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Comparative study of the metal pollution treatment from leachates by physical and biological methods

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Abstract

The purpose of this study is a comparative study of the treatment of the metallic pollution of the leachates of the controlled public landfill of the city of Fez by application of the biological processes by aeration and physical by filtration. The treatment of leachates by aeration allows an accumulation of heavy metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) by specific aerobic microorganisms present in the leachate, mainly Mn^{2+} ions with arate of reduction between 90,8% and 93,3%. For the physical treatment by infiltration- percolation, we carried out a comparative study of the filtrations on different matrices inorder to choose the best filter medium. We used as filter media: three types of clay, fly ash, bottom ash and marine sand. The best reductions in heavy metals are observed with the filtering substrate S_3 formed of clays designated A1 and fly ash, with concentrations lower than Moroccan standards for direct discharges and reduction rates higher than those found after 7 days of leachate treatment by aeration. The results obtained by the best filter bed F_3 are evaluated at a reduction of 87,67% for Aluminum, 95,6% for Chromium, 76,36% for Cu ions, an abatement rate greater than 99,31% for Fer, more than 95% for Mn ions, an abatement go up to 88,1% for Nickel and 93, 98% for Zn ions, meeting the standards of rejection in force.

1. Introduction

In Morocco, the increasing production of household waste and industrial waste leads to critical pollution problems. The increasingly complex and heterogeneous nature of this waste involves difficulties in their treatment and management. A large part is landfilled, without precautions, which constitutes a real and permanent threat to the environment. The controlled landfill of Fez receives more than 1000 tons per day of waste of all kinds. This quantity is much higher than that received by the Mohammedia landfill (200 tons/day) [1].

Indeed, from the disposal phase, the waste is subject to degradation processes linked to complex biological and physico-chemical reactions. The water infiltrates it and produces leachate and biogas loaded with organic and mineral substances, which generate pollution essentially of the organic and metallic type, in relation to the natural biodegradation of the confined waste and with their anthropogenic components, which release numerous substances toxic in the natural environment, particularly in the atmosphere, groundwater and waterways. The metal pollution from buried waste is a long-term problem, which raises many concerns about its release. The metal contents measured in the leachates are however, according to the literature, quite low and the majority of heavy metals, mainly copper, nickel, lead, iron, zinc and cadmium actually remain trapped within of the mass of waste.

Salam etal [2] estimate that more than 99,9% of heavy metals are still trapped in the landfill after 30 years. According to a study carried out on columns withand without recirculation, 95% of the metals remained trapped within the waste mass after 4 years [3].The concentration and the mobility of heavy metals have been widely studied in the last decades [4,5]. Although, many heavy metals are necessary in small amounts for the normal development of the biological cycles, most of them become toxic at high concentrations. Heavy metals are introduced into the environment through natural phenomena and human activities, such as agricultural practices, transport, industrial activities and waste disposal [6]. Certain metals are more or less mobile depending on their oxidation-reduction state. Redox conditions can influence the mobility of an element in three different ways [7]: a change in the oxidation state of the element itself, a change in the oxidation state of elements binding with the element itself to form a complex and formation or dissolution of phases carrying the trace element. Between 10 and 30°C, the temperature has only a negligible direct effect on the mobility of metals [8]. But, in the presence of organic matter, it can have an indirect role, for example by increasing its degradation, which can produce acidic and complexing substances [9]. It can also affect bacterial activity. The action of microorganisms can go in the direction of solubilization (production of acid and complexing compounds, etc.) or insolubilization (formation of insoluble metal sulphides, bioaccumulation and biosorption by microorganisms) of metals heavy. The effect of competition on the surface sites between metals or between metals and major cations can also play an important role by different mechanisms [10]:

- Adsorption: Surface phenomenon by which atoms or molecules attach themselves to the solid surface of a substrate according to various processes. Some minerals, such as clays, are excellent adsorbents, thanks to their very large specific surface areas. We call desorption the reverse transformation of adsorption, by which the adsorbed molecules or atoms are detached from the substrate.

There are two types of adsorption, depending on the mechanisms involved:

  - ➢ Physical adsorption (or physisorption): It is attributable to the electrostatic attraction of a solute by a polarized surface, in order to maintain electroneutrality.
  - ➢ Chemical adsorption (or chemisorption): In this case, the molecule adheres to the surface by ionic or covalent bonds.

- Precipitation: It is the passage of a species from the dissolved state to the solid state. Metals can precipitate in water from pores or on the surface of solid particles.
- Substitution in the crystal lattice: An atom can substitute for another in the crystal lattice; its

load and size should then be similar. It is, for example, the case of a metal ion incorporated into the crystal lattice during its precipitation, or which diffuses into the solid to fill a void or replace an atom of the solid.

