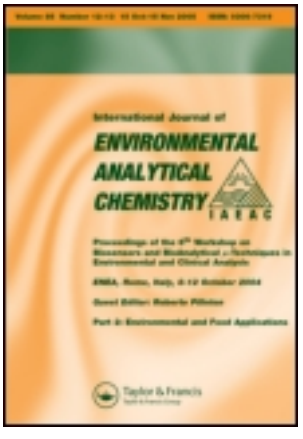

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Pharmaceuticals sorption behaviour in granulated cork for the selection of a support matrix for a constructed wetlands system

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Biosorbents have been recently gaining importance, with an increasing number of publications on their environmental applications, especially for removal of organic pollutants from aqueous media. The aim of this work was to evaluate the sorption capacity of a biosorbent, namely granulated cork, to remove mixtures of ibuprofen (IB), carbamazepine (CB) and clofibric acid (CA) from water and wastewater. High removal efficiencies were attained for IB and CB while a less satisfactory performance was observed for CA. Simultaneous removal of the three compounds mixed in the same aqueous solution showed no significant differences in comparison to the removal of the isolated compounds in separate solutions, which indicates that no competitive sorption effects occurred at the highest concentrations tested. On the other hand, in wastewater medium the mixture of pharmaceuticals underwent a decrease in the sorbed amounts of all the three substances, probably due to the presence of dissolved organic matter which increases their solubilities. These compounds were removed in the following order of efficiencies in all the tested conditions: IB > CB > CA. The sorption kinetics were characterised by an initial fast step within the first 6 h, during which most of the removed pharmaceuticals amounts were sorbed. After the first 6 h, CA attained equilibrium concentrations whereas the sorption kinetics for IB and CB were characterised by two pseudo-second order stages, the first one up to 48 h and a slower one beyond 48 h. Shorter equilibration times and larger removed amounts of pharmaceuticals per unit weight of sorbent were observed in this study for granulated cork in comparison with a previously studied clay material (LECA). The results of this study showed the sorptive qualities of granulated cork but are only a first step in the evaluation of this material for use as support matrix in constructed wetlands designed for removal of pharmaceuticals from wastewaters.

Keywords: biosorbents; carbamazepine; clofibric acid; constructed wetlands; ibuprofen; pharmaceuticals; sorption

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1. Introduction

In recent years, the occurrence of pharmaceuticals in the aquatic environment has become one of the emerging issues in environmental chemistry. The increasing use of these substances and the inadequacy of the conventional wastewater treatment processes used in most wastewater treatment plants (WWTPs) in dealing with these pollutants are the main reasons for the frequent detection of many of these compounds at concentrations typically ranging from $\mu g\,L^{-1}$ to $ng\,L^{-1}$ in WWTP effluents, surface water, groundwater and even in drinking water worldwide [1–4]. In order to improve the efficiencies of WWTPs in removing many of these and other types of trace organic pollutants, some advanced treatment technologies have been evaluated such as advanced oxidation processes, activated carbon adsorption, membrane filtration and membrane bioreactors. However, despite the sometimes high pollutant removal efficiencies attained by these processes, they are not widely used, mainly owing to the much larger costs involved in their application [1,2]. Consequently, there is a growing need for alternative wastewater treatment processes that can achieve higher efficiencies in removing pharmaceuticals from water and that do so at reasonable costs of operation/maintenance.

Subsurface flow constructed wetlands (SSF-CW) are low-cost wastewater treatment systems that have already been used with success to clean up wastewaters from some organic xenobiotics, including some pharmaceutical compounds [5–8]. Treatment in SSF-CWs involves processes such as microbial degradation, plant uptake, sorption, precipitation, sedimentation or filtration. The relative importance of each of these processes depends on the type of pollutants to be treated and on the characteristics of the SSF-CW components. In particular, the role played by sorption onto the solid matrix of the SSF-CW can be of particular relevance for the overall efficiency of the system. Significance of sorption processes can be enhanced by the appropriate selection of a solid matrix material with a high sorption capacity for the pollutants, which in turn must be based on the physico-chemical characteristics of the materials. Previous studies have shown that some clay materials such as expanded clay (LECA) present a high sorptive affinity for the pharmaceuticals carbamazepine, ibuprofen and clofibric acid [9].

Some choices of agro-industrial wastes (e.g. rice husk, pine bark) for the solid matrix of SSF-CWs are often considered as interesting alternatives to other more common choices (e.g. gravel) due to the usually low-cost of such materials and the economical value for the local economies in finding reuses for such wastes [10–12]. In addition, biosorbents (sorbents of natural origin) have been gaining in importance, as some of these materials can have an increased affinity for some types of contaminants and they are, in general, easily disposed of by incineration [13,14].

Cork sorbents, in particular, have become an attractive choice as, in addition to the low-cost of the wastes of the important Mediterranean cork stopper industry (especially in Portugal), they display good performances as complexing materials. Cork sorbents have already been shown to be capable of significantly retaining some organic xenobiotics such as some pesticides [14,15].

The aim of the present work was to evaluate the capacity of granulated cork for removing, from water and wastewater, three pharmaceuticals commonly detected in environmental monitoring studies, namely carbamazepine, clofibric acid and ibuprofen. A comparison was also made between removal efficiencies attained with this material and those obtained with LECA 2/4 in a previous study [9]. Furthermore, the structure and surface characteristics of cork were characterised as well as some of its physical

and chemical properties that may determine cork's sorptive behaviour. Ultimately, the results of this study may provide an evaluation on the potential of this material to be used as support matrix in SSF-CWs designed for the removal of pharmaceuticals from wastewater.

