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Extended Abstract

Heavy Metals Removal from Reclaimed Water in a Laboratory Column Using a Granitic Residual Soil †

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Abstract: The removal of five heavy metals was evaluated in vertical downflow column, with a granitic residual soil, operated in discontinuous and continuous mode. The results show higher removal rates of the five metals for the continuous mode, with highest values to Zn and Pb followed by Ni, Cu and Cr. The removal of all metals occurs mainly at the top 5 cm essentially through complexation and precipitation in the form of hydroxides.

Keywords: reclaimed water; heavy metals removal; sorption; residual soil

1. Introduction

The artificial recharge of aquifers with reclaimed water is a practice that can be useful for water management practices. Soil Aquifer Treatment (SAT) has been shown to be a technical and economical feasible alternative for the refining of secondary treatment effluents prior to their inclusion in aquifers. However, if the soil does not present favourable conditions for the infiltration of reclaimed water, the pollutant residual loads of these waters, such as heavy metals, can be a disadvantage to groundwater quality. The clays present in the soil have reactive properties that allow them to remove metallic cations essentially by sorption mechanisms (e.g., adsorption, cation exchange and complexation-precipitation), as demonstrated by several studies [1–6]. Thus, the objective of this work was to evaluate the removal of five heavy metals, namely chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), using a granitic residual soil and laboratory experiments in downflow column, namely for verifying the main sorption mechanisms responsible for their removal.

2. Materials and Methods

2.1. Characterization Tests of the Residual Soil

The residual soil was picked up at the Quinta de Gonçalo Martins (Guarda, Portugal), as suggested in a previous study [7]. In order to verify the importance of the soil properties for the heavy

metals removal, some physical (particle size, specific surface area, solid particle density, porosity and permeability), chemical (oxides analysis, cation exchange capacity, organic matter content and the soil pH determined in H₂O) and mineralogical properties (mineralogy of the clay fraction, <2 μm) of the soil were determined according to the procedures described in Silva [1].

2.2. Column Experiments

A vertical downflow column of acrylic was used in the experiments (Figure 1c). The experiments run in discontinuous and continuous mode.

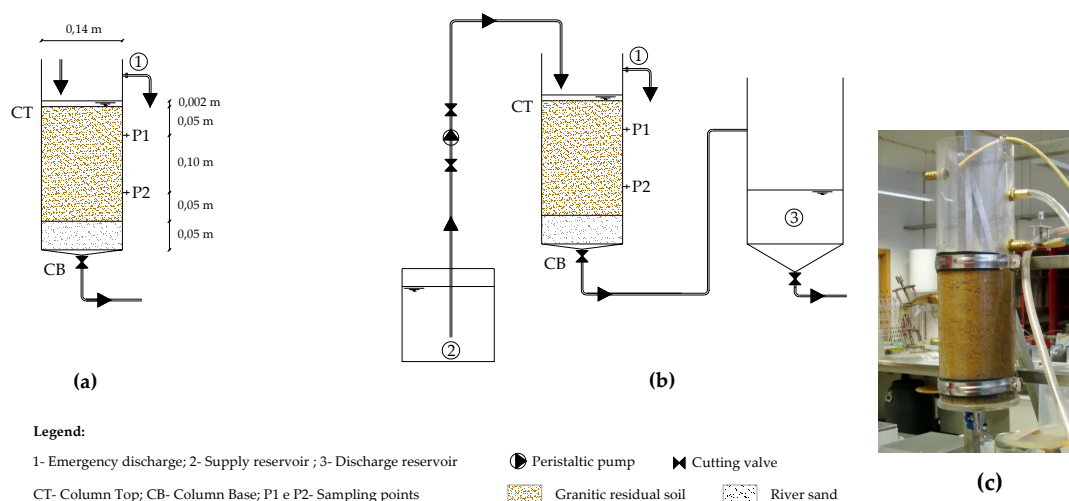


Figure 1. Scheme of the column tests: (a) discontinuous (fed-batch) mode; (b) continuous mode; (c) column in operation.

Four sampling points were used (column top (CT), P1, P2 and column base (CB)). The soil media had a total height of 25 cm, a void volume (V_u) of 1.48 L (from CT to CB) and two distinguished layers: a superior one with 20 cm of soil (weight of 4467.4 g) and a lower one with 5 cm of river sand (weight of 891.4 g).

