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Elimination of Heavy Metals (Cu, Zn, Cr, Ni and Pb) Contained in the Stabilized Leachate of the Agadir Landfill by Percolation-Infiltration on Titaniferous Medium

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This study focuses on the treatment of heavy metals in the stabilized leachate of Agadir landfill by means of infiltration percolation technique on filters at different heights 0.5, 1 and 1.5 m filled with titaniferous medium (TFM). It also deals with the effectiveness of the TFM from the region of Agadir (Morocco) in the retention of heavy metals. Through this study, it appears that the leachate of the city is loaded with heavy metals (Zn, Cu, Cr and Pb) and that there is absence of Cadmium and Nickel. The comparison of the total concentration of these metals with the standards of discharge re-use revealed that the zinc, the chromium and the plumb, exceed the maximums recommended by the World Health Organization. The experimental device makes it possible to reduce the load in Zn, in Cr, in Cu and in Pb with interesting outcomes in proportional to the heights of the filters. For the 1.5 m height column, the abatement rates were respectively Cu, Zn, Cr and Pb at 58.25 %, 65.04 %, 69.62 % and 60.26 %. This treatment technique has shown significant purification performance in the removal of heavy metals in the leachate.

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Introduction

The different types of waste (urban, rural and industrial), that Agadir landfill can accommodate cause a very large volume of leachates that is stored in the basins of this landfill. This ever increasing amount represents a big problem for the landfill and the environment. Many studies have shown that leachates contain large heavy metals. However, some exceed discharge standards, and recent work [1] has demonstrated that groundwater pollution from landfill is almost undetectable. Generally, the presence of heavy metals such as Cr, Cd, Pb, Hg, Ni, Cu, Zn and Fe, in the leachate can have a negative impact on the environment and human health [2, 3].In front of this problem their elimination is a major concern. The processes used to treat leachate include coagulation and flocculation [4], membrane filtration [5], electrochemical destruction [6], ozonisation [7]. However, these methods have a number of limitations including, high cost equipment, and intensive energy requirements

The system of removing heavy metals in leachate by the titaniferous medium (TFM) used in our work is infiltration-percolation. This approach has been applied to the semi-pilot model base. It consists of PVC columns of 11 centimeters in inner diameter, filled with different heights of TFM. The chemical analyses that have been carried out relate to the purifying power of TFM based on complementation/precipitation, the ion exchanges, the electrostatic interactions and the adsorption of heavy metals

[8]. The objective of this study is to determine the concentrations of heavy metals in the leachate before and after treatment and the rate of reduction of the filter mass.

Material and methods

Sampling of leachate and purification method

The leachate samples used in this work are stabilized leachates from the Agadir Grand dump. They are contained in plastic bottles of ten liters for each sample. The samples intended for analysis are fixed by concentrated nitric acid (1 mL of acid per 100 mL) after passing through the TFM columns.

The experimental setup consists of three PVC columns that are simulated in infiltration-percolation basins. These columns have a dimension of 11 cm internal diameter, filled with profiles of 0.5m, 1m and 1.50 cm of TFM. This experimental device is located in the materials and environment laboratory at the Faculty of Sciences of Agadir (see Fig. 1). Before the use of TFM, the coarse particles which may be at the origin of preferential currents within the columns have been eliminated. Indeed, the porosity of the massif influences the purification.

Each column is equipped with a perforated drainage system at the bottom base installed over a plastic film, to ensure a complete water tightness of the system. The PVC drain diameter is five centimetres and that of the pores is a few millimetres (~ 3 mm). The drain is surrounded by a 15-centimeter layer of gravel of varying shape to prevent the loss of fines from the TFM and clog the outlets of the effluent, and a support is placed to secure the filter bed. The experimental setup used is shown schematically in the Fig. 1. The purification is ensured by the passage of a volume of 2 litres of leachate for each column through the filter beds. The dynamic approach can be used to determine the retention capacity of heavy metals by TFM by percolating the contaminated effluents and by following the Cu (Zn, Cr and Pb) contents in the purified outflow leachate.