2. Experimental

2.1 *Reagents and materials*

Clofibric acid (CA) (97% purity), ibuprofen (IB) (99.8% purity) and carbamazepine (CB) (>99% purity) were obtained from Sigma-Aldrich (Steinheim, Germany).

All other high purity chemicals and solvents were supplied either by Sigma-Aldrich (Steinheim, Germany), Merck (Darmstadt, Germany) or Panreac Química S.A.U. (Barcelona, Spain) and were used without further purification. Ultra-pure water was obtained with a Milli-Q water purification system (Simplicity® UV, Millipore Corp., France).

Granulated cork with a diameter of 3–4 mm was supplied by Granaz (Azaruja, Portugal).

LiChrolut® RP-18 (500 mg, 3 mL) cartridges for solid phase extraction (SPE) were obtained from Merck (Darmstadt, Germany). Filters with 0.45 μm nylon membrane were purchased from VWR International (West Chester, PA, USA).

2.2 *Physical and chemical characterisation of cork media*

The supplied granulated cork contained considerable amounts of fine materials. In order to remove the excess powder, the granulated material was washed several times with Millipore water. The washed material was then dried at $105 \pm 5^{\circ}C$ for 3 days and used throughout this study.

The particle-size distribution on a weight basis was analysed in triplicate by the conventional dry-sieving technique [16]. Grain-size distribution plots were used to estimate d_{10} (effective grain size) and d_{60}, and the uniformity of the particle size distribution (the uniformity coefficient) was calculated as the ratio between d_{60} and d_{10}. The apparent porosity (void space) of the granulated cork samples was determined from the amount of water needed to saturate a known volume of the solid (number of replicate $n = 5$). Bulk density was determined based on the ratio between the dry weight and the bulk volume of the material ($n = 5$).

The microstructural properties of the media were investigated by secondary electrons and backscattering electrons micrographs taken on freshly cut cork samples using a variable pressure scanning electron microscope Hitachi Model S-3700N coupled with an Energy Dispersive X-ray Spectrometer Bruker Contact 200. Samples were coated with a thin conductive layer of gold-palladium on an EMITECH SC7620 sputter coater. A textural characterisation of the cork was also determined using a mercury porosimeter apparatus (Micromeritics AutoPore IV 9500 V1.07).

2.3 *Studies of pharmaceuticals sorption onto cork*

Sorption studies were performed on CA, CB and IB solutions prepared with Millipore water at concentrations of 1, 5, 10, 25 and 35 mg L^{-1}. In addition to studies using

single-compound solutions, some studies were also carried out with solutions (in water and in wastewater) containing a mixture of the three compounds such that each compound would be at a concentration of 35 mg L^{-1}.

The sorptive medium was previously sterilised and the experiments were conducted in darkness (to avoid photodegradation) and without stirring to provide a better simulation of the hydraulic behaviour in an SSF-CW, where low flow rates are normally used. Experiments were done in triplicate and at a controlled temperature of 20°C.

The amounts of pharmaceuticals sorbed by the cork material were determined by taking aliquots of the liquid every 24 hours from each assay container and calculating the difference between initial concentrations and the measured remaining concentrations in liquid at any given time. Quantification was performed using the high performance liquid chromatography (HPLC) technique as described in Section 2.4.

2.3.1 *Sorption assays for single pharmaceuticals in water*

Three series of batch assays, one for each of the three studied pharmaceuticals CA, CB or IB (each series consisting of a set of five assays carried out with aqueous solutions at each of the five studied concentrations, 1–35 mg L^{-1}), were set up in 5 litre plastic containers filled with cork. A solid to liquid ratio of 0.1 kg L^{-1} was used in each assay, corresponding to a flooding rate close to 100%.

The possibility of sorption of the compounds onto the containers walls was investigated for all the concentrations tested and using the same assay set up but without adding any sorbent material. This effect was found to be negligible both for plastic as well as for glass vessels.

2.3.2 *Sorption assays for pharmaceuticals mixtures in water and in wastewater*

Two additional batch assays were performed, one using an aqueous solution of the mixture of the three pharmaceuticals and the other conducted on wastewater spiked with the same mixture. In both cases each compound was present at the highest concentration of 35 mg L^{-1}. These assays were carried out for assessing possible competition effects in the simultaneous sorption of these compounds at such high concentration levels, and also to study the effect that a complex medium such as a wastewater has in the pharmaceuticals removal efficiency.

The wastewater used in these assays was collected after secondary treatment stage in a WWTP serving a small rural community population of *ca.* 400 inhabitants. The treatment processes used in this WWTP include screening, primary sedimentation and conventional activated sludge treatment. The collected effluent was characterised by the determination of the following wastewater quality parameters, according to the APHA-AWWA-WPCF methods [17]: total suspended solids (TSS), pH and total and soluble chemical oxygen demand (COD_t and COD_s) of samples filtered through 0.2 μm.

2.4 *Pharmaceuticals quantification and analytical method validation*

Pharmaceuticals quantification was performed on an Elite LaChrom HPLC system with UV detection (Hitachi, Japan). The reversed phase analytical column used was a Zorbax Eclipse XDB-C18 with 5 μm particle size. The analytical procedure used for the quantification of CA, IB and CB has been described in Dordio *et al.* [8].

Table 1. Parameters for the analytical methodology validation.

