



Selective removal of heavy metals from landfill leachate by reactive granular filters

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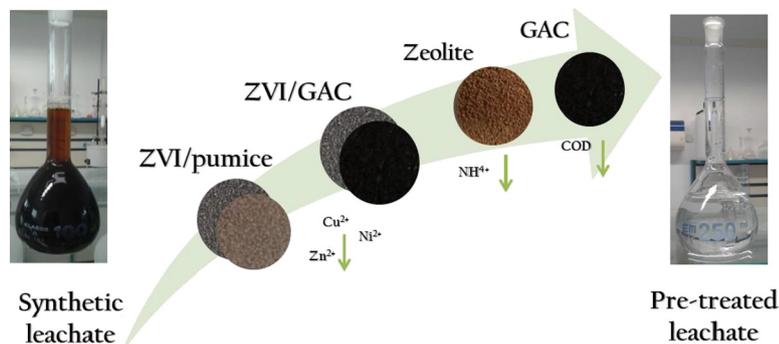
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HIGHLIGHTS

- A new chemical-physical pre-treatment for leachate was presented
- ZVI, GAC and a zeolite efficiently remove heavy metals contained into the leachate
- The proposed method could be used as an on-site technology for leachate pre-treatment
- Pre-treatment allows to safely co-treat leachate in municipal WWTPs

GRAPHICAL ABSTRACT



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ABSTRACT

The pre-treatment of landfill leachate prior to its co-treatment in the municipal plants of waste water processing could represent an appropriate and cost-effective solution for its management. Pre-treatment is necessary especially to remove heavy metals, which may be transferred to the excess sludge preventing its valorisation. In the present paper, we propose a chemical-physical pre-treatment of leachate using four different granular reactive media able to selectively remove the contaminants present in the leachate. The efficiency of these materials was investigated using synthetic leachate through batch tests and a column test. In the latter case the four materials were placed in two columns connected in series and fed an under constant upward flow (0.5 mL/min). The first column was filled half (50 cm) with a granular mixture of zero valent iron (ZVI) and pumice and half (50 cm) with a granular mixture of ZVI and granular activated carbon (GAC). The second column, which was fed with the effluent of the first column, was filled half with zeolite (chabazite) and half with GAC. Heavy metals were mainly removed by the ZVI/pumice and ZVI/GAC steps with a removal efficiency that was higher than 98, 94 and 90% for copper, nickel and zinc, respectively, after 70 days of operation. Ammonium was removed by zeolite with a removal efficiency of 99% up to 23 days. The average reduction of the chemical oxygen demand (COD) was of 40% for 85 days, whereas chloride and sulphate removal was negligible.

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1. Introduction

One of the most important issues for the overall sustainability (economic and environmental) of a modern landfill is leachate management; in fact, leachate is a complex and highly polluted matrix containing a large amount of dissolved organic matter, which is

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Table 1
Pre-treatment typologies of sanitary landfill leachate.

Pre-treatment typology	Contaminant	Leachate typology	Removal efficiency [%]	Reference
Stripping process	Ammonia (ammoniacal nitrogen)	Stabilised leachate (methanogenic phase)	70–90	(Cheung et al., 1997)
	COD		24–47	
Coagulation–flocculation	COD	Stabilised leachate	42–55	(Amokrane et al., 1997)
Coagulation–flocculation	Organic matter	Raw and partially stabilised	25–80	(Tatsi et al., 2003)
Fenton's reagent	COD	Old municipal landfill leachate	60	(Lopez et al., 2004)
Coagulation–flocculation	COD	Raw leachate	21–28	(Zazouli and Yousefi, 2008)
	Heavy metals		68–91	
Air stripping	Ammonia nitrogen	Raw leachate	88.6	(Pi et al., 2009)
Coagulation and ultrafiltration	COD	Raw leachate	84.8	(Zazouli et al., 2010)
	COD		25	
Precipitation process	Heavy metals	Stabilised leachate	79–88	(Liu et al., 2012)
	COD		55.87–68.65	
Coagulation–flocculation	Humic acids	Stabilised leachate	53.64–80.18	(Gandhimathi et al., 2013)
	COD		25–80	
Coagulation and adsorption	COD	Young and stabilised leachate	85	(Poveda et al., 2016)
Air stripping, chemical coagulation, electro-coagulation advanced oxidation with sodium ferrate	Ammonia	Stabilised leachate	50	(Silva and Palmeira, 2017)
	COD		42	
Geotextile filters	COD	Stabilised leachate	0–51	
	Heavy metals		0–51	