- Inclusion (mechanical entrapment): These are impurities trapped mechanically in non-opening pores during the growth of minerals. It can be in dissolved or solid form.

2. Methodology

2.1. The controlled public landfill of the city of Fez

2.1.1. Geographical location of the landfill

The controlled public landfill of the city of Fez (situation in Morocco: article will be read by foreigners and the situation in Morocco is essential) was located at the Sidi Harazem Road in the commune of Ain Bida, 11 km from the city center (**Figure 1**). It coversan area of 120 hectares and processes more than 1000 tons of solid waste per day, including nearly 900 tons of household waste.

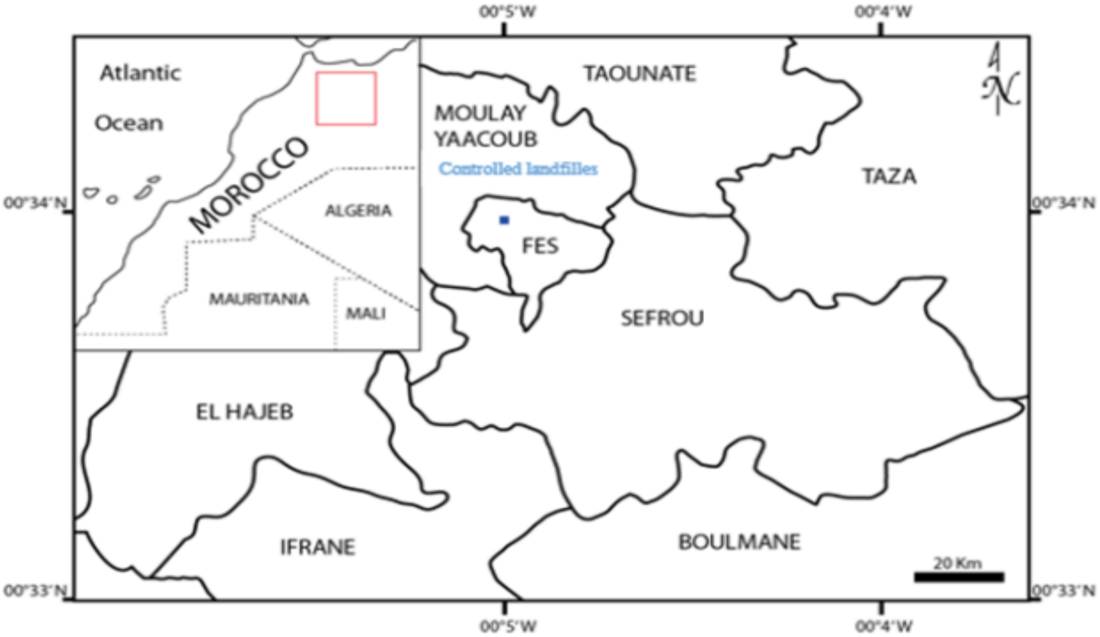

Figure 1. Georgraphical location of the study site

2.1.2. Geological setting of the landfill

Analysis of soil samples taken from the site showed that the land is formed by plastic blue marl and yellow clay. The clay layer is more than 30 m deep, thus avoiding groundwater pollution, while that of the marls is 596 m. The land is also characterized by the absence of exploitable mineral resources, classified geological deposits, and lateral water supply at the location of the site.

2.1.3. Fes leachate collection network

The leachate management consists of collecting, storing and treating it. In the case of the Fez controlled landfill, leachate is currently stored in five basins without being treated. Leachate can be evacuated to storage basins in two ways:

- Either by gravity through collectors;
- Either by pumping through manholes and submerged pumps.

The most pronounced problem at the landfill level lies in the production of enormous quantities of leachate despite the installation of a leachate drainage system and the construction of rainwater collection and evacuation structures. The Fez controlled landfill produces approximately 21600 liters of leachate per day, which are pumped to the five storage basins.

2.2 Treatment processes

The choice of treatment technique for metal pollution in leachates can be particularly difficult because of its variable physico-chemical characteristics over time [11]. The objective of this study is to contribute to the treatment of metal pollution from the leachate of the controlled public landfill of the city of Fez, by applying a biological treatment by aeration and physical treatment by infiltration-percolation, using substrates based on clay, fly ash, bottom ash and marine sand, given their availability, efficiency and simplicity of implementation.

