REMOVAL OF HEAVY METALS FROM LANDFILL LEACHATE USING ZERO VALENT IRON AND GRANULAR ACTIVATED CARBON

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Keywords:	Leachate, granular activated carbon, nickel, zero valent iron, zinc

REMOVAL OF HEAVY METALS FROM LANDFILL LEACHATE USING ZERO VALENT IRON AND GRANULAR ACTIVATED CARBON

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Abstract

The possibility of a landfill leachate pre-treatment, aiming at heavy metals removal, by either zero valent iron (ZVI), or granular activated carbon (GAC) or by a mixture of the two materials, was investigated in this paper through batch and column experiments. For this purpose a synthetic landfill leachate containing heavy metals (i.e. Cu, Ni, Zn), chloride, sulphates, ammonium and organic matter was formulated.

Batch tests results demonstrated the efficiency of ZVI, GAC and ZVI/GAC mixture in heavy metals removal (efficiency > 90 %) and their negligible effect on the other contaminants. Column tests showed as pure ZVI is by far more efficient than pure GAC in the long term.

The influence of humic acids (HA) on the reactive and hydraulic behaviour of ZVI was also studied through column tests. The presence of HA in the leachate caused a reduction of ZVI removal efficiency and a considerable decrease of its hydraulic conductivity.

Results of a column test carried out using the ZVI/GAC granular mixture showed as the removal efficiency over time ranges from 100 to 89 % for Cu, from 93 to 80 % for Ni, and from 98 to 95 % for Zn. The use of a filter filled with the ZVI/GAC mixture could find application for leachate pre-treatment having the objective of removing heavy metals prior the final co-treatment with municipal wastewater minimizing adverse side effect on the process (e.g. transfer of heavy metals in excess sludge to be used in agriculture).

Keywords: Leachate, copper, granular activated carbon, nickel, zero valent iron, zinc

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1. Introduction

The management of leachate is one of the main issues connected to the use of sanitary landfill technology. In particular, the presence of heavy metals in leachate can cause different problems to its co-treatment with municipal wastewater into wastewater treatment plants (WWTPs). This latter being one of the most frequent solution adopted worldwide [1]. In fact, unlike nitrogen and biodegradable organic pollutants, heavy metals are not affected by biological treatment. Their presence not only may reduce overall treatment efficiency but they are also transferred to excess sludge, derived from the treatment, preventing its direct or indirect (composting) use in agriculture [2][3].

A cost-effective pre-treatment of landfill leachate able to remove heavy metals would allow to minimize the drawbacks connected to leachate co-treatment in municipal WWTPs.

In this paper the efficiency of granular materials as zero valent iron (ZVI), granular activated carbon (GAC) and of a granular mixture of ZVI and GAC, was tested through laboratory tests.

In the scientific literature the use of granular materials (like ZVI, zeolite or GAC) for leachate treatment was investigated by different authors with two main objectives: evaluating their application as reactive media in permeable reactive barriers (an in situ groundwater remediation technology) for the remediation of landfill leachate-contaminated groundwater [4][5][6], or in landfill leachate treatment system [7]. The reactive materials, the heavy metals, the test typology (column test -CT- or batch test -BT-) and the main results obtained in the above mentioned studies are summarized in Table 1.

It can be observed as ZVI is the most used reactive medium. Its diffusion is due to its capacity of activating several reaction mechanisms for contaminants removal (e.g., redox reactions, precipitation, and sorption) [8][9][10]. However, the use of pure ZVI has limitations with regard to the long-term hydraulic and removal properties [11][12]. In fact, the inevitable corrosion of the material and gas formation can cause the clogging of the medium pores and the reduction of its reactivity [13][14][15][16]. However, the use of granular mixtures of ZVI with other reactive or inert materials, in various weight or volume ratios, allows to extend its efficiency in the long term [17][18][19][20][21][22].

GAC also can remove a large number of contaminants, organic and inorganic, through sorption mechanisms [23][24][6]. In particular, GAC removes heavy metals by complexation or by electrostatic attraction of metal ions to various surface oxygen-containing functional groups [25] [26]. Like ZVI, it has limitations in the long term due to the inevitable exhaustion of the sorption sites.

