

1 **SELECTIVE REMOVAL OF HEAVY METALS FROM LANDFILL LEACHATE BY**
2 **REACTIVE GRANULAR FILTERS**

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9
10 **Abstract**

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

27 **Keywords:** Granular activated carbon, heavy metals, leachate pre-treatment, zeolite, zero valent
28 iron.

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30 **1. Introduction**

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32 One of the most important issues for the overall sustainability (economic and environmental) of a
33 modern landfill is leachate management; in fact, leachate is a complex and highly polluted matrix
34 containing a large amount of dissolved organic matter, which is biodegradable or refractory to
35 biodegradation (e.g. humic acid), and of inorganic compounds such as: (i) light metals (Al, K, Na,
36 Mg, etc.); (ii) heavy metals and metalloids (As, Ca, Cd, Cu, Fe, Pb; Zn, etc.); (iii) anions (Cl^- , NO_2^- ,
37 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;
38 Slack et al., 2005; Wiszniowski et al., 2006). Whereas anions and light metals are generally present
39 in non-toxic concentrations, the toxicity of heavy metals and As may be considered a threat (Heyer
40 and Stegmann, 2002; Wiszniowski et al., 2006).

41 According to landfill age, leachate is generally classified as young or stabilised (or mature): young
42 leachate generally presents low pH values (< 6.5) and higher values of organic matter content and
43 biodegradability (i.e. COD up to 50.000 mg/L and ratio between biological and chemical oxygen
44 demand - BOD/COD > 0.4) and of heavy metals. Old or stabilised leachate usually presents higher
45 values of pH (> 7.5) and $\text{NH}_4\text{-N}$ (> 400 mg/L) and lower values of COD ($< 3000 - 4000$ mg/L), of
46 the BOD/COD ratio (down to 0.1) and of heavy metals (adapted from Gandhimathi et al., 2013,
47 Foo and Hameed, 2009, Renou et al., 2008).

48 Conventional landfill leachate treatments can be classified into four major groups: i) recycling of
49 leachate into the landfill body, ii) combined treatment with domestic sewage in external wastewater
50 treatment plants (WWTPs), iii) biodegradation: aerobic and anaerobic processes, and iv) chemical
51 and physical methods: chemical oxidation, adsorption, chemical precipitation,

52 coagulation/flocculation, sedimentation/flotation and air stripping (Hermosilla et al., 2009;
53 Kurniawan et al., 2006; Renou et al., 2008).

54 The co-treatment of landfill leachate with municipal sewage in WWTPs, after its transportation by
55 trucks, together with the on-site treatment by reverse osmosis, represents the method most
56 commonly used in many countries and in Italy, in particular, for leachate treatment (Calabrò et al.,
57 2018).

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

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

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

69 As results from the literature, several studies have focused on the pre-treatment of leachate, prior to
70 biological treatment or reverse osmosis, by applying different methods. The most common pre-
71 treatment method is the coagulation–flocculation process (Amokrane et al., 1997; Liu et al., 2012;
72 Tatsi et al., 2003; Zazouli and Yousefi, 2008). Other methods include: stripping (Cheung et al.,
73 1997), precipitation (Zazouli et al., 2010), combined processes as air stripping followed by
74 coagulation/ultrafiltration processes (Pi et al., 2009), coagulation and adsorption (Gandhimathi et
75 al., 2013), different physical-chemical methods (Poveda et al., 2016), Fenton’s reagent (Hermosilla
76 et al., 2009; Lopez et al., 2004) or use of nonwoven geotextiles (Silva and Palmeira, 2017).

