Solvent-free method for lipid extraction from sewage sludge: a dual and synergistic approach for reducing emerging pollutants

L. di Bitonto, V. Locaputo, C. Pastore

[1]Water Research Institute (IRSA), National Research Council (CNR), Bari, 70132, Italy
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Presenting author email: vito.locaputo@cnr.it

Abstract
This study investigates the synergistic effects of hydrochloric acid and hydrogen peroxide treatment in the extraction of lipid components from municipal wastewater while reducing the pollutant content. A detailed analysis of the main "emerging pollutants" in the samples collected during the process phases was carried out to determine the content of existing pollutants and the reduction rates due to the chemical treatment. After HCl/H_2O_2 treatment, a reduction of more than 70% was observed, highlighting the effectiveness of the treatment in promoting a more sustainable approach to waste management.

Introduction
The increasing scarcity of fossil fuels has prompted researchers to explore alternative renewable energy sources that are not intended for human consumption. In this context, municipal sewage sludge represents a sustainable and economical resource for the production of liquid fuels and oleochemicals through the extraction of the lipid component, which can be converted into biofuels. In addition, its use can promote technological innovation in the bioenergy sector and improve waste management, turning a problem into an opportunity. In a recent study, a novel solvent-free technology was developed to recover lipids from municipal sewage sludge (Bitonto *et al.*, 2024). Specifically, sedimented sewage sludge was dewatered by centrifugation, acidified, treated with hydrogen peroxide at 80 °C and then centrifuged again to extract the lipid fraction. The combined use of HCl and H_2O_2 allowed more than 70 % of the lipids present to be recovered, which also resulted in additional thickening of the final residual sludge (TS > 30%) without the need for polyelectrolytes or additional treatments (e.g. anaerobic digestion). However, despite the considerable reduction in the amount of sludge to be disposed of, the residual sludge needs to be destined for new applications. One of the main problems associated with the use of sewage sludge in agriculture is the presence of "emerging pollutants", natural or artificial compounds of various origins (e.g. plasticizers, additives, pharmaceuticals), which can be harmful to the environment and human health. In this work, the effect of the addition of HCl and H_2O_2, which are necessary to promote the solvent-free recovery of grease, on the degradation of emerging pollutants in municipal sewage sludge was investigated. The composition of the sewage sludge before and after chemical treatment was compared to evaluate the reduction of pollutants and to estimate the efficiency of the process to facilitate its application in other industrial contexts.

Materials and methods
Sewage sludge samples
Centrifuged primary sludge, sewage sludge treated with HCl and H_2O_2 and the residual sludge obtained at the end of lipid extraction were collected in the pilot plant for the recovery of lipids from municipal sewage sludge of Bari West. The samples were dried at 40 °C and immediately processed for the analysis.

Determination of emerging pollutants
1 g of dried and homogenized dry sample was added to a 20 mL Pyrex glass reactor containing 10 mL of acetone and 2 g copper (Cu). The system was sealed and stirred at 30 °C for 20 min. At the end of the process, the extract was separated by centrifugation, and this procedure was repeated twice. The extracts were collected and concentrated to 1 mL under nitrogen flow and then redissolved in 200 mL of Milli-Q water. The solid phase extraction method (SPE) was used to purify and enrich the extracts (Nie et *al.*, 2009). Samples were then silanized and analyzed by GC-MS using a Shimadzu Nexis gas chromatograph interfaced with a QP2020 NX spectrometer (Bitonto *et al.*, 2021). 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 to 320 °C at a rate of 25 °C min^{-1}. Helium was used as the carrier gas at a constant flow of 1 mL min^{-1}. The ion source was operated at 70 eV and kept at 250 °C during the analysis. The main list of m/z ions used for the identification and quantification of the main emerging pollutants detected is shown in Table 1.

Table 1. Emerging pollutants and their main m/z ions after the silanization operation.

Emerging pollutants	Retention time (min)	Ions (m/z)	
		Quantifier	Qualifiers
Nonylphenol (NP)	19.0	179	292
Nonylphenol Monoethoxylate (NP-1EO)	22.5	251	265
Nonylphenol Diethoxylate (NP-2EO)	28.5	309	295, 323
Diethyl hexyl Phthalate (DEHP)	32.5	149	167
Bisphenol A (BPA)	25.4	357	372, 191
Ibuprofen	12.6	160	263, 278
Naproxen	22.5	185	243, 302
Diclofenac	27.2	214	242

Analysis of results

Effect of chemical treatment with HCl/H_2O_2 on the reduction of emerging pollutants

Table 1 shows the list of the main pollutants found and analyzed in the centrifuged sludge and in the sewage sludge after chemical treatment with HCl and H_2O_2. Nonylphenol (NP), Nonylphenol Monoethoxylate (NP-1EO), Nonylphenol Diethoxylate (NP-2EO) and Diethylhexyl Phthalate (DEHP) were identified as the main contaminants. In addition, bisphenol A (BPA), Ibuprofen, Naproxen and Diclofenac were also detected (0.1-0.7 ppm), with the specific amounts as reported in Table 2.

Table 2. Analysis of pollutants for centrifuged sludge and sludge after chemical treatment with HCl and H_2O_2. LOD = 50 ppb.

Emerging pollutants	Dried solids (ppm)	
	Centrifuged Sludge	Sludge after treatment with HCl/H_2O_2
Nonylphenol (NP)	6.1 ± 1.7	6.6 ± 1.5
Nonylphenol Monoethoxylate (NP-1EO)	1.7 ± 0.9	1.9 ± 1.1
Nonylphenol Diethoxylate (NP-2EO)	2.9 ± 1.4	1.3 ± 0.6
Diethyl hexyl Phthalate (DEHP)	18.4 ± 3.0	7.4 ± 3.2
Bisphenol A (BPA)	0.2	< LOD
Ibuprofen	0.1	< LOD
Naproxen	0.2	< LOD
Diclofenac	0.7	0.2

After the chemical treatment with HCl and H_2O_2, a significant reduction of the pollutants was observed, corresponding to a degradation of 0.36, 2.39, 0.04, 0.02, 0.04 and 0.10 g per ton of treated centrifuged sludge of NP-2EO, DEHP, BPA, Ibuprofen, Naproxen and Diclofenac, respectively. In addition, this chemical treatment facilitated the desorption of the remaining contaminants from the surface of the sludge so that they could be easily removed in the subsequent centrifugation phase after the extraction of the lipid component (Bitonto *et al.*, 2024). The concentration of emerging contaminants in the residual sludge was found to be significantly reduced compared to the initial content present in the centrifuged wet sludge.

Conclusions

The combined use of HCl and H_2O_2 to recover lipids from sewage sludge has proven to be a promising approach that not only enables the recovery of lipids for biofuel production but also reduces the level of organic pollutants in the sewage sludge itself, thereby improving environmental safety and human health benefits. The dual benefit of biofuel production and pollutant reduction in the residues underlines the potential of this technology as a sustainable solution for urban sewage sludge management and resource recovery.

Acknowledges

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