2.2.1. Biological treatment by aeration

In aerobic processes, heterotrophic bacteria use organic matter whose carbon is a source of pollution and of energy, and oxygen as a final electron acceptor. Thus, the pollution, essentially in soluble form at the start, is partly eliminated and transformed into micro-organisms present in solid form. For our aerobic leachate treatment, we carried out continuous leachate aeration in a bioreactor with a capacity of 4L and a volume of leachate to be treated of 50 mL (**Photo 1**).

The variation in the concentration of dissolved oxygen in our bioreactor during the aerobic treatment of leachates shows that: At the start of aeration, the dissolved oxygen value recorded is 1,3 mg/L. After 3 hours of aeration, the dissolved oxygen reaches a high value of 5,4 mg/L. This value remains constant for 17 hours, then the bioreactor undergoes a slight increase in dissolved oxygen to a value of 5,7 mg/L for 3 hours. The recorded value of dissolved oxygen in the bioreactor decreases after wards to 5,5 mg/L then to 1,7 mg/L.From these results, it can be concluded that our bioreactor is well aerated and therefore the amount of oxygen in the bioreactor is sufficient for the optimal growth of bacteria.

Photo 1. Aerobic process for leachate treatment

2.2.2. Physical treatment of leachate by filtration

This part of the work was devoted to a comparative study of leachate filtration through different substrates in order to choose the best filtering matrix having given the best rate of reduction of the metallic pollution of the leachates, the filtering materials are natural clay soils designated by A_1, A_2 and A_3, fly ash and bottom ash. For this comparative filtration study, we used the experimental device, shown in **photo 2**. The effective height of the filter bed is 7cm (H) and the section S of the filtering device is 78,5 cm^2. Each substrate is taken with a concentration of 5 mg/L.

Photo 2. The experimental device

2.2.2.1. Leachate filtering matrices

We used different types of filter substrates: clay soils, charcoal ash and marine sand. The choice of these filtering substrates for the treatment of metal pollution is because these same matrices have given a satisfactory reduction of the physicochemical pollution for the same leachates [12].

2.2.2.1.1. Clay soil

The clay linings have been used as barriers in landfills to prevent contamination of groundwater and subsoil by leachates containing metals. We used three types of natural clay soils designated A_1, A_2 and A_3, taken from the Fez region of the Ouagriine site:

- The Soil A_1 is a solid gray calcareous clay in the dry state;
- The Soil A_2 is a rust-colored Upper Miocene silt;
- The Soil A_3 is a calcareous clay, hard and gray in color.

The choice of these materials is justified by the following characteristics:

- Abundance of these soils in the region of Fez.
- Rich in very fine mineral constituents. The latter make them more active in solution, which gives them a high adsorbent power [13].
- Their ferric ion content.

The soil samples (A_1, A_2 and A_3) are first crushed, sieved and dried at 100°C. This last operation eliminates the water of hydration. The attachment of organic matter to the surface of the adsorbent material is generally greater when the particle size of the material is small. For this reason, we chose fractions of 500 µm of the powders prepared to carry out the various leachate filtration tests. The powders prepared from the soils were also used for the physicochemical characterization of the different materials.

2.2.2.1.2. Fly ash

Following the combustion of the pulverized coal in the boiler, the fly ash is entrained by the combustion smoke and then captured by electrostatic precipitators.

This captured dust is transported to storage and homogenization silos [14]. From these silos, the ashes can either be loaded into tanks in a dry state (dry ashes), or humidified (wet ashes) to be delivered to customers or evacuated to the heaps. This system is designed to facilitate the recovery of fly ash by tank trucks that transport it to cement plants. We took samples directly from the trucks. Several samples were taken from several trucks and then mixed to obtain a representative sample. The fly ash collected all comes from the combustion of coal from South Africa. The sample obtained by quartering from several samples of 5 kg. Quartering consists of dividing the sample into four equal parts. Two opposite parts are collected and then homogenized. One of these last two parts is the subject of a new quarter and so on. The operation can be repeated three or four times in order to obtain a representative sample (**photo 3**).

Photo 3. Visual Appearance of Fly Ash

Under an optical microscope, fly ash appears as shiny grains of more or less spherical shape and different colors. Their particle size varies between 0,5 and 200 µm. This is a very fine material, its granularity is relatively tight, almost all of the material being between 5 and 20 microns. The oversize on the 80 microns sieve is generally between 10 and 20% by weight and the oversize on the 50 microns sieve is between 15 and 40%. It should be noted that within the same production, the granularity of the fly ashes seems quite variable.

2.2.2.1.3. Bottom ash

The taking of representative samples is done at two levels. We took the materials from the top, bottom, middle and inside the bottom ash heap from the Jorf Lasfar Electric Company (JLEC) and placed them outside the Civil Engineering laboratory of the Hassania School of Public Works. This quantity thus with drawn was sampled again by a sampler. This device makes it possible to divide the entire initial sample into two equal parts. Each half is obtained in a tank separately, after three or four passages, the representative quantity necessary for the tests envisaged is obtained.

