Research Article

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Removal of Cr, Cu and Zn from liquid effluents using the fine component of granitic residual soils

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Abstract: The practice of reuse of treated wastewater (TWW) is seen as a strategy for water conservation in regions where water scarcity is a natural reality and in those where population growth and/or climate change foresee this scarcity. In situations of lower water scarcity, reuse is practiced by imperatives of environmental protection of the receiving media, reducing the discharge of effluents from wastewater treatment plants. The artificial recharge of aquifers (RAQ) with TWW is a very common practice at the international level, but little considered in Portugal. However, residual waste from TWW (*e.g.* heavy metals), when deposited in soil or water, can cause significant environmental impacts on its uses, and cause serious health problems in several animal species due to their bioaccumulation in food chains. The present study intends to show that the granitic residual soils of the Quinta de Gonçalo Martins (Guarda), in the Beira Interior region of Portugal, present physical-chemical and mineralogical characteristics favorable to the infiltration of TWW into RAQ. The results of the batch sorption tests indicate that the soil has a reactive capacity to remove the Cu and Zn residual load at TWW at high efficiencies by adsorption and ion exchange mechanisms. The pseudo-first order model explained the reaction kinetics for the three heavy metals removal and when the sorption equilibrium state was reached, the removal of these metals was explained by the Freundlich isotherm.

Keywords: Treated wastewater reuse, artificial recharge of aquifers, heavy metals removal, residual soils, sorption

1 Introduction

Liquid effluents produced in wastewater treatment plants (WWTP) can be discharged into water bodies, if they meet the discharge limits for various quality parameters, as defined in legislation [1, 2]. There is thus a residual pollutant load that is allowed to enter into natural water bodies, if there is no risk of negative and significant environmental impacts for the water resources and its uses. However, climate change has been affecting the hydrological regime in several regions of the world, which has been manifested by periods of longer and more frequent droughts, which are interspersed with periods of floods, and which have led to the reduction of volumes of water for recharging surface and underground water bodies [3]. Therefore, the discharge of treated urban effluents into low flow water masses can produce negative and significant environmental impacts, especially in periods of low or no rainfall.

It should be noted that international and national strategies for integrated water management include reuse of treated wastewater (TWW) as part of the solution to meet water needs and to ensure the sustainability of water services. The reuse of TWW is a well-studied practice for uses such as agricultural irrigation, landscape irrigation, industry, artificial recharge of aquifers (RAQ), recreational and environmental uses and non-potable urban uses. The RAQ with TWW is a practice that is already very common at international level, with examples of success in Spain [4], Israel [5], USA [6], Finland [7] and Cyprus [8], but little considered in Portugal. It can contribute to the replenishment of volumes of water in the soil, which can be very advantageous in areas with water deficit or over-exploitation of groundwater. The Soil Aquifer Treatment (SAT) has been shown to be a technically and economically viable alternative for refining secondary treatment effluents prior to their inclusion in aquifers, as demonstrated by some studies [9–12]. However, if the soil does not present favorable conditions for the infiltration of TWW, the residual loads of these waters (*e.g.* heavy metals) can be a disadvantage to groundwater quality. It should be noted that the soil can act as a reactive filter capable of removing the residual load of the TWW.

