DYNAMIC TESTING IN COLUMNS FOR SOIL HEAVY METAL REMOVAL FOR A CAR PARK SUDS

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ABSTRACT

The increase in urban runoff brought about by a rise in impermeable surfaces has triggered the alteration and pollution of many aquatic systems. The overall goal of this research was to design a 'Sustainable Urban Drainage System'(SUDS) for the retention of heavy metals from a car park consisting of mixing autochthonous soil (70%) with sand (30%) to improve the hydrological conductivity and adsorption capacity. To quantify the retention of metals we characterize the adsorption kinetics and isotherms of the soil mixture and perform dynamic experiments. The proposed methodology allowed us to work out the amount of heavy metal retention by the adsorbent and the retention mechanisms. The retention capacity of the adsorbent mixture was as follows: $Cr^{3+} \approx Cu^{2+} >> Zn^{2+} > Ni^{2+} > Cd^{2+}$. Chromium and copper ions were mainly retained by precipitation, whereas zinc, nickel and cadmium were retained by ionic exchange with calcium ions that saturate the soil colloids. The soil mixture buffered pH was found to change when fed with an acid solution of metallic ions.

Keywords: Heavy metal adsorption, Stormwater runoff, Sustainable Urban Drainage Systems (SUDS), Car park stormwater.

1 INTRODUCTION

The increase in impermeable surfaces due to urban development alters the urban hydrological cycle, augmenting surface runoff as well as the frequency and magnitude of floods and the pollution of surface aquatic systems (Göbel *et al*., 2007; Hatt *et al*., 2006, 2009; Hou *et al*., 2019; Li *et al*., 2009). Urban runoff water pollution is normally linked to anthropogenic activities like vehicle traffic, industrial activity and street cleaning (Barbosa *et al*., 2012; Huber *et al*., 2016). At present, the discharges of this water are considered diffuse or nonpoint-source pollution (Fuerhacker *et al*., 2011; Ma *et al*., 2018).

The nature and origin of runoff water contamination is highly variable. Most studies identify urban water contaminants as solids in suspension (SS), soluble salts, heavy metals (Cu, Zn, Cd, Pb, Ni and Cr), pesticides, nutrients from fertilizers, biodegradable organic matter, polycyclic aromatic hydrocarbons (PAHs), and pathogenic microorganisms. All these pollutants contribute to water quality degradation (Barbosa *et al*., 2012; Bressy *et al*., 2012; Göbel *et al*., 2007; Tedoldi *et al*., 2016).

The amount and characteristics of the pollutant load are affected by hydrological factors, such as rainfall intensity, duration, and intervals between rainfall events. They are also affected by vehicle traffic movement (in car parks or in the street), industrial activity, or the maintenance of green spaces (Crabtree *et al*., 2006; Helmreich *et al*., 2010; Lee *et al*., 2004). Another important aspect is the way in which the contaminants are transferred from one place to another, either dissolved or adsorbed to particles. This, together with the release of coarser particles in pavings, has been the subject of specific studies such as those by Borris *et al*. (2016); Helmreich *et al*. (2010); Huber *et al*. (2016).

One of the urban spaces with greater impacts on the quality of urban runoff water are public car parks, particularly those in high demand areas like in large commercial spaces, hospitals or universities. These surfaces generate large quantities of heavy metals and hydrocarbons (Gnecco *et al*., 2019; Huber *et al*., 2016; Monrabal-Martinez et al., 2019; Salim Akhter & Madany, 1993; Schiff *et al*., 2016).

A number of techniques have been developed in order to improve urban runoff water management form areas like car parks. These have been given different terms, like “Low Impact Development (LID)”, “Water Sensitive Urban Design (WSUD)” or “Sustainable Urban Drainage Systems (SUDS)” (Fletcher *et al*., 2015). In this work we focus on SUDS,

63 which constitute a set of tools that aim to reproduce the natural conditions of urban runoff
64 reducing the hydrological impact of urban design, facilitating infiltration where the
65 terrain's conditions permit it, controlling the excess rainwater, and transferring it slowly to
66 water areas (Andrés-Doménech *et al*., 2018; Charlesworth *et al*., 2012; Dietz and Clausen,
67 2008; Eckart *et al*., 2017). These systems have proven effective in the management of
68 suspended sediments, heavy metals and nutrients (Davis *et al*., 2001; Jia *et al*., 2015; Zinger
69 *et al*., 2007).

70 The efficiency of SUDS to remove heavy metals from runoff water depends on
71 several factors, among them the adsorption capacity and hydraulic conductivy of the
72 surface medium, runoff first flush volume and composition, as well as the presence of
73 vegetation that prevents clogging and erosion (Allabashi *et al.*, 2019; Flanagan *et al*., 2019;
74 Kandra *et al*., 2014; Tedoldi *et al.,* 2016; Tedoldi et al., 2017b). A comprehensive analysis
75 of different factors controlling heavy metal pollution from urban runoff is presented in
76 previous reviews (Eckart et al., 2017; Huber et al., 2016; Kabir et al., 2014; Tedoldi et al.,
77 2016; Vardhan et al., 2019).

78 The soil hydraulic characteristics of the SUDS may vary depending on their function.
79 In general, the medium should have enough permeability to prevent permanent
80 waterlogging, but it should be low enough for the system to be capable of adsorbing the
81 contaminants that it receives (Le Coustumer *et al*., 2012). Another factor in SUDS design
82 is the balance between the adsorption efficiency of the material and its economic and
83 environmental cost. Local materials should be preferred for reducing transport costs and
84 carbon footprint.

85 It is of great importance to make an exhaustive study of the bed material in order to
86 determine its future behaviour as a pollutant load retainer. Faced with this challenge, a
87 number of questions arise, both at a design and at a maintenance level. At a design level:
88 What type of adsorbent is the most adequate for retaining the largest amount of heavy
89 metals while maintaining an infiltration intensity? What characteristics should it have?
90 With respect to maintenance: What pollutant load (heavy metals) can the soil retain? How
91 much runoff can be managed? What lifespan can the medium have before causing problems
92 for the environment?