biodegradable or refractory to biodegradation (e.g. humic acid), and of inorganic compounds such as: (i) light metals (Al, K, Na, Mg, etc.); (ii) heavy metals and metalloids (As, Ca, Cd, Cu, Fe, Pb; Zn, etc.); (iii) anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , S^{2-} etc.), and (iv) NH_3 (Fan et al., 2006; Kjeldsen et al., 2002; Qasim, 2017; Slack et al., 2005; Wiszniowski et al., 2006). Whereas anions and light metals are generally present in non-toxic concentrations, the toxicity of heavy metals and As may be considered a threat (Heyer and Stegmann, 2002; Wiszniowski et al., 2006).

According to landfill age, leachate is generally classified as young or stabilised (or mature): young leachate generally presents low pH values (<6.5) and higher values of organic matter content and biodegradability (i.e. COD up to 50,000 mg/L and ratio between biological and chemical oxygen demand - BOD/COD > 0.4) and of heavy metals. Old or stabilised leachate usually presents higher values of pH (>7.5) and $\text{NH}_4\text{-N}$ (>400 mg/L) and lower values of COD (<3000–4000 mg/L), of the BOD/COD ratio (down to 0.1) and of heavy metals (adapted from Gandhimathi et al., 2013, Foo and Hameed, 2009, Renou et al., 2008).

Conventional landfill leachate treatments can be classified into four major groups: i) recycling of leachate into the landfill body, ii) combined treatment with domestic sewage in external wastewater treatment plants (WWTPs), iii) biodegradation: aerobic and anaerobic processes, and iv) chemical and physical methods: chemical oxidation, adsorption, chemical precipitation, coagulation/flocculation, sedimentation/flotation and air stripping (Hermosilla et al., 2009; Kurniawan et al., 2006; Renou et al., 2008).

The co-treatment of landfill leachate with municipal sewage in WWTPs, after its transportation by trucks, together with the on-site treatment by reverse osmosis, represents the method most commonly used in many countries and in Italy, in particular, for leachate treatment (Calabrò et al., 2018).

However, as suggested by Calabrò and co-workers (Calabrò et al., 2010, 2018) these solutions still present many issues to be solved, the main problems being the following:

- the transfer of heavy metals and of other toxic substances, during the treatment in WWTPs, in the excess sludge and in purified water;
- the presence of compounds (e.g. ammonium, heavy metals) that could inhibit the biological process in WWTPs.

In this context, an appropriate and cost-effective solution, could be a leachate pre-treatment before co-treatment into municipal WWTPs (Gao et al., 2015; Wiszniowski et al., 2006). The aim of the pre-treatment would be the removal of organic and inorganic inhibitory compounds, such as heavy metals, that, as already mentioned, could reduce treatment efficiency or could be transferred to the excess sludge preventing its valorisation (e.g. composting, direct use in agriculture).

As results from the literature, several studies have focused on the pre-treatment of leachate, prior to biological treatment or reverse osmosis, by applying different methods. The most common pre-treatment method is the coagulation–flocculation process (Amokrane et al., 1997; Liu et al., 2012; Tatsi et al., 2003; Zazouli and Yousefi,

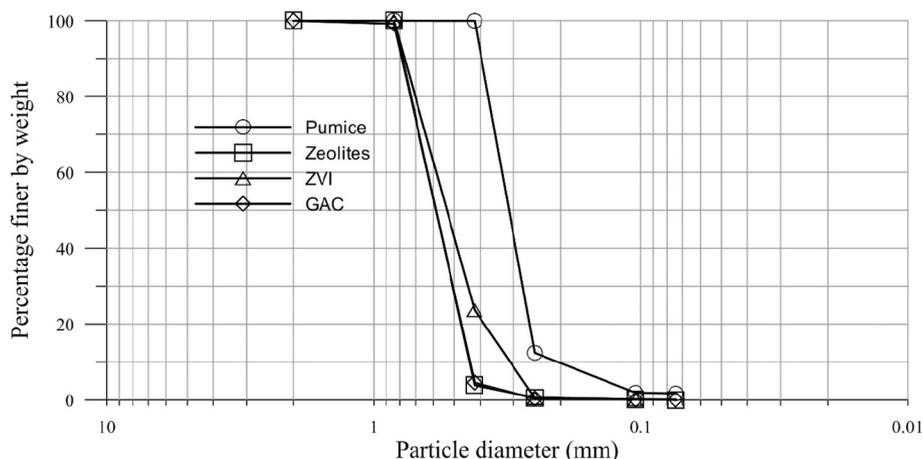


Fig. 1. Grain size distributions of ZVI, GAC, zeolites and pumice.

