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Physico-chemical characterization of landfill leachates: a comparison case between Tangier and Agadir(Morocco)

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Abstract
Leachate, the liquid percolating through solid waste, remains a major concern for managers of the new controlled landfills in Morocco, especially those built under European standards i.e., with waterproof membrane and leachate collecting systems. The center of urban waste disposal of Agadir is one of these controlled landfills. After a few years of operation, the involved stakeholders are now facing the major challenge, which is dealing with the quantitative and qualitative issues of the subsequent leachate,. The aim of this study is to characterize and compare two different leachate; one from the controlled landfill of Agadir, where the analysis of the composition of heavy metals revealed a significant iron load of these effluents (36.01 mg / l), whereas, the other from the uncontrolled waste disposal of Tangier, where analyzes shows a heavy load of the leachate TSS, chlorides and iron probably due to industrial activities. Leachate samples were collected, quarterly between January 2012 and February 2013, and analyzed for various physico-chemical parameters to estimate its pollution potential. Monitoring the variation over time of the relevant physico-chemical parameters of leachate in a storage center of urban waste is an important tool for controlling the nature of the waste flow, which allows the detection of abnormalities not normally seen by visual inspection.

Keywords: Leachate, Physico-chemical characterization, Agadir Landfill, Tangier's uncontrolled waste disposal, Morocco

1. Introduction
The demographical development and the intensification of the economical activities in Morocco, are accompanied by an increase of solid waste production [1-3] with 4.5 million tons/year of urban wastes and 800000tons/year of industrial wastes being dumped. This leads to an average of 1kg of waste per day and per inhabitant, however Morocco, like other developed countries, is showing a strong commitment to environmental protection. The adoption of law 28-00 regarding the management of waste and their disposal was a major step forward.
The rational management of solid waste is a challenge for all the concerned stakeholders i.e., producers, policy makers, researchers and professionals.
European standard landfills are well installed and successfully operating in developed countries. However, experience from managing the controlled landfills of Agadir (build under the same standards), have revealed that the implementation of this landfill model to Morocco raises some specific issues (leachate, odors, etc).
Else the waste water leakage, leachate in majority come from the rainfall water, and contains several minerals, often highly toxic contaminants. Their composition is specific for each landfill, and varies depending on the nature of the incoming wastes, the age of the landfill, the technical and operating conditions.
The objective of the present study is to determine the degree of pollution of leachate from the controlled landfill of Agadir Tamellast and compare it with that of the old and uncontrolled waste disposal of Tangier. The leachate from the former accumulates in the collecting system whereas, the leachate from the latter directly evacuate in

the bay of the city through Mghogha Channel and his small effluent Ghilane flow, This then that some of these leachate seeps into underground waters.

Study location

The Tamellast site of the controlled landfill of Agadir region, is located about 6 km north-east of Agadir with Lambert coordinates (X : 104 182 to 105 182 Y : 388 640 to 389 926) (Fig.1). It corresponds to the contact area between the High Atlas and the western plains of Souss [4].

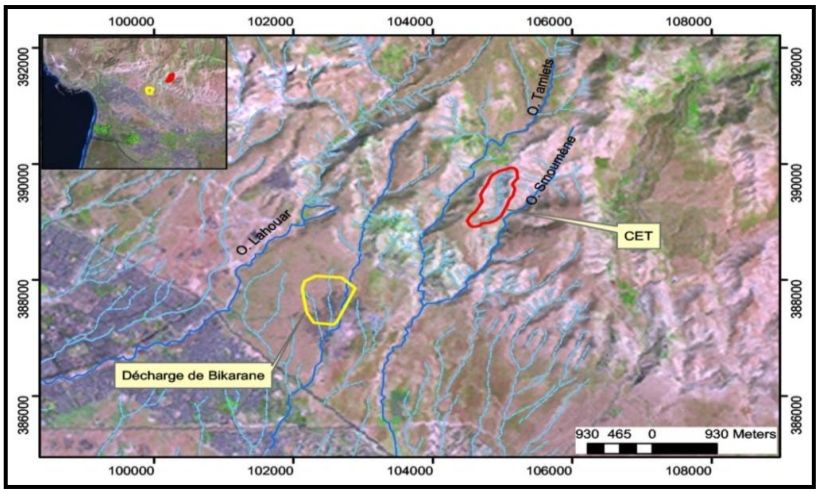

Figure 1. Satellite image showing the location of the existing landfill and the CSD of Agadir Tamellast