93 Thus, the main objective of this research is to answer these questions, that is, to

94 determine the heavy metal retention capacity of a given type of medium or soil for a SUDS.
95 To define the medium, an autochthonous soil from the site has been employed and three
96 types of sand tested to improve infiltration conditions. Thus, the specific objectives were
97 as follows: (a) to obtain the kinetics and the sorption isotherms of the metals in the soil and
98 in the three types of sand, (b) to select an adsorbent bed with appropriate hydraulic
99 conductivity and retention capacity, (c) to determine the breakthrough curves in dynamic
100 retention assays, and (d) to identify the retention mechanisms of the metals in the filter bed.
101 To explore these questions, we identified an effective medium for the design of a SUDS
102 pilot project in the car park of the Public University of Navarre (UPNA) campus in Tudela
103 (Spain). This SUDS aims to be a prototype for interventions in other places or with other
104 pollutants. For this we develop a methodology for evaluating the system and reach a
105 balance between hydraulic conductivity and adsorption capacity of heavy metals in the
106 runoff water, particularly: Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+}.

107 ## 2 MATERIAL AND METHODS

108 ### 2.1 Materials and reagents

109 The soil was obtained from a plot near the SUDS project located in Tudela (Navarre-
110 Spain). The project involved the transformation of a traditional urban stormwater drainage
111 system from the car park into a SUDS (Fig. SI1). Samples from the top 30-cms of surface
112 soil were collected in four different areas in the plot. The samples were dried in a laboratory
113 at room temperature for two weeks until a constant mass was obtained, then sieved through
114 a 2 mm mesh. According to the USDA soil taxonomy the soil was classified as *Typic*
115 *Calciustept* and the soil texture distribution was as follows: clay, 28.7% (< 2 μm); silt,
116 48.5% (2 – 20 μm); sand, 22.8% (> 50 μm). To select a type of sand which could improve
117 the soil's infiltration capacity, three commercial sand-types were compared: one of them
118 was river sand (RS) with a heterogeneous particle size, in which coarse grains of different
119 shapes and brownish-coloured fines were observed; the other two were washed sands
120 (WS), which differed in their granulometry (WS_1, with a granulometry between 0.2 and 1.0
121 mm; and WS_2, with a granulometry between 1.0 and 2.0 mm). The saturated hydraulic
122 conductivity of the different types of sand were measured using the constant head method
123 established in the ASTM 2434-68 (2006) standard.

2.2 Chemical characterization of the adsorbents

The pH was measured under saturated paste conditions (Jackson and Beltrán Martínez, 1982). For this, samples of the adsorbent mixture were placed in 50 mL beakers, to which deionized water was added until a paste was obtained. The ζ-Zeta was determined by photon correlation spectrometry (Malvern model Zetasizer 3000), with an He-Ne laser of 633 nm wavelength and a maximum power of 10 mW. To measure the size of the colloids, approximately 3 mL of leachate was added to standard polystyrene cuvettes. The Zeta-potential was obtained from measurements of the electrophoretic mobility using 50 mm quartz capillary cells (Mulligan *et al*., 2001). For each adsorbent, 200 mg of sample and 25 mL of deionized water were added to a 50-mL centrifuge tube. The tubes were subsequently shaken with the solids and the water, and they were centrifuged at 3000 rpm for 2 minutes in order to separate the largest sized colloidal particles that might interfere in the reading (Mulligan *et al*., 2001).

The inorganic carbon concentration influences the pH of the adsorbent which, in turn, affects the material's retention capacity. The inorganic carbon was determined from the content of $CaCO_3$ in the soils following the Loeppert *et al*. (1984) procedure.

2.3 Adsorption kinetics and isotherms

To determine the equilibrium time, 200.0 ± 0.3 mg aliquots of the adsorbent were placed in 50 mL centrifuge tubes (García *et al*., 1996). To each tube we added 0.25 mL of 1.0 M $NaNO_3$ solution and 25 mL of a metal solution of a known concentration (Table SI1). The centrifuge tubes were kept at 25.0 ± 0.1 ºC under continuous agitation. When the established times (1, 2, 3, 4, 5, 6, 12 and 24 h) elapsed the suspensions were filtered and 100 μL of HNO_3 was added to prevent the hydrolysis of the cations (Echeverría *et al*., 1998). The concentration of metals in the filtrate was determined by Atomic Absorption Spectroscopy (ASS) (García *et al*., 1996; Oliveira *et al*., 2007). The amount of metal sorbed by the adsorbent was found from the difference between the initial concentration and the concentration in the solution.

The adsorption isotherms of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} were obtained by adding 25 mL of an appropriate metal solution to 200 mg of each adsorbent in 50 mL centrifuge tubes. The metal solutions were prepared by diluting 1.000 g L^{-1} of a standard solution (Titrisol™ – Merck) in deionized water. The initial concentrations of the metal solutions were

155 increased to reach the isotherm monolayer. The maximum initial concentration for each
156 ion and adsorbent is shown in Table SI2. The centrifuge tubes were maintained at 25 ± 0.1
157 ºC and agitated for 24 h with a frequency of 5 oscillations per second. Then the suspensions
158 were filtered, acidified with 100 μL of HNO_3 and the concentration of metal was analysed
159 in the supernatant by ASS. A blank was prepared including 200 mg of the soil-sand mixture
160 and 25 mL of deionized water.

161 The adsorption parameters were determined using the models of Langmuir and
162 Freundlich (Ahalya *et al*., 2003). Although Langmuir's (1918) model assumes a series of
163 premises that are difficult to meet in the case of adsorption in a solution, it allows the
164 deduction of the capacity of the monolayer (Veith and Sposito, 1977), where the amount
165 adsorbed, n^a, is expressed by,

$$n^a = \frac{n_m^a B_L c_e}{1 + B_L c_e} \quad (1)$$

166 where n_m^a represents the concentration of adsorbate corresponding to the covering of the
167 monolayer; B_L is a coefficient of adsorption related to adsorption enthalpy; and C_e is the
168 concentration in equilibrium.

169 Despite its empirical origin and applications (Ahalya *et al*., 2003), the Freundlich
170 model is rigorous in the sorption to heterogeneous surfaces (Sposito, 1980). Its general
171 expression is as follows:

$$n^a = k_F c_e^n \quad (2)$$

172 where k_F is the Freundlich parameter related to the adsorption capacity and is equivalent to
173 the amount retained for an equilibrium concentration equal to unity; and n is an
174 adimensional parameter. The coefficients were determined through the logarithmic
175 transformation of Equation (2).