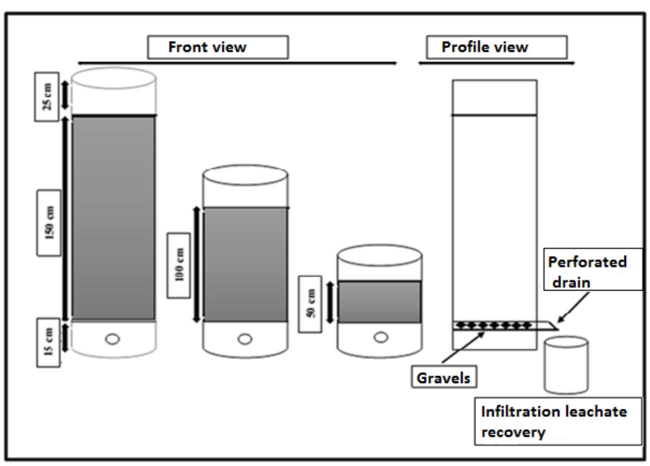


Fig. 1 : Experimental setup of infiltration-percolation on TFM.

Characterization of samples

The concentrations of heavy metal ions in the leachate were determined by atomic absorption of the AA-7000 graphite furnace. The morphology and elemental composition of TFM were observed using a scanning electron microscope (SEM supra 40VP, France) equipped with a dispersive X-ray spectrometer (EDX). The molecular structure was analyzed by a Fourier Transform Infrared Spectrometer (FTIR Hitachi I-2001 Dual Beam, over the 400-4000 cm-1 range. BET surface measurements (Brunauer-Emmett-Teller) were performed on a Micromeritics ASAP 2020M Surface Analyzer.

Results and discussion

Analysis and Characterization

We tested the efficiency of Cu, Zn, Cr and Pb metal removal through the black iron-rich TFM filtration process. To avoid the precipitation of metals and biological growth, a few drops of concentrated nitric acid were added to the samples to obtain a pH below 2.5 [9] followed by filtration on a filter paper, The samples were stored at 4°C for analysis with an AA-7000 graphite furnace atomic absorption spectrometry. Tab. 1 shows the concentrations of heavy metals (Cu (II), Zn (II), Cr (II), Pb (II), Cd (II) and Ni (II)) at the pilot system inlet.

Tab 1 : The concentrations (mg/L) of heavy metals in leachate stabilized

Trials	Cu	Zn	Cr	Pb	Cd	Ni
1	1.3378	10.6029	0.2635	1.2720	-	-
2	1.2536	9.4379	0.2010	1.2804	-	-
3	0.9826	9.8956	0.3009	1.2841	-	-
4	1.0028	6.3136	0.3105	1.2840	-	-
5	0.8599	7.5896	0.2543	1.2902	-	-
6	1.3509	7.5845	0.2513	1.2780	-	-
7	1.2458	8.5963	0.2440	1.2713	-	-
8	0.9989	8.5466	0.2463	1.2601	-	-
9	1.1024	9.1203	0.2635	1.0948	-	-
10	1.1389	7.2451	0.2875	1.3001	-	-
Average	1,1274	8,4932	0,2623	1,2615	-	-
standards	3.0	5.0	0.10	1.0	0.2	5

The results showed that some heavy metals found in leachate such as zinc, chromium and lead exceeded the standards of wastewater reuse. They also revealed the absence of cadmium and nickel. This study indicated that leachate generated from the Agadir landfill contains large quantities of different heavy metals. The average concentration of Zn, Cu, Cr, and Pb is 8.49, 1.12, 0.26, 1.26 ml/L, respectively. The concentration of Zn, Cr and Pb in the landfill leachate is higher than the allowed standard value hence the importance of treating these effluents as they have a negative impact on the environment.

The characterization of TFM was previously reported. The chemical composition (wt %) determined by X-ray fluorescence spectrometer is Fe_2O_3, 84.4; TiO_2, 8.1; SiO_2, 2.79;

ZrO_2, 5.15; Al_2O_3, 0.57; CaO, 0.51; MgO, 0.338; SO_3, 0.15; K_2O, 0.13; Na_2O, 0.15 and lost in ignition, 0.51. Nevertheless, it is important to note that the TFM explored in this study contains a considerably higher Fe_2O_3 content than that found in the siliceous sands frequently encountered in the water purification [10]. Fig. 2 reveals the EDX spectra and SEM image. The SEM observation of TFM reveals a rather different particle size and geometry with a low agglomeration of grains, ranging from a hundred micrometres to more than 300 µm.

The specific surface area, total pore volume and average pore diameter obtained from the N_2 equilibrium adsorption isotherms were found to be 0.84 m^2/g, 0.0132 cm^3/g and 2.64 nm, respectively. Fig. 3a shows the distribution of pore size (PSD) according to the BJH method. The PSD curve, in this case, has a population due to the existence of mesoporous grains.