2008). Other methods include: stripping (Cheung et al., 1997), precipitation (Zazouli et al., 2010), combined processes as air stripping followed by coagulation/ultrafiltration processes (Pi et al., 2009), coagulation and adsorption (Gandhimathi et al., 2013), different physical-chemical methods (Poveda et al., 2016), Fenton's reagent (Hermosilla et al., 2009; Lopez et al., 2004) or use of nonwoven geotextiles (Silva and Palmeira, 2017).

The objective of these pre-treatment methods was mainly to reduce the concentration of organic matter, ammonium and heavy metals present in young and/or stabilised leachate. Some of these pre-treatment typologies are summarized in Table 1.

Here we attempt to reduce the concentration of organic matter, ammonium and especially heavy metals present in a synthetic landfill leachate, by mimicking the situation of a young leachate, through the combined use of different granular reactive media able to selectively remove the contaminants.

The materials used were zero valent iron (ZVI), pumice, granular activated carbon (GAC) and a zeolite (chabazite).

ZVI has demonstrated to be effective for the treatment of a wide range of contaminants among which sulphates, nitrates and heavy metals (Fu et al., 2014). It is mostly used for groundwater remediation through the technology of permeable reactive barriers (PRB). The main limitation of ZVI is the long-term preservation of its hydraulic and removal properties (Bilardi et al., 2013; Moraci et al., 2016a; Moraci et al., 2016b). In particular, the inevitable corrosion of the material is responsible of the reduction of its reactivity and hydraulic conductivity (Caré et al., 2013).

In order to extend its efficiency in the long term and optimise its use (Noubactep and Caré, 2010), ZVI was mixed to pumice, a porous volcanic rock, which is generated during explosive eruptions due to the vigorous gas escape in lavas.

As reported in the literature, ZVI has been largely tested as reactive material to be used in the PRB technology as pure material, or mixed with a reactive/inert material (Madaffari et al., 2017; Moraci et al., 2015; Ndé-Tchoupé et al., 2018) or in sequence with others materials (Obiri-Nyarko et al., 2014). In the latter case (multi-barrier system) the granular iron was tested in sequence either with a biosparged zone (Morkin et al., 2000), or with GAC (Köber et al., 2002) or even with a biologically active tire (Lee et al., 2007) for the removal of organic contaminants. Other possible applications, already proposed in the scientific literature (Mwakabona et al., 2017; Chiu, 2013) and coherent with the research here presented, are the decentralized treatment of drinking water, water treatment for urban agriculture, stormwater treatment prior to discharge or reuse.

Zeolites are materials that have demonstrated to be effective in the removal of various contaminants thanks to their high ion exchange capacity. In particular, they have proved to be effective in the removal of ammoniacal nitrogen, COD and heavy metals contained in sanitary leachate (Lim et al., 2016). The zeolite used in this paper was a chabazite.

GAC was reported to be effective in the removal of various types of organic and inorganic contaminants through sorption mechanisms owing to its large surface area, micro porous structure and nonpolar characteristics. In particular, GAC was found to be effective to remove organic materials susceptible of biodegradation (Halim et al., 2010) and heavy metals (Goher et al., 2015; Yin et al., 2007) and is a common adsorbent used for colour removal in wastewater treatment.

Table 2
Coefficient of uniformity, mean grain size and particle density of materials.

	ZVI	GAC	Zeolite	Pumice
U	2	1.45	1.34	1.4
D ₅₀ (mm)	0.5	0.4	0.5	0.3
ρ (g/cm ³)	7.87	N.A.	2.17	2

Table 3
Composition of the synthetic leachate.

Element	Reagent	C(mg/L)
Cu	CuCl ₂	2
Ni	NiCl ₂ ·6H ₂ O	2
Zn	ZnCl ₂	10
NH ₄ ⁺	NH ₄ Cl	750
Cl ⁻	CuCl ₂ ; NiCl ₂ ·6H ₂ O; ZnCl ₂ ; NH ₄ Cl	1500
SO ₄ ²⁻	Na ₂ SO ₄	300
CO ₃ ²⁻	NaHCO ₃	1500
Biodegradable substance	CH ₃ COOH and humic acids ^a	2500

^a Approximately in equal amounts in terms of COD.