176 **2.4 Dynamic column assays of metal retention**

177 Due to the limited saturated hydraulic conductivity of the the soil collected from the
178 sampling plots, an adsorbing bed was prepared from a mixture of soil (70%) and washed
179 sand WS_1 (30%), which combined the original soil's metal retention capacity with the
180 permeability of the sand. The WS_1 sand was selected because of the smaller size of its
181 particles. The assays were made with a glass column having a porous disc at the bottom,

182 also made of glass, as a support for the adsorbent (Fig. 1). The column was 432 mm long
183 with a diameter of 34 mm. The sand/soil mixture or adsorbent was added to the column
184 until reaching a height of 200 mm in all the assays. Next, the adsorbent was compacted
185 with a vibrator (Tecnokartell model TK3S). Given that the height of the material in the
186 column diminished due to vibration, the filling and compacting process was repeated until
187 filling the height of 200 mm pre-established in these tests. Cotton was placed on top of the
188 adsorbent material to prevent erosion and splashing of the adsorbent during the dosing of
189 the solution. To condition the material, and for the first washing of the adsorbent, 200 mL
190 of deionized water was added after packing.

191 400 mL of a 10 mM solution of each metal ion (Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) was
192 added to the column. The solution had been previously adjusted to pH 3 in order to prevent
193 the precipitation of the metal ions in the solution. The concentration of this aqueous
194 solution was high enough for the assays to be completed with a single application of the
195 solution. Therefore, it was much higher than the concentrations that are typical in a parking
196 lot with a high intensity of motor vehicles (Göbel *et al*., 2007). The metal solution was
197 dosed with a pump (ProMinent Model Beta/5) at pumping conditions of a 30% run and
198 20% pulsation. These conditions were chosen taking into account the hydraulic
199 conductivity of the material/mixture and the pump's characteristics achieving an average
200 inflow rate of 5.5 mL/min.

201 Aliquots of 30 mL were taken from the drained solution at the outlet of the column
202 in order to measure the zeta-potential, the pH and the concentration of ions in the solution
203 (Alcántara *et al*., 2012). After adding 400 mL of the 10 mM solution of each metal ion, the
204 column was washed with 200 mL of deionized water to eliminate the remains of the
205 solution retained in the pores of the adsorbent (Hatt *et al*., 2008). The pump's dosing
206 conditions were the same as those described in the previous stage and the leaching samples
207 were collected in the same way as described in the above paragraph.

208 The zeta potential was determined as described in Section 2.2 and the leaching pH
209 was measured with a Metrohm pHmeter and a combined electrode. After measuring the pH
210 of each aliquot, 100 µL of concentrated HNO_3 was added to prevent hydrolysis and
211 precipitation processes in the metal ions (Davis *et al*., 2001).

212 The concentration of metals in dissolution was determined, either directly or after

213 dilution, by atomic absorption spectroscopy (Perkin-Elmer model 2100). An air-acetylene
214 flame was used and the flows were 2.5 L min^{-1} of air and 8 L min^{-1} of acetylene (Davis *et*
215 *al*., 2001; Fuerhacker *et al*., 2011; Garcia *et al*., 1996; Oliveira *et al*., 2007). The presence
216 of Ca^{2+} in the leaching was also analysed to find out whether any metals were retained due
217 to ion exchange (Singh and Sekhon, 1983).

218 Once the adsorbent was washed, some aliquots were taken from the adsorbent bed in
219 order to measure the distribution of the ions retained throughout the column. Samples were
220 taken from each 5 cm layer of the filter bed (Fig. SI2) and were dried in an oven at 105 ºC
221 until a constant mass was obtained (Hatt *et al*., 2008). Once dried, we added 1,000 ± 0.3
222 mg of each portion to 100 mL Erlenmeyer flasks, together with 6 mL of 60% HNO_3 and 4
223 mL of 36.5% HCl (Ahalya *et al.*, 2003; Davis *et al.*, 2001; Garcia *et al*., 1996). We included
224 another Erlenmeyer flask containing 1,000 mg of the original soil-sample mixture as a
225 blank. The flasks were placed on hotplates with constant agitation and the samples were
226 kept boiling under reflux for 1 hour (Fig. SI3). Then the samples were cooled, the
227 supernatant filtered into a 100 ml volumetric flask and the content of the flasks was made
228 up to the mark with deionized water. Cation concentrations in the extracts were determined
229 by AAS as was described above (Garcia *et al*., 1996; Oliveira *et al.*, 2007).

230 Given that the column infiltration was under laminar flow conditions, the hydrauic
231 conductivity, $k_{s,}$ was determined from the Darcy equation by measuring the flow at the
232 column outlet and the increase in hydraulic load between the entry and exit points of the
233 adsorbent medium in the column. A digital manometer (Keller LEO 1) was placed at the
234 upper part of the column to measure the hydraulic load. The hydraulic properties of the
235 WS_1 sand and of the mixture of soil/sand were determined in triplicate.

236 ## 3 RESULTS AND DISCUSSION

237 ### 3.1 Characterization of adsorbent material

238 Table 1 shows the inorganic carbon content, expressed as a percentage of calcium
239 carbonate, the pH and the zeta potential. The inorganic carbon content ranged from 34.9%
240 for soil to 0.38% for washed sands. The carbonate content is related to the origin of each
241 of the samples. The soil comes from an arid zone, which is rich in calcium carbonate. The
242 scarce percentage of carbonates in the WS_1 and WS_2 sand samples could be due to washing

prior to their commercialization. Therefore, on the basis of the inorganic carbon content in the samples, the soil had a greater capacity than sand samples to buffer the pH and favour the retention of metal ions.

The pH was basic in all the cases, with values between 7.9 for the soil and 8.7 for the WS_1 sand sample. The values of ζ-Zeta obtained in the assays for the four materials analysed were around -20.0 mV, a favourable potential for the retention of metal cations in solution. There were no significant differences between the values of ζ-Zeta in the samples analysed.