The particle size of the bottom ashes depends on that of the coal burned and the cooking conditions in the boiler. In general, they have a size that varies between 30 µm and 30 mm (**photo 4**).

Photo 4. Visual Appearance of Bottom

2.2.2.1.4. Marine sand

The marine sand that we used in our filtration-percolation experiments were lifted along the coast of the city of EL Jadida. The sands are washed with distilled water then dried in an oven at a temperature of 50°C for 24 hours.

3. Results and Discussion

3.1.The leachates studied

Table 1 summarizes the main physical and chemical properties of the leachate**,** the leachates from the controlled landfill of the city of Fez did not meet the rejection standards. The COD values obtained during this study reached up to 6720 mg/L, with an average of 5200 mg/L, the BOD_5 values of the leachates studied were 1520 mg/L with an average of 1375,12 mg/L.

The BOD_5/COD ratio is an indicator of the proportion of biodegradable organic matter in relation to total organic matter and therefore an indicator of leachate maturity **[15]**. This ratio decreases with the age of the waste implying that the biodegradability of dissolved organic material tends to decrease with the age of the waste **[16,17]**. The studies conducted by Sillet **[18]** have in fact made it possible to classify leachates according to their more or less biodegradable nature using the BOD_5/COD ratio. This ratio calculated in this study in order to assess the biodegradability of leachates. The BOD_5/COD ratio of the leachates from the controlled public landfill of the city of Fez gives an average of 0,22; which makes it possible to classify them among the intermediate leachates, poorly biodegradable **[19]**. In addition, there was a high concentration of TKN up to 3520 mg/L, which is an indicator of pollution caused by urban waste. In addition, a slightly high concentration of SS was noted, this could be explained by the high organic and mineral load, which was due to the nature of the waste. Besides, the pH of 8,16 was slightly basic. These values are in the range of Moroccan standards of the general limit values for discharges into surface and underground waters (**Table 1**).

For the three types of soil, the sum of the proportions of the metal oxides identified is around 100%.It follows that the clays studied are quantitatively different and consist mainly of silica in the quartz state

(40 to 62%). Similarly, they contain a high content of alumina (3,8 to 12,7%) and calcium oxide(12,5 to 20,6%).

Table 1. **Results of leachates pysico-chemical**

	Maximum values	Minimum values	Average values	Limit values of discharges into surface and underground waters
pH	8,38	7,94	8,16	5,5-9,5
Temperature	29,8	28,2	29	-
Electrical conductivity (ms/cm)	38,4	37,4	37,9	-
SS (mg/L)	604	352	478	100
COD (mg d'O2/L)	6720	3680	5200	500
BOD_5 (mg d'O2/L)	1520	1230,24	1375,12	100
TKN	3520	2772	3146	-

3.2. X-ray fluorescence analysis of clay soils

The average values expressed as a percentage of metal oxides of the various elements contained in claysoils A_1, A_2 and A_3 are represented in Figure 2.