To study the removal of the metals ions Cr, Cu, Ni, Pb and Zn, it was used concentrated solutions of 1.0 g L⁻¹ of potassium chromate (K₂Cr₄), copper sulphate (CuSO₄), nickel chloride (NiCl₂), lead nitrate (Pb(NO₃)₂) and zinc chloride (ZnCl₂), respectively. The feeding solution included the solutions of the five heavy metals with concentration of 5 mg L⁻¹ from each metal. In a first phase, the column was operated in a discontinuous (fed-batch) mode, including the phases of filling, reaction during 3.5 days (35 days in the total for 10 cycles), drainage and sampling, as suggested by Opoku [8]. In a second phase, the column was operated in a continuous mode, with a flow rate of 0.36 L d⁻¹ and a hydraulic load of 2.34 cm d⁻¹, values previously tested in the laboratory and which are in according with the ones observed by [9,10] in similar studies. For measurement of pH and temperature a SenTix 41 probe attached to a Multi 340i meter from WTW (Germany) was used. The determination of heavy metals concentration was carried out by means of an atomic absorption spectrophotometer GBC-906 (Australia), according to standard [11].

3. Results and Discussion

3.1. Characterization of the Residual Soil

The soil has around 4.94% of clay (≈60% of kaolinite) and a d_{50} of 0.59 mm. To avoid soil clogging and to ensure the polishing of the wastewater, the soil must have less than 10% of clay [12]. It has a density of 2.65, typical of granitic residual soils, porosity of 38.5%, specific surface (in the fraction less than 0.075 mm) of 0.29 m² g⁻¹ and permeability (k) in situ of 4.5×10^{-5} m s⁻¹. Soils with permeability of 6.94×10^{-6} m s⁻¹ are suitable for controlled infiltration of reclaimed water [13]. The cation exchange

capacity (at pH = 7) is low (6.09 cmol_c kg⁻¹) favouring the exchange of the Ca²⁺ cation in relation to Mg²⁺, K⁺ and Na⁺ cations. The organic matter content is very low (0.25%) and the soil is acidic (pH = 4.91). It contains mainly silica (58.64%) and alumina (33.17%) with lower levels of iron (3.96%) and potassium (4.23%). The clay-colloidal complex of this soil presents reactive properties that can allow it to remove heavy metals by sorption mechanisms [1].

3.2. Evaluation of the Heavy Metals Removal

The Figure 2a,b shows the pH and temperature variation, in the discontinuous and continuous mode experiments, respectively, at the sampling points. The variation of the concentration of Cr, Cu, Ni, Pb and Zn is shown in Figure 2c,d over the 10 operating cycles, at the CB point.

