Chemosphere 193 (2018) 635–644

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Sorption of albendazole in sediments and soils: Isotherms and kinetics

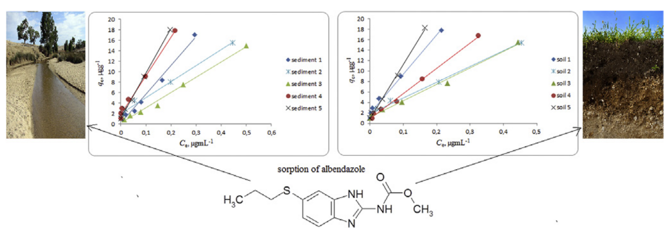
Dragana Mutavdžić Pavlović [a, *], Antonija Glavač [a], Mihaela Gluhak [a], Mislav Runje [b]

[a] Department of Analytical Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia
[b] Pliva Croatia TAPI R&D, Prilaz baruna Filipovića 25, 10000 Zagreb, Croatia

HIGHLIGHTS

- The sorption of albendazole was studied in five soil and five sediment from Croatia.
- Equilibrium data were tested using linear, Freundlich and Langmuir sorption isotherms.
- K_d values indicated that albendazole is moderately mobile/immobile in environment.
- pH, ionic strength and properties of sediment/soil have great impact on ALBA sorption.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 July 2017
Received in revised form
24 October 2017
Accepted 6 November 2017
Available online 9 November 2017

Handling Editor: I. Cousins

Keywords:
Albendazole
Sediment and soil
Sorption isotherm
Ionic strength
pH
Kinetic study

ABSTRACT

Albendazole is a broad-spectrum anthelmintic drug effective against gastrointestinal parasites in humans and animals. Despite the fact that it has been detected in environment (water, sediment and soil), there is no information on its fate in the environment. So, in order to understand the sorption process of albendazole in environment, the sorption mechanism and kinetic properties were investigated through sorption equilibrium and sorption rate experiments. For that purpose, batch sorption of albendazole on five sediment samples and five soil samples from Croatia's region with different physico-chemical properties was investigated. Except physico-chemical properties of used environmental solid samples, the effects of various parameters such as contact time, initial concentration, ionic strength and pH on the albendazole sorption were studied. The K_d parameter from linear sorption model was determined by linear regression analysis, while the Freundlich and Langmuir sorption models were applied to describe the equilibrium isotherms. The estimated K_d values varied from 29.438 to 104.43 mLg^{-1} at 0.01 M $CaCl_2$ and for natural pH value of albendazole solution (pH 6.6). Experimental data showed that the best agreement was obtained with the linear model ($R^2 > 0.99$), while the rate of albendazole sorption is the best described with the kinetic model of pseudo-second-order. Obtained results point to a medium or even strong sorption of albendazole for soil or sediment particles, which is particularly dependent on the proportion of organic matter, pH, copper and zinc in them.

1. Introduction

Pharmaceuticals represent a major class of pollutants with high usage and consumption worldwide. Although the effects of pharmaceuticals have already been identified as an emerging problem in environmental chemistry (Vazquez-Roiga et al., 2010), the potential environmental impacts of their production and use are only slightly understood and have recently become a topic of research interest (Ferreira da Silva et al., 2011). Veterinary pharmaceuticals

* Corresponding author.
E-mail address: dmutavdz@fkit.hr (D. Mutavdžić Pavlović).

https://doi.org/10.1016/j.chemosphere.2017.11.025

(VPs) are administered to livestock to treat disease and maintain herd health. After administration, the metabolites or the parent VP compounds are excreted into the environment via urine and feces, either in an unchanged form or in a microbiologically inactive form. VPs can be released into the environment either directly through treatment of animals in pasture or indirectly through slurry and manure spreading (Boxall et al., 2002; Figueroa et al., 2004). Anthelmintics, especially benzimidazole anthelmintics, have recently caught attention due to their high production and potential adverse effects. Anthelmintics, in general, are drugs that act against helminthic infections (caused by parasitic worms) and they are administrated to a wide range of animals in agriculture and aquaculture, so they comprise a large sector of pharmaceutical industry (McKellar and Jackson, 2004). After their use for intended purpose, once released in the environment, these pollutants are transported and distributed in soil, sediment and most of all water, as an unchanged compound or in the form of degradation products which are often very difficult to remove (Vasudevan et al., 2009). The ecological consequences, including the ecotoxicology of these compounds, of their release into environment are not well characterized (Jones et al., 2004). Because of that, Oh et al. (2006) evaluated aquatic toxicities of six benzimidazoles with a freshwater invertebrate, *Daphnia magna* and a marine bacterium, *Vibrio fischeri*. Results reflected the differences in species sensitivity and suggested lower bioavailability of investigated benzimidazoles. Benzimidazole that was the most toxic to the daphnids was fenbendazole (48-h median effective concentration (EC50), 16.5 μg/L), whereas albendazole (48-h EC50, 67.9 μg/L) was the third most harmful of the six investigated benzimidazoles. Escher et al. (2008) reported the baseline toxicity of albendazole and morantel, and concluded that they do not pose a hazard to the aquatic environment.