3.2 Sorption kinetics and isotherms of the metal ions

Figure 2 shows the sorption of Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by the soil and the three sand-types as a function of time. Due to the different adsorption capacity of the soil and sand samples, the amount of retained metal is expressed as a percentage with respect to the initial concentration in solution. We kept the adsorbent-mass/solution-volume ratio constant and varied the initial concentration of the aqueous solution (Supplementary information, Table SI1). Despite the differences in the total amount retained by the soil and the three sand samples, over 70% of the retention occurred in the first three hours of the trial, and the initial slope for the sorption was larger for the soil than for the sand samples. For all the metals, the initial slope for the sorption is steep and decreases towards equilibirum after the first hour. These results are similar to those obtained by Søberg *et al*., (2019). Except in the case of Cu^{2+}, adsorption in the washed sand samples (WS_1 and WS_2) was lower than 50%, whereas in the RS the percentage retained varied according to the metal. The lower sorption of cations in samples WS_1 and WS_2 in comparison to the soil and RS can be ascribed to the carbonate content. Metal solutions were acidified to prevent the hydrolysis and precipitation reactions of cations. Carbonate content in the soil and river sand was enough to buffer the hydronium ions from the metal solutions, but in the case of WS_1 and WS_2 samples it couldn't amortiguate the acidification from metal solutions. The equilibrium time of the samples ranged from 4 hours for the retention of Cu^{2+} and Cr^{3+} in the soil sample to 12 hours for the retention of Cd^{2+} in the sand samples. To facilitate the reproducibility of the assays, the sorption isotherms were determined after 24 hours, so that the equilibrium times were reached for all the samples in all the metals analysed.

The shape of the adsorption isotherm is related to the energy of the interaction,

whereas the amount retained depends on its retention ability or monolayer capacity. Figure 3 depicts the isotherms of the five cations for the soil and the three sand samples. Because the soil had greater capacity to retain metals than the sand, the sand sample isotherms have been inserted in the graph of the soil isotherms but on a different scale. The isotherms reveal differences in retention among metals, as well as among the soil and the sand samples. The isotherm of Cr^{3+} in the soil belongs to type H2 of the Giles *et al*. (1960) classification. These isotherms are characterized by an almost vertical slope at low equilibrium concentrations, and a plateau in which the amount adsorbed scarcely varied with the equilibrium concentration. The isotherms of the rest of the cations belong to group L2 of the Giles classification. In these isotherms, the amount retained is proportional to the equilibrium concentration in the initial part of the isotherm; the initial section is followed by a knee related to the saturation of the active adsorption centers, and another section whose slope reflects the soil's hetereogeneity. The isotherms of the metals in the sands have a lower initial slope and reach a plateau at lower equilibrium concentrations than the soil, which demonstrates that they are adsorbents with limited metal cation retention capacity.

Table 2 shows the adsorption parameters obtained when applying the Langmuir and Freundlich models to experimental data from isotherms. The capacity of the monolayer, n_m^a, and Freundlich's constant, k_F, are parameters related to the retention capacity, although n_m^a is the amount of retention in the plateau of the isotherm and k_F is the amount retained for an equilibrium concentration equal to one, in this research 1 mg L^{-1}. Despite the differences observed in the magnitude of these parameters, their trends are similar for the adsorbents and metals. The parameters n_m^a and k_F were much greater for the soil than for the sand samples, which could be attributed to the higher proportion of clay and silt, as well as to the contribution of the soil's laminar silicates. In the sand samples, RS retained more metals than WS_1 and WS_2, which might be related to its larger content in $CaCO_3$. In any case, the adsorption capacity of heavy metals was significantly larger in the soil than in the sand samples, which is in line with the results found by other authors such as Reddy *et al.* (2014).

The order of the quantitative retention of the cations in the soil was as follows: $Cr^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cd^{2+}$. Cr^{3+} has a higher oxidation number than the rest of the ions and thus it has a greater affinity for exchanging with ions like $Ca^{2+}$and Mg^{2+} that are present

306 in the clay-humic complex of the soil. The higher formal charge and smaller size of the
307 cation Cr^{3+} also facilitates the hydrolysis reactions that can induce precipitation in the form
308 of oxides. The steep initial slope and the sharp knee of the Cr^{3+} isotherm are typical of a
309 high interaction between adsorbent and adsorbate (Figure 3). The monolayer capacity and
310 Freundlich constant of cadmium retained by the soil was smaller than the other cations, in
311 consonance with the heavy metal retention results in soils of a different composition
312 (Echeverria *et al*., 1998).

313 **3.3 Dynamic assays and breakthrough curves**

314 The saturated hydraulic conductivity of WS_1 was $6.23 \times 10^{-3} \pm 8.80 \times 10^{-5}$ cm s^{-1},
315 whereas that of the soil-sand mixture was $4.33 \times 10^{-4} \pm 1.04 \times 10^{-4}$ cm s^{-1}, which is an
316 improvement of one order of magnitude. Contrasting these values with those provided by
317 Kutilek and Nielsen (1994) for the classification of soils in terms of their permeability, the
318 soil-WS_1 sand mixture had an average permeability. As expected, it was observed that the
319 conductivity values of the sand samples displayed less variability than the soil-sand
320 mixture.

321 Figure 4 shows the concentration and standard deviation, expressed in mmol/L, of
322 heavy metal ions and Ca^{2+} in the leached solution as a function of the total volume leached.
323 Two trends are shown in the concentration curves: first, $Cu^{2+}$and Cr^{3+} concentrations in the
324 leachate were lower than the detection limits of the experimental technique; second, Ni^{2+}
325 ions in the permeate were detected at 200 mL, and Cd^{2+}, Zn^{2+} ions at 240 mL. Therefore,
326 in the experimental conditions reported in this research, the amount of metals retained up
327 to a lixiviate volume of 200 mL would be the upper limit for SUDS. With these values of
328 the breakthrough point for each metal, the atomic masses and the initial solution
329 concentration, the retention capacities of the filter medium for each metal were as follows:
330 Cd^{2+}, 2.13 kg m^{-3}; Zn^{2+}, 1.24 kg m^{-3}; and Ni^{2+}, 0.97 kg m^{-3}.