The group Urbaser & Tecmed-Maroc is managing the landfills, under a 10 years delegated management contract, signed with the City of Agadir. The contract aims to ensure the rehabilitation of the old landfill Bikarrane and the construction, management and operation of a repository urban waste of Tamellast.

The uncontrolled waste disposal of Tangier, is located about 5 km south-east of the town center (Fig.2), between two rivers; M'ghougha and Mlaleh. The coordinates of the location are: latitude 35°44'35.32 "N and longitude 5°45'17.39" W, operating since beginning of the 1970s [5].

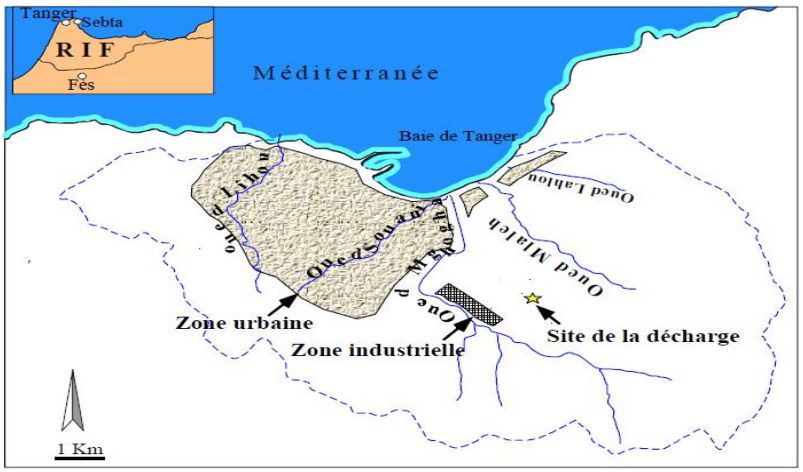

Figure 2. A map showing the location of the existing landfill of Tangier [5].

Nature of solid waste

The average composition of municipal solid waste in Morocco is characterized by the predominance of the organic fraction, about 77% for the case of large Agadir and 65.3 for Tangier city, which explains the relatively high rate of humidity (Fig. 3).

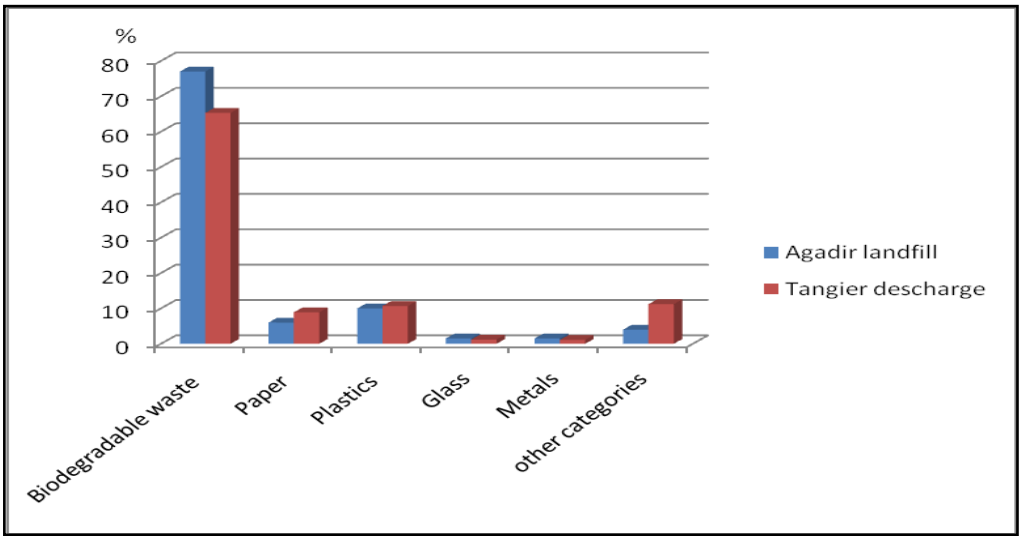

Figure 3. Percentage of the different components of municipal waste of Agadir and Tangier. [6]