In the present study batch and column tests were performed using granular pure materials, ZVI and GAC, and a mixture of the two at a weight ratio 30:70 respectively. A synthetic landfill leachate containing heavy metals (i.e. Cu, Ni, Zn), chloride, sulphates, ammonium and organic substance was formulated. The influence of humic acids (HA) on the reactive and hydraulic behaviour of the ZVI was also studied through a column test.

2. Materials and methods

The reactive granular materials used in this study were ZVI and GAC. The ZVI is of type FERBLAST RI 850/3.5, distributed by Pometon S.P.A. (Mestre, Italy) and it is mainly composed by iron (> 99.74 %).

The GAC is of the type CARBOSORB 2040 (20 x 40 mesh) and was provided by Comelt srl (Milan, Italy). It is a high quality product derived by physical activation of selected raw material of mineral origin.

The materials are characterized by a uniform grain size distribution, the coefficient of uniformity, $U = d_{60}/d_{10}$, is 2 and 1.45 for ZVI and GAC respectively, the mean grain size (d_{50}) is 0.5 and 0.4 for ZVI and GAC respectively.

Two synthetic landfill leachates, one with and the other without HA, representative of the acidic phase of a landfill, were prepared by dissolving specific reagents of the appropriate grade, provided from Sigma Aldrich, into distilled water. The concentrations of the elements and the reagents used are summarized in Table 2. For the leachate containing HA the contribution of CH_3COOH and HA in terms of COD was approximatively equal.

The pH of the synthetic solution was adjusted to the desired value equal to 5 with 0.1M NaOH.

In this research batch and column tests were carried out. Batch tests were carried out using a rotary shaker at 30 rpm (Stuart Scientific Rotator Drive STR/4). Each batch was prepared by mixing 52 ml of aqueous solution with 5.2 g of the reactive medium (solid-liquid ratio equal to 1:10). The liquid samples were collected at preset time intervals (i.e. 4, 24, 48, 72 and 96 hours) sacrificing the vial. The vials was then centrifuged, for 3 min at 6000 rpm, before the analyses.

Columns tests were carried out using polymethyl methacrylate (PMMA—Plexiglas™) columns (internal diameter of 5±0.1 cm and a height of 50 cm), equipped with sampling ports located at different distances from the inlet. The columns were fed with a peristaltic pump (Watson Marlow 205S) under constant upward flow rate. During the test hydraulic conductivity was determined by using the falling-head or constant-head permeability methods as appropriate [27].

Two column tests using ZVI and the two leachates (Table 2) were carried out in order to evaluate the influence of HA on the reactive and hydraulic behaviour of ZVI. These tests were carried out filling the columns with 500 g of pure ZVI (thickness of 6 cm) and the remaining space with quartz gravel.

The column tests using GAC or the ZVI/GAC granular mixture, at weigh ratio 30:70, were carried out filling the entire column with 477 and 750 g (225 of ZVI and 525 of GAC) of reactive medium respectively.

A flow rate of 0.5 ml/min was used for the tests performed using the pure materials and a flow rate of 0.1 ml/min was used for the column test carried out with the mixture.

In Tables 3 and 4 is shown the experimental program for respectively batch and column tests.

On aqueous samples, withdrawn from vials or from sampling ports in, respectively, batch and column tests, pH and redox potential (Eh) were measured with a multiparametric instrument (PCD

65) and subsequently the same samples were analysed using ICP-OES (Perkin Elmer OPTIMA 8000), for determining heavy metals concentration, and using a ion chromatograph (Metrohm 883 basic IC plus) for cations and anions measurements according to conventional Standard Methods [28].

The removal efficiency (R_E) of contaminants was calculated through equation 1:

$$R_E = \frac{C_0 - C_f}{C_0} \cdot 100 \qquad (1)$$

where C_0 and C_f are respectively the initial and final concentration of the contaminant in the leachate (mg/L).

3. Results and discussion

3.1 Batch tests

The results of batch tests are shown in Figure 1 in terms of contaminants normalized concentration (C/C_0) as a function of time, for the different contaminants used in the research.

