



Adsorption behavior of 17 α -ethynylestradiol onto soils followed by fluorescence spectral deconvolution

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ABSTRACT

In this study, a simple and rapid procedure for monitoring adsorption of 17 α -ethynylestradiol (EE2) onto soil samples was developed. The used method is based on a multiwavelength fluorescence spectral deconvolution (FSD) where the emission fluorescence spectrum of a sample is considered as a linear combination of emission spectra, named reference spectra. The combination of the reference spectra allows the restitution of the shape of the emission spectrum of any unknown sample. This approach was applied to follow EE2 adsorption onto four soil samples and is an easy and low cost alternative.

Adsorption experimental data showed a good fit with the Hill equation, mathematically equivalent to the Langmuir–Freundlich model assuming that the adsorption is a cooperative process influenced by adsorbate–adsorbate interactions. Molecular modelling studies clearly support the “co-operative adsorption” model, showing that after the adsorption of the first layer of EE2 molecules onto the soil, at least one more layer of EE2 is adsorbed, due to interactions established with the first adsorbed layer. Notwithstanding, packing a third row would imply interactions between two EE2 molecules that differ from the ones verified in the lowest energy structure, which also explains the plateau achieved in the adsorption curve.

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1. Introduction

The concern about Endocrine Disrupting Chemicals (EDCs) effects on environment has generated worldwide interest (Emmerik et al., 2003; Robinson and Hellou, 2009; Feng et al., 2010). EDCs have been defined as “exogenous agents that interfere with the production, release, transport, metabolism, binding, action, or elimination of the natural hormones in the body [of a human and/or wildlife species] responsible for the maintenance of homeostasis and the regulation of development process” (Lee et al., 2003). Natural estrogens, such as estrone (E1), estradiol (E2) and Estriol (E3) are biologically active steroid hormones mainly released by humans (e.g. human urine and feces) and also by livestock (e.g. animal manure) and wildlife (Yu et al., 2004; Fan et al., 2007; Feng et al., 2010). EE2 (17 α -ethynylestradiol) is a synthetic chemical used for birth control and medical treatments of cancer, hormonal imbalance, osteoporosis, and other ailments (Yu et al., 2004), is usually released from conjugated glucuronides or sulphate complexes present in urine (Feng et al., 2010) and has an estrogenic potency about ten times that of natural hormones (Stumpe and Marschner, 2009). The knowledge about interactions between

EDCs and soil/sediment components is limited since the potential threat of these compounds was only recognized recently (Emmerik et al., 2003). After being released into the environment, adsorption to natural solids is an important process that affects transport, degradation, biological activity and fate of EDCs (Pignatello and Xing, 1996; Fan et al., 2007; Sun et al., 2007). Several studies have shown that estrogens tend to quickly sorb onto soils or sediments, potentially limiting the mobility and transport of estrogens from soils to aquatic ecosystems where they seem to cause more damage (Hildebrand et al., 2006).

The most common method for direct measurement of the adsorption coefficient of an organic molecule, such as EE2, in soils is batch experiments. The main advantage of this method is the possibility to separate soil and solution, obtaining a large volume of solution for analysis. Also, the method can be easily used for routine laboratory following the OECD Guideline TG 106 (2000). The two most common analytical techniques to follow the adsorption studies are High Performance Liquid Chromatography (HPLC) (Emmerik et al., 2003; Lee et al., 2003; Yu et al., 2004; Sun et al., 2007; Sarmah et al., 2008; Robinson and Hellou, 2009; Feng et al., 2010) and Liquid Scintillation Counting (LSC) (Fan et al., 2007; Stumpe and Marschner, 2007, 2009, 2010; Caron et al., 2010). LSC requires an appropriate apparatus to read radioactivity as well as radiolabeled chemicals that are rather expensive. HPLC requires a long sample preparation due to clean-up procedures

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performed before analysis in order to remove interferents, such as organic matter, from solution (Lima et al., 2010). The need of a clean-up procedure before HPLC analysis becomes clear in the work of Sun et al. (2007) that used solid phase extraction before the analysis and Sarmah et al. (2008) that used liquid–liquid extraction. These methods are rather expensive or time consuming and the development of a faster, easier and less expensive technique, to follow adsorption phenomena, seems to be a requirement. UV spectral deconvolution (UVSD) is a multiwavelength deterministic or semi-deterministic procedure with UV spectrum exploitation based on the fact that the UV spectrum of a sample is a linear combination of pre-selected representative absorption spectra (called reference spectra) and that the combination of the pre-defined reference spectra allows the restitution of the UV spectrum of any unknown sample (Lima et al., 2010). This approach was applied by the authors (Lima et al., 2010) to follow atrazine sorption onto soils and seems to be an easy and low cost alternative to follow EE2 adsorption onto soils using the same principle. The aim of this work was to develop a simple, fast and low cost methodology to follow adsorption of EE2 onto soils based on the principle of spectral deconvolution and also to elucidate the adsorption behaviour of EE2 molecules onto soil particles.

2. Materials and methods

2.1. Principle of fluorescence spectral deconvolution

Initially, UVSD was tested for EE2; however, the obtained residuals plot and the recovery tests performed (based on a previous work of the authors (Lima et al., 2010)) were not satisfactory. These first findings are probably explained by the low UV light absorbance that characterizes these compounds. Due to the high fluorescence capacity of these compounds it was decided to test the same spectral deconvolution principle, but using EE2 fluorescence emission spectra.