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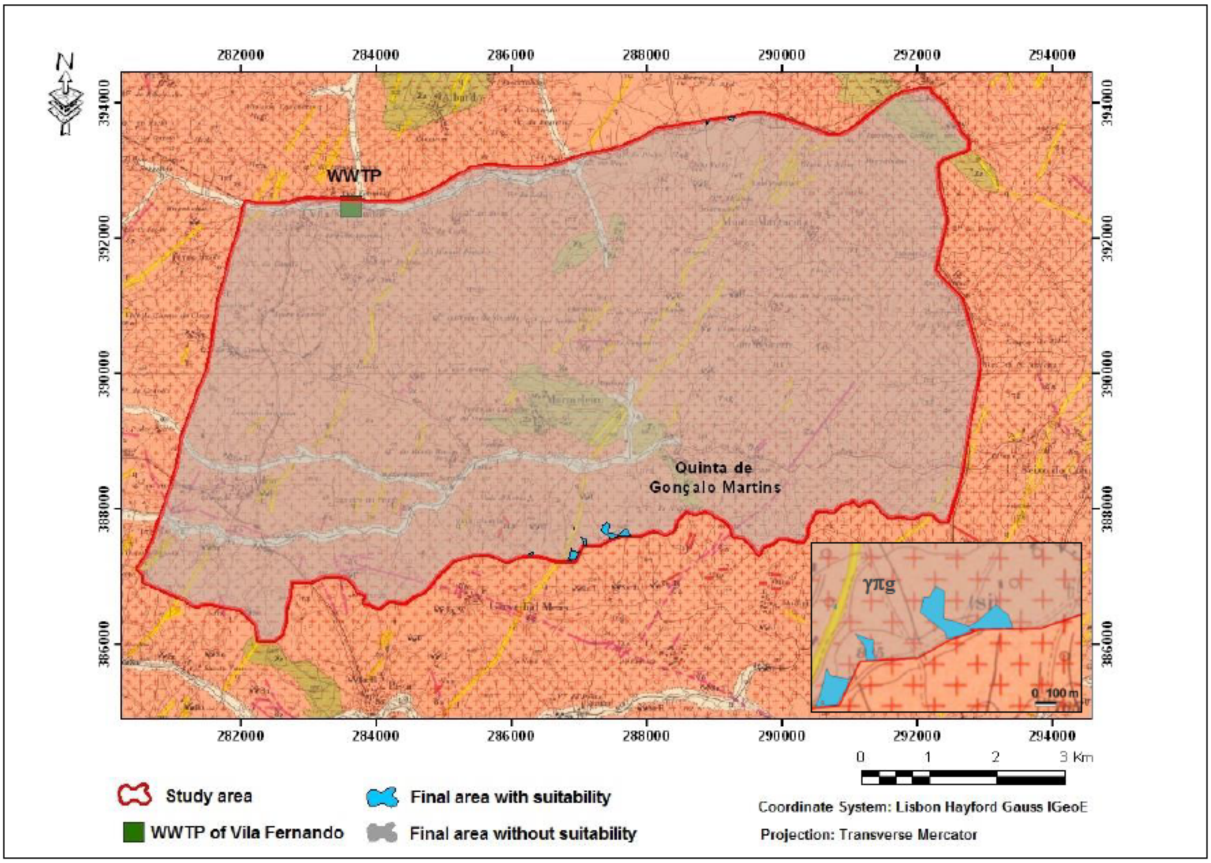

Figure 1: Location of the soil sampling area for infiltration of treated wastewater (blue spots) in an extract map from the Geological Chart of Guarda: Sheet 18-C

Clay minerals, such as a kaolinite, illite, montmorillonite, among others, have reactive properties that allow the removal of metallic cations, as well as inorganic cations, essentially by sorption mechanisms, as proved in [13–20]. However, it is difficult to assess the efficiency and mode of removal of heavy metals in situ, and it is more practical to use laboratory experiments (*e.g.* batch tests). Thus, the objective of this work was to evaluate the ability to remove three heavy metals, namely chromium (Cr), copper (Cu), and zinc (Zn), using the fine component of residual soils of Quinta de Gonçalo Martins (Guarda, Portugal), using batch tests, and to verify the sorption mechanisms responsible for the removal of these pollutants.

2 Methodology

2.1 Characterization of the granitic residual soil

The Quinta de Gonçalo Martins (Guarda), in the Beira Interior region of Portugal, was selected for TWW infiltration from the WWTP of Vila Fernando [21, 22] (Figure 1), using for example infiltration, retention or detention basins, like suggested by [19]. From a soil sample (Figure 2(a)) a fraction with less than 0.075 mm (fine soil) was extracted (Figure 2(b)) for the sorption experiments, as it is the most reactive fractions of the soil, namely silt and clay.

For understanding the importance of soil properties in the removal of heavy metals, some physical, chemical and mineralogical properties were determined. The differential and cumulative volumes of the fine soil as a function of the particle size, as well as the specific surface, were determined by laser diffraction using the Coulter LS200. The density of the solid particles was determined by the pycnometer method [23] and the porosity using the pro-


(a)


(b)

Figure 2: Pickling process for collecting the soil sample, in the selected site for the infiltration of treated wastewater (Quinta Gonçalo Martins, Guarda, coordinates M = 287699 m and P = 387657 m): colleting raw samples (a); sample of fine soil (b)

cedures described in [19]. The clay mineral fraction (< 2 μm) was determined by X-ray Diffraction (XRD) using a Philips Analytical X-Ray BV diffractometer, consisting of a 3710 mpd/00 PW controller and a PW high voltage generator 1830, P, operating at 40 KV and 30 mA with a copper ampoule (Cu Kα radiation). The chemical composition (oxides analysis) was determined with the Dispersive Energy Spectrometer (EDS) coupled to the Scanning Electron Microscope (SEM), Hitachi S-2700, USA. The cation exchange capacity was determined by the method of ammonium acetate buffered at pH 7, described in [24]. The organic matter by the Walkley-Black method, described in [25] and the soil pH, determined in H_2O and KCl by potentiometric method, suspended (soil: water, 1: 2.5), described in [26].

