Monitoring and behaviour of organic pollutants in sewage sludge after the anaerobic digestion process

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Abstract

Nowadays, there is a growing concern about the presence of contaminants in the aquatic environment that can be introduced by wastewater after its incomplete removal in wastewater treatment plants (WWTPs). In this work, the presence of the organic pollutants in sedimented Primary Sludge (PS) and the degradation efficiency in Digested Sludge (DS) after the anaerobic digestion were evaluated. Firstly, sludge samples were screened by gas-chromatography coupled to mass spectrometry (GC-MS) for the identification of pollutants present. Nonylphenol (NP), Nonylphenol Monoethoxylate (NP-1EO), Nonylphenol Diethoxylate (NP-2EO) and Diethyl Hexyl Phthalate (DEHP) were identified as the main contaminants. Subsequently, a quantitative method was applied for the pollutants identified in the previous screening, using calibration curves with certified standards. Most of the compounds analysed showed an increase in their concentrations as a result of anaerobic digestion, indicating that they were preferentially adsorbed on solid particles without being subjected to any degradation process. This underlines the need to use integrated processes to promote their degradation.

Introduction

Organic pollutants are receiving an increasing attention with respect to their toxicological properties and behaviour in the environment. They include compounds such as additives, plasticizers, pesticides and pharmaceuticals that are not currently covered by existing water-quality regulations. Most of these pollutants end up in the environment after consumption and incomplete elimination in wastewater treatment plants (WWTPs). Until now, research has mainly focused on monitoring these pollutants in influent and effluent wastewater, not paying attention to sewage sludge. Sewage sludge is the final residue resulting from the WWTPs from domestic, industrial or mixed settlements. One of the possible alternatives to landfilling is to use it as a soil improver for the benefit of agriculture. This practice, if properly implemented, would allow the recovery of the fertilizing value of the sludge (thanks to its mineral and organic content). On the other hand, it makes it possible to alleviate environmental problems and the cost of disposal, saving the use of synthetic fertilisers and soil improvers. For these reasons, the European Union has developed a sector-specific regulation promoting and supporting the use of sewage sludge in agriculture as an alternative to incineration or landfilling. Nevertheless, the use of sludge in agriculture also has some critical aspects due to the possible presence of harmful organic compounds, heavy metals, pathogenic organisms and microorganisms. Anaerobic digestion has been widely used and proven to be an effective biological treatment to stabilize organic substrates in sewage. However, due to the complexity of the samples and the low concentration levels commonly present, a detailed analysis protocol should be used to identify and quantify the organic pollutants that may be present before allowing their reuse. The aim of this work was to assess the behaviour and potential elimination of organic pollutants after anaerobic digestion in a sewage sludge treatment system. Primary Sludge and Digested Sludge obtained after the anaerobic digestion were screened by gas-chromatography coupled to mass spectrometry (GC-MS) for the identification of major organic pollutants present. Subsequently, a quantitative method was used for the quantification of the contaminants by the use of calibration curves with certified standards.

Materials and Methods

Sewage Sludge samples

Primary Sludge (PS) and Digested Sludge (DG) were up-taken from WWTPs of Bari Ovest (240.000 Population Equivalent, PE), located in southern Italy. Samples were treated immediately to prevent a long storage period (up to 48 h, 4 °C) and analyzed for the determination of the starting alkalinity, pH and total solids (TS) content. At the same time, the samples were dried at 40 °C for 72 h until to a constant weight was obtained, verifying that residual solids were equivalent to TS found at 105 °C. Finally, esterifiable lipids and ashes content were quantified, adopting the experimental procedures described by di Bitonto et al. (2020). The average chemical composition of sewage sludge samples is reported in Table 1.

Table 1. Chemical composition of PS and DG up-taken from the WWTP of Bari Ovest.