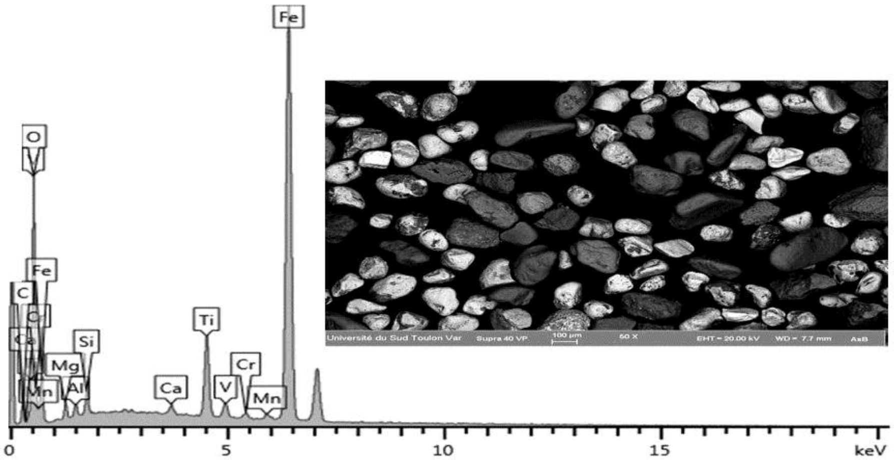
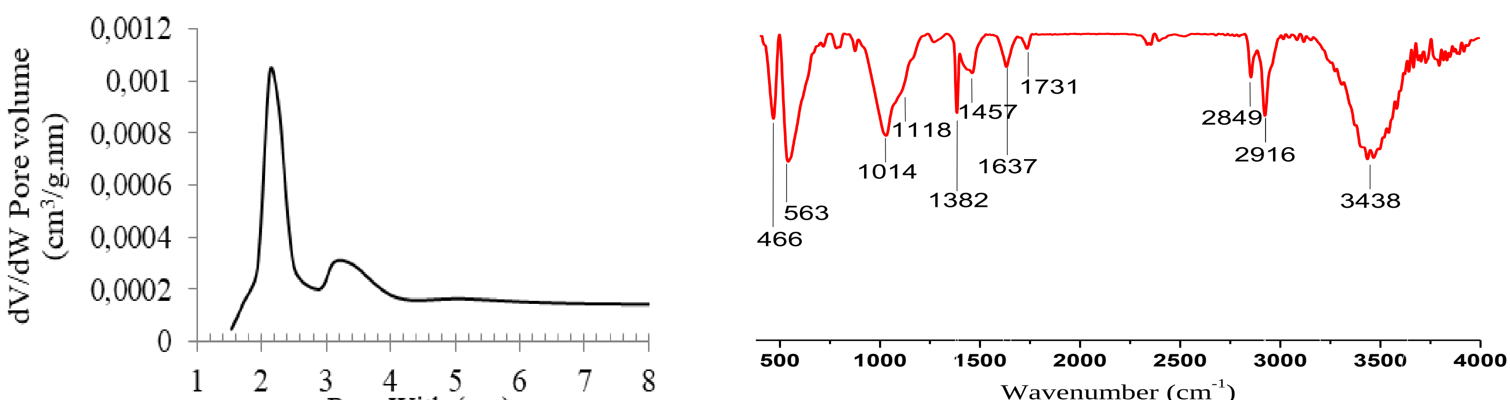


Fig. 2: EDX spectrum of TFM with SEM images

The IR spectrum of the TFM is illustrated in Fig. 3b. The presence of a wide band at about 3438 cm^{-1} and an absorption at 1637 cm^{-1} are noted. This band is attributed to the OH elongation and angular deformation of physisorbed molecular water [11] on metallic elements (M = Fe, Ti, Zr, Si, etc.) in the form of M-OH [12, 13] on the grain surface. The fine and intense bands observed between 420 and 560 cm^{-1} are attributed to the characteristic Si-O deformation bands at the abundant silica oxides. This observation has been confirmed, in perfect agreement with the EDX and X-ray fluorescence analysis. Very low absorptions around 2393 cm^{-1} are attributed to the presence of organic matter (CH elongation) [14] probably due to a contamination during the pelletizing operation.