331 With regard to Ca^{2+}, its leached concentration was lower than 10 mM, up to a total
332 volume of 60 mL (Fig. 4). Starting from this volume, the amount in solution increased to
333 45 mM. From there on, and throughout the assay, the concentration of Ca^{2+} in the leachate
334 diminished from 45 mM to 35 mM. These results imply that the ions of Cd^{2+}, Ni^{2+} and Zn^{2+}
335 were retained in the adsorbent mixture due to an ion exchange with the Ca^{2+} ions that
336 saturate the adsorbent's colloids.

Figure 5 shows the variation in pH and in ζ-Zeta as a function of the volume of leachate. The pH of the lixiviate was measured to assess the buffering capacity of the soil-sand mixture, given that the solution of metals had a pH 3 to prevent hydrolysis and precipitation of the ions. In Figure 5 three sections can be distinguished. Up to 200 mL of leachate, the pH fell to 6.5. For volumes higher than 200 mL, the pH value tended to be maintained between 6.5 and 6.0. This was due to the buffering capacity of the mixture of soil and sand resulting from the action of the carbonates present in the medium. From 400 mL upwards, the system was fed with deionized water that leached away the metal solution that may have remained in the gaps of the soil/sand system. For this reason, there was a general trend towards incrementing the pH of the leachate mixtures, from values of 6.0 to approximately 6.75. Considering that the pH of runoff water is similar to to that of rain, i.e. between 5 and 5.5 for the study zone (Vet *et al.*, 2014), the acidification of the adsorbent can be expected to be less than that described in the experimental conditions.

Figure 5 also shows the variation in ζ-Zeta (secondary axis), expressed in mV, as a function of the volume of leachate. The variation in the zeta potential of the leachate displays two sections. The negative charge of the colloids was neutralized when 90 mL had been leached corresponding to the application of the metal solution. The rest of the ζ-Zeta measurements were within the interval 0 ± 5 mV, which corresponds to the variability of the deionized water blank. Therefore, the cations neutralized the negative load of the colloids in the first retention stages. When the load of colloids had been neutralized, the metal retention could be attributed to ion exchange or to precipitation reactions.

Given that $Cu^{2+}$and Cr^{3+} could not be detected in the leachate, it would be appropriate to pose the question as to whether these ions were retained in the column and, if so, what this retention mechanism is. To obtain more information, samples of the adsorbent bed were taken from different sections of the column, then they were dried, and heated to mix with HNO_3 and HCl in order to extract the retained metals (Ahalya *et al*., 2003). Fig. 6 shows the concentration of metals retained in terms of the height of the adsorbent bed.

As was described in the adsorption isotherms, two adsorption trends were observed in the extraction of metals from the adsorbent. The Cu^{2+} and Cr^{2+} ions were retained at a higher proportion in the top 5-cm of the column, but they could not be detected in the extract from the bottom of the column (20- cm). In calcareous soils, carbonated chemical

species control the reactivity and mobility of metals. The larger affinity of soil-Cu and soil-Cr systems is in line with the first hydrolysis constant of the cations under study Cr, pK_a = 4.7; Cu, pK_a = 7.7; Zn, pK_a = 9.0; Ni, pK_a = 9.9; and Cd, pK_a = 10.1. (Basta and Tabatabai, 1992; Brümmer, 1986). The relation between metal sorption and cation hydrolysis suggests that OH groups bind to metals in solutions and at mineral surfaces in an energetically similar manner (Brady, 1992). The fact that Cu^{2+} and of Cr^{3+} were detected in the readings of the leachates at the top of the column but not at the bottom suggests that both ions precipitate in the column. From a design perspective, a 20-cm layer of this material would be enough to reduce the load of $Cu^{2+}$and of Cr^{3+} to below detection limits. At the breaking point, Cd^{2+}, Ni^{2+} and Zn^{2+} were homogeneously distributed throughout the height of the column, with the adsorbent retention spread equally through it. So, the profile of these ions in the column rules out their precipitation in the head of the adsorbent bed, and indicates that they were retained by ion exchange, as is suggested by the increased leaching of calcium ions.

The results from sorption kinetics, adsorption isotherms and breakthrough curves are crucial to design systems that use soils to filter and retain contaminants in stormwater management. These SUDS infiltration systems currently pose major challenges related to the design, maintenance and optimization of the contaminant retention (Tedoldi *et al*., 2017b). The metal input in the "Green Water Infrastructures (GWI)" implies that the soils may be under a slow and persistent increase in their concentration of metals (Kabir *et al*., 2014). Furthermore, given that the complex set of reaction pathways in GWIs is not fully understood and characterized, it is not possible to establish *a priori* their long-term retention capacities. Therefore, this research develops a method to assess the retention capacity of a given soil-type to adsorb heavy metals dissolved in runoff water. Reddy *et al*. (2014) and Søberg *et al*. (2019) have characterized the properties of several materials needed to adsorb contaminants under static conditions. However, we have assessed the retention of metals both under static and dynamic conditions of the fluid, which provides experimental data for characterizing the adsorbent and estimating the runoff volume.

As an example of estimating potential values of runoff volume, we applied the results obtained under dynamic conditions to the filtering medium in the bioretention unit (SUDS) designed in Tudela car park. The SUDS surface measures 288 m^2, the soil depth 30 cm and it receives the runoff from a parking lot of 1,985 m^2. The retention capacities of the filtering

medium obtained for each metal are 2.13 kg of Cd^{2+} m^{-3}, 1.24 kg of Zn^{2+} m^{-3} and 0.97 kg of Ni^{2+} m^{-3} of adsorbent. Starting from these values, and taking into account the concentration values of these metals in urban runoff in areas with a high density of traffic, as compiled in the literature (Göbel *et al*., 2007), we obtained the Total Treatable Runoff Volume (TTRV) per m^3 of the adsorbent medium that the system can handle by retaining each metal. We have taken the average of the maximum and minimum values from Göbel *et al*. (2007) review (Table 3). Dividing the volume calculated by the surface of the parking lot, and multiplying it by the surface of the SUDS, determines the height of effective precipitation (EP) per meter of the medium depth that the system can handle. Finally, by multiplying this value by the depth of the soil, it was obtained the value of the total effective precipitation (TEP) that the soil of the SUDS can handle under ideal conditions. Table 3 gives all the values associated with the these calculations. Those values, along with the precipitation of Cu^{2+} and of Cr^{3+}, demonstrate the great potential of the local soil for retaining heavy metals. The obtained values are consistent with those published by Kabir *et al*. (2014), who reported the promising capacity of GWIs to be used effectively as systems for urban environment quality improvement.

