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Research article

Furosemide removal in constructed wetlands: Comparative efficiency of LECA and Cork granulates as support matrix

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ABSTRACT

The removal efficiency of LECA and cork granulates as support matrix for pharmaceuticals active compounds in a constructed wetland system was investigated using the diuretic drug Furosemide. Kinetics studies were performed testing three different concentrations of Furosemide in an ultrapure water matrix, along seven days. LECA achieved higher removal values compared to cork granulates. However, cork granulates presented a higher removal in the first 24 h of contact time compared to the other adsorbent. The kinetic studies showed that LECA and cork granulates have different adsorption behaviours for Furosemide which is controlled by different adsorption mechanisms. Both materials showed good removal efficiencies and a combination of the two should be further explored in order to applied both materials as support matrix to cope with different furosemide concentrations.

1. Introduction

Pharmaceutical active compounds (PhACs) presence in water bodies is a current concern to the public health. These substances have been found in effluents previously treated in wastewater treatment plants (WWTPs) (Andreozzi et al., 2003; Ternes, 1998), surface water (Alonso et al., 2010), river sediments (Beretta et al., 2014), groundwater (López-Serna et al., 2013; Paíga and Delerue-Matos 2016) as well as in drinking water treatment facilities (Huerta-Fontela et al., 2011; Kuster et al., 2008). The main source of these pollutants is WWTPs effluents, especially if these facilities receive hospital effluents (Orias and Perrodin, 2013). So far, WWTPs are still not capable of removing all these pollutants and cost-effective solutions have to be provided. Hence, constructed wetlands (CWs) being a low-cost technology can be a good option as secondary or tertiary treatment for further improving PhACs removal efficiency in WWTPs. Although CWs have been mainly used to remove more common contaminants such as nutrients, heavy metals and pathogens (Machado et al., 2016), they can also be effective to retain and eliminate emerging contaminants like PhACs, as referred by Verlicchi and Zambello (2014). To achieve better removal performance, the optimization of the several elements of CWs (design, hydraulic parameters, type of support matrix and macrophytes) should be considered.

The most common materials used as support matrix in CWs are gravel and sand, usually cheap, worldwide available and easily accessible. However, these materials typically have poor adsorptive qualities. Therefore, other low budget materials have been tested on their capability to adsorb pollutants.

Light Expanded Clay Aggregates (LECA) is an artificially modified natural material that is produced by subjecting clay to high temperatures. LECA is mostly chosen as CW support matrix because of its high porosity and specific surface area (Kalhori et al., 2013), having a good biofilm adhesion as well as a better pollutants retaining capacity. This material is characterized by being chemically inert, non-biodegradable and having a neutral to slightly

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alkaline character (depending on the origin and composition of the original raw clay materials) (Nkansah et al., 2012). However to lower the cost of CWs, different types of biomaterials produced as by-product have been studied and tested on their pollutants removal efficiency (Dordio et al., 2011; Tee et al., 2009).

In Portugal, cork oak is the second most abundant tree after Eucalypt with 23% of the forest area, occupying a total of 736.775 ha. This value represents 34% of the world cork oak area (APCOR, 2015), generating export values of 899.3 million euros, in 2015. The production of cork stoppers and disks for wine industry is the main use for this material. However, many applications have been further explored, being nowadays a trend in fashion and souvenirs field. Another important use is for construction, where it can be used as thermic and acoustic insulation walls and floor (Gil, 2007). From cork transformation processes cork granulates and powder result as by-product, having different granulometries and densities (Pintor et al., 2012). This material has high porosity and adsorption capacity being a material with a big potential to be applied in the water/wastewater purification (Pintor et al., 2012).

Both LECA and Cork have been studied on their adsorption capacity of pollutants from different water matrices, such as wastewater, storm water and agriculture runoff (Domingues et al., 2005; Pintor et al., 2012) but few works exist on their capacity to remove PhACs (Dordio et al., 2007, 2011, 2017; and Villaescusa et al., 2011).

