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Innovative application of *biobed* bioremediation systems to remove emerging contaminants: Adsorption, degradation and bioaccesibility

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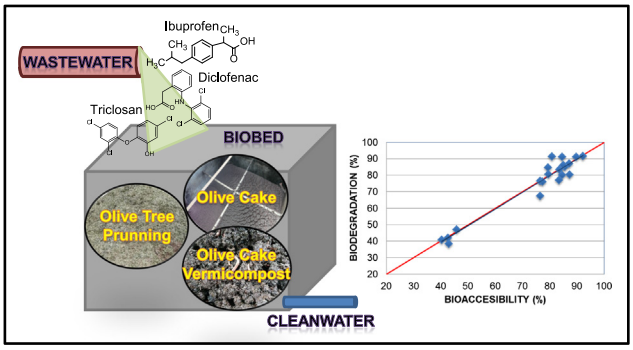
HIGHLIGHTS

- *Biobeds* were tested for removal of emerging contaminants (ECs) from wastewater.
- Sustainable *biobed* biomixtures were made from olive oil agro-industry waste.
- Biomixture with olive cake vermicompost showed the highest removal efficiency.
- Contaminant bioaccesibility and biodegradation were strongly correlated.
- Bioaccesible fraction has the ability to predict ECs biodegradation endpoints.

GRAPHICAL ABSTRACT



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ABSTRACT

Biobed bioremediation systems (BBSs) are widely used to prevent point-source pesticide contamination of water. However, these systems have never been investigated for possible elimination of emerging contaminants (ECs). In this study, two biobed systems, involving biomixtures elaborated with soil and raw olive mill cake (SCP) or its vermicompost (SVP), were assayed to determine their effectiveness in removing the ECs diclofenac, ibuprofen and triclosan from effluent wastewater. Adsorption, incubation and bioaccesibility experiments were carried out. The SCP and SVP biomixtures showed greater adsorption capacity than the soil (S), used as reference. In SVP and S, the degradation rates of the ECs applied were similar and over 94% of these compounds was removed after 84 days of incubation. However, SCP biomixture had a lower removal rate and the percentage of ECs removed ranged from 32 to 68%. In SVP, the bioaccesible fraction (*E*) reveals that approximately 82% of triclosan and diclofenac adsorption occurred in bioaccesible sites, thus explaining the more efficient decontamination observed in this biomixture. The relationship established between the bioaccesible and biodegradable fractions suggests that *E* values are a useful tool for predicting the endpoints of ECs biodegradation in bioremediation systems. UPLC/Q-TOF-MS analysis of samples showed different metabolite products.

1. Introduction

Bioaccesibility is a key concept which has been received increasing attention as a tool for pollution risk assessment (Semple et al., 2004). Bioaccesibility, which determines the removal efficiency of pollutants, has also become particularly important in bioremediation systems

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(Ehlers and Luthy, 2003). An effective bioremediation system should ensure the retention of pollutants, avoiding their spread to other compartments, while making them available to microorganisms. Thus, the sorption process in the adsorbent matrix regulates the bioaccessibility of the contaminants to be degraded. Several studies have used bioaccessibility measurements in order to predict bioremediation endpoints of hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons in contaminated soils to determine whether bioremediation technology was effective (Diplock et al., 2009; Juhasz et al., 2014). However, to the best of our knowledge, no studies have focused on emerging contaminants such as pharmaceuticals and personal care products (PPCPs), which include a wide group of chemicals with different polarities and properties. These contaminants have been a cause of increasing concern due to being frequently detected in the environment and their potential toxicological effect on living organisms (Bolong et al., 2009). Agricultural practices, such as the land application of biosolids, irrigation with reclaimed wastewater as well as the discharge of sludge and wastewater from pharmaceutical industries and hospitals, are the main sources of entry of these compounds into the environment (Bourdat-Deschamps et al., 2017; Petrović et al., 2003), as PPCPs can persist through currently available wastewater treatments (Akhtar et al., 2016; Evgenidou et al., 2015). Given the goal of recycling and safe reuse of wastewaters set by European countries to be achieved by 2030 (UN Sustainable Development Goal on Water, SDG 6) to alleviate water stress and to improve human sustainability (Angelakis et al., 2018), strategies to remove PPCPs from wastewater are therefore required. *Biobed* bioremediation systems, which have been extensively and successfully used for removing pesticides from agricultural wastewater (Castillo et al., 2008; Karanasios et al., 2012), might be implemented in the pharmaceutical industry, hospitals and urban wastewater treatment plants as a new, inexpensive and sustainable system to minimize the release of PPCPs into the environment.