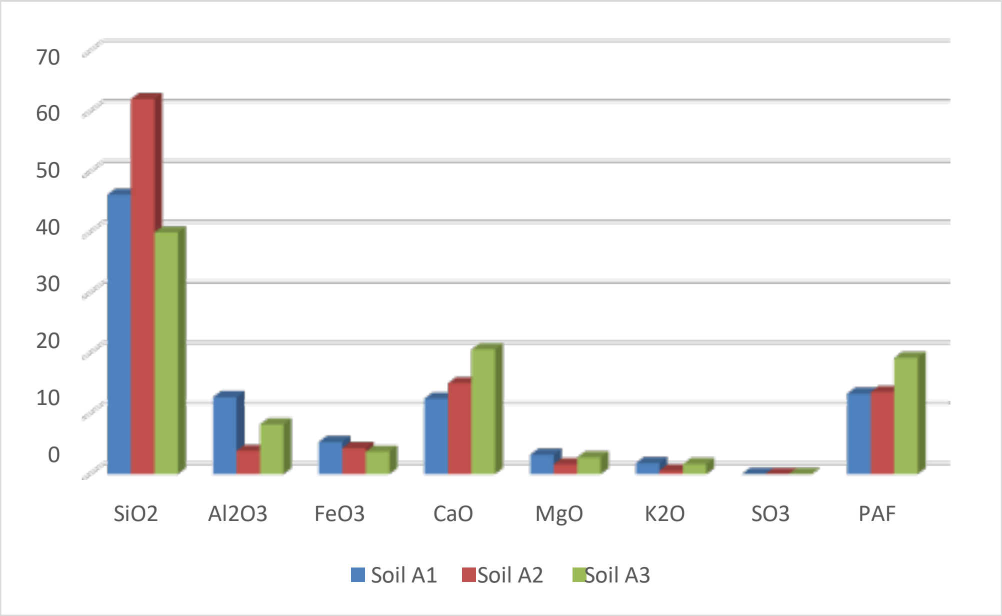

Figure 2. Chemical composition of clay soils expressed as percentage

3.3. Chemial composition of fly ash and bottom ash

Table 2 summarizes the results of the chemical analysis of the bottom ashes. We notice that more than 80% of the chemical composition of the bottom ashes is made up of the elements SiO_2, Al_2O_3 and Fe_2O_3. As for lime, it does not exceed 2%. This chemical composition reminds us of that of silicoaluminous ashes. In addition,the low free lime content predicts low swelling in a humid environment.

Table 2. Chemical composition of bottom ash obtained by ICP

Chemical element	SiO_2	Al_2O_3	Fe_2O_3	$\sum SiO_2 + Al_2O_3 + Fe_2O_3$	CaO	MgO	SO_3	K_2O
Percentage (%)	57	34	3,4	94,4	10	0,02	0,5	1,2

In general, the chemical composition of fly ash depends on that of the original coal. The results of the chemical analysis, reported in the table 3, show that for the fly ash, the sum of the percentages of the elements: SiO_2, Al_2O_3, and Fe_2O_3 is 94,4%, which makes it possible to classify them among the silicoaluminous ashes.

Table 3. Chemical composition of bottom ash

Chemical element	CaO	SiO_2	Fe_2O_3	Al_2O_3	K_2O	Na_2O	ZnO	PbO	SO_3	MgO	CaO Free
Percentage (%)	1,92	52,07	8,86	23,34	1,9	0,4	0,01	0,01	1,87	1,09	0,29

3.4.Particle size distribution curve of marine sands

For this reason, we used the standardized method NF P 18-560, this method consists in passing a quantity of 100 g of filtering substrate through 12 sieves whose meshes are classified in descending order of 2000 µm, 800 µm, 630 µm, 500 µm, 400 µm, 315 µm, 250 µm, 200 µm, 160 µm, 125 µm, 100 µm and 50 µm. A manual or mechanical vibratory movement applied for 5 to 30 minutes. Sieve over size weights, expressed as a percentage of the total sample weight (weight percentages), determined for each sample. Among nine samples of marine sands studied, taken along the coast of EL Jadida, we chose the marine sand whose particle size distribution curve indicated in the figure 3, which represents the particle size distribution of the sand particles as a function of its size. This particle size distribution allowed us to deduce the uniformity coefficient which is the ratio of the sieve mesh opening which allows the passage of 60% of the particles, to the sieve mesh opening allowing the passage of 10% of the particles (UC= d60/d10).

This particle size distribution allowed us to deduce that the marine sand studied is characterized by:

- A small particle size (160 µm) therefore, it will present a better leachate treatment performance by increasing the adsorption surface thanks to the reduction in the size of the adsorbent grains [20].
- Its uniformity coefficient (UC) which is and must be less than 1,5[20] knowing that more the value of UC is close to 1, the homogeneity for the filter bed is better [20].

This sand was then analyzed by ICP for, on the one hand to know the exact constitution of the chemical elements which constitute it, and on the other hand to know if there is a probable contamination in heavy metals, knowing that this sample of sand will be the subject of a filtering substrate, to filter the leachate.