2.2 Sorption experiments with Cr, Cu and Zn

In the batch sorption tests, concentrated solutions of 1.0 g/L of potassium chromate (K_2CrO_4), copper sulphate ($CuSO_4$) and zinc chloride ($ZnCl_2$) were used to study the removal of Cr, Cu and Zn metal ions, respectively. For the reaction kinetics, were used aqueous solutions of K_2CrO_4, $CuSO_4$ and $ZnCl_2$ with the following theoretical concentrations (C_t): 0; 1; 2.5; 5; 7.5 and 10 mg/L. Samples of 0.5 g of fine soil were placed in six 500 mL glass vessels. To each vessel were added 200 mL of aqueous solution of ions at the mentioned concentrations. The vessels were shaken for 24 hours, and 5 mL of liquid sample was withdrawn at the following times: 0, 0.25; 0.75; 2; 5; 11 and 24 hours and the pH and temperature values were measures. The experimental equipment used consisted of a Flask Shaker SF1 mechanical stirrer from Stuart Scientific (England), which was calibrated to promote a constant rotation and equal to 120 oscillations per minute, as used by [27]. For measurement of pH and temperature a SenTix 41 probe attached to a Multi 340i meter from WTW, Germany, was used. The determination of metals was carried out by means of an atomic absorption spectrophotometer GBC-906 (Australia), according to standard [28]. For the study of sorption isotherms, the same aqueous solutions were used, with the following theoretical concentrations (C_t): 0; 1; 5 and 10 mg/L and for three soil masses: 0.1, 0.5 and 1.0 g.

3 Analysis and discussion of results

3.1 Characteristics of the granitic residual soil

The residual soil has about 4.94% of clay (particle size less than 2 μm). According to [29], in order to avoid soil sealing and to ensure the treatment of residual water, the soil should have a low fraction of clay, namely less than 10%. The sample had a density of 2.65, porosity of 48.0% and specific surface of 0.29 m^2/g (Figure 3). It contains mainly silica (60.44%) and alumina (31.76%), with lower levels of iron (3.99%) and potassium (3.81%). Cation exchange capacity (at pH = 7) it considered a median value (11.68 $cmol_c$/kg) according to [30], the organic matter content is very low (0.45%) and the soil is very acidic (pH = 4.44). The study of the clay fraction (< 2 μm) by X-ray diffraction (XRD) (Figure 4) revealed the presence of kaolinite (K), illite (I) and smectite (S), with kaolinite account-

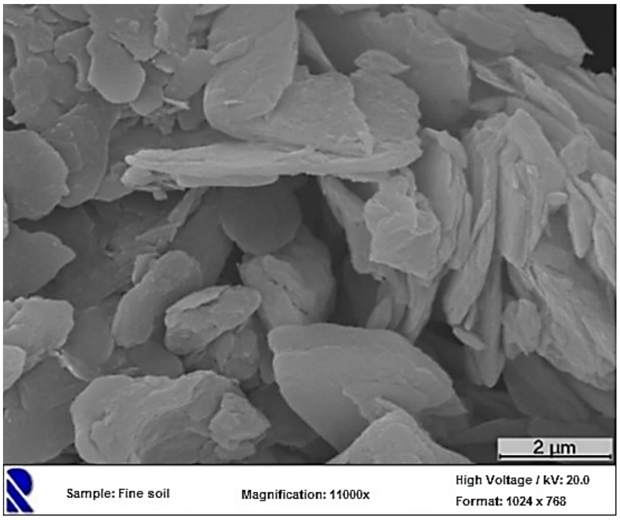

Figure 3: SEM image of the fine soil, magnification of 11000x

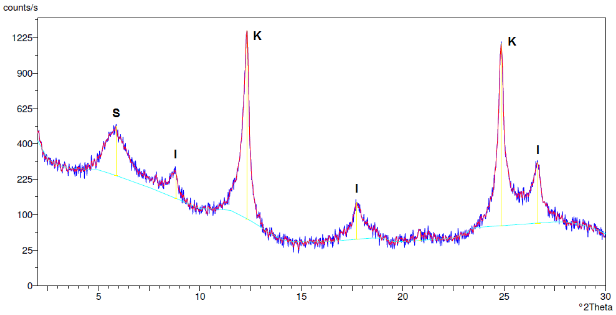

Figure 4: X-ray diffraction of the soil sample (< 2 µm)

