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Behaviour of emerging contaminants in sewage sludge after anaerobic digestion

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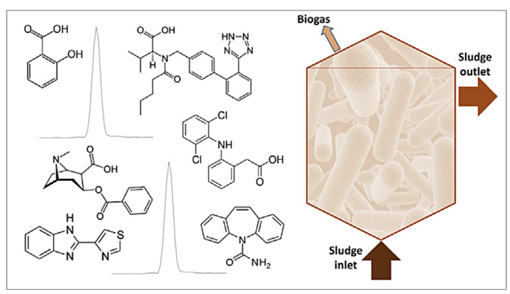
HIGHLIGHTS

- Anaerobic digestion of 13 emerging pollutants was studied in sewage sludge.
- Mesophilic and thermophilic anaerobic bacteria were tested.
- Concentrations of contaminants were evaluated in aqueous and solid phases of the sludge.
- Irbesartan and benzoylecgonine seemed to be degraded in both phases of the sludge.
- Concentrations in solid phase were commonly higher than in aqueous phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays, there is an increasing concern over the presence of contaminants in the aquatic environment, where they can be introduced from wastewater after their incomplete removal in the treatment plants. In this work, degradation of selected emerging pollutants in the aqueous and solid phases of sewage sludge has been investigated after anaerobic digestion using two different digesters: mesophilic and thermophilic. Initially, sludge samples were screened by ultra-high-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UHPLC-QTOF MS) for identification of emerging contaminants in the samples. In a second step, a target quantitative method based on LC coupled to tandem MS was applied for selected pollutants identified in the previous screening. The behaviour of the compounds under anaerobic conditions was studied estimating the degradation efficiency and distribution of compounds between both sludge phases. Irbesartan and benzoylecgonine seemed to be notably degraded in both phases of the sludge. Venlafaxine showed a significant concentration decrease in the aqueous phase in parallel to an increase in the solid phase. The majority of the compounds showed an increase of their concentrations in both phases after the digestion. Concentrations in the solid phase were commonly higher than in the aqueous for most contaminants, indicating that they were preferentially adsorbed onto the solid particles.

1. Introduction

Organic contaminants are receiving an increasing attention with

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respect to their environmental fate and toxicological properties (Evgenidou et al., 2015; Jelic et al., 2012; Petrie et al., 2014). Traditionally, research has been focused on the priority pollutants; however, in the last decade, there has been a clear trend towards the investigation of the so-called emerging contaminants. Emerging contaminants include compounds such as pharmaceuticals, veterinary drugs or drugs of abuse, that are not currently covered by existing water-quality regulations. The wide majority of these contaminants reach the environment after its consumption and excretion as unchanged compound or metabolites, and subsequent incomplete elimination in wastewater treatment plants (WWTPs) (Malmborg and Magnér, 2015). The low concentrations usually found for pharmaceuticals (typically at low ng/L levels) in treated waters are not expected to cause immediate adverse effects on human and on aquatic environment, but however not reliable data are currently available about long-term risk derived from their continuous input in the natural environment (Gracia-Lor et al., 2012; Petrovic et al., 2005). Until now, most of research has been focused on reporting concentration data for these contaminants in influent and effluent wastewater, but less attention has been paid to the sewage sludge (Gago-Ferrero et al., 2015).

Sewage sludge, also called biosolid, is the organic material resulting from the wastewater treatment plant. It is often reused in agricultural applications, principally as a fertilizer (Herrero et al., 2014; Li, 2014; Zhou et al., 2014). Although there is not current legislation on the use of biosolids on agricultural land with respect to the concentration of emerging contaminants (in part due to the scarce data reported on such analysis (Petrie et al., 2014)), it is important to perform effective removal to decrease, as much as possible, the potential risk to the environment and agriculture. In the biological treatment, bacteria degrade, metabolize or even mineralize, the dissolved and emulsified solid pollutants contained in municipal and/or industrial wastewater (De Sena et al., 2010). Anaerobic digestion (AD) has been extensively used and proven to be an efficient biological treatment to stabilize organic substrates in sewage (Zhou et al., 2014). The bacteria commonly present in anaerobic digestion can operate in different conditions of temperature: mesophilic, with working temperature ranges from 12 to 45 °C, the most efficient being 37 ± 2 °C; and thermophilic, which working conditions range from 37 to 65 °C, with an ideal temperature of 55 ± 2 °C (Malmborg and Magnér, 2015; Zhou et al., 2014). Thermophilic digestion uses to be more efficient than mesophilic, but requires more strict temperature control (Zhou et al., 2014). The investigation of the fate and behaviour of organic pollutants in WWTPs requires a previous knowledge on the presence and potential transformation of the compounds in both, liquid and solid phases, to identify whether the removal from the liquid phase is due to biological processes or sorption in the solid sludge phase (Topuz et al., 2014).