The landfilled waste mainly consist of ordinary waste from food preparation and normal cleaning of homes and offices, waste from commercial and artisanal businesses, products of cleaning of public roads, squares, parks, cemeteries and their dependencies, trash halls, fairs, markets, places of public holidays, waste from schools, barracks, hospitals (uncontaminated), hospices, prisons and all public buildings, industrial and commercial solid waste similar to household waste banal, but other waste such as rubble and debris are accepted without remuneration.

Table 1: Primary sorting categories commonly used in the reviewed methods for waste component studies [7]

Common primary components	**Alternative or subordinated terms (all used as primary components)**
Biodegradable waste	Biowaste, fermentable waste, food waste, yard waste, organic waste, degradable waste, kitchen and garden wastes, 'biowaste
	and undefined residue (fines)', bread, animal refuse, natural organic products
Paper	Newsprint, paper and newsprint, paper and cardboard, cardboard, mixed paper, total paper, high grade paper, corrugated
	paper, paper packaging, other non-packaging paper
Plastics	Plastic packaging, plastic film packaging, dense plastic packaging, foamed plastic packaging, non-packaging plastic
Glass	Glass packaging, non-packaging glass
Metals	Metal packaging, non-packaging metal, aluminum, iron, ferrous metals, non-ferrous metals
Other categories **Wood** **Textiles** **Hazardous waste** **Other organics** **Other inorganic** **Fines**	 Textiles and leather, health-care textiles, carpeting and mats Hazardous household waste, medical waste, special waste, small chemical waste Unclassified combustibles, other combustibles, miscellaneous combustibles Unclassified incombustibles, other non-combustibles, miscellaneous non-combustibles, ceramics, minerals Residue

Reliable generation of waste data is useful. Yet, there is neither a European [8-9] nor a Moroccan standard of solid waste component analysis.

Quantities of solid waste

The total quantities of wastes received in 2012 for the controlled landfill of Agadir and Tangier discharge are238 436.26 and 310 380.60 tones/year, with a daily average of 651.47 and 848.03 tons respectively. Both have a maximum in the summer season (Fig.4).

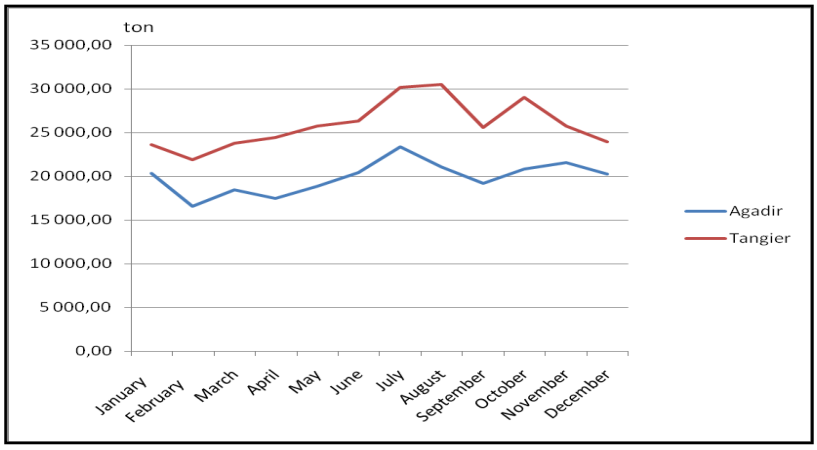

Figure 4. Monthly quantities of waste received at the controlled landfill of Agadir and discharge of Tangier for the year of 2012 [10-11]

Leachate Generation and Characterization

The amount generated and the extraction of potential pollutants from the waste depend upon several factors; including solid waste quantity, composition, age, degree of compaction, and the absorptive capacity of the waste, as well as seasonal weather variations, hydro-geological conditions in the vicinity of the landfill site, engineering and operational factors of the landfill, pH, and landfill chemical and biological activities [12-15].