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

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

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

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

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

95 As reported in the literature, ZVI has been largely tested as reactive material to be used in the PRB
96 technology as pure material, or mixed with a reactive/inert material (Madaffari et al., 2017; Moraci
97 et al., 2015; Ndé-Tchoupé et al., 2018) or in sequence with others materials (Obiri-Nyarko et al.,
98 2014). In the latter case (multi-barrier system) the granular iron was tested in sequence either with a
99 biosparged zone (Morkin et al., 2000), or with GAC (Köber et al., 2002) or even with a biologically
100 active tire (Lee et al., 2007) for the removal of organic contaminants. Other possible applications,
101 already proposed in the scientific literature (Mwakabona et al., 2017; Chiu, 2013) and coherent with

102 the research here presented, are the decentralized treatment of drinking water, water treatment for
103 urban agriculture, stormwater treatment prior to discharge or reuse.

104 Zeolites are materials that have demonstrated to be effective in the removal of various contaminants
105 thanks to their high ion exchange capacity. In particular, they have proved to be effective in the
106 removal of ammoniacal nitrogen, COD and heavy metals contained in sanitary leachate (Lim et al.,
107 2016). The zeolite used in this paper was a chabazite.

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

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

118 This sequence allowed to selectively remove the contaminants. In particular, the ZVI present in the
119 first two compartments allowed the removal of heavy metals but also to preserve the ion exchange
120 and adsorption capacity of the zeolite and of GAC, respectively. This choice allowed to preserve the
121 ability of the zeolite and of GAC to remove ammonium and organic substances, respectively, for a
122 longer period and to eventually remove the residual heavy metals present.

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124 **2. Materials and methods**

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126 *2.1 Solid materials*

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

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

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

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

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

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143 *2.2 Chemical reagents*

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

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

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

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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 Figure 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 equation 1:

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$$R_E = \frac{M_{input} - M_{output}}{M_{input}} \cdot 100 \quad [1]$$

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

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184 **3. Results and discussion**

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186 *3.1 Results of the batch tests*

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188 The results of the batch tests are summarized in Table 4. Batch tests on ZVI and GAC were carried
189 out with the leachate having the composition as shown in Table 3 but without humic acids. All three
190 reactive media were efficient in the removal of heavy metals (R_E ranged from 70 to 100 %) according to the sequence Cu>Ni>Zn for ZVI, Cu>Zn>Ni for GAC and Zn>Cu>Ni for zeolite
191 (Table 4).

192 Ammonium was significantly reduced only by zeolite ($R_E = 81\%$), chlorides were not removed
193 efficiently by either of the three materials, whereas sulphates were reduced to a certain extent (about
194 40%) by ZVI (Table 4).

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196 *3.2 Column test: removal of heavy metals*

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

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207 As can be observed from Tables 5-7 the removal efficiency calculated at the outlet of the column
208 (200 cm) was always higher than 94%.

209 When the single reactive media were considered, the first (i.e. ZVI/pumice) was shown to be
210 effective in removing all three of the heavy metals taken into consideration. More specifically, Cu
211 removal efficiency was always higher than 93% (Table 5), whereas Ni removal efficiency was
212 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).
213 Compared to Cu or Ni, the ZVI/pumice mixture showed a lower efficiency in removing Zn most
214 likely due to its higher concentration in the leachate. In particular, the removal efficiency was
215 higher than 50% up to 1512 h, but it decreased to 26.3% by the end of the test (Table 7).

216 We also observed that Cu was completely removed by the ZVI/pumice mixture up to 216 h while
217 afterwards, when the ZVI started to slightly reduce its reactivity, zeolite and GAC removed the
218 remaining mass (Table 5). It is interesting to note that the ZVI/GAC section was not able to remove
219 the limited Cu residual concentration, most likely because of the partial loss of reactivity of ZVI
220 due to its passivation (formation of oxide layer) for the presence of water and the action of other
221 contaminants in the previous period. This is specific to Cu that is the only metal that can be
222 quantitatively removed by electrochemical reduction to Cu^0 (cementation process, Bartzas et al.,
223 2006) thanks to the fact that the standard electrode potential of the couple Cu^{2+}/Cu is significantly
224 higher than the couple Fe^{2+}/Fe ($E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$, $E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44\text{V}$).