In this research paper, we studied the efficiency of these reactive materials through batch tests and a column test. The batch tests were used for a preliminary evaluation while the column test was used to more effectively simulate the real hydraulic conditions in a potential full-scale application. During the column test the materials were placed according to the following sequence: granular mixture of ZVI and pumice, granular mixture of ZVI and GAC, zeolite and GAC.

This sequence allowed to selectively remove the contaminants. In particular, the ZVI present in the first two compartments allowed the removal of heavy metals but also to preserve the ion exchange and adsorption capacity of the zeolite and of GAC, respectively. This choice

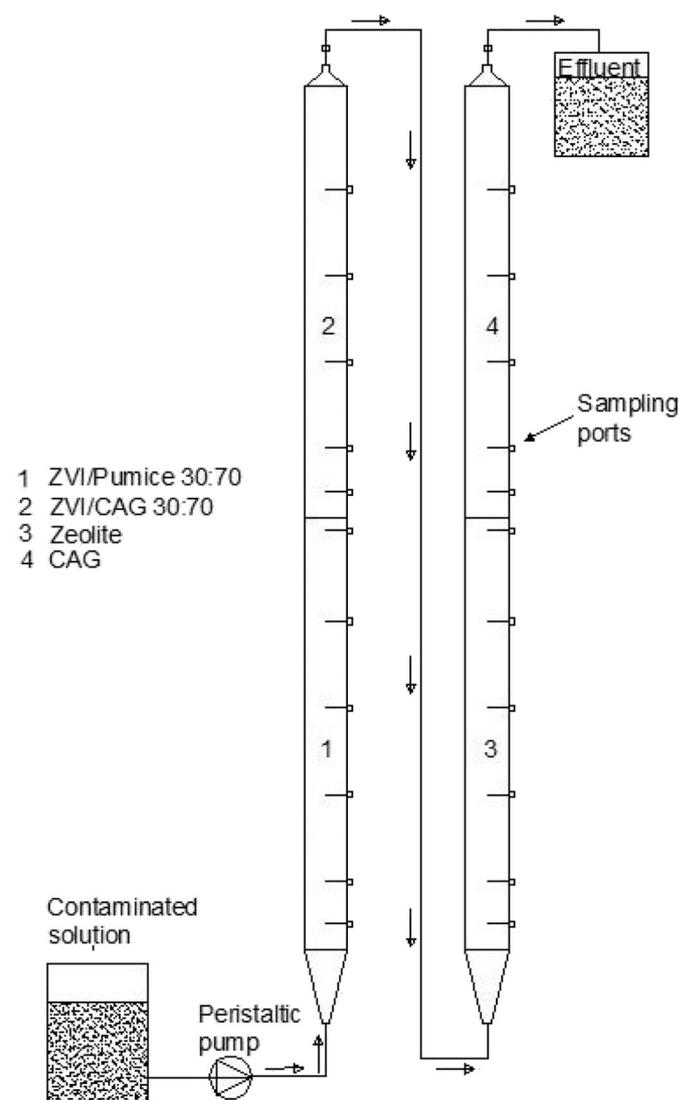


Fig. 2. Schematic overview of the apparatus used in the column tests.

Table 4
Batch tests results.

Contaminants	R _E [%]		
	ZVI	GAC	Zeolite
Cu	100	99	94
Ni	99	86	70
Zn	88	95	96
Ammonium	8	8	81
Chlorides	11	10	3
Sulphates	38	14	6

allowed to preserve the ability of the zeolite and of GAC to remove ammonium and organic substances, respectively, for a longer period and to eventually remove the residual heavy metals present.

2. Materials and methods

2.1. Solid materials

The typology of ZVI used in this research was FERBLAST RI 850/3.5, distributed by Pometon S.p.A. (Mestre, Italy) and mainly composed by iron (>99.74%).

The pumice came from the quarries of Lipari (Aeolian Islands, Sicily). Its mineralogical composition was determined as follows: SiO₂: 71.75%; Al₂O₃: 12.33%; K₂O: 4.47%; Na₂O: 3.59% and Fe₂O₃: 1.98%.