The drainage leachate comprises a transverse main and branch pipes as the backbone of the fish. Water leaching, via infiltration between the rollers installed at the bottom, is routed through the main manifold to the retention ponds and storage located downstream of the discharge. The optimal storage capacity is 22.000 m3. The stock have reached now 65.000 m3. Thus, even the reserved site for future exploitation is occupied by the leachate.

Google earth image of Agadir landfill between 2012 (left) and 2014 (right)

The company responsible for operating the discharge has made the work of setting up the sprinkler system and leachate recirculation, fueled by a pumping system. In orderto control the amount recirculated every day, the pumping system isequipped with a flow meter. A portion of leachate is sprayed on repressed traps whereas; the remaining portion is poured through a system that was proposed for summer evaporation on the slopes and berms. Thus, in the quantity of leachate stock (in m^3) is positively correlated with the precipitations (in mm) (Fig 5).

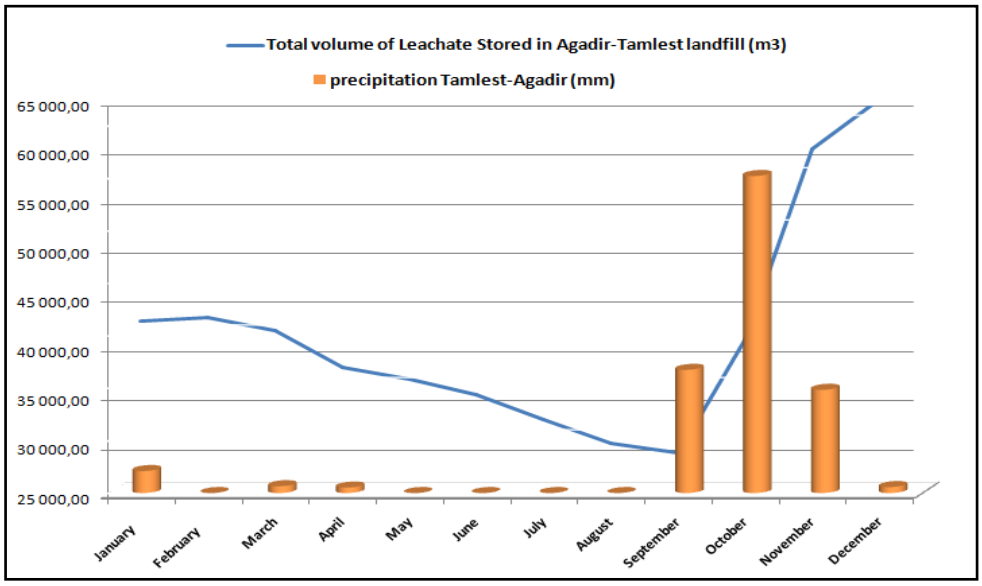

Figure 5. Precipitation and stocked leachate evolution in Agadir landfill for 2012 [10].

However, for Tangier discharge, all leachates produced are directly/naturally drained to the Mediterranean Sea. The quantity of leachate discharged to the bay of Tangier can be estimated by extrapolating the results from Agadir, using the quantity of waste of Tangier and its precipitation data,

2. Materials and methods

2.1. Leachate sampling and analysis

Leachate monitoring of the controlled landfill of Agadir was performed systematically on the analytical laboratory of the physico-chemical composition.

The leachate samples subject to analysis in this study were carefully collected:

- For great Agadir landfill at the outlet of operating area and storage ponds such way as to be as representative as possible. The point at the exit is the main collector of the leachate drainage system installed in the form of fish bones at the bottom of operating area, with the collection of sampled at storage ponds was done manually in the middle of basin to a definite depth, but at the same point for all campaigns.
- However, in Tangier the samples were collected downstream of the discharge but at the same point for all campaigns.