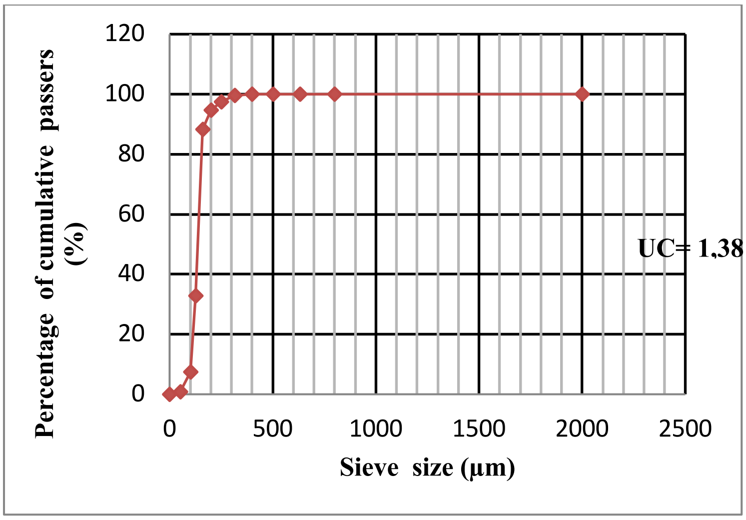

Figure 3. Particle size Distribution Curves of marine sand

3.5. Analysis of chemical element contents in marine sand

The results of this mineralogical analysis by ICP are reported in the histogram of Figure 4. This sand sample contains different chemical elements: The highest contents are recorded by SiO_2 (50,87%) and CaO (21,87%), followed by MgO (6,19%) and Al_2O_3 (4,52%). Fe_2O_3 and K_2O values remain relatively low; they reach 4,19% and 0,82% respectively. However, the lowest contents (<< 1%) are recorded by TiO_2 and MnO. These results find their explanation in the structure of marine flora and fauna, silica is stored by certain living organisms such as diatoms, which are brown algae, very abundant in marine environments. By radiolarians, which are Protozoa belonging to the class of Actinopoda marine and pelagic and by the sponges (Spongiaria), which build an internal skeleton made up of rods incorporated in a matrix of spongine **[21]**.

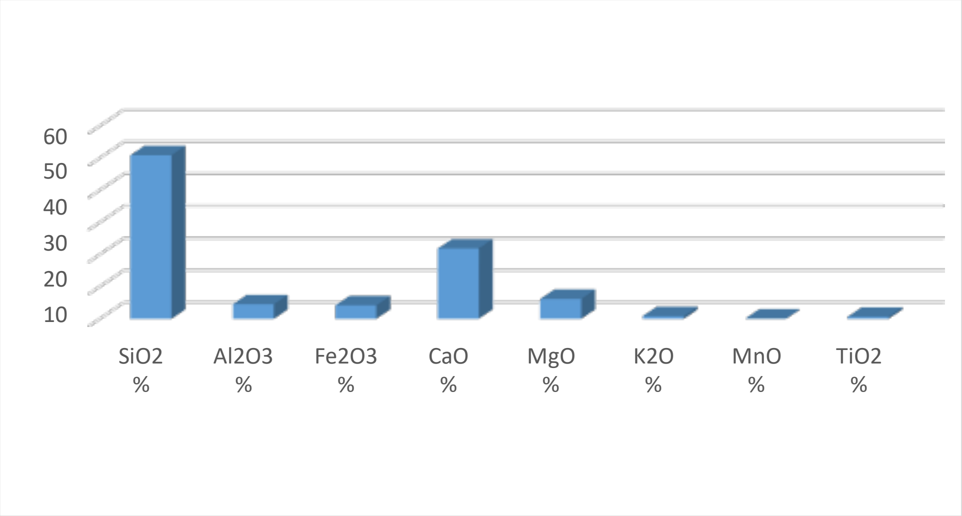

Figure 4. Result of ICP analysis of marine sand

The ability of the cells to produce mineralized materials, limestone or silica, involves the constitution of "skeletal" structures of the support. Most of the cells of multicellular organisms are in contact with a tangle of locally secreted macromolecules, which constitute the extracellular matrix and which build special structures such as tendons with a high content of elastic fibers, or bones, cuticles, shells or fibers are gradually saturated with deposits of calcium and silica crystals [21].

3.6.Results of metal pollution treatment for leachate

3.6.1. Analysis of heavy metals before and after aeration treatment

For the leachates studied, we analyzed the metallic elements (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the raw and treated leachates after 2 and 7 days of aeration. The choice of these elements is based on their high toxicity and high concentration in the raw leachates, in addition they are classified among the elements most commonly designated by the term heavy metal. [22].

Each value is the average obtained after 4 sampling campaigns. Table 4 summarizes the results of this analysis. Iron is the metal present in the greatest quantity with a concentration of the order of 14,65 mg/L whichis in agreement with the bibliographic data [23-25]. Iron is mainly present in the metallic materials of the landfill. It is considered among the important steels playing a great role in innumerable fields: dailylife, mechanical industry, food industry, chemistry, transport, medicine and surgery [26]. The Chromium concentration in the leachate reaches 4,554 mg/L. This measured value agrees with the concentration detected in the leachate from the Mohammedia landfill (5 mg/L) [1] and remains higher than that measured at the Akreuch landfill (Wilaya Rabat-Salé) (35-120 µg/L) [27]. This is because several industrial tannery units are installed in Fez. This presence of chromium can come from other types of waste collected with household waste such as paper, cardboard and wood (total Cr = 25 mg/g of paper and 80 mg/g of wood) [28].