ing for about 60% of the clayey material present in the soil. Other clay minerals similar proportions, that is, illite (21.41%) and smectite (18.73%). The clay-colloidal complex of this soil allow considered that has reactive properties that allow it to remove pollutants by sorption mechanisms, as well as a specific surface suitable for the development of the biofilm with the capacity to remove pollutants and pathogens through biodegradation mechanisms, as demonstrated in [19].

3.2 Sorption experiments with Cr, Cu and Zn

Tables 1 to 3 show the results of the tests performed for the study of reaction kinetics with Cr, Cu and Zn and 0.5 g of fine soil. The results show that the equilibrium concentrations (C_e) were reached between 2h and 5h of contact, for Cr (Table 1), between 5h and 11h for Cu (Table 2) and at 2h for Zn (Table 3). In general, a decrease in pH was observed shortly after 15 minutes of contact, continuing to decrease over time to the 24 hour duration of the assays. pH values for the Cr tests ranged from 6.95 (beginning) to 5.60 (final), although it was almost always above 6.00), for Cu assays changed from 6.09 (beginning) to 4.89 (final) and for the Zn assays ranged from 6.10 (beginning) to 5.00 (final). Temperature values were recorded between 18.8°C (minimum value) and 24.1°C (maximum value).

The removal efficiency (RE), in percentage, of the metals over time, was calculated through Eq. (1).

$$RE = \left(\frac{C_i - C_n}{C_i}\right) \times 100 \tag{1}$$

where C_i and C_n are the initial concentration and in the time n of solute in solution (mg/L), respectively.

There were observed RE of Cr of 10.1%, of Cu of 68.3% and of Zn of 79.5% for the C_e of 8.68 mg Cr/L, 0.71 mg Cu/L e 0.23 mg Zn/L, respectively.

The sorption rates (q_s), in (mg/g), were compiled through Eq. (2), which means, for each instant, the mass of metal retained in 0.5 g of fine soil.

$$q_s = \left(\frac{C_i - C_f}{m_s}\right) \times V \tag{2}$$

where, C_i is the initial concentration of solute in solution (mg/L), C_f is the final concentration or the equilibrium concentration of solute in solution (mg/L), V is the volume of the assays (L) and m_s is the mass of fine soil (g).

The sorption kinetics for the three heavy metals were explained by Lagergren's pseudo-first order kinetic model [31] according to Eq. (3).

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303}t \tag{3}$$

where q_e and q_t in (mg/g) are the sorption rate in the equilibrium and in the time t, respectively, and k_1 is the pseudo-first order kinetic constant (min^{-1}).

The mean square error (MSE) was used as the fitting measure [32, 33], using Eq. (4). This methodology allowed to fit the values of the variables characteristic of the model by minimizing the sum of the square of the difference between the values calculated by the model and the experimental values.

$$MSE = \sqrt{\frac{\sum_{i=1}^{j}\left[\left(X_{sim(i)} - X_{\exp(i)}\right)^2\right]}{\sum_{i=1}^{j}\left[\left(X_{\exp(i)}\right)^2\right]}} \tag{4}$$

where i is the number of values, j the maximum number of values, X_{exp} the experimental values and X_{sim} the simulated values with the model.

The sorption rate (q_e) were 0.392 mg Cr/g, 0.833 mg Cu/g and 1.360 mg Zn/g for the initial higher concentrations (C_i) (namely 9.66 mg Cr/L, 10.13 mg Cu/L and 10.33