		HPLC-UV system			Full analytical method
Compound	Linearity (R^2)	IDL ($mg\,L^{-1}$)	IQL ($mg\,L^{-1}$)	Repeatability (%RSD)	LOQ ($mg\,L^{-1}$)
CB	0.9998	0.3676	1.225	2.2	0.01279
IB	0.9999	0.2693	0.8976	1.9	0.009076
CA	0.9999	0.1079	0.3598	0.42	0.003634

Linearity, sensitivity (limits of detection and of quantification) and repeatability were determined to establish the accuracy and precision of the full analytical method. Linearity between peak area and concentration was determined by regression analysis of calibration curves constructed with standard solutions of CB, IB and CA. Standard solutions of $100\,mg\,L^{-1}$ were used to prepare standards between 0.5 and $50\,mg\,L^{-1}$ of each compound. Three replicates were made for each standard solution and each solution was injected five times. Instrumental detection and quantification limits (IDL and IQL) were obtained by determining the concentrations corresponding, respectively, to signal-to-noise ratios of 3 and 10 for the chromatographic measurements and the limit of quantification (LOQ) of the entire analytical method (including pre-concentration by solid phase extraction, SPE) was calculated according to Vieno *et al*. [18]. The repeatability of the HPLC-UV system was tested by performing six consecutive replicate injections of same standard solution using the same mobile phase, and it was evaluated as the dispersion (relative standard deviation) of the measured peak areas. Data concerning the validation of the analytical methodology which has been developed for the quantification of CB, CA and IB in water and wastewater are presented in Table 1.

The low IQL obtained for direct sample analysis were still too high for the requirements of some of the samples and it was necessary in some cases to carry out a pre-concentration step of those samples prior to their chromatographic analysis. This pre-concentration step consisted of a previously developed, optimised SPE procedure using a reversed phase C18 silica cartridge (LiChrolut® RP-18) with sample pH adjusted to 7 [8]. Analyte recovery by this SPE procedure was above 95% for all the individual compounds and their mixture. Coupled to the SPE pre-concentration step, the LOQ for the entire analytical method was lower than $0.013\,mg\,L^{-1}$ for all compounds, a value low enough for the requirements of this study.

2.5 *Statistical analysis*

Statistical comparison of data was made by the analysis of variance method (ANOVA, single factor) at significance level of $P < 0.05$.

3. Results and discussion

3.1 *Physical and chemical characterisation of the granulated cork*

The sorption capacity of the solid medium is related to its physical and chemical properties. Some of the most relevant ones were determined in this work for the granulated cork that was used in the sorption assays and are presented in Table 2.

Table 2. Physical and chemical characteristics of granulated cork. The values for d_{10}, d_{60} and uniformity coefficient ($U = d_{60}/d_{10}$) are means of triplicate analyses. The values for the apparent porosity, bulk density, pH and electrical conductivity are means ± 1 SD ($n = 5$).

Parameters	Cork
d_{10} (mm)	3.00
d_{60} (mm)	3.75
Uniformity coefficient (U)	1.25
Apparent porosity/Void space (%)	52 ± 2
Bulk density ($kg\,m^{-3}$)	77 ± 3
pH (in water)	5.32 ± 0.16
Electrical conductivity at 20°C ($mS\,cm^{-1}$)	0.072 ± 0.002

The granulated cork samples used throughout this work can be considered a quite uniform material in terms of particle size ($U = 1.25$) with most of its particles (~90%) having diameters within 5–2.83 mm. The apparent porosity is quite large, due not only to inter-granules void space but also to the porous cellular surface which can absorb and accommodate substantial amounts of water (Figure 1). The extensively porous nature of this material is also responsible for a very low bulk density, which raises some practical problems in terms of maintaining compactness of cork beds at high flooding rates.

The alveolar (honeycomb-like) structure of the cork material is well visible on its surface, as captured in SEM micrographs (Figure 1). The thin-walled cells are closed and hollow, forming shapes of predominantly 4, 5 and 6-sided polygons, without intercellular space. Usually, either three or four cell walls meet at each vertex of the network.

In order to characterise the cork textural properties, different parameters, such as surface area, the average pore diameter and the porosity were determined. The surface area, the average pore diameter and the porosity (%) are $38.5\,m^2\,g^{-1}$, 0.4763 μm and 81%, respectively.

Cork is a complex organic material with a chemical composition mainly consisting of suberin, lignin, waxes and polysaccharides (cellulose and hemicellulose) as structural components and other extractables such as tannins [13,19]. The mineral content is low, the most abundant element being calcium [19]. This composition, poor in electrolytes, accounts for the weekly acidic character of cork and the low electrical conductivity of the solutions resulting from water in contact with cork. Sorption onto cork is, thus, expected to be essentially due to interactions of van der Waals type.

3.2 *Efficiency of pharmaceuticals removal by granulated cork*

The capacity of granulated cork to remove each of the three pharmaceuticals studied (CB, IB and CA) was tested initially in ideal conditions consisting of each compound dissolved individually in pure water (single-compound solutions) and, subsequently, in more realistic assays using solutions of mixtures of the three compounds, both in water and in treated wastewater.