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

The zeolite used was of the type UOP MOLSIVTM AW-500 Adsorbent, provided by UOP MS S.p.A. (Reggio Calabria, Italy). The AW-500 is a chabazite and was formulated for the dehydration and purification of industrial gases and liquids. The zeolite was purchased as pellet and powdered through a miller to obtain the desired grain size distribution (Fig. 1).

The coefficient of uniformity, $U = d_{60}/d_{10}$, the mean grain size (d_{50}) and particle density (ρ) of the four reactive media are summarized in Table 2.

2.2. Chemical reagents

A realistic synthetic landfill leachate is not easy to formulate and the choice of the right chemical reagents and concentrations is crucial to simulate this complex matrix and avoid the precipitation of solid compounds.

The synthetic landfill leachate used in this experiment was representative of a young landfill. It was prepared by dissolving specific reagents into distilled water. The composition of the synthetic leachate and the reagents used are summarized in Table 3.

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

2.3. Batch and column tests

Before performing the column test, the preliminary evaluation of the reactivity of ZVI, GAC and of zeolite was carried out through batch tests. To this end, vials containing 52 mL of aqueous solution and 5.2 g of the selected reactive medium (solid-liquid ratio equal to 1:10) were placed on a rotary shaker at 30 rpm (Stuart Scientific Rotator Drive STR/4) for 96 h. At the end of the experiment, the vials were centrifuged for 3 min at 6000 rpm.

The column test was carried out using two polymethyl methacrylate (PMMA–Plexiglas™) columns having an internal diameter of 5 ± 0.1 cm and a height of 100 cm. The two columns were equipped with sampling ports located at different distances from the inlet and were connected in series. A peristaltic pump (Watson Marlow 205S) was used to feed the columns under a constant upward flow equal to 0.5 mL/min. The first column was fed from a single PE container (50 L) containing the synthetic leachate and the second one was fed with the effluent of the first column as depicted in Fig. 2.

The first column was filled half (50 cm) with the granular mixture of ZVI/pumice at weigh ratio (w.r.) 30:70 and half (50 cm) with the granular mixture of ZVI/GAC at the same w.r. The second column was filled half (50 cm) with zeolite and half (50 cm) with GAC.

pH and redox potential (Eh) were measured in each sample collected (PCD 65 multi-parametric instrument).

Samples were then filtered through 0.45 μ m filters, stored at 4 °C and further analysed for Cu, Ni and Zn content by ICP-OES (Perkin Elmer OPTIMA 8000), for ammonium, nitrate and chloride content by ion exchange chromatography (Metrohm 883 basic IC plus) and for COD by a photometer (WTW Photolab S12) using specific pre-dosed cuvettes.

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

$$R_E = \frac{M_{\text{input}} - M_{\text{output}}}{M_{\text{input}}} \cdot 100 \quad (1)$$

where M_{input} and M_{output} were, respectively, the mass of contaminant at input and at output from the reactive medium (mg).

3. Results and discussion

3.1. Results of the batch tests

The results of the batch tests are summarized in Table 4. Batch tests on ZVI and GAC were carried out with the leachate having the composition as shown in Table 3 but without humic acids. All three reactive media were efficient in the removal of heavy metals (R_E ranged from

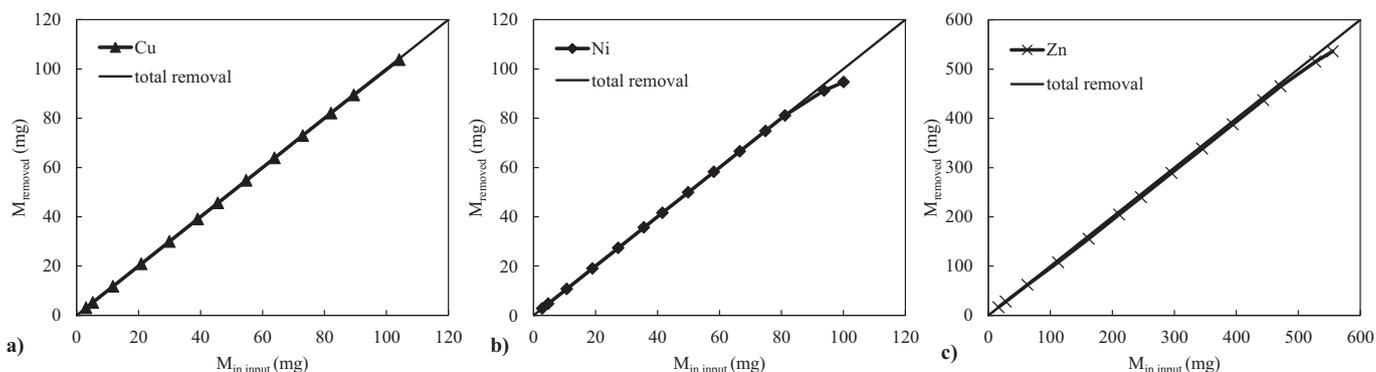


Fig. 3. Removed mass [mg] of Cu (a), Ni (b) and Zn (c) versus mass in input [mg].