This study aims, for the first time, to use a *biobed* system to remove PPCPs from water. For this purpose, two biomixtures composed of agro-industrial wastes from the olive oil industry were evaluated at a microcosm scale to determine their effectiveness in retaining and eliminating different PPCPs. To better understand the functioning of these bioremediation systems, the bioaccesible fraction of these contaminants was measured using the isotope dilution method. The relationship between biodegradation and bioaccesibiliy as a potential screening tool was also evaluated in order to predict the endpoint of the biodegradable fraction of each PCPP in the biomixtures. Diclofenac, ibuprofen and triclosan, which are frequently detected in reclaimed and surface water, were selected for this study (Bouju et al., 2016; Bourdat-Deschamps et al., 2017; Maassen et al., 2017; Poirier-Larabie et al., 2016; Singer et al., 2002), and their presence in soil, surface water and groundwater has been shown to cause toxicological problems (Bedoux et al., 2012; Fent et al., 2006; Oaks et al., 2004; Rubasinghege et al., 2018).

2. Material and methods

2.1. Chemicals

Two pharmaceuticals, ibuprofen (IBP) and diclofenac (DCF) sodium salt and the personal care product triclosan (TCS), all with a purity of ≥97%, were purchased from Sigma-Aldrich (Steinheim, Germany). Their structure and physical-chemical properties are outlined in Fig. 1. Deuterated diclofenac (d-DCF; phenyl-d_4-acetic, 98% purity) and deuterated triclosan (d-TCS; 2,4-dichlorophenoxy-d_3, 97% purity) were provided by Cluzeau Info Labo (Sainte-Foy-La-Grande, France) and C/D/N Isotopes Inc. (Point-Claire, Canada), respectively. Standard solutions of IBP, DCF, TCS, d-DCF and d-TCF were prepared in acetone. All other solvents used were of HPLC grade.

2.2. Biomixtures

Soil (S), wet olive cake (C) or its vermicompost (V) and olive tree prunings (P) were the materials used in the biomixtures. Arable silty clay loam soil (Chromic vertisol) containing 34, 56 and 10% of clay, silt and sand, respectively, was collected from a Spanish olive orchard (S2, 0436148-4211209, zone 30S) at a depth of 0–25 cm. Wet olive cake from the two-phase olive oil extraction process was provided by Romeroliva, S.L. (Deifontes, Spain). Vermicomposting was carried out by the earthworm *Eisenia andrei* on a pilot scale by mixing wet olive cake and manure at a 4:1 (dw/dw) ratio. The whole process lasted 6 months, with an additional 2 months for maturation and drying. Olive tree prunings were collected from an olive farm in Granada (Spain). All biomixture components were air-dried, ground and sieved through a 4-mm mesh prior to use.

Two biomixtures were elaborated using the aforementioned materials: i) SVP containing S, V and P (25:25:50, v:v:v) and ii) SCP containing S, C and P (25:25:50, v:v:v). The physical and chemical properties of these biomixtures and their components are shown in Table 1.

2.3. Batch adsorption experiments

Adsorption isotherms were developed using 0.5 g (dry weight.) of the biomixture weighed in triplicate in 30 mL Pyrex centrifuge tubes. Samples were spiked with different aliquots of a mixture containing the three PPCPs in acetone in order to obtain concentrations ranging from 25 to 500 mg kg^{-1}. Following acetone evaporation, 25 mL of the 0.01 M $CaCl_2$ solution were added to each sample. The tubes were placed in an end-over-end shaker at 20 ± 1 °C, for 24 h. Preliminary kinetic studies revealed that equilibrium was reached after 4 h. Samples were then centrifuged at 1811*g* for 15 min at 20 ± 1 °C. After centrifugation, an aliquot of the supernatant was analyzed using high performance liquid cromatography (HPLC), and the biomixture was extracted using the QuEChERS method described below.

Adsorption experiments in S, used as reference, were run in parallel under the same experimental conditions.

A linear model ($C_s = K_d \times C_w$) was used to fit the sorption isotherms; C_s (mg kg^{-1}) and C_w (mg L^{-1}) are the concentrations of the PPCPs in the solid and water phase, respectively, at equilibrium; K_d (L kg^{-1}) is the solid-water distribution coefficient. The distribution coefficient normalized to organic carbon content (K_{OC}, L kg^{-1}) was calculated using the formula (K_d/ % OC) × 100, where %OC is the percentage of organic carbon in the adsorbent.

2.4. Degradation study

SVP and SCP were contaminated with the PPCPs at a nominal concentration of 20 μg g^{-1}. For this purpose, silica sand (1 g), which was placed in a glass beaker, was spiked with a mixture of PPCPs in acetone; following solvent evaporation, it was mixed with 20 g (dry weight) of the biomixture and homogenized using an end-over-end shaker for 15 min at room temperature. The moisture content of the samples was adjusted to 75% of their field capacity. Samples were incubated in the dark at 20 ± 1 °C. Moisture content was maintained by weighing and adding ultra-pure water when necessary.

Incubation experiments with S were also carried out in parallel under experimental conditions similar to those described for the biomixtures.

To control abiotic degradation, the degradation study was run in parallel in sterile SVP, SCP and S samples (SVPs, SCPs and Ss). Sterilization was carried out in an autoclave at 121 °C for 20 min. This process was repeated three times to ensure the complete elimination of microorganisms.

Incubation was carried out in triplicate with 24 microcosm systems per biomixture or soil. After 0, 3, 5, 10, 15, 21, 42 and 84 days,