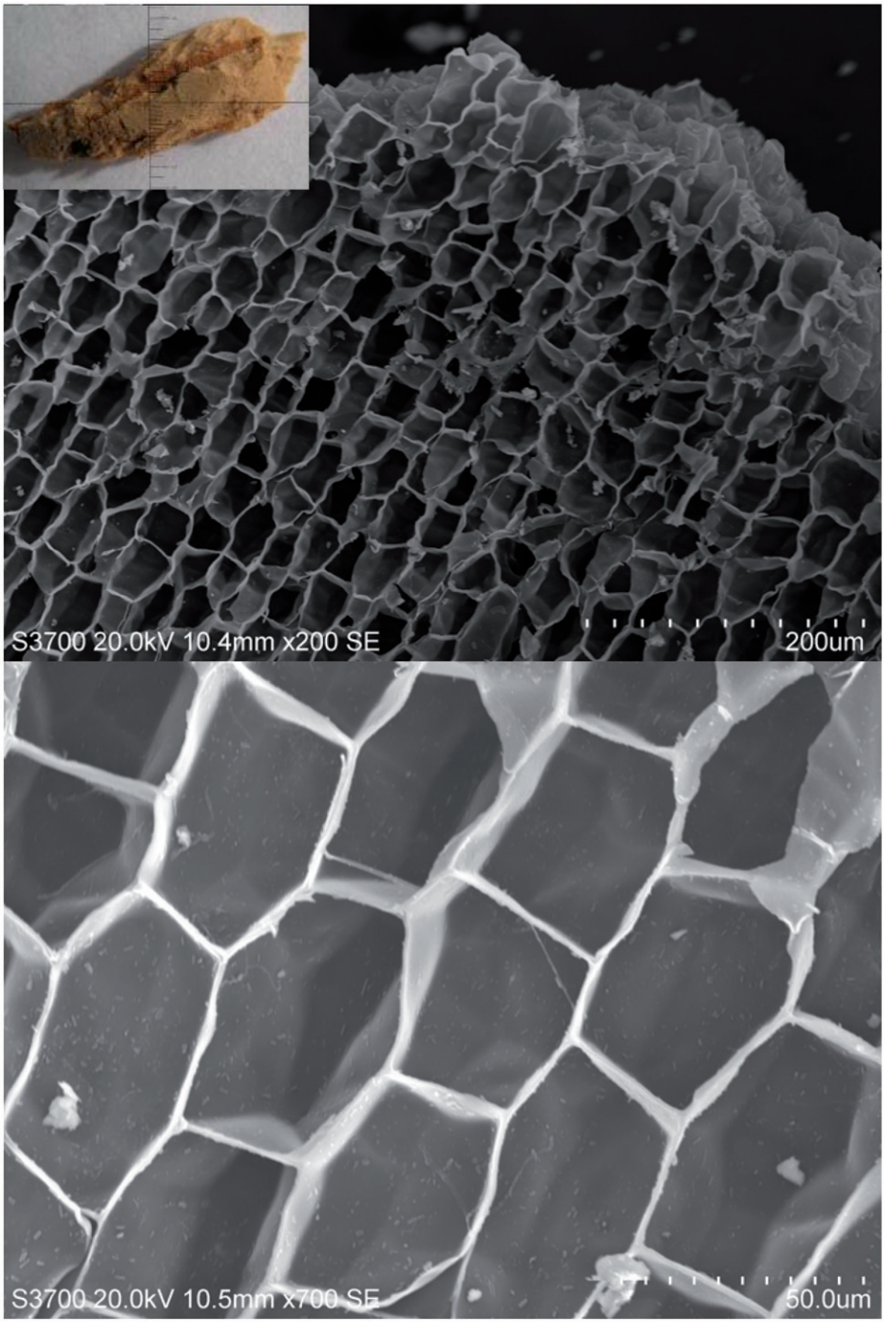

Figure 1. Scanning electron micrographs of cork granules.

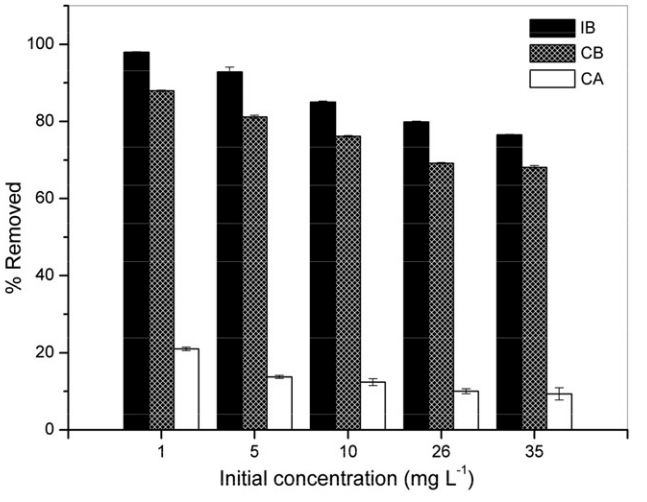

Figure 2. Removal efficiencies of the individual pharmaceuticals (CA, IB and CB) in water by granulated cork for each initial concentrations after 144 h of contact time. Vertical bars represent the averages of 3 replicates and error bars represent the range of ±1 S.D. All removal efficiencies are ANOVA significantly different at $P < 0.05$ within each initial concentration class.

3.2.1 *Individual compounds in water*

In the assays using the single-compound aqueous solutions (Figure 2) granulated cork displayed a great affinity for IB and CB, while much lower removals were attained for CA. IB was the compound sorbed in greater extent with percentages of removal of 76.5%–97.9% for initial concentrations in the range of 1–35 mg L^{-1}. CB was also extensively sorbed (removal percentages of 68.1%–87.9%) whereas CA was, by far, the least sorbed of the three compounds (removal percentages of 9.3%–21.0%). The observed low affinity of CA for cork may be explained by its higher water solubility, which disfavours its partition to this solid medium. In fact, as noted in Section 3.1, interactions with cork surface should be essentially of van der Waals type whereas ionic interactions with the ionised acidic pharmaceuticals in solution should play a negligible role in cork's sorptive behaviour. However, CA's larger water solubility may have led it to remain in solution instead of being sorbed by cork. In addition, steric effects due to the large volume of the chlorine atom bonded in an ortho position to the aromatic ring of the CA molecule may have been responsible for such lower amounts of this compound entering the pores in cork surface.

It is noticeable that percentage removal decreased with increasing load. Thus, higher percent removals were obtained for lower initial concentrations. Despite the lower percentage removals at higher concentrations, the actual absolute removed amounts kept increasing with increasing initial concentrations. In fact, there seems to be a linear relationship between the sorbed amount and the initial concentration of each pharmaceutical in the tested concentrations range (Figure 3). For the highest initial concentration of 35 mg L^{-1}, the sorption capacity of granulated cork was not yet exhausted for any of the compounds as the sorbed amounts continued to be in an increasing trend.

