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Ibuprofen adsorption in four agricultural volcanic soils

Esmeralda Estevez [a], Jose Manuel Hernandez-Moreno [b], Juan Ramon Fernandez-Vera [c], Maria Pino Palacios-Diaz [d,*]

[a] Department of Physics, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain
[b] Department of Soil Science and Geology, Universidad de La Laguna, 38204 La Laguna, Spain
[c] Laboratorio Agroalimentario y Fitopatológico del Cabildo de Gran Canaria, 35413 Arucas, Spain
[d] Department of Animal Production, Universidad de Las Palmas de Gran Canaria, 35413 Arucas, Spain

HIGHLIGHTS

- Ibuprofen adsorption at 1-200 mgL^{-1} in four volcanic soils, at 1:1 and 1:5 S/W ratios
- Non-linear and linearized Langmuir and Freundlich equations were well fitted
- 1:1 S/W better simulates field conditions and provides lower parameters than 1:5
- Similar K_d, R_F, and higher S_{max} in andic soils comparing to literature
- IB adsorption is related to S/W, DOC and soil properties, including andic ones

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ABSTRACT

Ibuprofen (IB) is a high environmental risk drug and one of the most frequently prescribed in human medicine. Recently, IB has been detected in Gran Canaria in reclaimed water for irrigation and in groundwater. Adsorption was studied in four volcanic soils from three islands of the Canarian Archipelago. Once the biodegradation process has been excluded from the experimental conditions, a batch method was applied using initial concentrations of 1-5-10-20-50-100-200 mgL^{-1} and two soil/water ratios (w/V): 1:5 (OECD, 2000) and 1:1. Non-linear and linearized Langmuir and Freundlich equations were well fitted. The wide IB range tested in our batch studies allowed us to measure experimental adsorption values close to the maximum adsorption capacity (S_{max}) as estimated by Langmuir, making it possible thereby to validate the use of the Langmuir equation when there is a burst of contamination at high concentration. The distribution coefficient (K_d), S_{max} and Retardation Factor (R_F) varied from 0.04 to 0.5 kgL^{-1}, 4-200 $mgkg^{-1}$ and 1.2-1.9, respectively. The lowest S_{max} and K_d values were found for the 1:1 S/W ratio whereas most batch studies employ 1:5 S/W ratios, thus obtaining higher adsorption parameters than when considering field conditions (1:1). Despite the high anion retention of andic soils, similar K_d and R_F to those reported for other soils were obtained in 1:5, while high S_{max} was found. Our results demonstrate that IB adsorption in volcanic areas responds not only to the soil properties commonly cited in adsorption studies, but also depends on andic properties, sorbent concentration and Dissolved Organic Carbon, the higher values of which are related to the lower K_d and S_{max}. The low R_F and low detection frequency of the IB in groundwater suggests that a) reclaimed water irrigation is not the main source of IB, and b) the existence of some uncontrolled water disposal points in the zone.

1. Introduction

Ibuprofen, IB, ((RS)-2-[(4-2- methylpropyl)phenyl] propanoic acid, CAS number: 15687-27-1) is a non-steroidal anti-inflammatory drug (NSAID) and one of the "Essential Drugs" listed by the World Health Organization (http://www.who.int/medicines/publications/essentialmedicines/en/index.html).

Its consumption in Spain increased from 0.39 in 1992 to 21.30 defined daily dose/1000 habitants per day in 2006 (AEMPS, 2006). It was the second NSAID and the third active compound most consumed in terms of number of packs sold in 2009 (DGFPS, 2009).

Given the widespread occurrence of IB in aquatic environments, its potential for ecological impact has become a matter of growing concern (Christensen et al., 2009). IB has been proposed as a priority substance to be identified under the Water Frame Directive. However, the inclusion of IB was rejected in January 2012 due to lack of evidence of significant risks to aquatic environments (EC, 2012). In spite of this, IB in the water environment has been shown to affect

* Corresponding author. Tel.: +34 928454353; fax: +34 928451142.
E-mail address: mpalacios@dpat.ulpgc.es (M.P. Palacios-Diaz).