2.2. Analytical work

- The pH, temperature, conductivity were measured in situ using a multi-parameter. Leachate samples (average 1 L) were carefully collected, in a systematic manner. For Agadir landfill, the samples were collected at the outlet of the operating area and storage ponds in order to be as representative as possible. However, in Tangier the samples were collected downstream of the discharge but at the same point for all campaigns.

The collected samples were in a cooler (< 4 °C), and immediately transported to the laboratory. In addition to in situ measurements, pH, temperature, and conductivity were also measured in the laboratory using (Jenco instruments 6173). Measurements of COD, BOD5, nitrates, chlorides and heavy metals were performed in accordance with national and international standards (see annex 1).

3. Results and discussion

3.1. Color and odor

The color of leachate samples were orange brown or dark brown and had a malodorous smell. The smell is most likely due to the presence of organic acids from the decomposition of the highly concentrated organic matter in the waste. The dark color in landfill leachate is also associated with the high concentration of the organic substances [16].

3.2. pH

The pH varied according to the age of landfills [17].Generally, the pH of a stabilized leachate is higher than that of a young leachate [18]. In general, leachates have pH between 4.5 and 9 [19]. The pH of young leachate is less than 6.5 whereas, pH of old landfill leachate has pH higher than 7.5 [20]. Initial low pH is due to high concentration of volatile fatty acids [21]. Stabilized leachate shows fairly constant pH with little variations and it may range between 7.5 and 9.

The pH of the collected samples was relatively stable (Figure 6) and varied between 7.6 and 7.9 for Agadir samples, and 6.8 and 7.6 for Tangier samples. These values are within the lower and higher pH limits of Moroccan standard limit, which are 6.5 and 8.5.

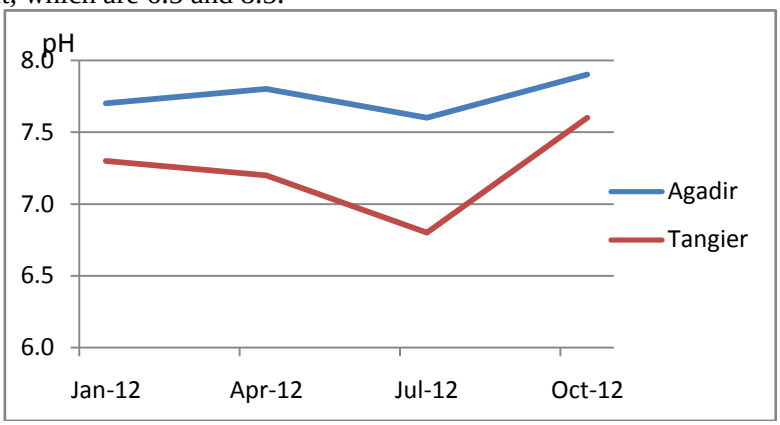

Figure 6. pH variation over time in leachate from Agadir and Tangier landfalls in 2012

3.3. Temperature

The temperature of the leachate varied according to the seasonal temperatures of the Agadir and Tangier cities (Fig.7):

- Agadir landfill: an average of 20.9 ° C, a peak in April of 27.1 ° C and a minimum of 17.6 ° C recorded in October 2012.
- Tangier discharge: an average of 27.6 ° C, a peak in July of 29.2 ° C and a minimum of 24.6 ° C recorded in January 2012.

