



Research article

Granulated cork as biosorbent for the removal of phenol derivatives and emerging contaminants

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ABSTRACT

This study evaluated the ability of cork to adsorb a broad range of phenolic, pharmaceutical and cosmetic compounds: phenol, 2-chlorophenol, 2-nitrophenol, 2,4-dichlorophenol, pentachlorophenol carbamazepine, naproxen, ketoprofen, diclofenac, triclosan, and methyl paraben. The effect of variables such as the compound concentrations and the amount of cork were studied resulting in a highly pH dependence in the case of phenolic compounds. Maximum removal percentages and uptake values of 75% (1.61 mg/g) for 2,4-dichlorophenol, 55% (1.25 mg/g) for 2-nitrophenol, 45% (1.47 mg/g) for 2-chlorophenol, 20% (0.63 mg/g) for phenol, and 100% for pentachlorophenol, were obtained for a 30 mg L⁻¹ solution at pH 6, showing that the adsorption process increased with greater electronegativity of the phenolic substituting group. Removal percentages and uptakes of 82% (3.56 mg/g) for naproxen, 57% (2.31 mg/g) for ketoprofen, 50% (1.84 mg/g) for carbamazepine, 50% (1.78 mg/g) for methyl paraben, 100% for sodium diclofenac, and 100% for triclosan, were obtained using 5 mg of cork and a 1 mg L⁻¹ solution of each compound. The adsorption process was almost complete after 30 min for all the micropollutants. Experimental equilibrium data were analysed by Freundlich and Langmuir adsorption models. Cork has proved to be an effective sorbent for the removal of phenols and emerging contaminants from contaminated waters and is a readily available material that can be acquired at minimal or no cost in cork-producing areas.

1. Introduction

The control of contamination caused by both regulated and non-regulated micropollutants is of great importance as compounds such as phenol derivatives and pharmaceuticals and personal care products are detected in almost all effluents. Among the regulated compounds, phenols are listed in the US Environmental Protection Agency (EPA) priority list of pollutants and in EEC directive 76/464, related to dangerous substances discharged into aquatic environments (García-Araya et al., 2003). Of the 21 chlorophenolic compounds included in these two lists, pentachlorophenol, a wood preservative, is now considered the highest priority pollutant (Liao et al., 2007). Chlorophenols are also found in industrial wastewater as residues of the bleaching process in the pulp industry and can be present in the aquatic environment as a result of both hydrolysis and photolysis of chlorinated phenoxy acid herbicides (Calace et al., 2002).

Pharmaceuticals and ingredients of personal care products (PPCPs),

also known as emerging contaminants, are detected together with their metabolites at trace levels, from ng L⁻¹ to µg L⁻¹, in surface waters as they are not completely removed at industrial and sewage treatment plants. Non-steroidal anti-inflammatory drugs (NSAIDs), such as sodium diclofenac, naproxen, ketoprofen and ibuprofen, as well as methyl-paraben, a preservative used in personal care products, tend to be easily transported and discharged due to their high polarity and low volatility (Breton and Boxall, 2003). Recently, sodium diclofenac was included in the EU priority contaminant list (EU Water Framework 2013/39/UE Directive). DCF and NAP have been detected in effluent waste waters as their biodegradability is poor (Joss et al., 2006).

The majority of micropollutants have not been identified as targets of conventional wastewater treatment plants (WWTPs). Process optimization (e.g. increasing sludge residence times), coagulation-flocculation and advanced technologies, such as reverse osmosis and ozonation and other advanced oxidation processes (AOP), are able to remove micropollutants from water, although their high cost limits the degree