Table 1: Results for experiments with Cr

Parameters	Theoretical concentration (C_t) (mg/L)	Sampling time (h)						
		0	0.25	0.75	2	5	11	24
C 1) (mg/L)	1.0	0.94	0.89	0.88	**0.85** 2)	0.88	0.86	0.85
pH		6.20	6.00	5.99	6.12	6.07	6.01	6.34
Temp. (°C)		19.90	20.30	20.60	20.70	21.10	20.30	19.90
C 1) (mg/L)	2.5	2.33	2.27	2.30	2.25	**2.22** 2)	2.24	2.20
pH		6.61	6.14	6.30	6.08	5.61	6.03	5.60
Temp. (°C)		19.90	20.30	20.70	20.90	21.30	20.60	20.20
C 1) (mg/L)	5.0	5.62	5.18	5.22	**5.08** 2)	5.16	5.23	5.21
pH		6.71	6.15	6.10	6.14	6.08	6.11	6.19
Temp. (°C)		19.90	20.40	20.70	20.90	21.20	20.60	21.10
C 1) (mg/L)	7.5	6.88	6.73	6.30	6.35	**6.31** 2)	6.36	6.35
pH		6.79	6.30	6.25	6.31	6.22	6.18	6.16
Temp. (°C)		20.00	20.50	20.70	21,10	21.40	20.40	20.10
C 1) (mg/L)	10.0	9.66	8.98	8.74	8.72	**8.68** 2)	8.70	8.73
pH		6.95	6.41	6.35	6.34	6.33	6.29	6.30
Temp. (°C)		20.00	20.40	20.60	20.90	21.10	20.40	19.90

1) Concentration after contact with the soil

2) Equilibrium concentration

Table 2: Results for experiments with Cu

Parameters	Theoretical concentration (C_t) (mg/L)	Sampling time (h)						
		0	0.25	0.75	2	5	11	24
C 1) (mg/L)	1.0	0.92	0.63	0.51	0.48	0.45	**0.44** 2)	0.46
pH		6.09	5.87	5.66	5.66	5.63	5.67	5.46
Temp. (°C)		19.80	19.70	19.90	19.80	19.60	19.20	19.60
C 1) (mg/L)	2.5	2.24	1.14	0.75	0.71	0.78	**0.71** 2)	0.70
pH		5.60	5.40	5.32	5.41	5.38	5.42	5.35
Temp. (°C)		19.80	19.80	19.90	19.90	19.60	19.10	19.80
C 1) (mg/L)	5.0	5.35	4.21	4.27	4.33	**4.31** 2)	4.36	4.38
pH		5.21	5.10	5.01	5.05	5.04	5.01	5.01
Temp. (°C)		19.80	19.90	20.10	20.30	19.70	19.40	19.80
C 1) (mg/L)	7.5	7.27	6.05	5.91	5.88	**5.84** 2)	5.88	5.90
pH		5.04	4.91	4.82	4.90	4.87	4.83	4.89
Temp. (°C)		19.00	19.90	20.10	20.30	19.60	19.40	19.60
C 1) (mg/L)	10.0	10.13	8.52	8.18	8.07	8.12	**8.05** 2)	8.13
pH		5.10	5.01	4.94	4.97	5.01	4.96	4.95
Temp. (°C)		19.90	19.90	20.00	19.80	19.60	19.10	19.60

1) Concentration after contact with the soil

2) Equilibrium concentration

Table 3: Results for experiments with Zn

Parameters	Theoretical concentration (C_t) (mg/L)	Sampling time (h)						
		0	0.25	0.75	2	5	11	24
C 1) (mg/L)	1.0	1.12	0.37	0.27	**0.23** 2)	0.22	0.25	0.21
pH		6.10	5.60	5.50	5.37	5.71	5.16	5.64
Temp. (°C)		19.10	19.00	23.50	24.10	20.90	18.80	21.80
C 1) (mg/L)	2.5	2.55	1.52	1.24	**1.21** 2)	1.22	1.24	1.22
pH		6.07	5.32	5.31	5.32	5.28	5.39	5.42
Temp. (°C)		18.90	19.00	22.60	23.70	20.60	19.30	22.10
C 1) (mg/L)	5.0	5.18	3.12	3.03	**3.08** 2)	3.06	3.10	3.07
pH		5.90	5.44	5.20	5.12	5.10	5.06	5.11
Temp. (°C)		19.00	19.10	22.70	23.00	20.70	19.00	22.30
C 1) (mg/L)	7.5	7.44	5.21	5.08	**5.03** 2)	5.05	5.03	5.09
pH		5.83	5.28	5.03	5.04	5.05	5.05	5.00
Temp. (°C)		19.00	19.30	23.10	22.80	20.60	19.20	22.30
C 1) (mg/L)	10.0	10.33	7.16	7.07	**6.93** 2)	6.91	6.97	7.00
pH		5.91	5.33	5.15	5.07	4.98	5.07	5.05
Temp. (°C)		19.00	19.70	22.80	22.80	20.60	19.60	22.50

1) Concentration after contact with the soil

2) Equilibrium concentration

mg Zn/L). For all metal the sorption rates were higher theoretical concentrations (10 mg/L). The sequence for the kinetics of sorption of metals is Cr < Cu < Zn.