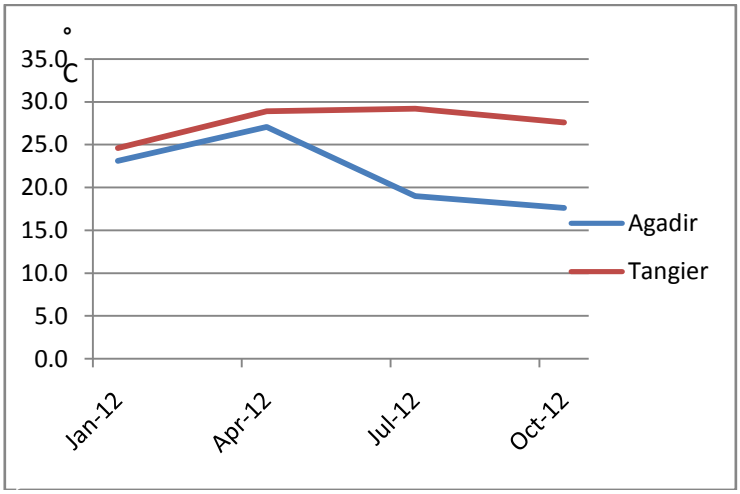

Figure 7. Temperature variation over time of the leachate from Agadir landfill and Tangier discharge in 2012

3.4. Conductivity

The average electrical conductivity at 20 ° C is of the order of 58.65mS/ cm, indicating a strong mineralization of leachate from Agadir landfill, which is most probably due to chloride ions (table 2). However, the average conductivity of the leachate from Tangier discharge was 33.23mS/cm, indicating a moderate mineralization. The low conductivity (16.10mS/cm) recorded in the leachate from Tangier in October 2012 is due to the beginning of winter season.

Table 2: Conductivity variation over time of leachate from Agadir landfall and Tangier discharge in 2012

Conductivity 20°C (mS/cm)	Outgoing leachate operation - Tangier	Outgoing leachate operation - Agadir
January-12	36.60	37.90
April-12	37.90	53.50
July-12	42.30	72.60
October-12	16.10	70.60
Mean	33.23	58.65

3.5. BOD_5

BOD_5 (biochemical oxygen demand in 5 days) is the measure of biodegradable organic mass of leachate. It typically decreases with time [22] and thus, indicates the maturity of the landfill. The BOD values in leachate from the two landfilling sites are reported in figure 8.

The leachate of pond 1 does not fall within the recirculation system and is used as a reference for monitoring the natural evaporation since 2010, which explains the accumulation of salts and the high conductivity.

The average BOD_5 outgoing of the operation area was 25395 mg O_2 / l, showing a high organic load in Agadir's leachate. it's the average BOD_5 is even higher in Tangier's leachate (11 705 mg O_2 / l). The measured BOD values were considerably higher than the standard limits. BOD value varies according to age of landfills. For new landfills, BOD values are between 2000-30000 mg/l whereas, for mature landfills, BOD values varies from 100-200 mg/l [23]

3.6. COD

COD represents the amount of oxygen required to completely oxidize the organic waste constituents to inorganic end products. Again, the measured COD values were considerably higher than the standard limit. Nevertheless, greater COD values were recorded by several other studies [24-28].

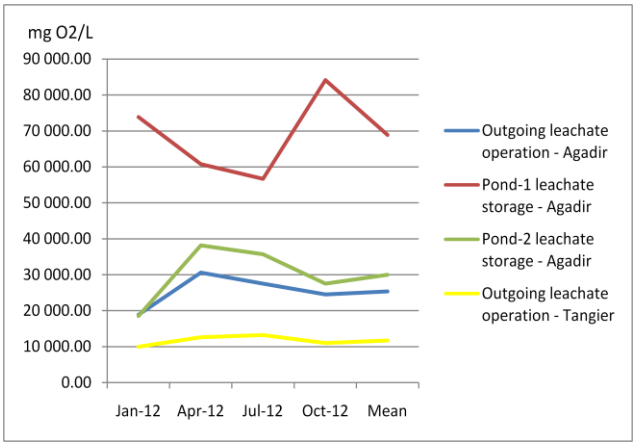

Figure 8. BOD_5 evolution of leachate of Agadir landfall and Tangier discharge in 2012