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to which they are employed and, in the case of AOP, toxic intermediate by-products can be generated (Zhang et al., 2014). A less costly, simple and efficient alternative is the use of adsorption processes, which are able to remove a variety of metallic and organic compounds from aqueous systems. Given its high adsorption capacity, granulated or powdered activated carbon has become the most widely used adsorbent (García-Araya et al., 2003). However, the need to constantly regenerate spent carbon, makes this material costly also in scaled-up use. Activated carbon can be obtained from different waste and natural materials such as pine bark, sawdust and cork bark among others (Pineo et al., 2004). Granular activated carbon (GAC) obtained from coal, coconut and wood has been used to remove phenols such as 2,4-dichlorophenol (Choi et al., 2006), and high surface area carbon adsorbents have been synthesized from pine-sawdust and applied to NSAIDS sorption (Álvarez-Torrellas et al., 2016). The direct use of biosorbents, including agriculture wastes, seaweed, fungal biomass, etc., is a low-cost alternative to activated carbon and their uptake capacities can be improved by physical or chemical modification of these biomaterials (Tran et al., 2015; Zhou et al., 2015). Paper mill sludge, activated sludge, fly ash, sawdust, bagasse pith, rice husk ash, jute fibres, rice bran ash, and brown algae have been applied to phenolic compounds removal as substitutes of GAC (Gholizadeh et al., 2013). Among them, lignocellulosic materials, which are derived from plants, have been widely studied to develop cost-efficient sorbent materials for the removal of metals and phenolic derivatives (Okasha and Ibrahim, 2010). Some of these natural materials, such as almond shells, have proved to be particularly efficient in adsorbing PCP (93%) (Estevinho et al., 2006) and pomegranate peel and banana peel are also efficient in adsorbing, 2,4-DCP and Ph, respectively (Achak et al., 2009; Soto et al., 2011).

Cork, a lignocellulosic natural material, has been used as a biosorbent for pollutants, such as insecticides, uranium, volatile phenols, paracetamol, chloroanisoles, polycyclic aromatic hydrocarbons, and heavy metals. The make-up of cork is approximately 45% suberin, 27% lignin, 12% polysaccharides, and 10% extractive compounds (Pintor et al., 2012). The interactions of cork with organic pollutants, which are essentially hydrophobic, are explained by the aromatic rings and carboxyl and hydroxyl groups of suberin and lignin. In the case of highly hydrophobic pesticides ($\log K_{ow} > 4$), such as chlorpyrifos, it has been established that raw cork is suitable for their retention. However, adsorption is less successful in the case of hydrophilic pesticides ($\log K_{ow} < 2$), such as methomylandoxamyl (Olivella et al., 2015). Moreover, the aromatic components of lignin interact with the aromatic moieties of the adsorbed compounds via π - π interactions, as is the case in paracetamol and phenanthrene sorption (Olivella et al., 2013; Villaescusa et al., 2011).

These findings have been confirmed by molecular modelling calculations, which reveal that π stacking, reinforced by hydrogen bonding, is the main contributor to the interaction between pesticides and lignin (Olivella et al., 2015). Granulated cork has also proved to be able to remove ibuprofen (IB), carbamazepine (CBZ) and clofibrac acid (CA) from water and wastewater (Dordio et al., 2011).

The objectives of this study are (i) to evaluate the sorption capacity of granulated cork towards regulated phenolic compounds (phenol (Ph), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 2,4-dichlorophenol (2,4-DCP), pentachlorophenol (PCP), and diclofenac (DCF)) and emerging contaminants (triclosan (TCS), naproxen (NAP), ketoprofen (KET), carbamazepine (CBZ), and methyl paraben (MPB)); (ii) to study the effect of several parameters, such as pH, compound concentration, and amount of cork on the efficiency of the adsorption process; and (iii) to characterize the sorption processes by analysing the experimental data by the Langmuir and Freundlich isotherm models. The results obtained are compared with the sorption capacities of other biosorbents and biosorbent-based activated carbons.

2. Experimental

2.1. Reagents and solutions

The cork, kindly supplied by the Cork Centre (Palafrugell, Spain), was sifted to attain powder particles of < 2 mm, cleaned three times thoroughly with bi-distilled water, and air dried before use.