When comparing the amounts of each pharmaceutical sorbed by granulated cork, the following order was consistently observed for all initial concentrations: IB > CB > CA.

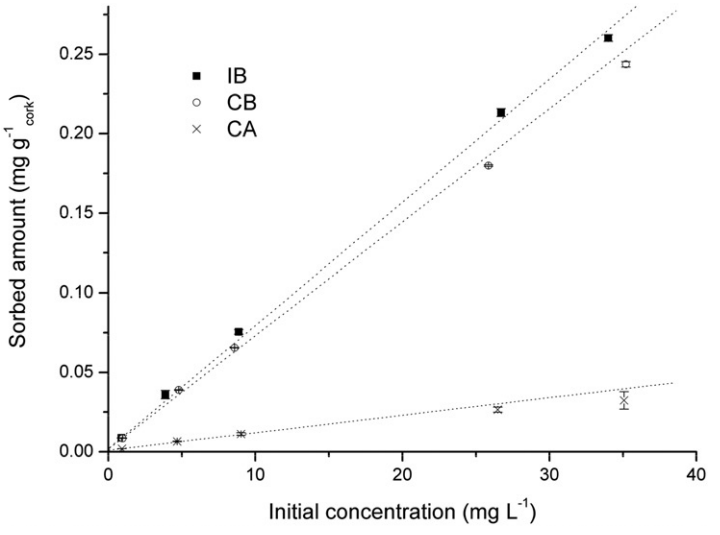

Figure 3. Total removed amounts of CA, IB and CB after 144 h of contact time for each initial concentration. Points represent the averages of 3 replicates and error bars represent the range of ±1 S.D. Lines are linear fits to the data ($R^2 > 0.995$).

3.2.2 *Mixtures of the three compounds in water and treated wastewater*

In order to assess possible efficiency losses arising under less than ideal conditions, the behaviour for the highest initial concentrations (35 mg L^{-1}) of the individual pharmaceuticals in solution was compared to that of the compounds mixed in the same aqueous solution as well as in a more realistic and complex liquid matrix such as a pre-treated wastewater.

Removal percentages of any of the pharmaceuticals in water did not show any noticeable differences, whether in the assays of single-compound solutions or in those with pharmaceuticals-mixture solutions (Figure 4). This seems to indicate that, within the tested concentrations range, no competitive sorption effects were observable that affected the removal performance, which may be suggestive that cork's capacity is still far from being exhausted.

The assays on the wastewater medium were performed using a wastewater sample with a pH of 8.30 and slightly high contents of suspended solids (TSS = 53 mg L^{-1}) and organic matter ($COD_t = 131$ mg L^{-1} and $COD_s = 77$ mg L^{-1}) that was spiked with 35 mg L^{-1} of each pharmaceutical. Removal of pharmaceuticals from this wastewater was somewhat reduced in comparison with the behaviour of the isolated compounds in water (Figure 4). Still significant removal efficiencies were observed for CB (63%) and IB (50%). For CA, the observed removal efficiencies remained, as expected, somewhat poor (8%).

3.3 *Sorption models*

Some insight into the processes of sorption can be gained by exploring how the equilibrium concentrations in solution, C_e, and corresponding sorbed amounts, n_{sorb}, fit

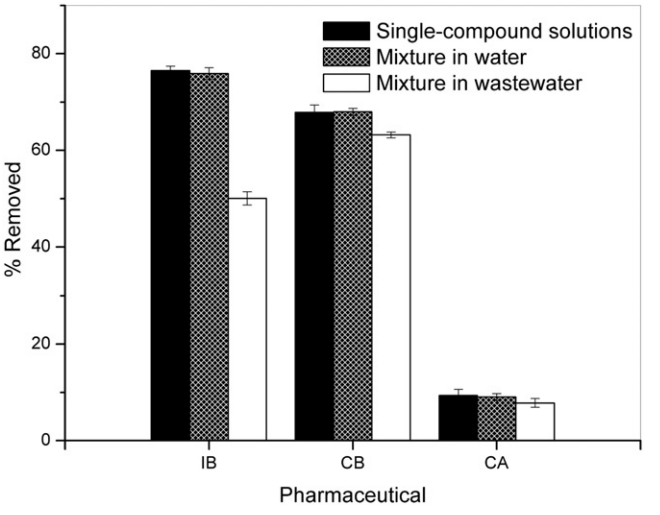

Figure 4. Comparison of removal efficiencies of CA, IB and CB by granulated cork (after 144 h of contact time) for initial concentrations of 35 mg L^{-1} of each compound in single-compound aqueous solutions, pharmaceutical-mixture aqueous solutions and wastewater spiked with the pharmaceutical mixture. Vertical bars represent the averages of 3 replicates and error bars represent the range of ±1 S.D. All removal efficiencies are ANOVA significantly different at $P < 0.05$ within each media-type class.

some of the most popular model isotherms equations for sorption from liquid phase, namely the Langmuir equation [20]:

$$\frac{n_{sorb}}{n_m} = \frac{K_L C_e}{1 + K_L C_e}$$

which can be written in a linear form as:

$$\frac{C_e}{n_{sorb}} = \frac{1}{K_L n_m} + \frac{1}{n_m} C_e$$

where K_L is the Langmuir constant, which relates to the energy of sorption, and n_m is the monolayer capacity, i.e. the maximum amount of sorbed compound, and the Freundlich equation [21]:

$$n_{sorb} = K_F C_e^{1/n}$$

which can also be written in a linear form as

$$\ln n_{sorb} = \ln K_F + \frac{1}{n} \ln C_e$$

where K_F is the Freundlich constant, which relates to the extent of sorption, and $1/n$ is the Freundlich exponent, which determines the concavity of the isotherm and in the special case of $1/n = 1$ corresponds to a partition equilibrium, in which case K_F is the Nernst partition coefficient K_d.