It is possible to observe that Cu was completely removed (R_E>99.8%) by both pure granular reactive materials (i.e. ZVI and GAC) and also by the granular mixture, Ni and Zn were removed with a removal efficiency higher than 90.9 and 93.1 % respectively by the three reactive granular media.

The use of the ZVI/GAC granular mixture allowed to enhance and accelerate the removal of heavy metals likely due to the increase of the number of mechanisms available for heavy metals removal. In fact, after only 24 hour all the three heavy metals were removed with a removal efficiency higher than 97.6 %. From the same figure it is possible to observe that unlike heavy metals, the removal efficiency of the three reactive media towards ammonium, chlorides and sulphates was negligible.

The values of the removal efficiency for the different contaminants and reactive granular materials are summarized in Table 5.

An increase of pH end a decrease of Eh was observed for the three granular reactive media as showed in figure 2. In particular, pH increase was slightly lower for pure GAC.

The change of pH in presence of ZVI was consistent with the effects of ZVI corrosion during its interaction with water and the consequent production of hydroxyl (OH^-).

3.2 Column tests with ZVI and GAC pure materials

In figure 3 the normalized concentration of heavy metals (i.e. Cu, Ni and Zn) determined at the outlet of the columns containing ZVI and GAC and permeated by the acidic leachate is shown as function of time.

Cu was completely removed by pure ZVI. Its removal was due to the cementation process which allows the precipitation of Cu [29][30]. The irregular behaviour shown between the 2500 and 3500 hours could be due to some form of release of previously removed copper. Ni and Zn were instead removed up to 900 and 2000 h respectively by ZVI. Ni and Zn removal can be mainly attributed to i) co-precipitation with iron (during precipitation iron corrosion products may entrap adsorbed contaminants in their mass), ii) adsorption on the surface of iron corrosion products and iii) adsorptive size-exclusion which occurs when the formation of iron oxides reduces the pore volume of the reactive medium and behave as a reactive filter towards the contaminants [31][32][33]. For the other contaminants the analyses carried out on samples withdrawn at the outlet of the ZVI column have shown a removal efficiency for ammonium equal to 15 % up to 216 h and the complete exhaustion of the reactive medium starting from 576 h. For chlorides and sulphates the removal efficiency was always lower than 20 %.

Referring to GAC column test, Cu was removed for the entire test duration at the outlet (Figure 3a) whereas, an increase of metal concentration, was observed at 912 h at the first sampling port (3 cm from column inlet) indicating the beginning of the reactive medium exhaustion. On the contrary, the total removal of Ni and Zn was observed only at the first sampling, carried out after 24 h, in fact afterwards the reactive medium showed its exhaustion along the entire thickness (Figure 3 b,c).

Referring to the other contaminants the ammonium removal was null at the outlet of the GAC column for the entire duration of the test, whereas chlorides and sulphates removal efficiency was always less than 20 %.

Notwithstanding batch tests results showed a similar behaviour of the ZVI and of the GAC towards heavy metals removal (Figure 1 and Table 4), column tests results showed as the ZVI is significantly more efficient than GAC in the long term.

The hydraulic conductivity of the two reactive materials is shown in Figure 4 as a function of time. It was constant for ZVI up to 2300 h afterwards it slightly reduced down to $7.3*10^{-4}$ cm/sec. No change was observed for GAC.

3.3 Influence of HA

In order to evaluate the influence of HA on the reactive and hydraulic behaviour of the ZVI a column test using a leachate containing HA was carried out.

In figure 5 the contaminant normalized concentration of Cu, Ni and Zn is plotted as function of time. It can be observed as i) the three heavy metals were not completely removed by the reactive medium, ii) the removal sequence observed was the following Cu > Ni > Zn iii) zinc was the metal most greatly influenced by the presence of HA.