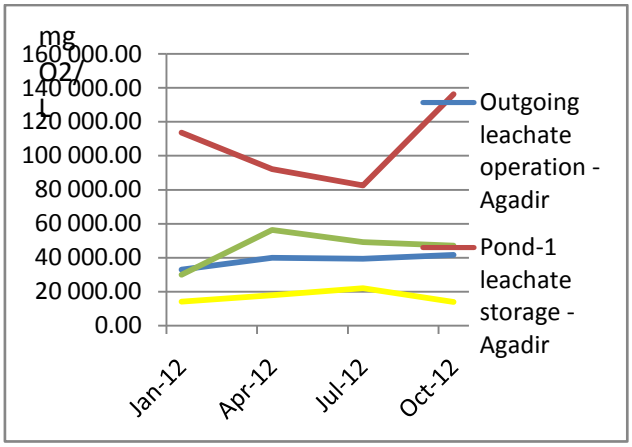

Figure 8. COD variation over time in leachate from Agadir landfall in 2012

The COD values for leachate samples of the Tangier's discharge site were between 13880-14000 mg/l and 17800-22060 mg/l during winter and summer, respectively. These measured values are also considerably higher than the standard limit. Yet, less than the outgoing leachate from operation area in Agadir controlled landfill; 33024 to 41664 mg/l and 39360 to 39936 mg/l during winter and summer respectively. However, the measured values of the stocked leachate in Agadir were largely higher (fig.9).

in general, young landfill leachate (the acid-phase landfill, <5 years) contain large amounts of biodegradable organic matter. More than 95% of the dissolved organic carbon (DOC) consists of volatile fatty acids, and some high molecular weight compounds. In mature landfills (the methanogenic-phase landfill), the organic fraction in the leachate becomes dominated by refractory compounds, and the DOC content consists of high molecular weight compounds [29-30].

3.7. BOD_5/COD Ratio

The ratio BOD5/COD of the leachate characterized in this study were higher than those obtained in the discharge of Fez, [31], Rabat [32], Mohammedia [33] and Alhoceima [34].

In this study, the mean ratio for the collected leachate samples of the landfilling sites was >0.65. This indicates that leachate studied is young and unstable [35] and thus, the discharge is in acidogenic phase [36].

Organics in leachate are characterized by different levels of biodegradability and the BOD5/COD ratio describes the degree of biodegradation the low BOD5/COD ratio shows the high concentration of non-biodegradable organic compounds and thus the difficulty to be biologically degraded [37].

3.8. Chlorides

The chloride values of leachate samples of the landfilling sites were between 10152to 22635 mg/l and 6345 to 11713 mg/l, respectively in Agadir and Tangier. The measured chloride values were considerably higher than the standard limit. Higher ranges of 490-1190, 360-4900 and 580-10100 mg/l were previously recorded by other researchers [38-40]. This is due to the contributions of waste industrial unit canned fish for Agadir landfill. According to Deng and Englehardt (2007), the concentration of chlorides may range between 200-3000 mg/l for a 1-2 year old landfill and the concentration decreases to 100-400 for a landfill greater than 5-10 years old [41].

The quantity of chloride ions influence the electrical conductivity, a strong positive correlation between the concentration of chloride ions and conductivity (table 2) was observed. This close relationship has been previously demonstrated [42] on the site of Etueffort.

3.9. Nitrate

The nitrate mean values for leachate at landfilling site of Agadir were 2.06 mg/l, 5.68 mg/l, and 2.48 mg/l respectively in outgoingoperation area, storage Pond-1 and storage Pond-2. However it was higher in the discharge of Tangier with 49 mg/l. Microbial decomposition of organic carbon influences several processes of the nitrogen cycle. Nitrogen concentration decreased due to microbial utilization of nitrate compounds and to the de-nitrificationinto ammonia gas [43]. Nitrates are the primary contaminant that leaches into groundwater.

3.10. Metallic composition of leachate

In household waste, heavy metals are made by plastic (Cd), batteries (Hg, Zn, Mn, Ni, Pb), scrap metal (Fe, Pb), rubber (Zn), leather (Cr), glasses (Cr), textile (Cu, Zn), paper, and cardboard (Pb, Cu, Cr) [35].