For the study of sorption isotherms with Cr, Cu and Zn and 0.1 g, 0.5 g and 1.0 g of fine soil, Freundlich model [34] (Eq. (5)) better explains the equilibrium isotherm, and the results are presented in Figures 5 to 7.

$$\log(q_e) = \log\left(k_f\right) + \frac{1}{n} \times \log(C_e) \tag{5}$$

where q_e (mg/g) is the sorption rate at the equilibrium, k_f is the Freundlich coefficient (L/g), C_e the equilibrium concentration of solute in solution (mg/L) and 1/n is a coefficient that depends on the solute, porous media and environmental conditions.

It is possible to observe that the q_e for Cr, Cu and Zn were higher for the higher values of C_t (10 mg/L) and also higher for lower values of mass (m = 0.1 g).

From the analysis of Figure 5(a) and 0.1 g of fine soil the q_e of Cr was 0.664 mg/g for the C_e of 9.46 mg/L. The pH ranged from 6.98 (beginning) to 6.59 (final). The temperature varied from 21.1°C (beginning) to 23.1°C (final).

For 0.1 g of fine soil (Figure 6(a)) the q_e of Cu was 2.939 mg/g for the C_e of 8.34 mg/L. The pH ranged from 5.54 (beginning) to 5.22 (final). The temperature varied from 21.1°C (beginning) to 23.2°C (final). The results are superior to those presented by [13], which used a clay rock in the El Hamma area of Tunisia, obtaining a q_e value of 0.021 mg Cu/g with a heavy metal C_i of 0.5 mg/L and using clay masses of 0.5 and 5.5 g. Although the clay has a high specific surface (about 490 m^2/g), the high pH of the solution (between 8 and 10) would not favor the adsorption of Cu, which was practically removed by complexation and precipitation in the form of hydroxides and carbonates. This seems to indicate that pH has much more influence on the removal of metals than the specific surface of the material. On the other hand, in a study with crude Egyptian kaolin and bentonites treated with calcium and sodium (Ca-B and Na-B) for the removal of heavy metals from polluted waters, [20] showed that q_e increased with increasing C_e, as observed in the present study, with higher values of removed mass and Cu mass in the aqueous solution, from about 12 mg Cu/g to C_e of 8 mg/L for the soil with Ca-B and 4 mg Cu/g for the case of crude kaolin. The Freundlich model was also the one that best fit the results obtained.

For 0.1 g of fine soil (Figure 7(a)), the q_e of Zn was 6.138 mg/g for the C_e of 6.34 mg/L. The pH ranged from 5.59 (beginning) to 5.37 (final). The temperature varied from 22.3°C (beginning) to 20.3°C (final). In the study by [20] q_e increased with increasing C_e, as in the present study, but presented generally higher values of removed mass and mass of Zn in the aqueous solution, with maximum values of 12