Future research will involve extending the retention of metals under dynamic conditions to soils varying in permeability and sorption capacity. Another aspect to be considered in future research is which metals are adsorbed to different types of solid particles, the amounts of which can end up being very significant (Borris *et al*., 2016; Gavrić *et al*., 2019; Huber *et al*., 2016; Loganathan *et al*., 2013; Zafra *et al*., 2011). These particles can be retained on the surface due to sedimentation in systems like grass swales or vegetative filter strips (Gavrić *et al*., 2019; Muñoz-Carpena et al., 2019). Sedimentation, together with the precipitation of copper and chromium, are supported by the results obtained by Tedoldi *et al*. (2017a), who showed how the vertical distribution of the concentration of heavy metals in soil is characterized by a significant accumulation of them on the surface, which continues decreasing with depth. Other authors like Søberg *et al*. (2017) and Wang *et al*. (2017) found metals that were adsorbed in the top 5 cm of the filtering material.

4 CONCLUSIONS

This research work has permitted the development of a technique for finding out the

retention capacity of heavy metals in the soil of a Sustainable Urban Drainage System (SUDS), and for identifying the retention process of each metal. This has some practical implications in the design and maintenance of a SUDS, as has been demonstrated.

The capacity of the soil to retain metal ions was far superior to that of the three sand samples analysed. The order of quantitative retention of the cations in the soil was as follows: $Cr^{3+}>Cu^{2+}>>Zn^{2+}\approx Ni^{2+}>Cd^{2+}$. The experiments under dynamic conditions with the adsorbent medium in the column made it possible to find out which metals are retained at breaking point, and their retention mechanisms. The analysis of the filtering medium after the assay allowed us to verify that the Cr^{3+} and Cu^{2+} ions were preferably retained in the first 5 cms of the column, and that the concentration of these cations decreased to a lower value than the technique's detection limit at the bottom of the column, which enables one to deduce that the principal retention mechanism was precipitation. In addition, at the breaking point, the concentration of Cd^{2+}, Ni^{2+} and Zn^{2+} was homogeneous throughout the column, and, given that the retention was accompanied by leaching of Ca^{2+} into the adsorbent bed, it can be inferred that the retention of these ions was produced mainly by ion exchange.

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Table 1. Content in inorganic carbon, pH, and ζ-Zeta for the sands and soil samples.

Table 2. Langmuir and Freundlich parameters deduced from the adsorption isotherms of ions Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} by the soil and sand samples.

Table 3. Total treatable runoff volume at the SUDS from a car park in Tudela (Spain).

Table 1. Content in inorganic carbon, pH, and ζ-Zeta for the sands and soil simple.

	Inorganic C (% $CaCO_3$)	pH saturation.	ζ-Zeta (mV)
Soil	34.9	7.9	-21
RS	20.1	8.4	-17
WS_1	0.38	8.3	-20
WS_2	0.38	8.7	-20

RS - river sand; WS_1 - washed sand 1, WS_2 - washed sand 2.

Table 2. Langmuir and Freundlich parameters deduced from the adsorption isotherms of ions Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} by the soil and sand samples.

	Langmuir		Freundlich	
	n_m^a (mmol/kg)	B_L (L/mg)	k_F (mmol/kg)	n
		Cr^{3+}		
Soil	61.3	2.63	15.4	0.176
RS	1.37	25.3	0.943	0.194
WS_1	1.11	33.7	0.772	0.126
WS_2	0.95	22.8	0.871	0.338
		Cu^{2+}		
Soil	52.9	0.190	10.80	0.812
RS	2.00	3.14	0.93	0.571
WS_1	5.34	1.83	1.39	0.500
WS_2	0.42	0.83	0.09	1.09
		Zn^{2+}		
Soil	24.6	1.76	8.75	0.739
RS	4.29	9.56	3.42	0.436
WS_1	0.40	40.1	0.31	0.197
WS_2	0.37	10.9	0.31	0.413
		Ni^{2+}		
Soil	22.79	1.48	6.29	0.613
RS	1.55	13.5	1.16	0.418
WS_1	1.42	0.81	0.44	0.760
WS_2	1.48	0.73	0.43	0.770
		Cd^{2+}		
Soil	11.4	0.69	4.36	0.945
RS	1.11	1.39	0.61	0.700
WS_1	0.17	1.74	0.12	0.345
WS_2	0.29	2.60	0.17	1.03

RS - river sand; WS_1 - washed sand 1, WS_2 - washed sand 2.

Table 3. Total treatable runoff volume at the SUDS from a car park in Tudela (Spain).

	BP[a]	MRC[b]	RCAM[c]	CRTA[d] (µg/L)		TTRV[e]	EP[f]	TEP[g]
	mL	g	Kg	Min	Max	L	(L/m^2)	(L/m^2)
Cd^{2+}	240	0.27	2.13	0.3	13	$3.2 \cdot 10^8$	$4.64 \cdot 10^7$	$1.39\ 10^7$
Zn^{2+}	240	0.16	1.24	120	2000	$1.17 \cdot 10^6$	$1.69 \cdot 10^5$	$5.08\ 10^4$
Ni^{2+}	210	0.12	0.97	4	70	$2.62 \cdot 10^7$	$3.81 \cdot 10^7$	$1.14\ 10^6$

[a] BP: Breaking Point
[b] MRC: Metal Retained in the Column
[c] RCAM: Retention Capacity per m^3 of Adsorbent Medium (soil)
[d] CRTA: Metal Concentration of Runoff from Traficked Areas with high density (Göbel et al., 2007)
[e] TTRV: Total Treatable Runoff Volume per m^3 of adsorbent medium (soil)
[f] EP: Effective Precipitation height per m of soil depth
[g] TEP: Total Effective Precipitation height that the SUDS can handle

Fig. 1. Setup for the dynamic experiments on the retention of metals by a mixture of soil (70%) and sand (30%)

Fig. 2. Sorption kinetics for Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by the soil and sand samples (RS, WS_1 and WS_2)

Fig. 3. Sorption isotherms at 25 ºC for the retention of Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} by the soil and sand samples (RS, WS_1 and WS_2). The plots include the isotherm type for the soil according to Giles et al. (1960) classification: H, high affinity; L, Lagmuir.