Sorption is one of the dominant processes among various physical, chemical and biological processes affecting transport of chemicals to surface water and groundwater and determining the fate of VPs in the environment (Schwarzenbach et al., 2003). Sorption behaviour of pharmaceuticals is controlled by their physico-chemical properties (water solubility, K_d, K_{oc}, K_{ow}, pK_a), the type of solid matrices (content of organic matter and soil minerals, CEC, pH, and ionic strength), and environmental conditions (pH, temperature) (Srinivasan et al., 2014; Kong et al., 2012; Bui and Choi, 2010). Pharmaceutical fate and transport in the natural environment is represented with the solid/water distribution coefficient, K_d, because sorption on solid samples influences the distribution of substances between an aqueous phase and solid surfaces (Schaffer et al., 2012; Bui and Choi, 2010). The compounds with poor sorption properties have a high mobility in soil and represent a potential risk for groundwater contamination when treated wastewater is used for irrigation. Relatively strong or moderate sorption indicates that compounds would have reduced mobility in soil and hence a decreased risk for leaching into the aquifer phase (Lin and Gan, 2011). The degree of sorption to soil materials and aquatic sediments vary for different pharmaceuticals, e.g. for sulfonamides from 0.6 to 4.9, for tetracyclines from 290 to 1620 and for fluoroquinolones from 310 to 6310. These variations are not only the consequence of the content of soil organic matter, which has been considered in most cases (Thiele-Bruhn, 2003). Accumulation of pharmaceuticals in solid matrices is also firmly governed by the ionization properties of pharmaceuticals whose pK_a values are within an environmentally significant pH range (Hörsing et al., 2011). The large range in reported K_d values is also the result of differences in pedo-climatic conditions, rainfall pattern and spatial variability of soils including carbon content, mineralogical characteristics and soil pH.

Benzimidazoles are not readily degraded in the environment (Kreuzig et al., 2007), so their sorption to soil and sediment is very important in assessing their predicted environmental concentration in the environmental risk assessment. However, K_d value is determined only for a very small number of anthelmintics (Supplementary information, Table S1). The mobility fate of flubendazole and fenbendazole was evaluated in soil (Kreuzig et al., 2007) and, based on their relatively high soil/water distribution coefficient, it was conducted that their leaching into groundwater was unlikely despite their refractory nature in soil.

Albendazole (ALBA) is a broad-spectrum activity anthelmintic, of the benzimidazole group, which is used to remove the parasite from the host. It interferes with the normal metabolism of the parasite and selectively prevents incorporation of glucose during its development (Vardanyan and Hruby, 2006; Nogrady and Weaver, 2005). Albendazole can end up in the soil via animal excretion or in water after inadequate treatment of wastewater from its production. It is still unknown what happens with albendazole in soil, water, or sediment-water ecosystem, and which mechanism of its elimination is worse for the environment.

Unlike the evaluation of ecotoxicity, sorption phenomena in aqueous and soil environments have rarely been investigated for benzimidazoles (and anthelmintics in general) and K_d of albendazole is unknown. The only study carried out on albendazole (according to available information) and other benzimidazoles is the determination of sorption coefficients on various dissolved organic matter surrogates and sewage sludge. That study (Kim et al., 2010) has established that albendazole, together with fenbendazole, has higher sorption coefficients than other benzimidazoles and that there is no significant difference in the obtained sorption coefficients between hydrophilic and hydrophobic organic matter. Obtained results suggested that specific hydrophilic interactions also play a significant role in the sorption of benzimidazole.

The goal of this study was to experimentally determine the K_d values of albendazole on five soil and five river sediments collected from Croatian territory as a function of soil/sediment properties: texture (% sand, silt and clay), pH, organic matter content (OM), electrical conductivity (EC), cation exchange capacity (CEC), calcium carbonate content and the content of affordable microelements (Cu, Fe, Zn and Mn). The influence of ionic strength and pH on sorption was also determined. Sorption is described by three models: the Linear isotherm (K_d) (Pereira Leal et al., 2013; Białk-Bielińska et al., 2012), Freundlich and Langmuir isotherms (Kim et al., 2012). Obtained K_d values were used to estimate the thermodynamic parameters, such as Gibbs free energy (ΔG°) at 25 °C, for the sorption of ALBA onto soil and sediment samples. The sorption data were analysed using three different kinetic models: Lagergren's pseudo first-order, pseudo-second-order and intraparticle diffusion model (IPD). In addition to the kinetics of sorption, desorption kinetics were also investigated to see if ALBA is reversibly or irreversibly sorbed on the investigated soil or sediment sample. Both sorption and desorption processes are very important and could affect the behaviour of a chemical in the environment. So, this study will be of significance for understanding the migration pattern of albendazole in environment, getting insight into the role of soil and sediment in albendazole transport in aquatic systems and will contribute to the environment protection and pollution control.

2. Materials and methods

2.1. Materials

The studied pharmaceutical albendazole (ALBA) of high purity (>99%) was obtained from Genera d.d. (Kalinovica, Croatia). Table 1 shows structural formula of ALBA and its physico-chemical