70 to 100%) according to the sequence Cu > Ni > Zn for ZVI, Cu > Zn > Ni for GAC and Zn > Cu > Ni for zeolite (Table 4).

Ammonium was significantly reduced only by zeolite ($R_E = 81\%$), chlorides were not removed efficiently by either of the three materials, whereas sulphates were reduced to a certain extent (about 40%) by ZVI (Table 4).

3.2. Column test: removal of heavy metals

In Fig. 3 the removed mass (mg) of the three heavy metals (Cu, Ni, Zn), determined at the output of the column (200 cm), is plotted as a function of the mass in input (mg), whereas Tables 5–7 summarise the values of the removal efficiency (Eq. (1)) for each of the three heavy metals taken separately ($R_{E,Cu}$, $R_{E,Ni}$ and $R_{E,Zn}$) and for each sampling time (h). The removal efficiency was calculated at the outlet of the column (200 cm) but the contribution provided by each reactive medium was also reported.

As can be observed from Tables 5–7 the removal efficiency calculated at the outlet of the column (200 cm) was always higher than 94%.

When the single reactive media were considered, the first (i.e. ZVI/pumice) was shown to be effective in removing all three of the heavy metals taken into consideration. More specifically, Cu removal efficiency was always higher than 93% (Table 5), whereas Ni removal efficiency was higher than 70% up to 1512 h, but it decreased to 30.8% by the end of the test (i.e. 2184 h; Table 6). Compared to Cu or Ni, the ZVI/pumice mixture showed a lower efficiency in removing Zn most likely due to its higher concentration in the leachate. In particular, the removal efficiency was higher than 50% up to 1512 h, but it decreased to 26.3% by the end of the test (Table 7).

We also observed that Cu was completely removed by the ZVI/pumice mixture up to 216 h while afterwards, when the ZVI started to slightly reduce its reactivity, zeolite and GAC removed the remaining mass (Table 5). It is interesting to note that the ZVI/GAC section was not able to remove the limited Cu residual concentration, most likely because of the partial loss of reactivity of ZVI due to its passivation (formation of oxide layer) for the presence of water and the action of other contaminants in the previous period. This is specific to Cu that is the only metal that can be quantitatively removed by electrochemical reduction to Cu^0 (cementation process, Bartzas et al., 2006) thanks to the fact that the standard electrode potential of the couple Cu^{2+}/Cu is significantly higher than the couple Fe^{2+}/Fe ($E_{Cu^{2+}/Cu}^0 = 0.34$ V, $E_{Fe^{2+}/Fe}^0 = -0.44$ V).

Ni was completely removed by the ZVI/pumice mixture up to 96 h and afterwards it was principally removed by the ZVI/GAC section, followed by zeolite whereas GAC was not effective in nickel removal (Table 6).

ZVI/pumice and ZVI/GAC showed a similar efficiency in Zn removal but the contribution of the zeolite was fundamental to remove the

Table 5
Copper removal efficiency $R_{E,Cu}$ (%).

Time [h]	$R_{E,Cu}$ [%]				
	Outlet	ZVI/Pumice	ZVI/GAC	Zeolite	GAC
56	100	100	–	–	–
96	100	100	–	–	–
216	100	100	–	–	–
384	100	99.4	–	0.6	0
552	100	99.0	–	1.0	0
720	100	98.9	–	0.9	0.2
840	100	99.0	–	0.6	0.4
1008	100	99.0	–	0.4	0.6
1176	100	99.1	–	0.3	0.6
1344	100	99.3	–	0.2	0.5
1512	100	99.3	–	0.2	0.5
1680	100	97.8	–	1.8	0.4
2016	99.7	94.0	1.2	4.0	0.5
2184	99.4	93.3	1.5	3.9	0.7

Table 6
Nickel removal efficiency $R_{E,Ni}$ (%).