Fig. 4. Concentration of heavy metals and calcium in solution as a function of leached volume.

Fig. 5. Variation of pH and ζ-Zeta as a function of the volume of lixiviate.

Fig. 6. Concentration of metals as a function of height for the sampling column.

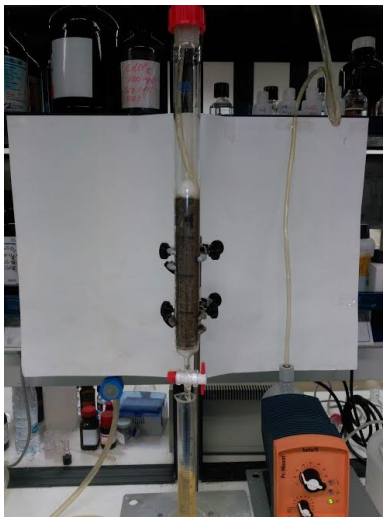

Fig. 1. Setup for the dynamic experiments on the retention of metals by a mixture of soil (70%) and sand (30%).

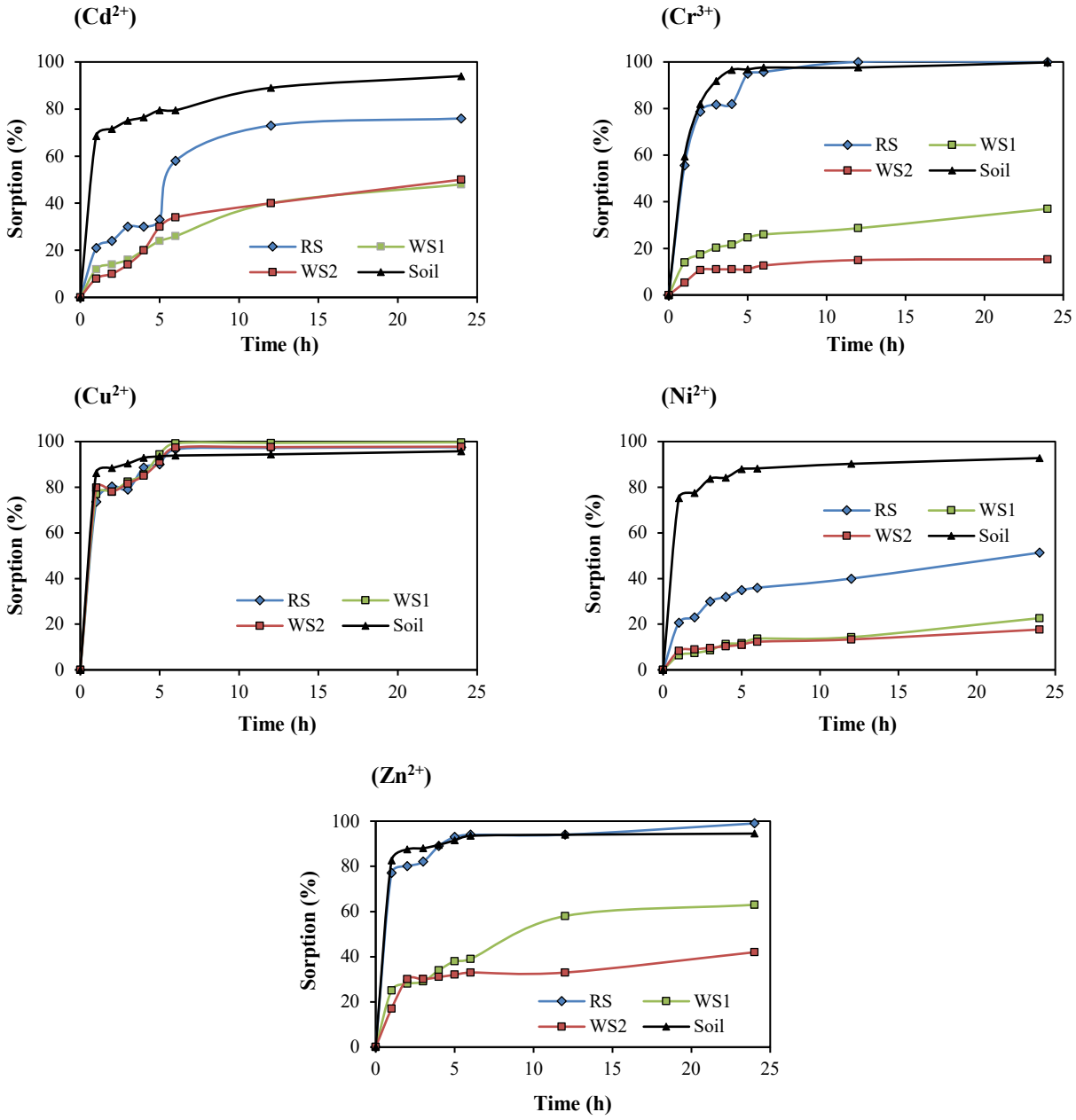

Fig. 2. Sorption kinetics for Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} by the soil and sand samples (RS, WS_1 and WS_2).