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

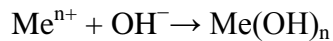
228 ZVI/pumice and ZVI/GAC showed a similar efficiency in Zn removal but the contribution of the
229 zeolite was fundamental to remove the residual concentration of this metal, in contrast to GAC
230 whose efficiency in Zn removal was null (Table 7).

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

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

240 Concerning the pH measurements, we noticed that the pH value increased by flowing through the
241 ZVI/Pumice mixture (from 5 to 6.5 up to 960 h) due to the ZVI interactions with the contaminants,
242 which caused the production of the hydroxyl ions (OH^-), as reported by Jun and co-workers (Jun et
243 al. 2009). The pH value remained unchanged when flowing through the ZVI/GAC mixture, whereas
244 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
245 - 8 up to 600 h). After 960 h a progressive decrease in the pH value was observed by flowing
246 through the reactive media containing ZVI, which was likely due to the reduction of iron corrosion
247 caused by the formation of an oxide layer at the ZVI surface. Subsequently, a slight increase of pH
248 was observed when the column was fed with the second batch of leachate, which was slightly more
249 acidic than the first one (pH equal to 5.29 and 4.88 for the first and the second solution,
250 respectively), which likely caused a partial dissolution of the oxides layer and a further corrosion of
251 ZVI.

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



257 *3.3 Column test: removal of COD and ammonium*

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

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

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

275 The ammonium at the outlet was reduced with a removal efficiency that was higher than 87.5% up
276 to 840 h. As expected, it was also efficiently removed in the section containing the zeolite showing
277 a removal efficiency that was higher than 90% up to 552 h whereas the contribution of the reactive
278 media containing ZVI and of GAC was negligible (Table 9). The measurements are reported up to

279 840 h because, as the experiment proceeded, zeolite lost its reactivity and the overall removal
280 efficiency became less than 5%.

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



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285 **4. Conclusions**

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

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

299 According to the results of this paper a filter, composed of the same reactive materials used in this
300 study and having a surface of 2.5 m² and a height of 1.5 m, could treat 1 m³/day of leachate, having
301 characteristics similar to the leachate formulated in this study, with an efficiency higher than 99%
302 for Cu, than 94% for Ni and than 96% for Zn for three months. If only the ZVI/pumice and
303 ZVI/GAC layers were to be used (height equal to 1 m) the efficiency would be reduced to about 93
304 % for Cu, 73 % for Ni and 71 % for Zn.

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445

Pre-treatment typology	Contaminant	Leachate typology	Removal efficiency [%]	Reference
Stripping process	Ammonia (ammoniacal-nitrogen) COD	stabilised leachate (methanogenic phase)	70-90 24-47	(Cheung et al., 1997)
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 Heavy metals	raw leachate	21-28 68-91	(Zazouli and Yousefi, 2008)
Air stripping Coagulation and ultrafiltration	ammonia nitrogen COD	raw leachate	88.6 84.8	(Pi et al., 2009)
Precipitation process	COD Heavy metals	raw leachate	25 79 - 88	(Zazouli et al., 2010)
Coagulation–flocculation	COD Humic acids	stabilised leachate	55.87 - 68.65 53.64 - 80.18	(Liu et al., 2012)
Coagulation and adsorption	COD	young and stabilised leachate	25 - 80	(Gandhimathi et al., 2013)
Air stripping, chemical coagulation, electro-coagulation advanced oxidation with sodium ferrate	COD ammonia	stabilised leachate	85 50	(Poveda et al., 2016)
Geotextile filters	COD Heavy metals	stabilised leachate	42 0-51	(Silva and Palmeira, 2017)

Table 1. Pre-treatment typologies of sanitary landfill leachate

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

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 ₂ ⁻	Na ₂ SO ₄	300
CO ₃ ²⁻	NaHCO ₃	1500
Biodegradable substance	CH ₃ COOH and humic acids *	2500