Time [h]	$R_{E,Ni}$ [%]				
	Outlet	ZVI/Pumice	ZVI/GAC	Zeolite	GAC
56	100	100	–	–	–
96	100	100	–	–	–
216	100	92.4	7.6	–	–
384	100	82.8	17.2	–	–
552	100	77.7	22.3	–	–
720	100	74.1	25.9	–	–
840	100	72.3	27.7	–	–
1008	100	70.6	29.4	–	–
1176	100	69.2	30.8	–	–
1344	100	70.1	29.6	0.2	0.1
1512	100	70.7	28.8	0.4	0.1
1680	100	62.5	31.7	5.7	0.1
2016	97.3	39.8	38.7	18.4	0.4
2184	94.6	30.8	42.8	20.3	0.7

residual concentration of this metal, in contrast to GAC whose efficiency in Zn removal was null (Table 7).

Contrary to Cu, the removal of Ni and Zn can mainly be attributed to co-precipitation, adsorption and adsorptive size-exclusion processes (Bilardi et al., 2015; Rangsvik and Jekel, 2005). Co-precipitation involves the entrapment of contaminants into iron corrosion products, adsorption can take place on the surface of iron corrosion products (for example into $Fe(OH)_3$ and $FeOOH$), whereas adsorptive size-exclusion processes occur when the formation of iron oxides reduces the pore volume of the reactive medium and behaves as a reactive filter towards the contaminants.

When both ZVI/pumice and ZVI/GAC mixtures started to lose their reactivity, the heavy metals were mostly entrapped by the zeolite or to a minimum extent by GAC (Tables 5–7). In fact, the contribution of the GAC section was almost negligible.

Concerning the pH measurements, we noticed that the pH value increased by flowing through the ZVI/Pumice mixture (from 5 to 6.5 up to 960 h) due to the ZVI interactions with the contaminants, which caused the production of the hydroxyl ions (OH^-), as reported by Jun and co-workers (Jun et al., 2009). The pH value remained unchanged when flowing through the ZVI/GAC mixture, whereas it slightly increased in the zeolite (from 6.5 to 7 up to 246 h) and in the GAC sections (from 7 to 7.5–8 up to 600 h). After 960 h a progressive decrease in the pH value was observed by flowing through the reactive media containing ZVI, which was likely due to the reduction of iron corrosion caused by the formation of an oxide layer at the ZVI surface. Subsequently, a slight increase of pH was observed when the column was fed with the second batch of leachate, which was slightly more acidic than the first one (pH equal to 5.29 and 4.88 for the first and the second solution,

Table 7
Zinc removal efficiency $R_{E,Zn}$ (%).

Time [h]	$R_{E,Zn}$ [%]				
	Outlet	ZVI/Pumice	ZVI/GAC	Zeolite	GAC
56	100	92.8	7.2	–	–
96	100	88.1	11.9	–	–
216	97.9	66.6	28.1	3.2	–
384	95.7	48.0	38.8	8.9	–
552	96.0	43.3	43.2	9.4	–
720	96.9	43.8	45.9	7.2	–
840	97.4	44.4	46.8	6.2	–
1008	97.8	45.5	47.1	5.2	–
1176	98.1	46.6	47.1	4.4	–
1344	98.4	50.1	44.4	3.9	–
1512	98.5	52.5	42.6	3.4	–
1680	98.6	46.8	43.4	8.4	–
2016	97.6	33.0	42.8	21.8	–
2184	96.5	26.3	45.0	25.2	–

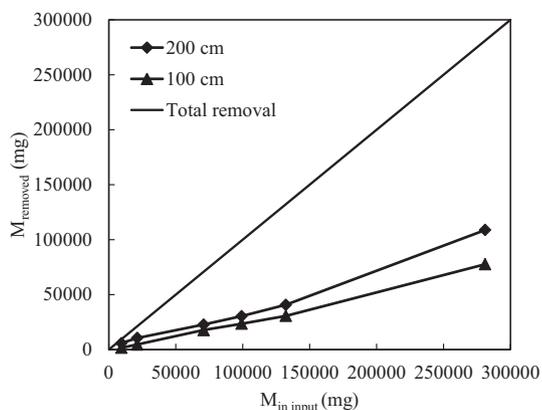
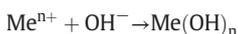


Fig. 4. COD removed mass [mg] versus mass in input [mg].

respectively), which likely caused a partial dissolution of the oxides layer and a further corrosion of ZVI.