Table 4. Analysis of heavy metals before and after aeration treatment

Heavy métals (mg/L)	Raw leachate (mg/L)	After 2 days (mg/L)	After 7 days (mg/L)	Rate reduction (%) after 2 days of aeration (mg/L)	Rate reduction after 7 days of aeration (mg/L)	Limit values of discharges into surface and underground waters
Al	3.245	1,311	0,189	59,6	63,3	10
Cd	0,028	0,016	0,012	42,8	57,1	0,25
Cr	4,554	2,17	1,843	52,3	59,5	0,5
Cu	0,428	0,093	0,085	78,3	80,1	0,5
Fe	14,65	6,21	4,29	57,6	70,7	2
Mn	2,002	0,184	0,133	90,8	93,3	1
Ni	0,841	0,622	0,417	26	50,4	0,5
Pb	0,215	0,092	0,075	57,2	65,1	0,5
Zn	1,663	0,575	0,484	65,4	71	5

The lead concentration reaches 0,215 mg/L, this is related to discharges from industrial units, particularly in the printing and lead-based paint manufacturing sectors.The contents found for the different metals verify the order of magnitude of the concentrations given by Dace and al **[29]** in the methanogenesis phase, namely Zn > Ni > Cu > Pb. This order is frequently found in the bibliography **[30]**. Nickel, Zinc and Copper are in fact the most leachable elements in fresh waste **[31]**. They come from special waste such as batteries, paint pigments, stabilizers, rubbers and waste from copperware factories in the old medina of Fez, which use these threemetals in electroplating. Copper can also come from printing inks or paints **[32]**. Metal concentrations are in fact strongly linked to the composition of the waste. The high variation in metal contents may be associated with the high heterogeneity of the waste.

Metals are also present in other families of waste such as plastics, glass, paper and cardboard, putrescibles and special waste. As a result, the wastecontains a large stock of heavy metals. Cuprys *et al* **[33]**, estimate that the concentrations of copper, cadmium, zinc, lead and mercury are 5 to 127 times higher in landfills than in soils.

From the results of table 4, we observed that leachate treatment by aeration further reduces heavy metals, mainly after one week of aeration. The reduction rates are greater after 7 days of aeration compared to 2 days of aeration. Indeed, it is the accumulation of metals in the biological sludge that was used for sowing.Mn^{2+} ions have the highest reduction rate compared to other metals and are between 90,8% and 93,3%.The variability of metal reduction rates is due to the ionic form of each metal, to the capacity of each bacterium to accumulate the metal and to the physico-chemical conditions, which differ from one germto another to ensure the reduction of the metals. After 7 days of aeration, the leachate meets the standards for direct discharges, except for Fe, which has a concentration slightly higher than that of the standard. This is because the concentration of this metal is higher in the raw leachate.

3.6.2. Physical treatment of metal pollution from leachate by filtration:

In this step, we analyzed the metallic elements (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the raw and filtered leachates through the substrates S_1, S_2 and S_3. Each value is the average obtained after 4 sampling campaigns. The results of this analysis reported in **Table 5**. These results reflect a reduction in metal ions in the three leachate filtrates. The best reductions in metals observed with the filtrate F_3 with concentrations below the Moroccan standards of the general limit values of discharges into surface and underground waters and reduction rates higher than obtained after seven days of leachate treatment by aeration. The iron ions which had the highest concentration in the raw leachates are effectively reduced with the highest reduction rate above 99,31% and a concentration below 0,1 mg/L,well below the standard (3mg/L). The chromium has an abatement rate of 95,6% with a concentration of 0,2 mg/L, well below the standard for direct discharges (2 mg/L). This metal, which has always presented a major problem for the leachates of Fez, whose presence is caused by solid waste discharged by industrial tannery units of the city without any prior treatment in the absence of regulations. The following points can explain this strong elimination:

- The richness of the A_1 soil and fly ash in silica (higher content than that of bottom ash), surface hydroxyl groups are formed by hydration which allows the adsorption of metal cations **[34];**

- Being good adsorbents, iron oxides and aluminum oxides present in fly ash (% ∑ Al2O3+Fe2O3 = 47,4%) and soil A_1 (18%) play an important role in the retention of ions metallic [35];
- The manganese oxides present in the filtering substrates also playan important role because they have a particular affinity for certain heavy metals (Cu, Zn, Ni, Pb, etc.), which they can adsorb in large quantities [36];
- The small particle size of the fly ash does not exceed 200 µm, which allows an increase of the adsorption surface resulted from the decrease of the dimensions of the adsorbent grains;
- The high content of SiO_2 (silico-aluminous structure) of the fly ash [37]. It is an adsorbent with a high electrical polarity.
- The pozzolanic activity of the fly ash used makes it possible to form, with the lime present in the sands, stable hydrated calcium-silicon gels in the form of C-S-H. This reaction allows further stabilization of heavy metals [22] by various mechanisms:

• Mechanical trapping: metallic contaminants can act as a nucleation center and remain trapped in the hydrates thus formed [38, 39].