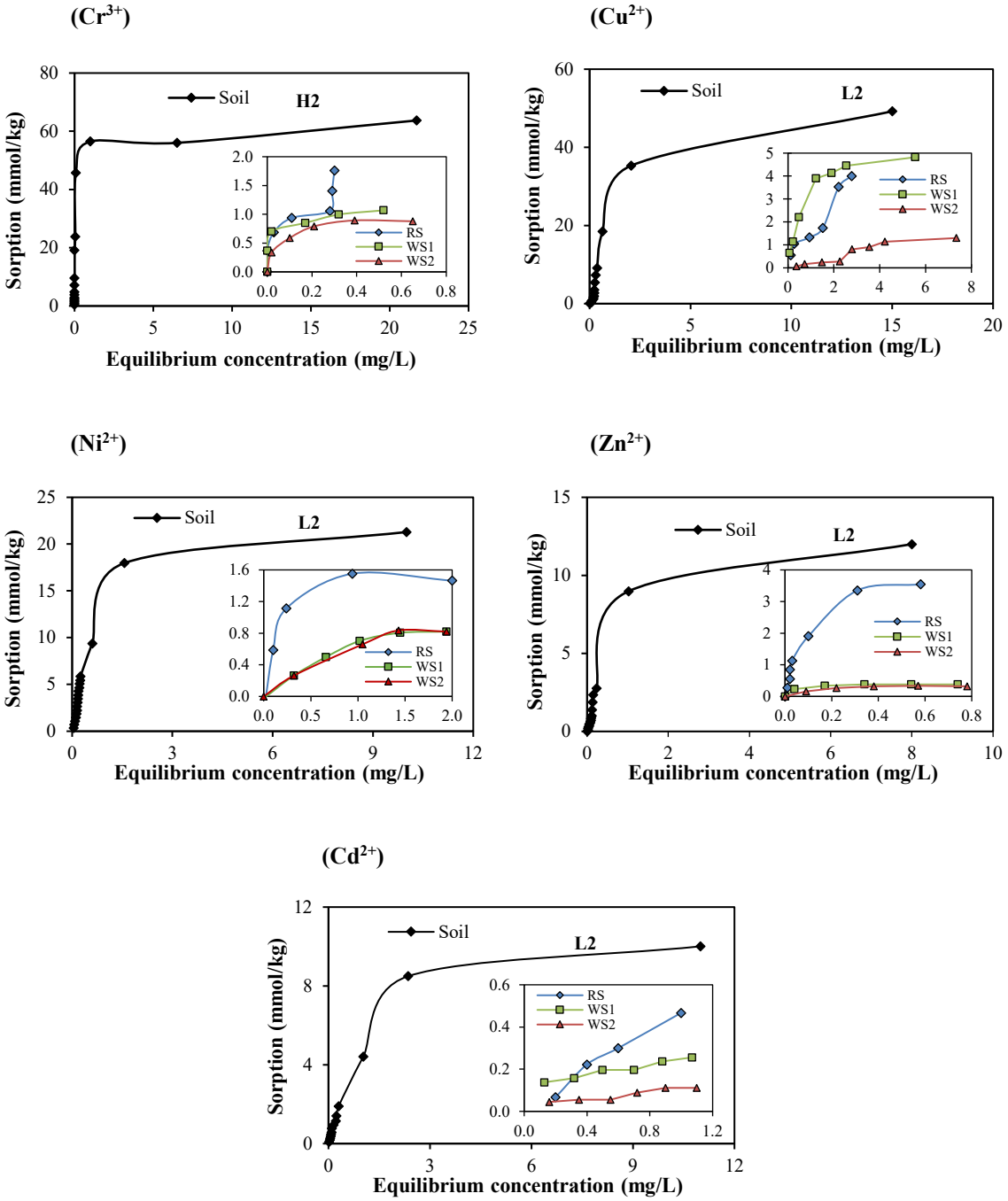

Fig. 3. Sorption isotherms at 25 ºC for the retention of Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} by the soil and sand samples (RS, WS_1 and WS_2). The plots include the isotherm type for the soil according to Giles et al. (1960) classification: H, high affinity; L, Lagmuir.

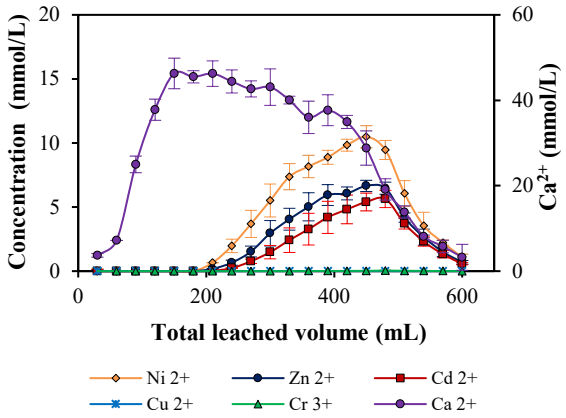

Fig. 4. Concentration of heavy metals and calcium in solution as a function of leached volume.

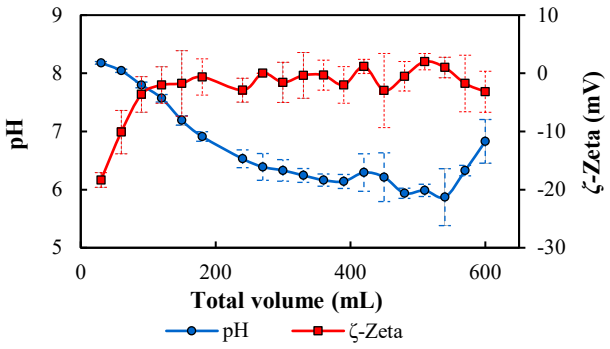

Fig. 5. Variation of pH and ζ-Zeta as a function of the volume of lixiviate.

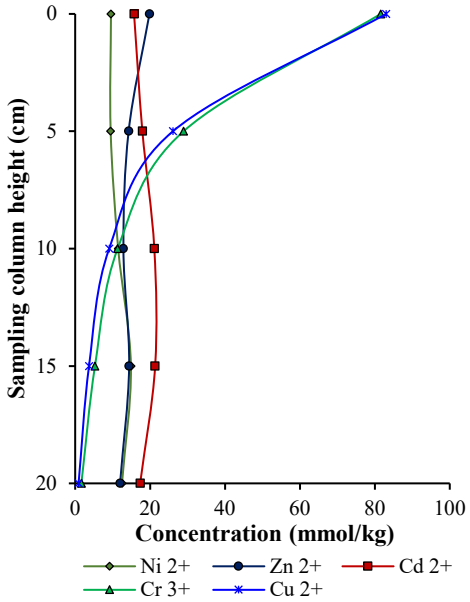

Fig. 6. Concentration of metals as a function of height for the sampling column.