Test solutions were prepared by diluting appropriate amounts of stock solution of Ph, 2-CP, 2-NP, 2,4-DCP, PCP (Dr. Ehrenstorfer GmbH, Germany) to concentrations ranging between 0.1 and 60 mg L^{-1} . A 100 mg L^{-1} stock solution was prepared by dissolving appropriate amounts of these phenolic compounds in bi-distilled water. All reagents (Panreac, Spain) were of analytical grade.

HPLC-grade acetonitrile (Carlo Erba, Spain), Milli-Q water and acetic acid for analysis (Sigma Aldrich, Spain) were used as the mobile phase. TCS, NAP, KET, CBZ, DCF sodium salt and MPB were purchased from Sigma Aldrich (Spain).

A stock solution containing 250 mg L^{-1} of each compound was prepared in methanol, stored in brown glass bottles and kept at 4°C in order to avoid degradation during the test period. This solution was prepared monthly. Working standard solutions of 0.5 and 1 mg L^{-1} were prepared daily by diluting this stock solution with ultrapure water obtained from a Millipore purification system (Millipore, USA). Chromatographic grade acetonitrile was provided by Fisher (USA) and sodium acetate and acetic acid were from Sigma Aldrich (Spain). NaOH and HCl solutions were used for the pH adjustment of the test solutions. All chemicals used in this study were of analytical grade. The physical and chemical properties of the emerging contaminants and phenolic compounds are given in Table 1.

2.2. Chromatographic analysis

Phenolic compound concentrations were determined by using a high-performance liquid chromatograph (Spectra SYSTEM, ThermoQuest, Italy) consisting of an SCM1000 vacuum membrane degasser, a P2000 gradient pump, and a UV6000LP diode-array detector. Control and data processing were performed with ChromCard version 1.21 software (ThermoQuest, Italy).

Chromatographic separation was achieved in a C18 reversed-phase column ($5 \mu\text{m}$, $20 \times 0.46 \text{ cm}$ i.d., Teknokroma, Spain) with a guard column ($5 \mu\text{m}$, $0.3 \times 0.46 \text{ cm}$ i.d., Teknokroma, Spain) of the same packing material. The injection volume was set at $100 \mu\text{L}$ and the flow rate was 1 mL min^{-1} . The mobile phase was an acetonitrile solution ($\text{CH}_3\text{CN}:\text{H}_2\text{O}:\text{CH}_3\text{COOH}$, 50:49:1) and the detection wavelength was set at 275 nm for Ph, 2-CP, and 2-NP, and at 286 nm for 2,4-DCP and PCP.

The determination of CBZ, NAP, KET, DCF, TCS, and MPB was performed with an Agilent 1200 series high performance liquid chromatography system equipped with two pumps (G13128), a degasser (G1379B), an autosampler (G1329B) and a DAD detector (G4212A), system control and data acquisition were performed using Agilent ChemStation software. The injection volume was $10 \mu\text{L}$. The mobile phase, consisted of (A) Milli-Q water, 0.1% acetic acid and 0.3852 g of sodium acetate and (B) acetonitrile, was passed through a C18 Kinetik column ($2.6 \mu\text{m}$, $50 \times 2.10 \text{ mm}$ i.d., Phenomenex, USA) in a gradient mode as follows: 0 min; 90% A, 5 min; 75% A, 15 min; 55% A, 20 min; 20% A, 23 min; 55% A, 25 min; 90% A. Total run time was 25 min. The flow rate was 0.3 mL min^{-1} and the detection wavelength was set at 242 nm for CBZ, NAP and TCS; 250 nm for KET and MPB, and 280 nm for DCF.

2.3. Adsorption studies

To clean the cork, weighted amounts of sieved ($\leq 0.2 \text{ mm}$) raw cork were put into contact with 10 mL of ultrapure water in 25 mL glass

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