The results of the linear fits of C_e/n_{sorb} vs. C_e (Langmuir model) and ln n_{sorb} vs. ln C_e (Freundlich model) are presented in Table 3. Clearly, the Freundlich equation models the

Table 3. Fits of experimental sorption data to the linear forms of Feundlich and Langmuir equations.

	Freundlich			Langmuir		
Pharmaceutical	K_F ($L^{1/n}\,mg^{(1-1/n)}\,g^{-1}$ cork)	$1/n$	R^2	K_L ($L\,mg^{-1}$)	n_m ($mg\,g^{-1}$ cork)	R^2
CB	0.04033	0.7224	0.9994	0.1366	0.3668	0.8783
CA	0.002385	0.7518	0.9990	0.03352	0.06056	0.8701
IB	0.07649	0.5598	0.9939	0.4366	0.3171	0.8757

experimental data very well for every pharmaceutical whereas the Langmuir equation fits are visibly much poorer.

The Langmuir equation describes a very simple model of adsorption by assuming an energetically homogenous surface, the absence of lateral interactions between sorbed molecules and that adsorption is restricted to the formation of a single layer of adsorbate molecules. The cases where these three assumptions are all simultaneously true are not very frequent. Nevertheless, in many cases the Langmuir equation fits experimental data surprisingly well. This success of the Langmuir model is probably due to a balance of opposing effects. As a matter of fact, Langmuir isotherm equations are frequently used to model even adsorption phenomena in liquid phase. In the present case, however, a Langmuir equation clearly fails to adequately fit the experimental data, as was noted.

The Freundlich equation has an empirical origin, but can be derived theoretically by considering an exponential variation of the sorption enthalpy with surface coverage. In fact, the Freundlich equation can be depicted as a summation of a distribution of Langmuir isotherms and hence it is able to account for the heterogeneity of the sorption process. In the present case, the best fit to the Freundlich equation reflects the heterogeneity of the sorbent material as well as possible lateral interactions between the sorbed molecules.

3.4 *Kinetic studies*

For the highest initial concentration of the pharmaceuticals studied ($35\,mg\,L^{-1}$), the profiles of the removed amounts of each compound as function of contact time with granulated cork are shown in Figure 5.

The kinetics of removal of every compound were characterised by an initial fast step in the first 6 h: for any of the compounds, at least 44% of the total amounts removed during the full period of contact with cork were removed just within this initial period. Subsequently, CA essentially attained a stable concentration profile corresponding to the state of sorption equilibrium whereas IB and CB continued to be removed at a slower rate, especially up to 48–72 h of contact time.

Table 4 presents the fits of sorption kinetics experimental data to zeroth order, first order and second order rate equations. A set comprising the full data as well as two subsets of the data corresponding to two periods (6–48 h and 48–144 h) have been considered. For CB and IB it is clear that the sorption process occurred in two stages as the fits for the complete data set are much poorer that those for each of the two subperiods. These two

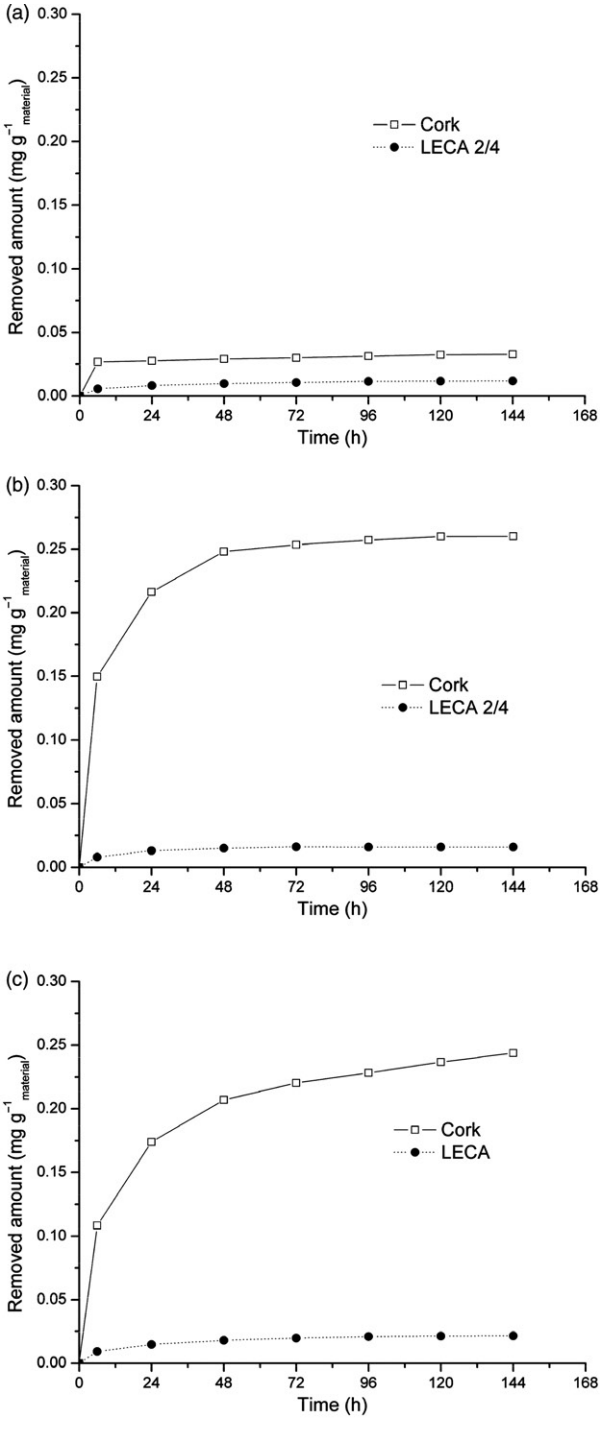

Figure 5. Effect of contact time on the removed amounts of (a) CA, (b) IB and (c) CB from aqueous solutions of 35 mg L^{-1} of each compound, by granulated cork. The points represent the averages of 3 replicates and error bars represent the range of ±1 S.D. For comparison, corresponding data on the removal of the same compounds by LECA 2/4 [9] is also presented.

