Green Extraction of Lipids from Sewage sludge: Towards Efficient Production of Sustainable Biolubricants

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Keywords: Sewage sludge; Lipid extraction; Ethyl hexanoate; Calcium soaps.

Introduction

Sewage sludge, a by-product of wastewater treatment, poses significant challenges due to its massive production volume, also destined to increase in the next future (Di Giacomo and Romano, 2022), and to its potential environmental hazards (Yakamercan et al., 2021). However, within this challenging waste lies potential for resource recovery and biorefinery applications. Harnessing these compounds not only offers a sustainable solution for managing sewage sludge but also contributes to the development of a circular economy by recovering/producing from this waste valuable products with diverse industrial applications. Primary sewage sludge is rich in lipid components, mainly fatty acids and calcium soaps, which can make up to 28 wt.% of the sludge's dry matter (di Bitonto et al. 2020; D'Ambrosio et al. 2021). Extracting these lipids from primary sewage sludge requires careful consideration of various parameters to maximize extraction yields. In this work, a sustainable approach for the recovery of lipids from primary sewage sludge, namely batch extraction using ethyl hexanoate, a bioderivabile and biodegradable solvent (D'Ambrosio et al., 2023) was investigated. Various sewage sludge pre-treatments (including dewatering and acidification) and extraction parameters (such as extraction time, temperature, and stirring mode) were systematically investigated to determine optimal conditions for achieving high lipid recoverability.

Material and Methods

Sewage sludge characterization

Primary Sludge (PS) was sampled from the Wastewater Treatment Plant (WWTP) of Lecce (Puglia, Italy, 120000 population equivalent) and characterized in terms of total solids (TS), volatile solids, ashes, and esterifiable lipids. In detail, esterifiable lipids were expressed as FAMEs content (wt.% with respect to TS) obtained after a methanolysis of the dry primary sludge. The methanolysis was carried out at 105 °C, overnight, under stirring, and at the end of the reaction an aliquot of the supernatant was injected into the GC-FID, determining FAMEs content.

Liquid-Liquid ethyl hexanoate batch extraction

Liquid-liquid extractions using ethyl hexanoate were carried out considering 20 g of dewatered primary sewage sludge (TS: 18.7 wt.%) and 20 g of ethyl hexanoate and performing the extraction for 1-4 h, at 25 °C or 70 °C. Esterifiable lipids recoverability from the sludge was expressed as follows:

$$\text{Esterifiable lipids recoverability (\%)}: \frac{F_{ex} \cdot E}{F_{tot}} \qquad \text{(Eq. 1)}$$

Where F_{ex} is the FAMEs content evaluated in the extract (wt.%), E is the extraction yield (wt.%) and F_{tot} is the FAMEs content evaluated in the dry sludge (wt.%). The extraction tests were performed in triplicate, and for each result, a standard deviation within 5% of the related value was determined.

Results and discussion

A complete lipids recoverability was achieved with the ethyl hexanoate batch extraction conducted on a dewatered primary sludge (TS: 18.7% wt) at 70 °C for 3 h, under magnetic stirring. In this case, extracted lipids consisted of insoluble calcium soaps (48.9%), which passed into the ethyl hexanoate phase as a fine suspension, and soluble lipids (51.1%), mainly composed of free fatty acids. Considering the possible direct industrial application of calcium soaps, including their use as solid lubricants and thickening agent in grease lubricants (Amrina et al., 2023; Sarma and Vinu, 2022), also fatty acids were converted into calcium soaps, by adding a stoichiometric amount of $Ca(OH)_2$ to the ethyl

hexanoate phase, observing their immediate precipitation as calcium soaps. Thus, a complete and cost-effective recovery of esterifiable lipids in the form of calcium soaps was achieved without the need for distillation of ethyl hexanoate, which can be directly reused for subsequent extraction cycles. Regarding the recoverability of ethyl hexanoate from the dewatered sludge, it was estimated to be 91.8% wt and could be potentially further improved by employing a high-performance centrifuge or distilling the residual sludge.

Conclusion

In conclusion, liquid-liquid ethyl hexanoate batch extraction proved highly effective in recovering esterifiable lipids from primary sewage sludge. Esterifiable lipids were completely recovered from the sludge in the form of insoluble calcium soaps, which can serve as solid lubricants or as thickening agent in grease lubricants. A low-energy process was proposed, including a single extraction cycle performed at 70 °C for 3 h, neutralization of fatty acids through $Ca(OH)_2$ for obtaining insoluble calcium soaps and an easy and complete recovery of calcium soaps though a simple phase separation. The positive outcomes achieved, together with the potential to further enhance ethyl hexanoate recoverability from the exhausted sludge, are promising indicators for the actual feasibility of the proposed extraction process.

Acknowledgments

This work was financially supported by the LIFE Programme of the European Union LIFE20 ENV/IT/000452.

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