD values of the leachate samples were ranking between 0.1 and 0.5. The studies performed by **Chian and Dewalle (1976)**, reported BOD₅/COD values from 0.5 to 0.7, thereby emphasizing the presence of large amounts of biodegradable organic matter. This could cause contamination by chemical species in dissolved or suspended forms of the environment (**Kurniawan et al., 2006**). In this study, phosphate content (i.e. $3.12 \pm 0.51 \text{ mg L}^{-1}$) was below FEPA's standard values (i.e. 5 mg L^{-1}) (See Table 1), but knowledge of the nitrates and phosphates contents is important to predict the nutritive state of the waters, since these ions are important nutrients for plants which generally appear following the decomposition and mineralization of organic matter (**Naveen et al., 2017**). Otherwise, most of the metallic trace element contents (i.e. Iron, Copper, Nickel, Zinc and Lead) were below FEPA's standard (See Table 1), as well as some literature values (**Aluko et al., 2003**) and identical to those of **Naveen et al. (2017)**.

Table 1: Physico-chemical characteristics of leachate from the Landfill of Akouédo (Abidjan, Côte d'Ivoire)

Parameters	Concentration of raw leachate	FEPA's standard (1991)
pH	8.85 ± 0.03	6-7
Conductivity ($\mu\text{S}/\text{Cm}$)	31994.6 ± 0.15	-
SS (mg L^{-1})	604.5 ± 0.5	< 30
Temperature ($^{\circ}\text{C}$)	26.3 ± 0.25	< 40
Nutrients		
Ammonium (NH_4^+) (mg L^{-1})	212.5 ± 0.31	-
Nitrites (NO_2^-) (mg L^{-1})	257.5 ± 0.42	< 1
Nitrates (NO_3^-) (mg L^{-1})	301.85 ± 0.16	< 20
Phosphates (PO_4^{3-}) (mg L^{-1})	3.116 ± 0.51	< 05
Organic matters		
DCO ($\text{mg O}_2 \text{ L}^{-1}$)	9640 ± 0.4	-
DBO ₅ ($\text{mg O}_2 \text{ L}^{-1}$)	1015 ± 0.12	< 50
DBO ₅ / DCO	0.1 ± 0.05	-
Metallic trace elements		
Iron (Fe) (mg L^{-1})	8.75 ± 0.47	20
Copper (Cu) (mg L^{-1})	0.10 ± 0.02	< 1
Nickel (Ni) (mg L^{-1})	0.12 ± 0.11	< 1
Zinc (Zn) (mg L^{-1})	0.52 ± 0.2	< 1
Lead (Pb) (mg L^{-1})	0.35 ± 0.04	< 1

3.2. Humic and Fulvic acids in leachate of the Landfill of Akouédo

Table 2 exhibits the essential fractions of humic substance (HS) contained in the leachate from the Landfill of Akouédo. These are humic acid (HA), fulvic acid (FA) and humin (H). Indeed, a large amount of HA (i.e. $\sim 91\%$) compared to FA + H (i.e. $\sim 9\%$) was obtained in the leachate (See Table 2). According to **Castagnoli et al. (1990)**, the predominance of humic acid is probably due to the stabilization and non-homogeneity of waste in the landfill. The FA/HA ratio value (i.e. 0.1) confirmed the previous results. In fact, **Fan et al. (2006)** also revealed a low FA/HA value (i.e. 0.36 vs 0.94) in the leachate of a landfill site in Central Taiwan, due to the lack of organic matter caused by the aging of the landfill.