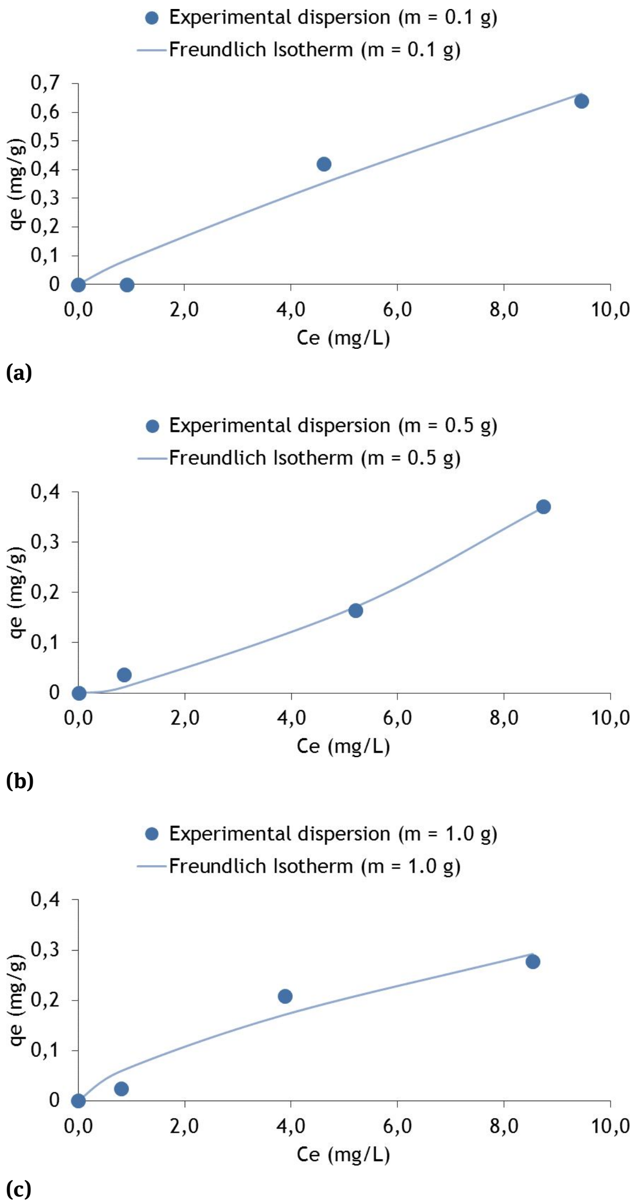

Figure 5: Sorption isotherms for the Freundlich model with Cr and soil masses of 0.1 g (a), 0.5 (b) and 1.0 g (c)

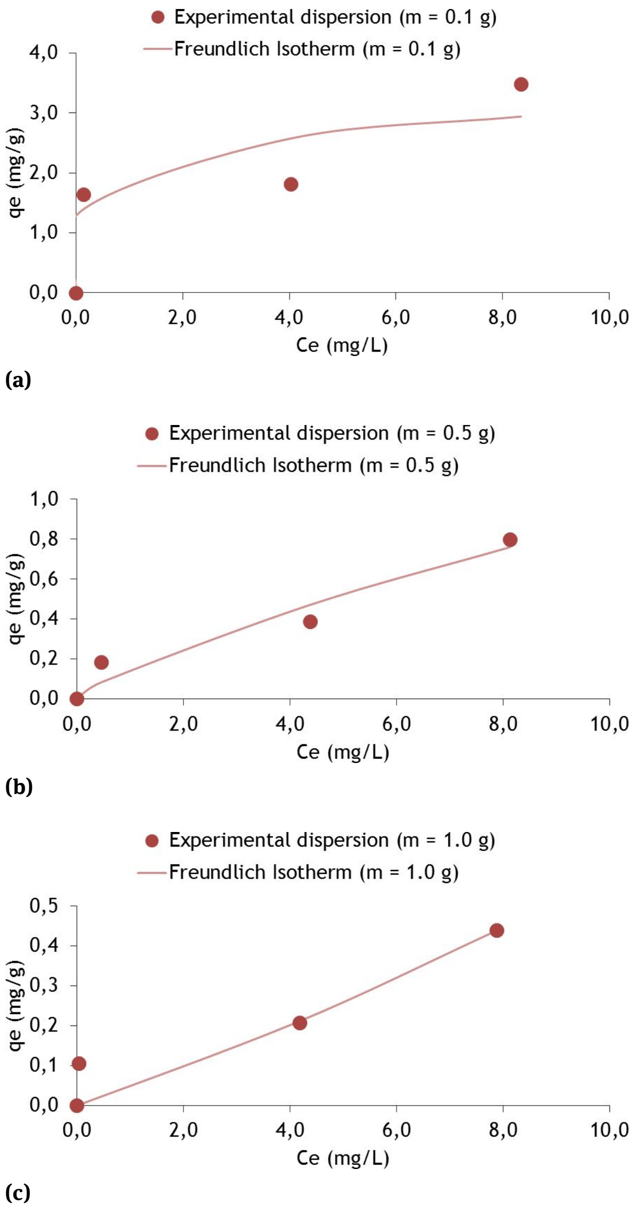

Figure 6: Sorption isotherms for the Freundlich model with Cu and soil masses of 0.1 g (a), 0.5 (b) and 1.0 g (c)

mg Zn/g for C_e of 8 mg/L (for Ca-B and Na-B soils) and from 6 mg Zn/g to 8 mg/L in the case of crude kaolin.

In general, in tests performed with Cr (where its removal was lower) although the pH dropped, it was almost always above 6. This decrease in pH would have been associated with the dissociation of H^+ ions from the clay-colloidal complex of the soil to the aqueous medium due to the hydrolysis of tetrahedral and octahedral structures [14, 35], as well as to possible hydration of aluminium and iron oxides, which may have reduced the OH^- concentration in the solution. The removal of Cr ion was low because the ideal pH for its electrostatic adsorption and ion exchange was between 2 and 4 [36]. On the other hand, removal by complexation and precipitation in the form of hydroxides only occurs significantly at pH values above 6 [13, 15, 37], which in general occurred with this ion.