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reproduction in both vertebrates and invertebrates (Han et al., 2010; Hayashi et al., 2008), the growth of several bacterial and fungal species (Pomati et al., 2006), the genotoxic effects for fish (Ragugnetti et al., 2011) and cyto-genetic effects in freshwater bivalves (Parolini et al., 2011).

The entry routes of pharmaceutical compounds (PCs) into the environment are related with wastewater treatment plants (WWTPs), septic tanks, hospital effluents and animal excreta (Kümmerer, 2004; Daughton and Ternes, 1999). In Spain, IB is frequently detected in WWTP effluents (Martinez-Bueno et al., 2012) and at higher levels than expected (Ferrando-Climent et al., 2012). The environment concentration in sediments and soils is in g kg^{-1} and in surface water and groundwater is within a range from ng L^{-1} to μg L^{-1} (Lapworth et al., 2012; Hernando et al., 2006). This ubiquitous contaminant has been found at concentrations greater than 0.1 μg L^{-1} in Spanish aquifers (Cabeza et al., 2012; Jurado et al., 2012). A recent study carried out in Gran Canaria detected IB concentrations below 100 ng L^{-1} in reclaimed water employed to irrigate a golf course and 50 ng L^{-1} in groundwater corresponding to the subjacent aquifer (Estevez et al., 2012).

The main removal mechanisms for IB are biodegradation and sorption. There are several studies on IB biodegradation in batch experiments and real WWTPs (Borges et al., 2011; Caviglioli et al., 2002; Gagnon et al., 2008; Onesios et al., 2009; Quintana et al., 2005; Winkler et al., 2001). Zwiener et al. (2002) concluded that the IB transformation products (TPs) account for less than 10% of the initial concentration in their degradation experiments in both biofilm reactors and batch experiments with activated sludge. Collado et al. (2012) pointed out the time-effect on the transformation rate of IB on its TPs relative to IB input, which declines from 32% (after 24 h) to 3% (after 72 h). Highly mobile organic compounds have the potential to leach into groundwater, whereas strongly sorbing PCs can accumulate in top soil layers. Therefore, adsorption is a determining process in the environmental fate of organic chemicals in soils (Pignatello and Xing, 1995). The extent of adsorption is related to the physicochemical properties of contaminants and another factors such as the soil organic matter content (OM), surface adsorption to mineral constituents, ion exchange capacity, H-bonding, pH and complex formation with metal ions such us Ca, Mg, Fe and Al (Drillia et al., 2005; Karickhoff et al., 1979). Several studies have demonstrated the low sorption affinity of IB in soils (González-Naranjo et al., 2013; Lin and Gan, 2011; Xu et al., 2009).

Volcanic soils frequently present large amounts of short-range-ordered minerals (allophane, Fe and Al oxyhydroxides) and/or Al–humus complexes (Tejedor et al., 2009). These components determine a high reactivity due their large surface areas and bonding capacity for anions and cations. The phosphate retention is used as an index of this reactivity. These properties are defined as "andic", whose higher expression is found in Andisols (Soil Survey Staff, 1999). A large macro- and mesoporosity, associated to a strong aggregation, is also common in andic soils, which favours the preferential flux of solutes. However, the amorphous components tend to crystallize with time (tens of thousands years) and the andic properties are increasingly lost. Soil management can also lead to a loss of the andic properties through a decrease of bulk density or the anion binding capacity; in consequence, the soil classification can easily shift to another soil Order (Tejedor et al., 2009). In the Soil Taxonomy System, andic properties (attenuated) appear at the Subgroup level of some soil Orders.