Samples	**TS (%wt)**	**pH**	**Alkalinity ($CaCO_3$ ppm)**	**Chemical composition (%wt$_{TS}$)**	
				Esterifiable Lipids	**Ashes**
PS	4.8 ± 0.2	6	7131 ± 125	16.5 ± 0.8	21.6 ± 0.6
DG	32.6 ± 0.6	7	38033 ± 423	2.7 ± 0.4	39.8 ± 0.4

Determination of organic pollutants

Organic pollutants were extracted from sewage sludge by using acetone as an extracting solvent. 2 g of dried (40 °C, 72 h) and homogenized sample were placed under stirring for 20 min at 30 °C with 10 mL of acetone and 1 g of Copper (Cu). The extract was separated by centrifugation, and the procedure was repeated two times. The extracts were combined, concentrated to an approximate volume of 1 mL under nitrogen flow and redissolved in 200 mL of milli-Q water. SPE method was used for cleanup and preconcentration of extracts (Petrovic´ and Barcelo´ (2000)). Finally, the sample were silanized and analyzed by GC-MS (Bitonto et al. (2021)). Identification and quantification of organic pollutants was conducted using a Perkin Elmer Clarus 500 gas-chromatograph interfaced with a Clarus 500 spectrometer. The instrument was configured for spitless injections (1 µL) using an HP-5MS capillary column (30 m; Ø 0.32 mm; 0.25 µm film). The column temperature was set as follows: 50°C for 3 min, then increased to 140 °C at a rate of 25 °C min^{-1} and finally at 320 °C at a rate of 25 °C min^{-1}. Helium was used as a carrier gas with a constant flow of 1 mL min^{-1}. The detector temperature was set to 280 °C. For the GC-MS, the ion source was operated at 70 eV and maintained at 250 °C during the analysis. The main list of m/z ions used for the identification and quantification of organic pollutants is shown in Table 2.

Table 2. Target organic contaminants and their main m/z ions after silanization process.

Organic pollutants	Retention time (min)	Ions (m/z)	
		Quantifier	Qualifiers
4n-Nonylphenol (4n-NP)	15.5	235	207
Nonylphenol (NP)	19.0	179	292
Nonylphenol Monoethoxylate (NP-1EO)	22.5	251	265
Penconazole	22.5	161	159, 248, 250
Carbamazepine	26.7	165	193
Diclofenac	27.2	214	242
Nonylphenol Diethoxylate (NP-2EO)	28.5	309	295, 323
Diethyl hexyl Phthalate (DEHP)	32.5	149	167
17α-Ethynylestradiol (EE2)	37.0	425	231, 440

Results and discussion

Analysis of organic pollutants for Primary and Digested Sludge

The analysis of the organic pollutants contained in the primary and digested sludge collected from WWTPs of Bari Ovest is reported in Table 3. From the analysis of data, Nonylphenol (NP), Nonylphenol Monoethoxylate (NP-1EO), Nonylphenol Dietoxylate (NP-2EO) and Diethyl Hexyl Phthalate (DEHP) have been identified as the main contaminants present. In addition, most of the pollutants analysed showed an increase in their concentration after the anaerobic digestion, indicating that they were preferentially adsorbed on solid particles without being subjected to any degradation process.

Table 3. Analysis of organic pollutants for PS and DG. LOD = 50 ppb.

Organic pollutants	Concentration dry sludge (ppm)	
	PS	DG
4n-Nonylphenol (4n-NP)	0.3	0.4
Nonylphenol (NP)	22.4 ± 0.1	27.2 ± 0.1
Nonylphenol Monoethoxylate (NP-1EO)	3.0	3.9
Penconazole	< LOD	< LOD
Carbamazepine	< LOD	< LOD
Diclofenac	< LOD	< LOD
Nonylphenol Diethoxylate (NP-2EO)	6.2 ± 0.1	8.6 ± 0.1
Diethyl hexyl Phthalate (DEHP)	53.6 ± 0.1	63.7 ± 0.1
17α-Ethynylestradiol (EE2)	< LOD	< LOD

Conclusions

In this work, the concentrations of the main organic pollutants were detected in the primary and digested sludge obtained from the $WWTP_S$ of Bari Ovest. Increasing their concentrations in digested sludge highlights that the anaerobic digestion is not sufficient to remove the contaminants present that remain adsorbed on the sludge surface. Further integrated processes will be developed to promote their degradation.

Acknowledges

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References

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