A few papers have been recently published dealing with the analysis of emerging compounds in both liquid and solid phases, although less information exists on the solid material due to the difficulty associated to the analytical measurements in these highly-complex matrices (Topuz et al., 2014). The most applied extraction technique for the aqueous phase is solid phase extraction (SPE) using different cartridges and conditions (Bijlsma et al., 2014; Diaz et al., 2013; Paíga et al., 2015). Regarding the solid phase of the sludge, the most frequent extraction procedures are based on Pressurized Liquid Extraction (PLE) (Benítez-Villalba et al., 2013; De Sena et al., 2010; Dorival-García et al., 2013; Masiá et al., 2015; Mastroianni et al., 2013; Ternes et al., 2005), the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) (Herrero et al., 2014; Masiá et al., 2015; Peysson and Vulliet, 2013) and UltraSonic Extraction (USE) (Benítez-Villalba et al., 2013; Dorival-García et al., 2013; Gago-Ferrero et al., 2015; Ternes et al., 2005; Topuz et al., 2014; Zhou et al., 2012).

The knowledge on the behaviour and distribution of emerging contaminants in sewage sludge can be only obtained from reliable concentration data in these matrices. Due to the complexity of the samples and the low concentration levels commonly present, it is necessary to apply advanced techniques to ensure quality data. Currently, the determination of pharmaceuticals, pesticides and illicit drugs in waters and sludge is mostly based on liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS), a robust, sensitive and well-established technique for quantification of these pollutants in different matrices (Bijlsma et al., 2009; Gago-Ferrero et al., 2015; Masiá et al., 2015; Mastroianni et al., 2013; Thomas et al., 2012). Moreover, High Resolution Mass Spectrometry (HRMS) (Bijlsma et al., 2013; Boix et al., 2014; Peysson and Vulliet, 2013; Wick et al., 2011) is an advanced analytical tool for both screening and identification/elucidation, thanks to the accurate-mass full-spectrum acquisition data provided by these analyzers, both in MS and MS/MS modes.

The goal of this work was to evaluate the behaviour and potential elimination of selected emerging contaminants after anaerobic digestion in a sewage sludge treatment system. For this purpose, anaerobic bacteria were used under two different conditions of temperature mesophilic and thermophilic. As sewage sludge contains both liquid and solid phases, the concentration levels and potential elimination of contaminants were evaluated in both matrices. In the first part of the study, a wide-scope screening using ultra-high-performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UHPLC-QTOF MS) was carried out in the sludge, in order to identify the emerging contaminants present in the sample. In a second step, a quantitative method based on HPLC-MS/MS with triple quadrupole was used for both sludge phases, in order to estimate the removal of 13 selected compounds. In addition, the analytic distribution in aqueous and solid phase of the sewage sludge was evaluated.

2. Methods

2.1. Reagents and chemicals

Reference compounds of 4-aminoantipyrine (4-AA), 4-acetyl aminoantipyrine (4-AAA), 4-formyl aminoantipyrine (4-FAA), thiabendazole, venlafaxine, carbamazepine, irbesartan, valsartan, diclofenac, salicylic acid, acesulfame and fenofibric acid were purchased from Sigma-Aldrich (St Louis, MO, USA), LGC Promochem (London, UK), Toronto Research Chemicals (Ontario, Canada), Across Organics (Geel, Belgium), Bayer Hispania (Barcelona, Spain), Fort Dodge Veterinaria (Gerona, Spain), Vetoquinol Industrial (Madrid, Spain) and Aventis Pharma (Madrid, Spain). The illicit drug studied was the main metabolite of cocaine, benzoylecgonine (BE), which was obtained from Cerilliant (Round Rock, TX, USA).

Isotopically-Labeled Internal Standards (ILIS) of diclofenac-d_4, valsartan-d_8, thiabendazole-d_6, venlafaxine-d_6, irbesartan-d_6 and salicylic acid-d_4 were obtained from CDN Isotopes (Quebec, Canada). Benzoylecgonine-d_3 was purchased from Cerilliant as solution in methanol at a concentration of 100 mg L^{-1}.

HPLC-grade methanol (MeOH), formic acid eluent additive for LC-MS (HCOOH, content>98%), sodium hydroxide (NaOH, >99%) and ammonium acetate (NH_4Ac, reagent grade) were purchased from Scharlab (Barcelona, Spain). Leucine enkephalin was purchased from Sigma Aldrich. HPLC-grade water was obtained from deionized water passed through a Milli-Q Gradient A10 (18.2 MΩ cm) water purification system (Millipore, Bedford, MA, USA).

Oasis HLB (200 mg) cartridges, used for solid-phase extraction, were purchased from Waters (Milford, MA, USA).