Comparing these results with those obtained using pure ZVI permeated by leachate in absence of HA (Figure 3), can be observed as the presence of HA reduces the removal capacity of the reactive medium towards the three heavy metals. The same conclusion was also reached in literature [34][35][36] using Cr(VI) and As(V). In particular, the decrease in the removal capacity for Cu can be attributed, as well as attributed in literature for Cr(VI) removal, to the deposition of HA aggregates on the ZVI surface since HA can form aggregates with cations such as Fe^{2+}, Fe^{3+} and Ca^{2+} that deposit on the iron surface inhibiting electron transfer from ZVI [35][34]. The reduction of the ZVI removal efficiency toward Ni or Zn can be attributed to the deposition of HA on ZVI surface causing a reduction in the formation of iron corrosion products effecting mechanisms of adsorption/co-precipitation as hypothesized in literature for As(V) removal [34]. Also [37] observed through batch tests a reduction of the ZVI removal capacity toward Zn and Ni in the presence of HA. This behaviour was attributed to the formation of HA–heavy metal complexes which prevented the removal reactions at ZVI surface.

In presence of HA the removal of chlorides, sulphates and ammonium was lower than 5 %.

Moreover the presence of HA greatly influenced the hydraulic behaviour of ZVI as shown in figure 6. In fact, the hydraulic conductivity reduced of almost three order of magnitude after only 768 h from test beginning for the column test carried out using HA.

3.4 ZVI/GAC column test

In order to improve the hydraulic behaviour of the ZVI, especially when it is permeated with a leachate containing HA, and to increase the removal efficiency respect to the use of pure GAC, the two materials were mixed using a weight ratio equal to 30:70 respectively. The column test was performed using a lower value of flow rate (equal to 0.1 ml/min) in order to guarantee the completion of the removal reactions.

In Figure 7 the normalized contaminant concentration (C/C_0) of Cu, Ni and Zn was plotted as a function of time (h).

The removal efficiency of heavy metals ranged from 100 to 89 % for Cu, from 93 to 80 % for Ni, and from 98 to 95 % for Zn.

In figure 8 the ZVI and the ZVI/GAC granular mixture are compared for the three heavy metals in terms of mass removed $M_{removed}$ [mg] as a function of the mass in input M_{input} [mg].

In general, the granular mixture ZVI/GAC allowed to improve the reactive behaviour of the pure ZVI when it is permeated by leachate having the same composition used in the experiment with mixture (i.e. in presence of HA) especially towards Zn removal. The improvement of the reactive behaviour was mainly attributed to the presence of the GAC instead that to the longer residence time guaranteed by the lower value of flow rate used during the experiment.

Ammonium was removed at the outlet with an efficiency of 95 % after 144 h of test, afterwards the removal capacity reduced up to 40 % after 288 h. At 1800 h the reactive medium was completely exhausted. In the case of chlorides and sulphates, no significant removal was observed.

The ammonium removal was main attributed to the ZVI since previously column tests results showed the inability of the pure GAC to remove this contaminant. The higher value of the ammonium removal efficiency determined at 144 h for the granular mixture respect to the value determined for the pure ZVI was attributed to the higher residence time.

In Figure 9 the hydraulic behaviour of the granular mixture is shown. A sudden reduction of the hydraulic conductivity was observed after 2000 h of test duration. In particular, after 2500 hours a value equal to $1.44 \cdot 10^{-4}$ cm/s was reached and the test was interrupted. A visual observation has shown the presence of gas bubbles and of filamentous mucilage at the inlet and outlet of the column. Since during disassembly of the column, a cementation phenomenon was not observed, clogging could be due to the presence of gas bubbles (likely hydrogen developed during anaerobic corrosion of ZVI) and to a biofilm formation.

4. Conclusions

In this study the efficiency of the ZVI, the GAC and of a mixture of the two materials was tested through laboratory tests (i.e. batch and column tests) in order to evaluate the efficiency of a leachate pre-treatment system which would allow to solve some of the issues linked to the co-treatment of leachate with municipal sewage.

Batch tests results showed a removal efficiency for Cu, Ni and Zn higher than 93.1 % for ZVI, 90.9 % for GAC and 97.6 % for the granular mixture ZVI/GAC. On the contrary, the efficiency of the three investigated reactive media towards the other contaminants contained into the formulated landfill leachate (i.e. chloride, sulphates and ammonium) was negligible.

Column tests, carried out using the pure materials (i.e. ZVI and GAC), confirmed the results obtained by batch tests for heavy metals removal, only in the short term, in fact, it was observed as ZVI was by far more efficient than pure GAC in the long term.