*approximately in equal amounts in terms of COD

Table 3. Composition of the synthetic leachate

Contaminants	ZVI	R _E [%]	
		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

Table 4. Batch tests results

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

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

Table 6. Nickel removal efficiency R_{E_Ni} (%)

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	-

Table 7. Zinc removal efficiency R_{E_Zn} (%)

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

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

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

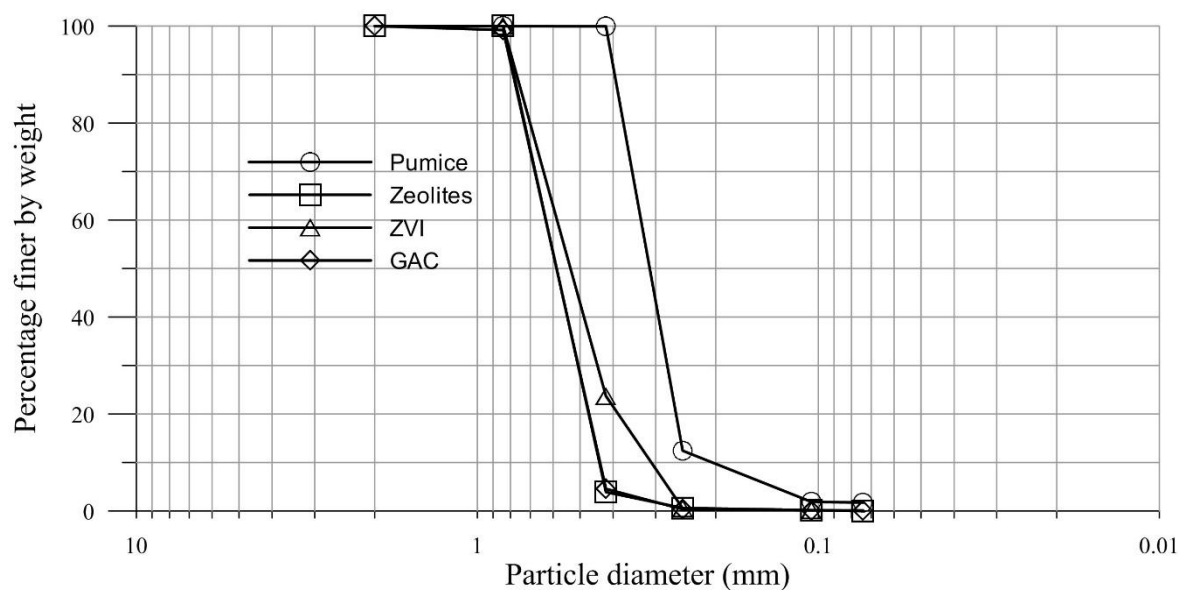


Figure 1. Grain size distributions of ZVI, GAC, zeolites and pumice

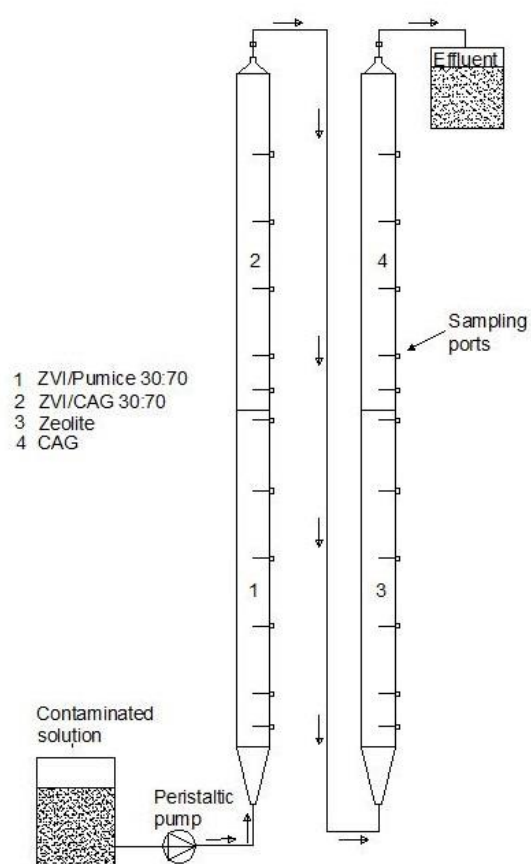


Figure 2. Schematic overview of the apparatus used in the column tests

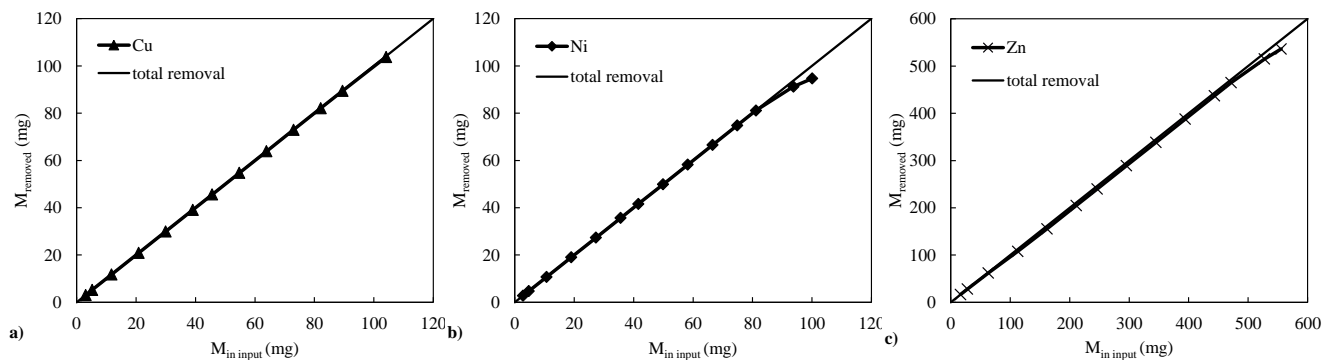


Figure 3. Removed mass [mg] of Cu (a), Ni (b) and Zn (c) versus mass in input [mg]

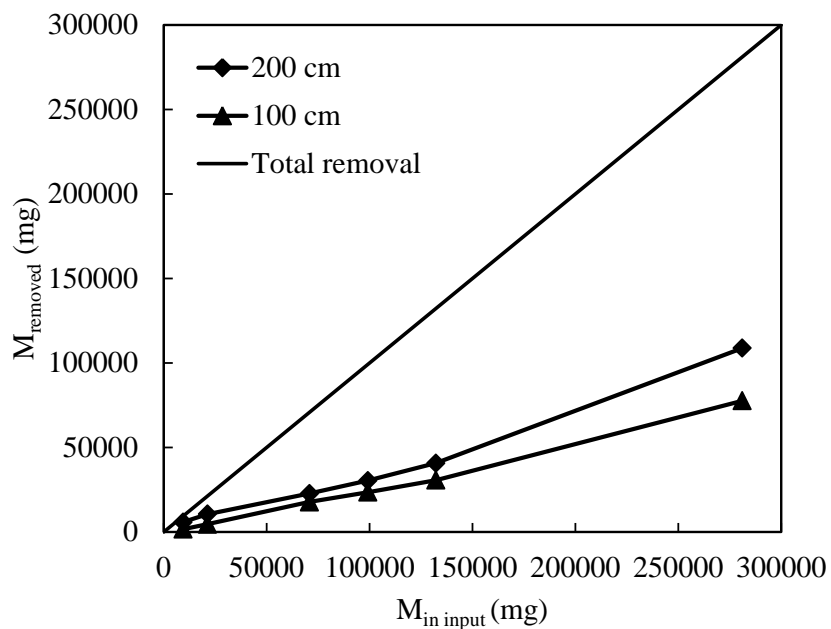


Figure 4. COD removed mass [mg] versus mass in input [mg]