Removal of nonylphenol, pyrene and phenanthrene from sewage sludge and biosolids by cyclodextrins and rhamnolipids

F. Madrid*, M. Rubio-Bellido, J. Villaverde, E. Morillo


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*Presenting author e-mail: fmadrid@irnase.csic.es

After the progressive implementation of the EU Directives 91/271/EEC and 98/15/EEC concerning urban wastewater treatment, many countries have increased the number of wastewater treatment plants (WWTP), and large amounts of sewage sludge are generated which require disposal. A useful and interesting option is the production of compost and the direct application of stabilised sludge to land. It has positive effects on soil, such as modification of soil structure and addition of organic matter and nutrients for plants, but there are potential hazards in this practice, such as spread of pathogens, odours, heavy metals and persistent organic contaminants.

The use of sewage sludge in agriculture is regulated by the European Union’s Council Directive 86/278/EEC, but it has not yet established maximum values for organic contaminants. However, the third draft of a working document on sludge to revise this Directive (EC 2010), although not being a formal regulation, limits the values for some organic compounds, such as some PAHs and nonylphenols (maximum concentration limits 6 and 450 mg kg⁻¹ dry matter).

PAHs are formed and released into the environment as by-products of incomplete combustions through natural and man-made sources (Morillo et al. 2007). They are highly toxic, present high persistence in the environment, low biodegradability and high lipophilicity. PAHs enter to wastewater-treatment plants through the sewerage and are almost completely concentrated in sludge because of their poor solubility in water and high adsorption capacity on solid particles.

NP is a biotransformation product of nonylphenol ethoxylates (NPnEOs), an important group of non-ionic surfactants that are widely used in many commercial and household functions (detergents, cosmetic products, textiles). Due to its formation in sewer system, NP is commonly detected in influent wastewater of sewage treatment plants. NP causes estrogenic responses on aquatic organisms and it was listed as a priority substance in the Water Framework Directive (EU, 2001).

Different methods are being proposed to remove PAHs and NPs from contaminated sewage sludge. Among these techniques, biological ones, based on their degradation by microorganisms are considered cost effective and environmentally friendly. However, the sequestration of these compounds in the sludge matrix declines their bioavailability and reduces the biodegradation of the contaminants. The reduction of bioavailability can be avoided with the use of amendments that increase the solubility of the contaminants.

Recently, biogenic compounds as cyclodextrins (CDs) or biosurfactants (BSs) have been used in environmental applications, because they increase the solubility of hydrophobic organic contaminants (Morillo and Villaverde, 2017). CDs form inclusion complexes with a wide range of guest hydrophobic molecules, which are located in the interior cavity of the CDs. The hydrophilic properties of the outer zone of the CDs solubilize the resulting complex, increasing its bioavailability. CDs are formed by glucose monomers, so microorganisms could also use CDs as a biostimulant. Biosurfactants are also biodegradable compounds produced by bacteria or yeast, and also from plants and animals. Their amphiphilic properties reduce interfacial tension and increase solubility and bioavailability of hydrophobic compounds. Rhamnolipids (RLs) are a type of BSs synthesized by Pseudomonas aeruginosa. Due to their special hydrophilic and lipophilic moieties, RLs have enhanced PAH extractability from soils (Madrid et al., 2019).

The objective of this study was to evaluate the performance of several CDs and a RL on the removal of Pyrene, Phenanthrene and Nonylphenol from several sewage sludge samples from different WWTPs located in Sevilla (Spain) and from a composted sludge.

Materials and Methods

Three fresh sewage sludges and one composted biosolid were dried by freezing and liophilization. Dry samples were spiked separately with three contaminants usually found in sewage sludge, pyrene, phenanthrene or nonylphenol at a rate of 10, 10 and 500 mg kg⁻¹ respectively. These concentrations are above the legal limits proposed for these contaminants in sewage sludges or biosolids for agricultural applications. Contaminated fresh and composted biosolids were aged for 60 days, and samples were taken at 1, 15, 30 and 60 days for analysis.

Different extractant solutions were selected and compared to extractions with distilled water: β-cyclodextrin (BCD), hydroxy-propyl-β-cyclodextrin (HPBCD), randomly methylated-β-cyclodextrin (RAMEB), and rhamnolipid JBR-425 (RL, supplied by Jeneil Biosurfactant, USA). Concentration (50 mM) was...
selected according to Reid et al. (2000). Soil:solution ratio for the extraction was 1g:20 mL. Contaminant concentration in the extractants were determined by HPLC coupled with a fluorescence detector, using a C-18 column, 250 mm length, 4 mm diameter and acetonitrile:water 90:10 as mobile phase. Excitation/emission wavelengths were 270/390, 244/360 and 222/305 nm for pyrene, phenanthrene and nonylphenol respectively.

**Results and Discussion**

Figure 1 shows the percentages of the three contaminants extracted from the composted biosolid and one of the sludges (T), as a summary of the global results. Water extracted very low amounts of the three pollutants, whereas CDs and RL extractions were sample, pollutant and incubation-time dependent. BCD extracted usually similar contents as water. The extractions with the other CDs, HPBCD and RAMEB, were more effective than BCD. In the cases of phenanthrene and nonylphenol, extractable amounts were higher than 20% of the initial content in many occasions when using HPBCD and RAMEB, whereas pyrene showed lower results.

![Graph showing extraction percentages](image)

Figure 1. Percentage of the initial pyrene, phenanthrene or nonylphenol content extracted in compost and sludge T during the incubation.

RL showed the highest extractions for pyrene, with contents even higher than 80% at the beginning of the incubation of the sludge T, and usually pyrene extractions were higher than 60% in the time period studied. These spectacular results were not reached for phenanthrene and nonylphenol. When using RL, generally the extraction was higher than 40% for phenanthrene but lower for nonylphenol (about 20%).

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**References**