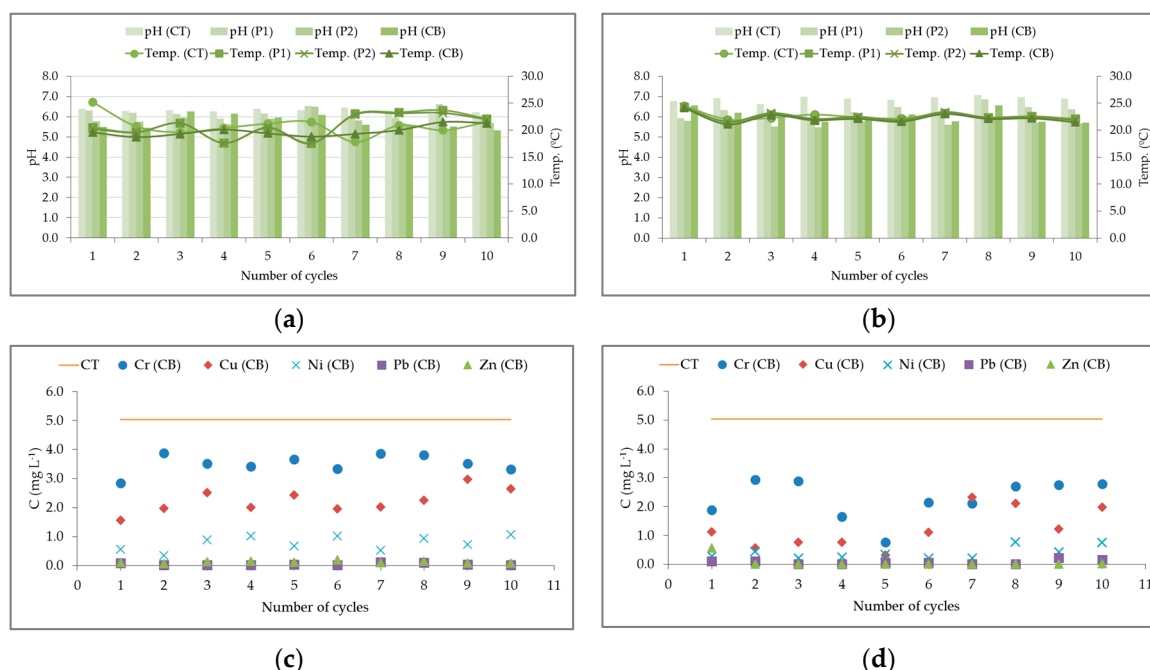


Figure 2. pH and temperature variation in the sampling points for the: (a) discontinuous mode and (b) continuous mode experiments; Variation of the concentration of Cr, Cu, Ni, Pb and Zn at the CB point for the: (c) discontinuous mode and (d) continuous mode experiments.

From the analysis of Figure 2a,b, in general, it can be seen a decrease in pH values from the CT to the CB points. The average temperature, in all sampling points, remained practically constant through all cycles. For the discontinuous experiments (Figure 2c) it was observed, in average, overall concentration removals of 1.44 mg Cr L⁻¹, 2.82 mg Cu L⁻¹, 4.25 mg Ni L⁻¹, 5.03 mg Pb L⁻¹ and 5.0 mg Zn L⁻¹, which corresponds to overall removal efficiencies of 28.8% for Cr, 55.89% for Cu, 84.6% for Ni, 99.1% for Pb and 97.69% for Zn. For the continuous experiments (Figure 2d) it was observed, in average, overall concentration removals of 2.78 mg Cr L⁻¹, 3.84 mg Cu L⁻¹, 4.75 mg Ni L⁻¹, 5.01 mg Pb L⁻¹ and 5.13 mg Zn L⁻¹, which corresponds to overall removal efficiencies of 54.85% for Cr, 75.93% for Cu, 92.42% for Ni, 98.53% for Pb and 98.8% for Zn, higher than the ones observed in discontinuous experiments (Figure 2c). The sorption rates (q_s) were estimated using the Equation (1):

$$q_s = \frac{C_i - C_f}{m_s} \cdot V_u \quad (1)$$

where, q_s is the sorption rate (mg g⁻¹), C_i and C_f are the initial and final metal concentration (mg L⁻¹), respectively, V_u is the void volume (L) and m_s is the mass of soil (g).

In the continuous experiments the q_s values were: 0.92 mg Cr mg⁻¹, 1.27 mg Cu mg⁻¹, 1.58 mg Ni mg⁻¹, 1.66 mg Pb mg⁻¹ and 1.70 mg Zn mg⁻¹, which, in general, are high than the ones found in the discontinuous experiments: 0.48 mg Cr mg⁻¹, 0.94 mg Cu mg⁻¹, 1.41 mg Ni mg⁻¹, 1.67 mg Pb mg⁻¹ and 1.66 mg Zn mg⁻¹. The pH values, associated with longer contact times, seem to favored the removal of the Cr, Cu, Ni, Pb and Zn metal ions by complexation and precipitation in the form of hydroxides [2,4,14]. However, it seems to have also occurred adsorption and cation exchange (with the exception of Cr), since the pH drops to values below 6 in several cycles. The minor removal of Cr may be related with the competition of the various species of metals in solution that, according to [2], favors the species with minor charge when there is variations in the ionic strength of the solution. In general, the removal of the five heavy metals occurred straight in the first 5 cm of soil, and was slightly superior in the continuous mode.

4. Conclusions

The granitic residual soil presents suitable characteristics for removing the five heavy metals. The higher removal rates occurred in the continuous experiments. Zn and Pb presented the highest removal rates, followed by Ni, Cu and Cr. Complexation and precipitation in the form of hydroxides seems to be the main sorption mechanism responsible by heavy metals removal.

Author Contributions: This study was developed by F.S. during her PhD and was supervised by A.A and V.C. Other contributes in the analysis and discussion of the results were given by A.C. and P.S.

Conflicts of Interest: The authors declare no conflict of interest.

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