Table 4. Fits of sorption kinetics experimental data to zeroth order, first order and second order rate equations.

			CA	CB	IB
Zeroth order	6–144 h period	equation	$C(t) = -0.0046\ t + 32.42$	$C(t) = -0.0831\ t + 21.59$	$C(t) = -0.0637\ t + 15.14$
		R^2	0.9862	0.7789	0.6282
	6–48 h period	equation	$C(t) = -0.0054\ t + 32.44$	$C(t) = -0.2298\ t + 25.47$	$C(t) = -0.2287\ t + 19.47$
		R^2	0.9791	0.9288	0.9208
	48–144 h period	equation	$C(t) = -0.0041\ t + 32.36$	$C(t) = -0.0375\ t + 16.67$	$C(t) = -0.0127\ t + 9.637$
		R^2	0.9779	0.9840	0.9069
First order	6–144 h period	equation	$\ln C(t) = -0.0001\ t + 3.479$	$\ln C(t) = -0.0050\ t + 3.075$	$\ln C(t) = -0.0054\ t + 2.691$
		R^2	0.9865	0.8607	0.7054
	6–48 h period	equation	$\ln C(t) = -0.0002\ t + 3.479$	$\ln C(t) = -0.0118\ t + 3.255$	$\ln C(t) = -0.0171\ t + 3.003$
		R^2	0.9789	0.9589	0.9645
	48–144 h period	equation	$\ln C(t) = -0.0001\ t + 3.477$	$\ln C(t) = -0.0029\ t + 2.840$	$\ln C(t) = -0.0015\ t + 2.272$
		R^2	0.9782	0.9925	0.9150
Second order	6–144 h period	equation	$1/C(t) = 4 \times 10^{-6}\ t + 0.031$	$1/C(t) = 0.0003\ t + 0.045$	$1/C(t) = 0.0005\ t + 0.069$
		R^2	0.9869	0.9278	0.7770
	6–48 h period	equation	$1/C(t) = 5 \times 10^{-6}\ t + 0.031$	$1/C(t) = 0.0006\ t + 0.037$	$1/C(t) = 0.013\ t + 0.046$
		R^2	0.9786	0.9820	0.9924
	48–144 h period	equation	$1/C(t) = 4 \times 10^{-6}\ t + 0.031$	$1/C(t) = 0.0002\ t + 0.056$	$1/C(t) = 0.0002\ t + 0.102$
		R^2	0.9784	0.9973	0.9224

stages are both pseudo-second order but with different rate constants, the second stage being correspondingly slower. In the case of CA, the kinetic profile from 6 h onwards is essentially a flat plot because effectively all the CA removal occurred within the first 6 h and, afterwards, CA concentrations in solution correspond to stable equilibrium concentrations.

Changing the conditions of the assays to the other two tested conditions, i.e. mixtures in water and in wastewater, did not appreciably affect the kinetics in any of the cases (data not shown). Still most of the compounds' removal occurred within the first 6 hours, and little compounds' removal occurred beyond the period up to 48–72 h of contact time.

The first hours of contact seemed, therefore, to be the most important stage of the whole process and, although the initial aim of the present work was to study the removal processes in a longer time frame, a better characterisation of the initial period would probably prove useful.

3.5 *Discussion regarding cork sorption performance in comparison with LECA*

In previous studies, some clay materials have been tested for the removal, by sorption, of CA, IB and CB from water and wastewater [9]. In particular, a bed composed of light expanded clay aggregates (LECA) was found to present high removal efficiencies of CB and IB and to have suitable characteristics to be used as a solid matrix in constructed wetlands [8], but the compound CA was only modestly removed by this material. Considering these previous tests, some questions arise: How does the sorptive qualities of LECA and granulated cork compare? Does this biosorbent have the potential to be considered as an alternative to LECA to be used as a solid matrix in constructed wetlands?

From the comparison of the absolute amounts of the three pharmaceuticals removed per unit weight of cork and LECA for several different initial concentrations (Figure 6) it is clear that cork has a much larger specific sorption capacity for all three compounds. In every case much larger amounts of the three pharmaceuticals were removed by cork and, in addition, the amounts removed also increased more steeply with their initial concentrations. However, the differences between amounts sorbed by cork and by LECA were much more pronounced for IB and CB than for CA. In fact, although CA was removed in larger extent by cork than it was by LECA, removed amounts of CA were still somewhat modest and this compound remained a difficult pollutant to be removed from water, even with this biosorbent. It was also observed that both materials showed a linear dependence between amounts sorbed and initial concentration of the pharmaceuticals and were far from exhausting their sorption capacity up to initial concentrations of 35 mg L^{-1}.

In terms of the kinetic behaviour of the removal process (Figure 5) in LECA and in cork for the case of the highest initial concentration (35 mg L^{-1}) the most salient difference in the kinetic profiles at the two materials was a clearly faster removal of CA in the initial 6 h of contact with cork in comparison with LECA.