Table 2: Concentrations of humic substance component in the leachate of the Landfill of Akouédo

Components	HA	FA + H	HA + FA + H	FA/HA
HS (mg.L^{-1})	872	90	962	0.1
Proportion (%)	90.64	9.36	100	-

3.3. DRIFT spectra analysis

The DRIFT spectra of leachate humic acid (LHA) and synthetic humic acid (SHA) are illustrated in **Figure 2**. Indeed, these spectra provided information on specific molecular structures and various functional groups (**Schnitzer and Khan, 1972**). For instance, $3200 - 3400 \text{ cm}^{-1}$ regions were assigned intermolecular O-H stretching or H-bounded OH, whereas $2850 - 2980 \text{ cm}^{-1}$ regions were ascribed asymmetrical and symmetrical stretching of methyl and methylene C-H bond. Moreover, $2900 - 1720 \text{ cm}^{-1}$ regions were attributed to aliphatic C-H stretching, C-O stretching in carboxylic acids and aldehydes and ketone groups, respectively, while $1690 - 1710 \text{ cm}^{-1}$ regions related to due to C=O stretching of COOH and ketonic C=O. A shoulder at 1650 cm^{-1} due to stretching of C=C bonds present in aromatic or asymmetric alkenes conjugated with C=O or carboxylate, and 1540 cm^{-1} region corresponded to amide II band (i.e. C=N stretching.), 1240 cm^{-1} (C-O stretching), 450 cm^{-1} was supposed to be due to S-S bonds (**Kang et al., 2002; Fan et al., 2006; Qi et al., 2012**). Therefore, it should be noted that within the present study, the characteristics of the functional groups of the LHA and SHA molecules were basically

similar.

However, the vibrational forces in the relative distribution of each functional group, have some differences, hence the decrease and stretching of some bands of SHA (See **Figure 2**).

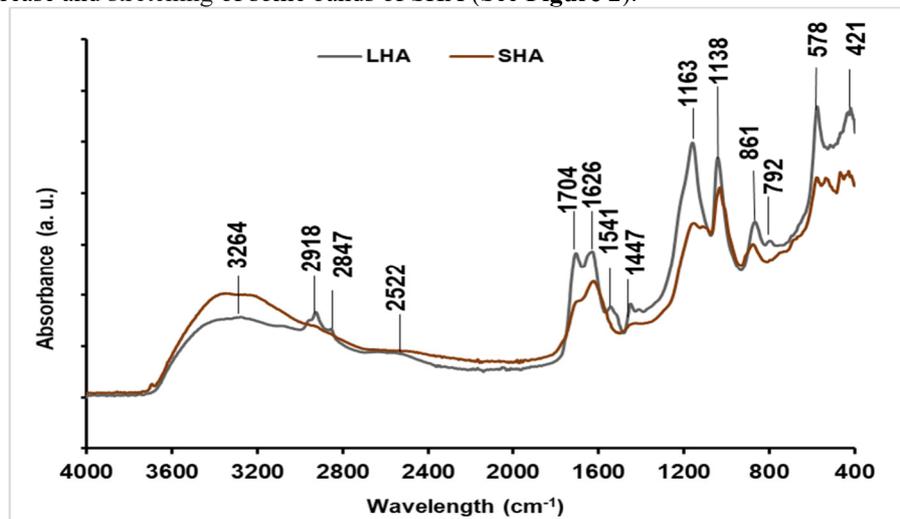


Figure 2 : DRIFT spectra of leachate humic acid (LHA) and synthetic humic acid (SHA).

Conclusion

In this work, we characterized the leachate from the Landfill of Akouédo despite the completion of filling operations. The Physico-chemical composition of the raw leachate suggested a stabilized landfill, with high pH values (i.e. $\sim 8.85 \pm 0.03$). The study revealed a weak load of inorganic pollutants (NH_4^+ , NO_2^- , NO_3^-), compared to the FEPA's standard (1991). The stabilization of the landfill was confirmed by a very low BOD₅/COD ratio which was approximately 0.1 ± 0.05 . Metallic trace element contents (i.e. Iron, Copper, Nickel, Zinc and Lead) were also below FEPA's standard (1991). The study showed that organic content of the leachate was predominantly humic acid since fulvic acid was less than 10 % in the leachate. This was confirmed through DRIFT analyses which showed that the characteristics of the functional groups of the LHA and SHA molecules were basically similar. The data on the humic substance (HS) characteristics shown in the results of the landfill leachate can be used in several related research areas, such as the optimization of leachate treatment processes and the remediation of groundwater contaminated with leachate.

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Conflicts of Interest

The authors do not declare any conflict of interest with respect to the publication of this article.

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