The aim of this paper is to determine the adsorption behaviour of IB in four volcanic soils from the Canary Islands under similar conditions to those used on agricultural farms. Another objective was to calculate adsorption parameters in extended concentration ranges. Furthermore, this work discusses exhaustively the regression methods and determines the best fit to the experimental equilibrium data by comparing the parameters provided by linear and non-linear models of the Langmuir and Freundlich isotherms.

2. Material and methods

2.1. Chemicals

IB sodium salt (98% purity) was purchased from SIGMA–Aldrich® (Spain). Some characteristics of IB are included in Table 1. Acetonitrile and methanol (HPLC, gradient grade) orthophosphoric acid, calcium chloride dihydrate and sodium chloride were purchased from Panreac (Spain), and deionised water was prepared in a Milli-Q purification system (Millipore).

The stock standard solution of IB (1 g L^{-1}) was prepared by dissolving 110 mg of the IB sodium dehydrated salt in 2 mL of methanol and thereafter in 100 mL of distilled water. The amount of methanol added to the batches was maintained at <0.4% of the liquid volume to avoid co-solvent effects. Working solutions (1-5-10-20-40-50-100-200 mg L^{-1}) were prepared by diluting the stock solution with a 0.01 M equimolar solution of $CaCl_2$ and NaCl prepared in distilled water.

2.2. Soil samples

Surface soils were collected over four locations on the Canary Islands (Fig. S1). The first came from an irrigated field on the El Hierro island (EH) and can be classified as Torriarents (Soil Survey Staff, 1999) with andic properties (including volcanic glasses). Two soils were sampled in a golf course situated on the NE coast of Gran Canaria, and both have been irrigated with reclaimed water since 1976. One of these soil samples represented the original soil of the golf course area: GC1, and the other one was sampled in fairways covered with transported soils from the middlands of the NE of the island: GC2 (Estevez et al., 2010). Soil GC1 is a Torriarents (adjacent natural soils are vitritorrands) and the transported soil GC2 corresponds to an Ustalfs dominated zone. The fourth soil, FV, from Fuerteventura Island was sampled from a wastewater-irrigated field in the SE area of this arid island. This carbonate-rich soil can be classified as Torriarents. After collection, soil samples were stored at 4 °C until use. All the soils were air-dried, homogenised and sieved through 2-mm meshes for the laboratory analysis. The main physical and chemical soil characteristics are presented in Table 2.

2.3. Adsorption experiments

A preliminary biodegradation experiment using 1 mgL^{-1} of IB was performed. Batch tests were performed using sterilized and non-sterilized soils. For each subsample 10 g of soil was incubated with 10 mL or 50 mL of 1 mgL^{-1} of IB to reach the 1:1 or 1:5 (w/V) soil/solution ratios, respectively. The method for sterilization of soil was based on the incubation of soil samples in an autoclave at 121 °C and 1.1 atm for 45 min (Alef and Nannipieri, 1995). After 24 h shaking, filtrated suspension was analyzed by HPLC-UV.

Adsorption of IB in the four soils was measured using the equilibrium batch method at room temperature (23 ± 2 °C) in triplicate, in 125 mL amber glass bottles with Teflon-lined caps. The adsorption

Table 1
Properties of Ibuprofen (IB).

PROPERTIES	
Melting point (°C)	76
pKa dissociation constant$_a$	4.91
Chemical formula	$C_{13}H_{18}O_2$
Water solubility of IB (mg/L)$_b$	21
Water solubility of IB sodium salt: $C_{13}H_{17}NaO_2$ (mg/L)$_c$	100,000
Vapor pressure (Pa)$_d$	2.47E^{-02}
Henry's law constant (atm m^3/mole)$_e$	1.50E^{-07}
log Kow$_f$	3.5

a: Rafols et al. (1997); b: Yalkowsky and Dannenfelser (1992); c: http://www.sigmaaldrich.com, d: Neely and Blau (1985); e: Meylan et al. (1996); f: Stuer-Lauridsen et al. (2000).