The principle of FSD approach is a multiwavelength based on a procedure of matrix algebra where each emission spectrum corresponds to a linear combination of a small number p of reference spectra (Lima et al., 2010). In the model, the coefficients a_i of the linear combination are calculated by solving a system based on the following relation established for each wavelength:

$$S_s = \sum_{i=1}^p a_i \text{REF}_i(\lambda) \pm r$$

where S_s is the sample emission fluorescence, $\text{REF}_i(\lambda)$ is the emission fluorescence of the i th REF at each wavelength λ , a_i the contribution coefficient of the i th REF in the linear combination, p the number of reference spectra and r is the error of restitution at each λ (Coulomb et al., 2006; Hassouna et al., 2007; Nam et al., 2008).

The associated contribution coefficients (a_i) of each reference spectra in the linear combination, the standard deviation of the calculation and also the deconvolution residuals can be calculated using the simple and commonly used Excel program (Lima et al., 2010).

2.2. Soil sample

Soil samples (0–30 cm) were collected 30 months after the last application of the organic fertilizers, from a long-term field experiment which was established in 1962, at the experimental farm of INRES – Institute of Plant Nutrition, University of Bonn, Germany, on a luvisol derived from loess (17.8% clay, 67.3% silt, 5.9% sand), following a cereal-root crop sequence (Scherer et al., 2003). The treatments selected for the present investigation were sewage sludge from municipal wastewater treatment facilities

(14.88 t ha⁻¹) (SLU), farmyard manure (9 t ha⁻¹) (FYM), compost from organic household waste (58 t ha⁻¹) (COM), and mineral fertilizer (MIN). These amounts (given on a dry weight basis) were applied every second year until 1997, then the amounts were changed to 10 t ha⁻¹ sewage sludge and 90 t ha⁻¹ compost once in 3 years, while the application rates of FYM and mineral fertilizer were kept on the same level. The soil's organic carbon content was 1.98% for sewage sludge, 1.47% for farmyard manure, 2.78% for compost and 1.24% for mineral soil and pH ranged from 6.1 and 7.1. Soil samples were air-dried and passed through a sieve, mesh size 2 mm.

The raw soil water extract containing 0.01 M CaCl₂ was prepared by adding 12.5 mL of 0.01 M CaCl₂ solution to 250 mg of soil and shaking them in a head over head shaker at 100 rpm for 15 h at 22 ± 1 °C. The mixture was then centrifuged at 1680g for 5 min and the supernatant filtered with a 0.22 μm pore resulting in the raw soil water extract referred.

2.3. Apparatus and reagents

The fluorescence spectra were obtained using the Spectrofluorometer Fluoromax-4 (Horiba Jobin Yvon).

Dissolved organic carbon (DOC) was determined using the Total organic carbon Analyser TOC-V_{CPH} from SHIMADZU.

All reagents were of analytical grade and all working solutions were prepared in ultra-pure water, obtained from a Milli-Q Millipore (Millipore Q plus 185) system. A stock standard solution of EE2 (98%, Sigma) was prepared in methanol and standard solutions were prepared by diluting this stock solution with 0.01 M CaCl₂.

2.4. Fluorescence spectra acquisition

The fluorescence spectra were obtained using an excitation wavelength of 280 nm and emission spectra were recorded between 295 and 350 nm. Excitation and emission slits were maintained at 5 nm.

For fluorescence intensities measurements, standard solutions with concentrations ranging from 0.4 to 4 mg L⁻¹, were prepared in the raw soil water extract containing 0.01 M CaCl₂. Fluorescence reference emission spectra (REF₁, REF₂, REF₃) were registered for the raw soil water extract, for the 0.01 M calcium chloride and for an EE2 solution in 0.01 M CaCl₂. Dissolved organic carbon (DOC) values of soil extracts (soil/solution ratio 1:50) were 6.4 ± 0.1 mg L⁻¹ for mineral soil, 10.82 ± 0.04 mg L⁻¹ for soil fertilized with compost from organic household waste, 6.71 ± 0.02 mg L⁻¹ for soil fertilized with sewage sludge from municipal wastewater treatment facilities and 6.79 ± 0.04 mg L⁻¹ for farmyard manure.

Ammonium hydroxide was added to standards, samples and reference solutions in order to obtain 0.1 M as final concentration and all of them were diluted 100 times prior to analysis, resulting in a calibration curve from 4 to 40 μg L⁻¹. Ammonium hydroxide was used to buffer the solution, as molecular fluorescence is pH dependent, improving the repeatability and to avoid the formation of aggregates of organic matter.

In order to evaluate the accuracy and precision of the deconvolution method, recovery tests with concentrations ranging from 4 to 40 μg L⁻¹ were made using samples spiked with EE2 and with or without soil organic extract in CaCl₂ 0.01 M. All experiments were made in triplicate.

2.5. Adsorption experiment

Selection of appropriate soil to solution ratio for adsorption studies depends on the distribution coefficient K_d and the relative degree of adsorption desired. Therefore, as a general practice, it is

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