In the Cu and Zn experiments, in addition to mentioned dissociation, ion exchange will also occur between the H^+ ions and Cu and Zn ions (hence the pH values are lower in the tests with these four ions, with values close to 5), although there also appears to have been ion exchange with the Al^{3+} and Fe^{3+} ions present in the clay-colloidal complex, and OH^- reduction due to the hydration of iron and aluminium oxides. The ion exchange of H^+, Al^{3+} and

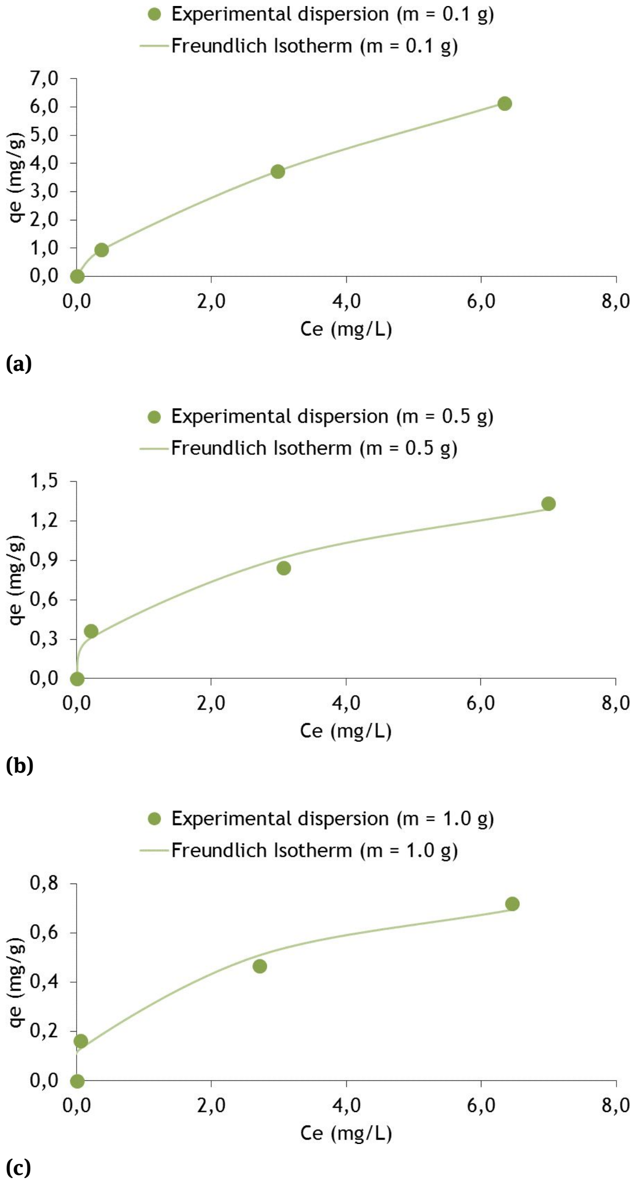

Figure 7: Sorption isotherms for the Freundlich model with Zn and soil masses of 0.1 g (a), 0.5 (b) and 1.0 g (c)

Fe^{3+} by Cu and Zn is favored at pH values below 5.5 as referred in [15]. The removal of Cu and Zn would not have occurred by complexation and precipitation in the form of hydroxides, since it only has significance for values above 6 [13, 15, 37].

4 Conclusions

The fine component of the granitic residual soil of Quinta de Gonçalo Martins (Guarda, Portugal), has reactive properties that give it a good capacity for removing Cu and Zn by sorption mechanisms, which allows it to act as a barrier to water contamination during the artificial recharge of aquifers with treated wastewater. With respect to the batch tests, Cu and Zn removal was observed to be high and occurred mainly by adsorption and ion exchange mechanisms, according to the pseudo-first order kinetics model. Sorption rates (q_e) of 0.833 mg Cu/g and 1.360 mg Zn/g were found for the highest theoretical concentrations (C_t) (10 mg/L) and for a fine soil mass of 0.5 g. The removal of Cr in the soil was low. When the sorption equilibrium state was reached, the removal of these pollutants was explained by the Freundlich isotherm. Sorption rates (q_e) were highest for the lowest fine mass value (m = 0.1 g), namely 2.939 mg Cu/g and 6.138 mg Zn/g. The use of this soil as a means of filling infiltration infrastructures can still become economically competitive when compared to the reactive materials currently used.

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