(a) **(b)**

Fig. 3: a) Pore size distribution curve and b) Infrared spectra of TFM

Elimination of heavy metals in leachate

We monitored the heavy metal concentrations in the leachate of the Agadir landfill for a period of three and a half months before and after the treatment using the infiltration-percolation process. The concentrations of heavy metals recorded at the outlet of the different heights show that all the sand thicknesses tested are effective in eliminating the particular fractions of the metals. However, this efficiency seems to depend on both the height of the TFM and the metal concentration in the leachate to be purified (Fig.4)

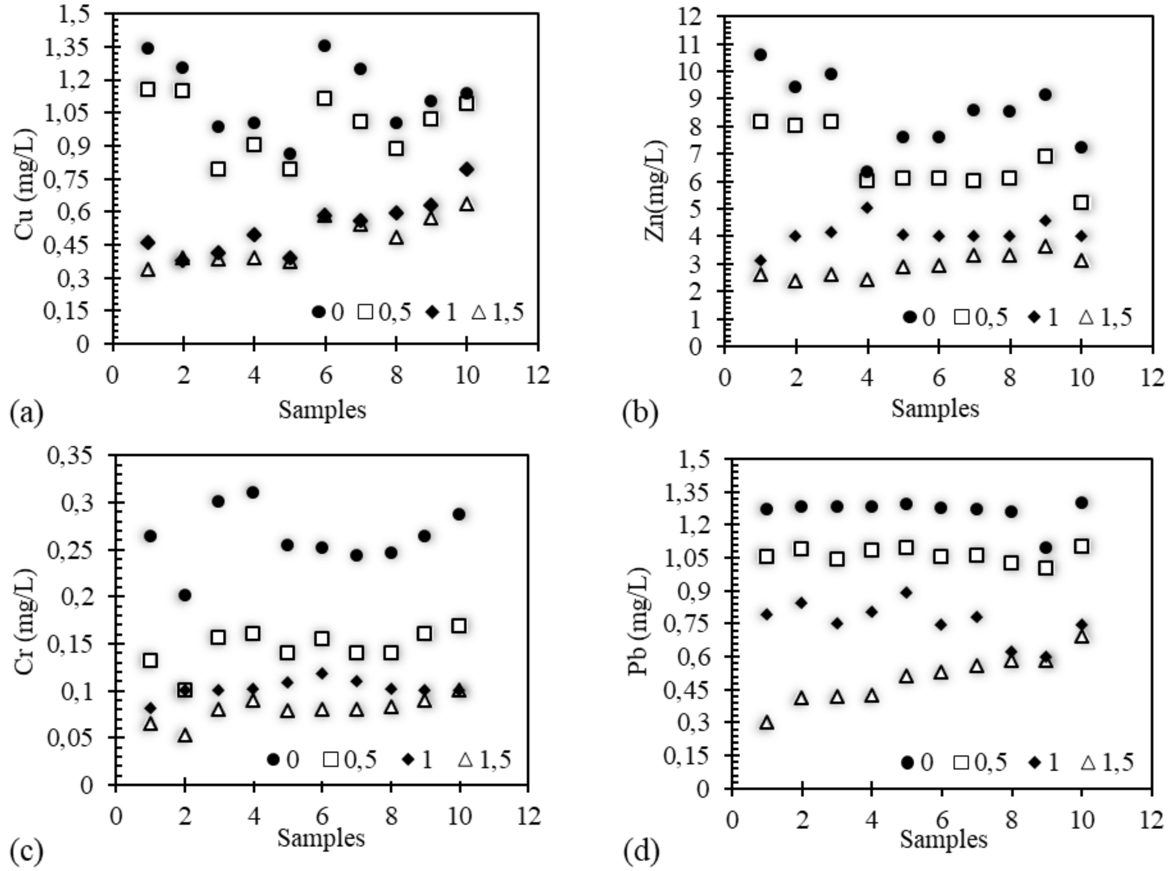


Fig. 4 : Changes in heavy metal concentrations in leachate before and after infiltration-percolation. a) shows changes in copper concentration in leachate, b) changes in zinc concentration in leachate, c) changes in chromium concentration in leachate, d) the evolution of lead concentration in leachate.