4. Conclusion

The results obtained with this work showed that granulated cork presents good sorption qualities for the removal of some pharmaceuticals from aqueous solutions. This material was shown to remove extensively two of the three pharmaceuticals tested, ibuprofen and carbamazepine, although the third one, clofibric acid, was removed only in modest

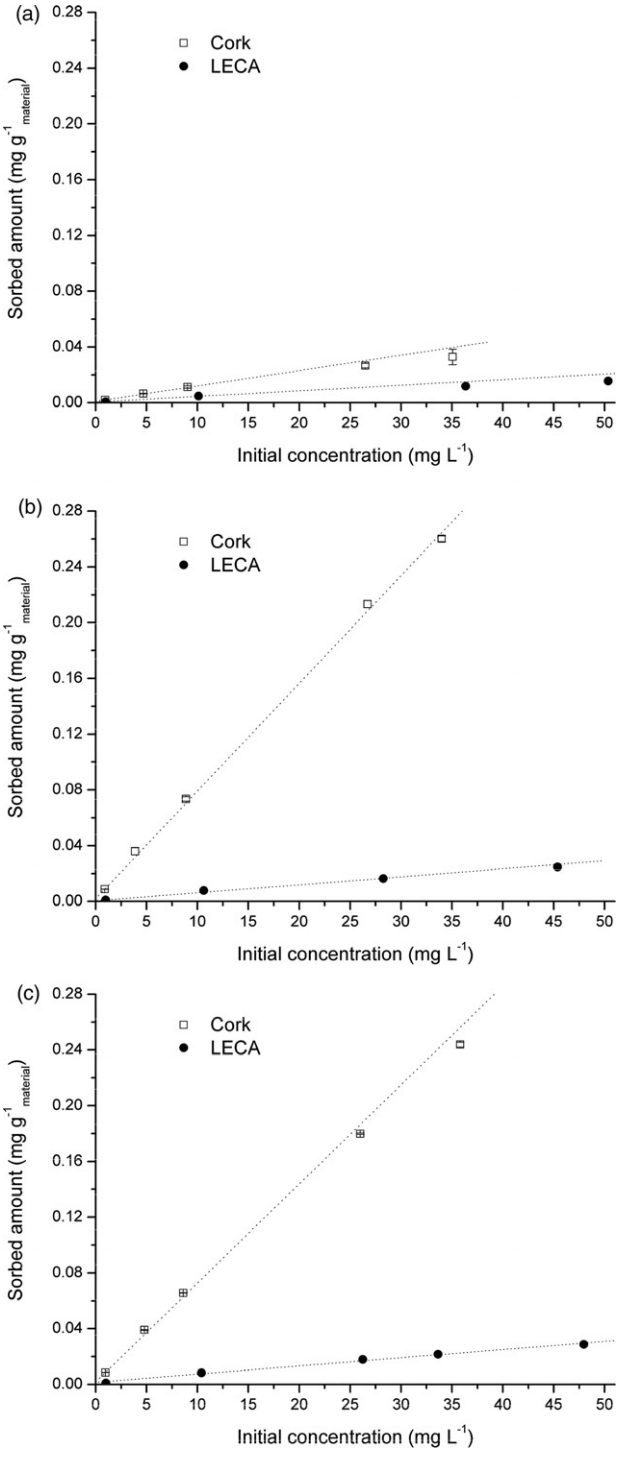

Figure 6. Comparison between the total amounts removed by granulated cork and by LECA, per unit weight of sorbent, of the pharmaceuticals (a) CA, (b) IB and (c) CB after 144 h of contact time for each initial concentration. Points represent the averages of 3 replicates and error bars represent the range of ±1 S.D.

amounts, in similarity with results obtained with other materials. This behaviour was observed in all the tested conditions (aqueous solutions of single compounds, aqueous solutions of mixtures of all three compounds and a treated wastewater spiked with the three compounds) and the amounts of each pharmaceutical removed always followed the order: ibuprofen > carbamazepine > clofibric acid.

When all the pharmaceuticals were present in the same aqueous solution to be removed simultaneously, negligible differences were observed in the amounts removed in comparison to the removal of each compound separately, which leads to the conclusion that competitive sorption effects were negligible for this material at these concentrations range. However, there was some loss of removal efficiency in the more complex liquid matrix provided by a pre-treated wastewater, where the sorbed amounts of all the pharmaceuticals were reduced, probably due to the increased solubility promoted by the wastewater's dissolved organic matter.

The first 6 h period seemed to be the most important stage of the whole sorption process. In fact, it was during this short initial period that occurred the removal of almost half of the total amounts removed during the full period of contact with cork. Equilibrium was attained for CA within this period while, for IB and CB some additional compound removal continued at a slower rate especially within the 6–48 h period. Experimental data was found to fit well a pseudo-second order kinetic model ($R^2 = 0.9224$–0.9973) but the kinetics clearly consisted of two stages, one in the 6–48 h period and a second stage beyond 48 h.

Comparison of amounts of pharmaceutical removed per unit weight of material obtained with granulated cork and another previously tested material, LECA 2/4, showed a much higher capacity of cork for sorption these compounds, although CA remained a problematic compound to be removed. Equilibrium was also attained slightly faster in granulated cork in comparison with LECA.

In summary, these laboratory studies showed important advantages presented by granulated cork as a sorbent material for the removal of certain pharmaceuticals from water. However, this work represents only a first step in the study of its use as a support material for constructed wetlands designed to treat pharmaceuticals contamination and further tests are still necessary in order to evaluate aspects such as its suitability for plants development (and which plant species would it be more suitable for), adequate wastewater flow in a continuous flow system, and the compactness of the material in the beds.

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