Concentration of heavy metals in a landfill is generally higher at earlier stages because of the higher metal solubility due to the low pH caused by production of organic acids [17].The results presented in (Table 3) show that the studied leachate has a very high pollution load. The average load of suspended matter MES is about 426.97 mg/l in Agadir and 900 mg/l in Tangier.

However, the average concentration of nitrate NO3- is between 3.639 mg/l and 49 mg/l, of phenol index is between 2.5mg/l for Tangier and 14.31 mg/l for Agadir site, the sulphides 21 mg/l, and the average concentration of oils and fats is 55.64 mg/l in the site of Agadir and 3 200 mg/l in the discharge of Tangier.

The concentration of heavy metals shows a large metal loading. This may be due to contributions from industrial waste. The classification of heavy metal concentrations of these leachates in ascending order is as follows: Fe>Mn> Ni> Al> Zn> Ba> As> CRT> Cu> Sn> Co>Pb> Sb> Se> Cd> Hg for Agadir landfill and Fe>Mn>Al>Zn>Ba>Ni>CrT>As>Co>Sb>Se>Cu>Pb>Sn>Cd>Hg for Tangier discharge [39]. The metal content of the leachate from both sites is typical of a discharge with a domestic dominant character [44-45]. Therefore, the presence of heavy metals in landfill leachate inhibits microbial growth. [46]

Concerning the discharge of Tangier, analyzes carried out between winter and summer of 2012, shows a heavy load of the leachate TSS, chlorides and iron probably due to industrial activities.

Conclusion

1. Characterization of leachate generated by the Centre of Waste Storage Tamellast-Agadir has revealed that the leachate is young and unstable, with an important pollution load.
2. The results obtained at the Centre of Waste Storage Agadir were compared to those collected at other landfills, and showed that the metal composition of the leachate is typical of a discharge with a domestic dominant character.

3. The analysis of the composition of heavy metals revealed a significant metal load of these effluents, where iron is the most abundant metal (36.01 mg / l).
4. The concentration of most of the analyzed elements in the leachate exceeds the recommended limits in developing countries, which constitutes a pertinent danger for the environment and public health.
5. Landfill site of Tangier City is non-engineered low lying open dump. It has neither bottom liner nor leachate collection and treatment system. Therefore, all the leachate generated finds its paths into the surrounding environment.
6. Leachate samples of landfill site were collected and analyzed for various physico-chemical parameters to estimate its pollution potential. The analyzed samples contained a high concentration of organic and inorganic compounds, beyond the permissible limits. While heavy metals concentration was in trace amount as the waste is domestic in nature, the measured leachate samples would need an appropriate treatment strategy to reduce the pollutants to a satisfactory level prior to discharge into the receiving system.
7. The data presented in this study indicated that with seasonal variations, particularly during rainy season, values of various parameters increased; reason being with time the solid waste material degraded and the waste constituents percolated down along with rainwater. Thus, the age and seasonal variations has a significant effect on leachate composition;

Annex 1

PARAMETERS	METHODS OF REFERENCE
Sampling	NF EN 25667 (ISO 5667)
pH	NF T 90-008 NMISO10523
Temperature	NF EN 25667 (ISO 5667) NM03.7.008
Conductivity	NF EN 27888 NM ISO 27888
Biochemical Oxygen Demand (BOD 5)	NF EN 1899
Chemical Oxygen Demand (COD)	NF T 90-101
SM (Suspended matter)	NF EN 872 NF T 90-105-2
Chlorides	NF ISO9297 NM 03.07.024
Nitrates	RODIER Method
Ni	NF EN ISO 11885
Co	NF EN ISO 11885
Pb	NF EN ISO 11885
Fe	NF EN ISO 11885
Mn	NF EN ISO 11885
Zn	NF EN ISO 11885
Cu	NF EN ISO 11885
CrT	NF EN ISO 11885
As	NF EN ISO 11885
Se	NF EN ISO 11885
Sb	NF EN ISO 11885
Cd	NF EN ISO 11885
Al	NF EN ISO 11885
Hg	RODIER NFT 90-007
Ba	NF EN ISO 11885
Co	NF EN ISO 11885

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