A column test carried out using the pure ZVI permeated with a leachate containing HA showed as their presence negatively influenced its reactive and hydraulic behaviour. In fact, HA reduced the removal capacity of the ZVI towards the three heavy metals (from 99.6 to 89 % for Cu, from 99.7 to 83 % for Ni, and, especially, from 99.8 to 0 % for Zn after 834 h from test beginning). Furthermore, the presence of HA reduced the ZVI hydraulic conductivity of almost three order of magnitude after only 768 h from test beginning.

Finally a column test, using a granular mixture of ZVI and GAC at weight ratio 30:70 permeated with a leachate containing HA, was performed. The mixture allowed to improve the reactive and hydraulic behaviour of pure ZVI. It was observed a removal efficiency variable from 100 to 89 % for Cu, from 93 to 80 % for Ni, from 98 to 95 % for Zn. A sudden reduction of the hydraulic conductivity was observed after 2000 h from test beginning, likely due to the formation of gas bubbles and of biofilm. Therefore, a monitoring of the reactivity and hydraulic behaviour of the reactive medium is fundamental in order to guarantee its correct use as leachate pre-treatment system.

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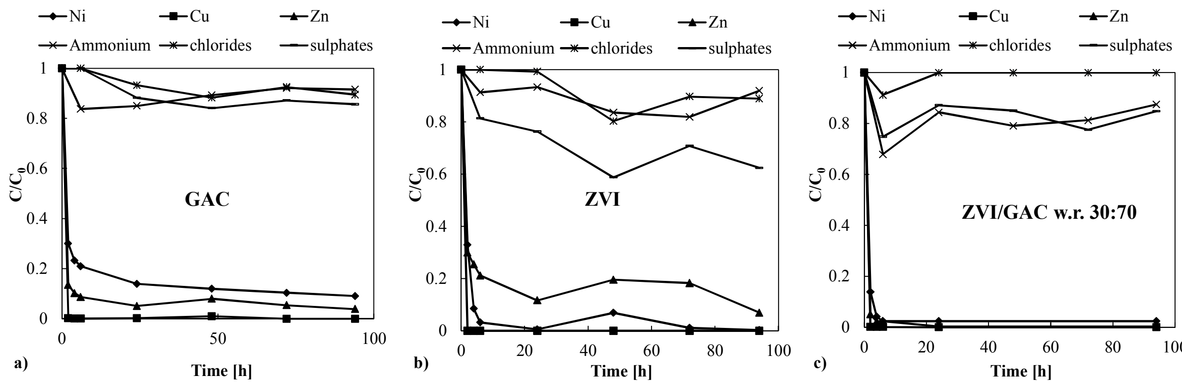

Figure 1: Contaminants normalized concentration (C/C_0) versus time in batch tests