An increase of OH^- concentration derived from ZVI corrosion would be favourable to form hydroxide precipitates with heavy metals, as described by the following reaction (Jun et al., 2009):



3.3. Column test: removal of COD and ammonium

As shown in Fig. 4, the removed mass of COD (mg), which was determined at 100 and 200 cm in thickness of the reactive medium, was plotted as a function of the mass in input (mg). The values of the removal efficiency R_{E_COD} (Eq. (1)), which were calculated at 200 cm (Outlet) and considering the contribution provided jointly by the first and second section (i.e. ZVI/pumice and ZVI/GAC) and by the third and fourth section (i.e. zeolite and GAC) are, instead, summarized in Table 8.

The average removal efficiency in COD was about 30–40% with the exception of the first 216 h when it was higher (50–60%; see Table 8 for details). The highest contribution in COD removal, observed at the beginning of the experiment, was given by the zeolite/GAC sections with the latter probably playing a major role. At later sampling times, the sections containing ZVI were more efficient suggesting that this material can be effective in COD removal, as reported by previous findings (Zhou et al., 2014). COD removal by ZVI is possible through a reaction of oxidation–reduction between ZVI and the organic matter or by entrapment in the matrix of iron corrosion products.

The values of the removal efficiency $R_{E_NH_4^+}$ (Eq. (1)) for ammonium, which were calculated at the outlet of the column (200 cm), and the contribution provided by the first two sections (i.e. ZVI/pumice and ZVI/GAC), by the zeolite and by the GAC are summarized in Table 9.

The ammonium at the outlet was reduced with a removal efficiency that was higher than 87.5% up to 840 h. As expected, it was also efficiently removed in the section containing the zeolite showing a removal efficiency that was higher than 90% up to 552 h whereas the

Table 8
COD removal efficiency R_{E_COD} (%).

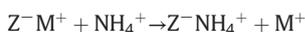
Time [h]	R_{E_COD} [%]		
	Outlet	ZVI/Pumice and ZVI/GAC	Zeolite and GAC
96	61.0	17.4	43.6
216	49.4	21.3	28.1
720	32.2	25.1	7.1
1008	30.6	23.6	7.0
1344	30.8	23.2	7.6
2856	38.7	27.6	11.1

Table 9
Ammonium removal efficiency $R_{E_NH_4^+}$ (%).

Time [h]	$R_{E_NH_4^+}$ [%]			
	Outlet	ZVI/Pumice and ZVI/GAC	Zeolite	GAC
56	100	6.06	93.93	0
216	100	5.14	94.86	0
384	100	3.67	96.32	0
552	100	2.80	97.20	0
840	87.55	2.27	84.43	0.85

contribution of the reactive media containing ZVI and of GAC was negligible (Table 9). The measurements are reported up to 840 h because, as the experiment proceeded, zeolite lost its reactivity and the overall removal efficiency became <5%.

Zeolite removes ammonium from aqueous solutions by ion exchange. Ammonium can be exchanged by cations according to the following reaction:



4. Conclusions

The results obtained in this paper show how the combined use of different granular reactive media (i.e. ZVI, GAC and zeolite) allows to remove heavy metals contained in the leachate and to safely treat it in WWTPs. This methodology of leachate pre-treatment could be economically advantageous to valorise the excess sludge via composting rather than landfilling it, which, in turn, could considerably reduce the cost of sludge disposal.

The methodology proposed could be used as an on-site technology for the pre-treatment of leachate having characteristics similar to those described in this study. The investigated reactive materials could be placed into a tank, which could include up to three slots connected in series and containing the ZVI/pumice mixture, the ZVI/GAC mixture and zeolite as reactive materials since, as shown by the results derived by this study, the contribution given by the GAC section towards contaminants removal was negligible. The system could allow the replacement or isolation of each reactive medium at any time when an exhaustion of one of the three media is observed.

According to the results of this paper a filter, composed of the same reactive materials used in this study and having a surface of 2.5 m² and a height of 1.5 m, could treat 1 m³/day of leachate, having characteristics similar to the leachate formulated in this study, with an efficiency higher than 99% for Cu, than 94% for Ni and than 96% for Zn for three months. If only the ZVI/pumice and ZVI/GAC layers were to be used (height equal to 1 m) the efficiency would be reduced to about 93% for Cu, 73% for Ni and 71% for Zn.

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