• Integration in hydrates: the C-S-H formed have, in addition, to integrate metal contaminants by substitution (especially Aluminum and Iron) in the crystal lattice, the ability to trap these contaminants in their interfoliar spaces [40]. This explains the strong reduction of Fe and Al ions in the leachate.

• Adsorption: C-S-H have good adsorption capacity [41].

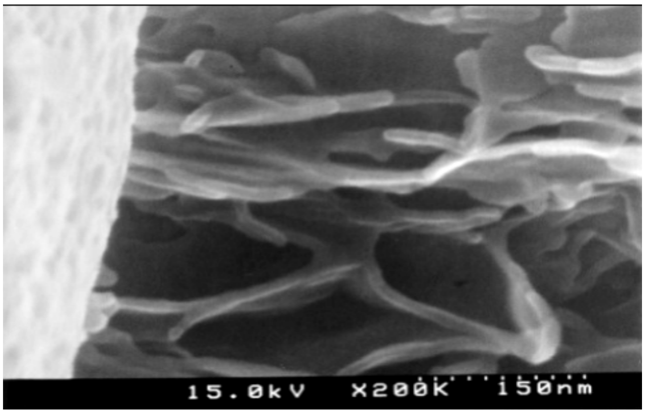

Photo 5. Zoomed image of the Pozzolanic reaction of fly ash [42]

The results obtained show the economic advantage provided by the use of coal ash and especially fly ash in the treatment of metal pollution from leachates. This is also done with a view to limiting the environmental risks due to the landfilling of these by-products. This filtration process reduces metal ion with substandard concentrations. The Fe ions which had the highest concentration in the raw leachates and which persisted before treatment by aeration arenow effectively reduced with the highest reduction rate of 99,32% and a concentration of less than 0,1mg/ L. Cr ions also record an abatement rate of over 97,8% with a concentration of less than 0,1 mg/L. It can be concluded that after this filtration, the heavy metal contents of the leachates effectively according the standards for direct discharges [43].

Table 5. Variation in the concentration of heavy metals in leachates before and after different filtartions

Heavy Metals	**Before filtration(mg/L)**	**After filtration (mg/L)**			**Rate réduction (%)**			**Limit values of discharges into surface and underground waters**
		(F_1)	(F_2)	(F_3)	(F_1)	(F_2)	(F_3)	
Al	3,245	0,3	3,8	0,4	90,75	-	87,67	10
Cd	0,028	<0,1	<0,1	<0,1	-	-	-	0,25
Cr	4,554	0,5	2,2	0,2	89,02	51,69	95,6	0,5
Cu	0,428	0,2	0,2	0,1	53,27	53,27	76,36	0,5
Fe	14,65	0,1	<0,1	<0,1	99,32	>99,31	>99,31	2
Mn	2,002	0,1	<0,1	<0,1	95	>95	>95	1
Ni	0,841	0,1	0,3	<0,1	88,1	64,32	>88,1	0,5
Pb	0,215	<0,1	<0,1	0,2	>53,49	>53,49	6,97	0,5
Zn	1,663	<0,1	<0,1	0,1	>93,98	>93,98	93,98	5

F1: Leachate filtrate through substrate S1: Soil A1+ Marine SandF2: Leachate filtrate through substrate S2: Soil A1 + Bottom ash F3: Leachate filtrate through substrate S3: Soil A1 + Fly ash

Conclusion

The filtration of leachates through the substrate S_3 formed by the clay soil designated A_1 and fly ash makes it possible to effectively reduce metal pollution, with concentrations respecting the Moroccan standards of the general limit values of discharges into surface and underground waters and an abatement rates higher than those found after 7 days of leachate treatment by aeration. The results obtained by the best filter bed F_3 are evaluated at a reduction of 87,67% for Aluminum with 0,4 mg/L; 95,6% for Chromium with 0,2mg/L; 76,36% for Cu ions with 0,1 mg/L; an abatement rate greater than 99,31% for Fer. An abatement more than 95% for Mn ions and go up to 88,1% for Nickel with concentrations respectively less than 0,1 mg/L; while Zn ions are effectively reduced to 93,98% with a concentration that does not exceed 0,1 mg/L.

In perspective, we propose to carry out a filtration of all the leachates on a filter formed by layers of well-chosen marine sands intercalated by the substrate S_3, and this for their efficiency and their simplicity of implementation, to better according the standards of rejection in force.

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