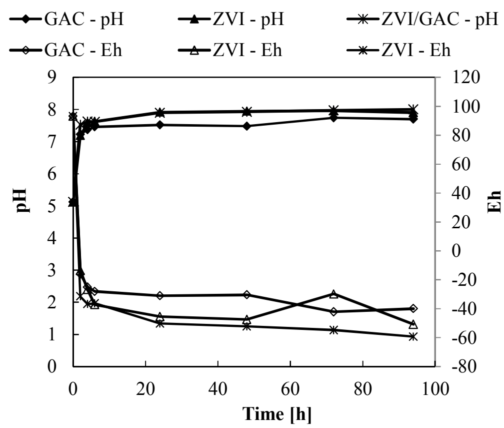

Figure 2: pH and Eh profiles versus time in batch tests

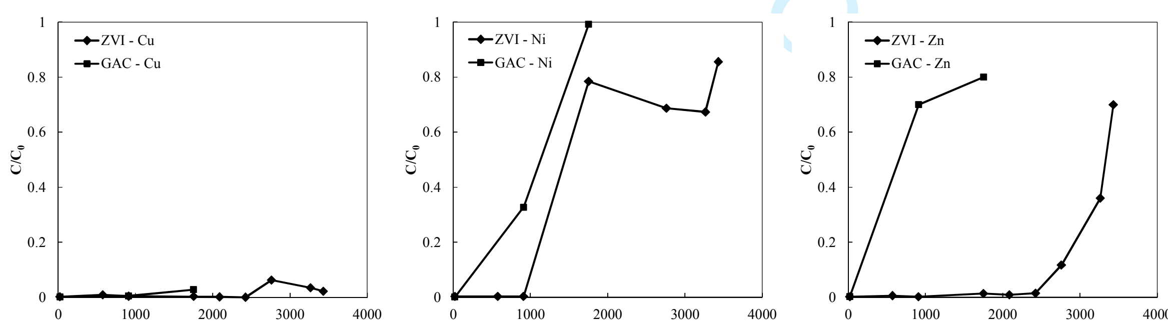

Figure 3: Contaminants normalized concentration (C/C_0) versus time in ZVI and GAC column test

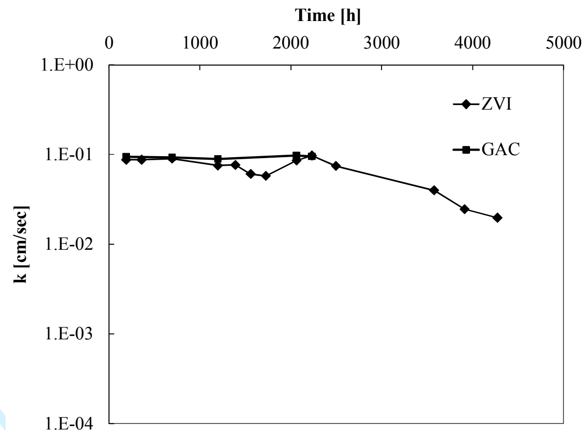

Figure 4: Hydraulic conductivity vs time for the ZVI and GAC column tests

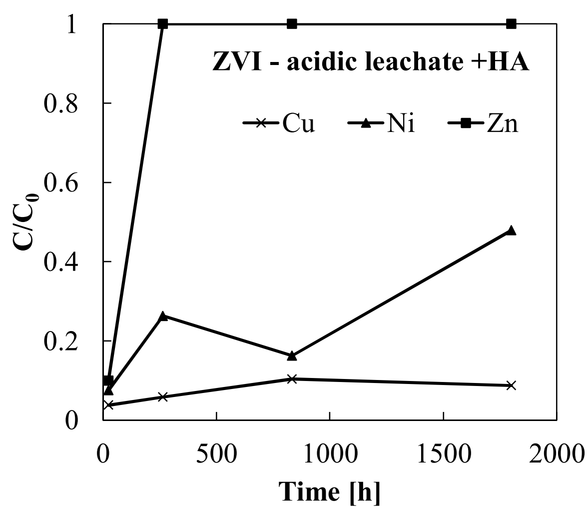

Figure 5: Contaminant normalized concentration (C/C_0) of Cu, Ni and Zn as a function of time [h] for the ZVI permeated with leachate containing HA

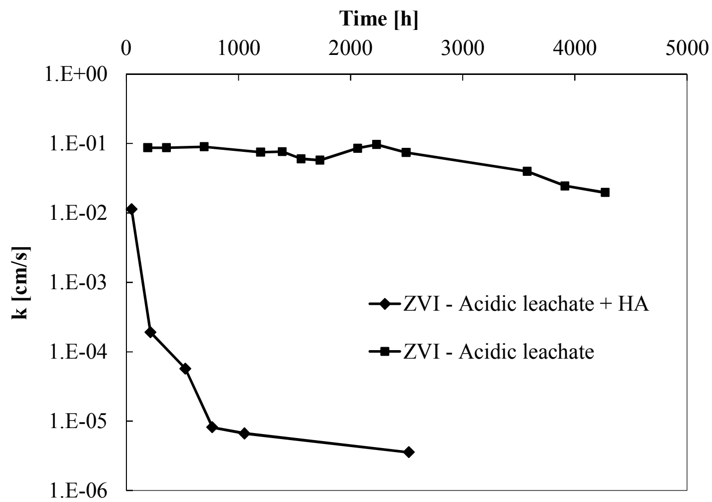

Figure 6: Hydraulic conductivity vs time for the ZVI permeated with leachate in presence or without HA