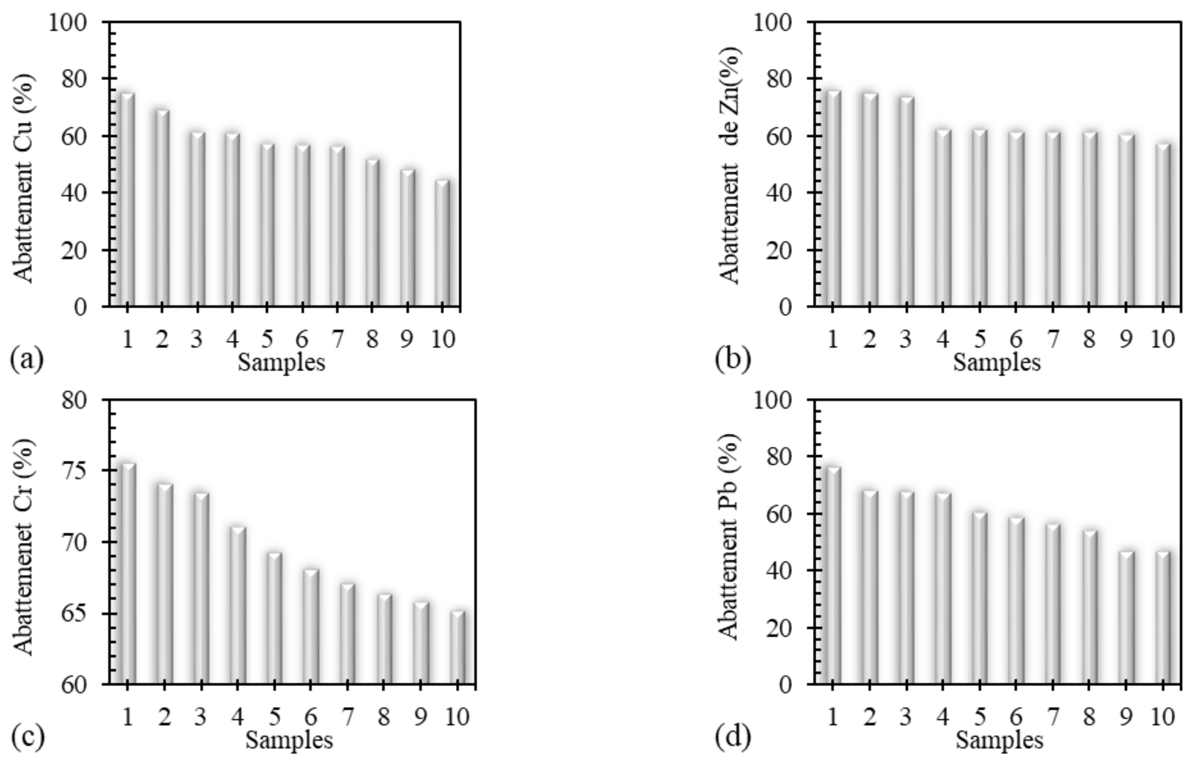


Fig. 5 : Abatement of a) copper, b) zinc, c) chromium and d) lead in leachate.

Many studies have proved that soils can remove heavy metals [15, 16]. The most important process that affects the behaviour of heavy metals in soil is the adsorption of metals from the liquid phase into their solid phase [17]. The results of this study demonstrate a high efficiency of the removal of heavy metals, which is in agreement with other reported studies, for which the types of the same sand were used [18]. However, the presence of iron oxides in the TFM significantly affects the mobility of heavy metals [19], including the role of organic matter in fixing much of the trace metals. Microorganisms can play a role in metal mobilization and can affect their bioavailability by attaching and releasing elements decomposing organic matter [20].

Fig. 5 describes the concentrations of heavy metals in leachate at different depths of the pilot system. The results show that the abatement rate decreases over time. This can be explained either by our TFM being clogged or the decreasing performance of the elements responsible for eliminating heavy metals in leachate (iron oxide and micro-organisms).

Conclusion

The results obtained during the treatment of leachates show that the concentrations of the heavy metals Cu, Zn, Cr and Pb are respectively 1.1274, 8.4932, 0.2623 and 1.2615 mg/L. They also show the absence of Cd and Ni. Values registered are above the standards of the Moroccan Ministry of Environment except copper. The use of iron-oxide-rich TFM component for leachate treatment has demonstrated its effectiveness at the pilot scale for the removal of heavy metals. The results obtained for the removal of heavy metals show improved performance; 58.17 % Cu (II), 59.2 % Zn (II), 69.61 % Cr (II), and 60.28 % Pb (II). These values are in line with the Moroccan water standards used for irrigation without forgetting that the height of TFM column has an influence on the rate of elimination. According to FTIR, XRD and EDX, the possible mechanisms for the removal of heavy metals on TFM are the interactions between the hydrogen bonding (OH^-) and Cu (II), Cr (II), Pb (II). These interactions can take different forms such as ion exchange process, electrostatic interactions or biological interactions.

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