Furosemide is a loop diuretic pharmaceutical used to treat cases of hypertension and edema. In Portugal, this drug occupies the 15th place of the Top 100 active substances with the highest number of packages sold in the National Health System (INFARMED, 2014). After ingestion, in average, 70% of the oral dose of Furosemide is absorbed by the organism (Prandota and Witkowska, 1976), and according to Zuccato et al. (2005) 90% of the non-absorbed is excreted as parent compound. Therefore in countries with high consumption of this PhAC its presence is to be expected in the WWTP influents. Santos et al., 2013, in north-centre of Portugal, evaluated the presence of PhACs in effluents from 4 hospitals and in the influent and effluent of the WWTP receiving them. Furosemide was present in all the flows analysed, in hospital effluents the concentration ranged from 32.6 to 0.43 $\mu g\ L^{-1}$ and in the WWTP the influent presented a mean of 2.73 $\mu g L^{-1}$ while the effluent had a concentration of 1.18 $\mu g\ L^{-1}$. In another work (Salgado et al., 2010) furosemide was also found in the influent of a WWTP in Portugal (3.62 $\mu g\ L^{-1}$), while in the effluent it was not detected. The presence of Furosemide in European WWTP effluents and surface waters has been documented in several studies (Jurado et al., 2012; Silva et al., 2011; Jelic et al., 2011), indicating that the conventional treatment technologies applied in these facilities are not effective for its removal. However, few are the studies that analyse the removal of this PhAC in constructed wetlands (Matamoros et al., 2009, 2012; Verlicchi et al., 2013).

The aim of the present work was to compare the potential of LECA and cork granulates as support matrix for constructed wetlands, targeting PhACs removal efficiency from water. Thus, adsorption capacity of both materials was evaluated to understand their performances in removing the diuretic PhAC Furosemide.

2. Material and method

2.1. Chemicals

Analytical grade Furosemide (99.8% purity) was purchased from Sigma-Aldrich (Lisbon, Portugal). Phosphoric acid (>85% purity) and HPLC-grade solvent acetonitrile were obtained from Enzymatic, S.A. (Loures, Portugal). Ultra-pure water was prepared from a Millipore Milli Q system.

2.2. Materials

Light Expanded Clay Aggregates (LECA) was provided by MaxitGroup Portugal (grade 2/4). Low-density cork granulates with particle size between 3 and 5 mm have been supplied by Amorim Cork Composites (Santa Maria da Feira, Portugal).

2.3. LECA and cork granulates cleansing and physical-chemical characterization

Both LECA and Cork granulates were thoroughly washed by distilled water to eliminate impurities. Microorganisms' minimization was obtained by sterilization during 24 h in the oven at 105 °C.

LECA physico-chemical characterization details are reported in Dordio et al. (2009a) and include: particle-size distribution on a weight basis, analysed according Day (1965); Apparent porosity and bulk density, determined as described in Brix et al. (2001) and Del Bubba et al. (2003) with 5 replicates; and additionally Point of Zero Charge (PZC) was analysed using the mass titration method. Table 1 shows the main physical and chemical characteristics of LECA.

Cork granulates particle distribution was determined according to ISO 2030–1989 standard, while bulk density was determined as referred in NP EN 1097-6:2003 (n = 3). Porosity was obtained through the NP EN 1097-3:2002. Determination of pH and electric conductivity (EC) was done according to EN 13037 and EN 13038 respectively (n = 3) (Table 1).

2.4. Batch adsorption experiments

Experimental set-up was established to simulate a subsurface CW. Therefore, along the duration of the experiment photodegradation was avoided and no agitation was implemented. Adsorption studies were performed in batch mode, using twelve 0.5 L cylindrical glass cups with a filling material/ultrapure water ratio of 0.80 and 0.15 g mL^{-1} for LECA and cork granulates, respectively. Three different concentrations of furosemide were tested ($\approx$1.0, 5.5 and 11.0 mg L^{-1}). The removal of the PhAC from each trial was compared with the initial concentration. A control set without the PhAC was implemented for each material to determine possible trace contaminations of the target PhAC. For each material and concentration the experiment was performed in 3 replicates. Each trial had the duration of 7 days and solution samples were taken in pre-defined time intervals along this period. All samples were filtered through a 0.45 μm PVDF filter of 13 mm before liquid chromatography analysis.

2.5. HPLC-UV apparatus

The chromatography PhAC measurements were carried out on a HPLC - Beckman Coulter System Gold, with a Solvent Module 126 and a Diode Array Detector 168, using the 32 Karat Software version

Table 1
Physical and chemical characteristics of the adsorbent materials studied.

	LECA	Cork granulates
d_{10} (mm)	3	3.14 ± 0.05
d_{60} (mm)	3.95	4.56 ± 0.15
d_{60}/d_{10}	1.32	1.45 ± 0.03
Apparent Porosity (%)	46 ± 1	51
Bulk density (kg m^{-3})	486 ± 7	70.13 ± 1.63
pH in water	9.93 ± 0.02	5.50 ± 0.03
PZC	10.54 ± 0.03	–
EC (mS cm^{-1})	537 ± 15	30 ± 1.7