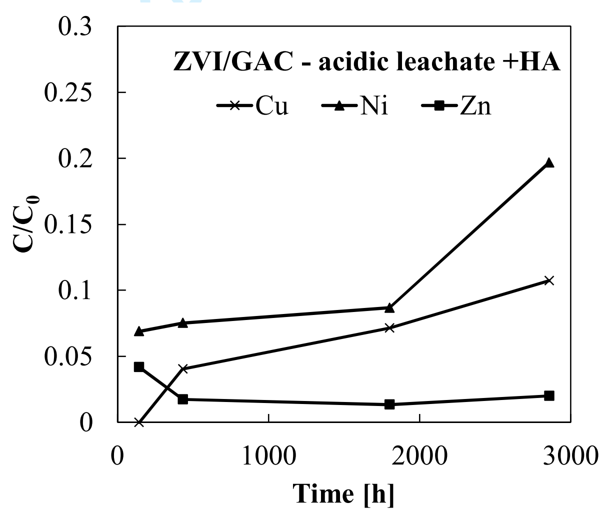

Figure 7: Contaminant normalized concentration (C/C_0) of Cu, Ni and Zn as a function of time [h] for the ZVI/GAC granular mixture permeated with leachate containing HA

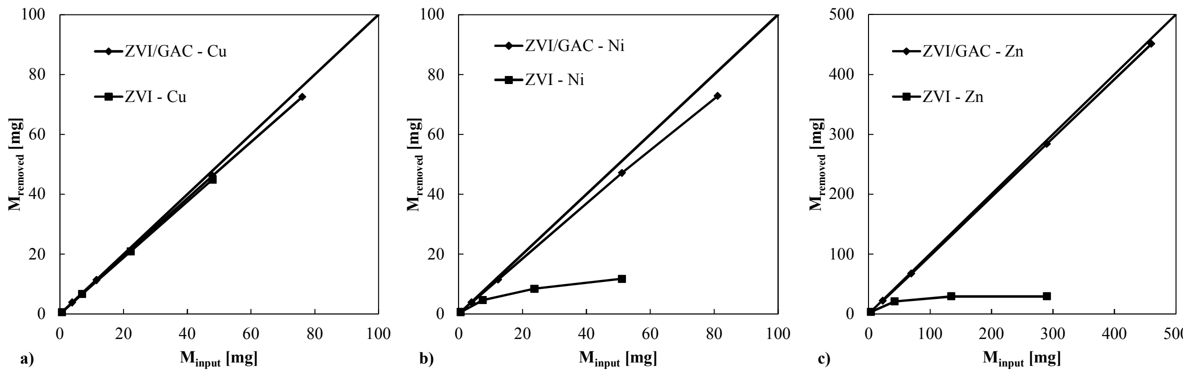

Figure 8: Mass removed ($M_{removed}$) versus mass in input (M_{input}) for a) Cu, b) Ni, c) Zn for ZVI and ZVI/GAC mixture

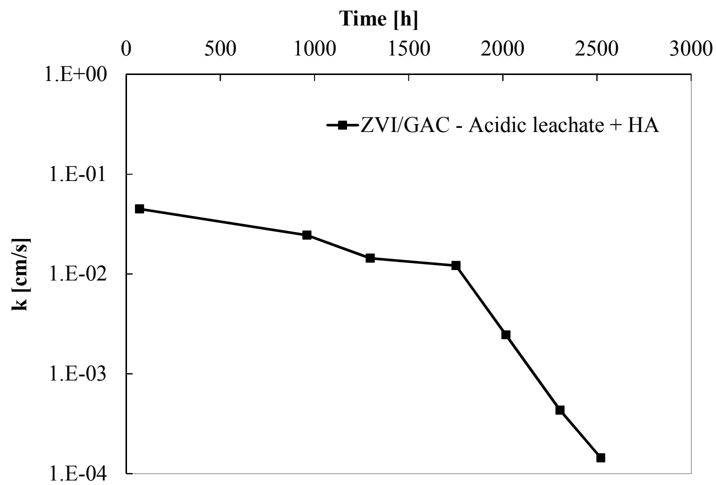

Figure 9: Hydraulic conductivity vs time for the ZVI/GAC granular mixture

Table 1: Literature studies regarding the use of granular reactive materials for the removal of heavy metals contained into sanitary landfill leachate.

Materials	**Contaminant – Concentration (mg/l)**	**Leachate typology**	**Study**	**Removal (%)**	**Reference**
Organic material, ZVI, fly ash or red mud	Cu, Zn, Ni and Mn (all 50)	Synthetic sulphate solutions (pH = 5.5)	CT	From 100 to 0	[5]
ZVI - ZVI/zeolite	COD (1027.1), BOD_5 (328.7), NH_4^+ (60.4), NO_3^- (5.3), NO_2^- (15.1), PO_4^{3-} (2.1) SO_4^{2-} (571.6), Zn (82.8), ∑Cr (0.2), Cd (0.08), ∑ Mn (13.8), Pb (0.3 mg/l), Ca (559.9), Mg (186.4), Ni (0.1), Cu (0.6).	Real landfill (pH = 6.9)	CT	Zn 93.2 - 97.2 Mn 90.2 - 99.6 Ca 77.4 - 81.7 Mg 52.6 - 95.9 Cd 88.0 - 95.2 Cr 67.4 - 70.7	[4]
ZVI, zeolite and activated carbon	COD (< 5500), NH_4^+(< 1500), NO_2^- (<10.00), NO_3^- (<18.70), As (< 0.1), Ba (< 0.3), Be (< 0.01), Cd (< 0.1), ∑Cr (< 1.6), Cu (< 3), Mn (< 1.4), Mo (< 0.2), Ni (< 1), Pb (< 0.3), Se (0.1), Zn (< 3), Co (< 0.1), 16PAHs (1)	Real landfill (pH = 7.9 - 8.61)	CT	COD 55.8 TN 70.8 Ammonium 89.2 Ni 70.7 Pb 92.7 16PAH 94.2	[6]
Municipal solid waste incineration fly ash	COD (5625.5), NH_3-N (66.8), Zn, Pb, Cr, Cd, Cu (all<1)	Real landfill (pH = 7.48)	BT	Zn 39.42 Pb 59.24 Cr 28.14 Cd 55.37 Cu 32.82	[7]

Table 2. Composition of the synthetic leachates

Element	Acidic leachate		Acidic leachate + HA	
	C(mg/L)	Reagents	C(mg/L)	Reagents
Cu	2	$CuCl_2$	1	$CuCl_2$
Ni	2	$NiCl_2 \cdot 6H_2O$	1	$NiCl_2 \cdot 6H_2O$
Zn	10	$ZnCl_2$	6	$ZnCl_2$
NH_4^+	750	NH_4Cl	750	NH_4Cl
Cl^-	1500	$CuCl_2$; $NiCl_2 \cdot 6H_2O$; $ZnCl_2$; NH_4Cl	1500	$CuCl_2$; $NiCl_2 \cdot 6H_2O$; $ZnCl_2$; NH_4Cl
SO_2^-	300	Na_2SO_4	300	Na_2SO_4
CO_3^{2-}	1500	$NaHCO_3$	1500	$NaHCO_3$
COD	2500	CH_3COOH	2500	CH_3COOH + HA

Table 3. Batch tests programme

Reactive medium	Solution
ZVI	Acidic leachate
GAC	Acidic leachate
ZVI/CAG 30:70	Acidic leachate

Table 4. Column tests programme

Reactive medium	Mass [g]	Thickness [cm]	Q [mL/min]	Duration [day]	Solution
ZVI	500	6	0.5	57	Acidic leachate
GAC	477	50	0.5	30	Acidic leachate
ZVI	500	6	0.5	30	Acidic leachate + HA
ZVI/CAG 30:70	750	50	0.1	48	Acidic leachate + HA

Table 5: Batch tests results (t = 96 h)

Reactive medium	R_E (%)					
	Cu	Ni	Zn	Ammonium	Chlorides	Sulphates
ZVI	99.9	99.7	93.1	8	11.1	37.6
GAC	99.8	90.9	96.1	8	10.5	14.3
ZVI/GAC	99.9	97.6	99.6	12.5	1	15.1