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Efficient extraction of lipids from primary sewage sludge using ionic liquids for biodiesel production

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A B S T R A C T

This study proposes a novel method to extract lipids from wet primary sludge for biodiesel production using ionic liquids. Tetrakis(hydroxymethyl)phosphonium chloride and widely used 1-butyl-3-methylimidazolium methyl sulfate were evaluated to extract lipids from raw and dried sludge (96% and 2%, wt. water content, respectively) and compared to the conventional Soxhlet method using organic solvents. Both these ionic liquids showed suitability for lipid extraction from raw sludge, giving even better results than expected from dried sludge. The $[C_4mim][MeSO_4]$ ionic liquid reached 18.5% and 26.9% of lipids, 14.1% and 18.4% of biodiesel from dried and raw sludge, respectively. The $[P(CH_2OH)_4]Cl$ ionic liquid gained 23.4% and 27.6% of lipids, 17.0% and 19.8% of biodiesel from dried and raw sludge respectively, reaching comparable results to the conventional Soxhlet method (27.2% of lipids, 19.4% of biodiesel). Therefore, the proposed ionic liquid process is efficient in lipid extraction directly from wet primary sludge, eliminating the expensive step of sludge drying and the use of volatile organic solvents. Under the optimised extraction conditions using $[P(CH_2OH)_4]Cl$ ionic liquid and raw sludge (1:5 sludge (g/TS):IL (cm^3) ratio, 100 °C and 3 h), the obtained yield of lipids and biodiesel amounted to 25.7% and 21.1%, respectively. Additionally, lipid extraction using $[P(CH_2OH)_4]Cl$ ionic liquid also precipitates cellulosic material, which allows for direct and easy cellulose-based co-product recovery, giving high additional value to the process. Consequently, the economic and environmental aspects of biodiesel production from sewage sludge could be improved.

1. Introduction

The energy demand from fossil fuels for transportation has been increasing during the last few years, and it will be the strongest growing energy demand sector in the future. However, the expected depletion of fossil fuels and the environmental problems associated with their combustion limit their utilisation in the future [1]. Therefore, the necessity of using alternative renewable fuels, with no environmental impact, is currently increasing. Biodiesel is one of the most promising renewable fuels in road transport, proposed as an alternative to fossil diesel. However, the competitive potential of biodiesel is currently limited by the high price of common lipid feedstocks, which constitutes between 70% and 85% of the overall biodiesel production cost, furthermore the cultivation of edible vegetable oils for biofuels raises the concerns of food shortage, which competes with fuel production [1,2]

Nowadays, due to a considerable amount of lipids, municipal wastewater sludge has been receiving progressive attention as a promising non-edible lipid feedstock for biodiesel production [2–9]. In fact, sewage sludge is a waste that needs specific treatment before disposal and represents a major cost in a wastewater treatment plant (WWTP) operation. Therefore, the sewage sludge can be envisaged as a relatively cheap, readily available and non-edible feedstock, which can make biodiesel production profitable. Furthermore, the use of sludge as a source of lipid for biodiesel production is also an alternative to exploit the excess of waste sludge.

Nevertheless, the main challenge to be faced by biodiesel production from waste sludge is the efficiency of lipid extraction from water, which can reach up to 95–98 wt%, as dewatering and drying constitutes more than 50% of the total biodiesel production cost [2,3]. Thus, the cost of energy necessary to eliminate the water, before lipid extraction, is a main limitation for scaling up. Despite

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this fact, the published data so far have reported only on the utilisation of dried or dewatered sludge in lipid extraction or *in situ* transesterification using organic solvents [2–7,9–11]. Solely, one previous study demonstrated the feasibility of lipid extraction from raw sludge (~96% of water) by direct liquid–liquid extraction using hexane as a solvent [8]. On the other hand, health, security, and regulatory problems related to the use of volatile organic solvents are also very important issues.

In recent years, ionic liquids (ILs) have attracted significant attention for their use as green replacements for harmful volatile organic solvents due to their non-volatile character, excellent chemical and thermal stability, potential recoverability, and design possibilities [12,13]. The use of ionic liquids for lipid extraction from dry biomass has been successfully studied [14–18]. In addition, the application of ionic liquids to extract lipids from wet biomass has been also noted [14,19]. It was suggested that direct dissolution of wet biomass by ionic liquids could lead to the recuperation of all organic components due to the dissolution of hard cell walls composed mainly by cellulose [19,20]. Hence, the rôle of ionic liquids in the lipid extraction is not only to replace organic solvents, but also the ability to dissolve wet biomass and thereby the possibility to recover other valuable components such as proteins and polysaccharides as cellulose. As municipal primary sludge, apart from lipids, contains proteins and high amount of cellulose, mainly from waste toilet paper [21–23], the recovery of all valuable materials will give added value to the process.

All of the studies about lipid extraction by ionic liquids which are listed above focused on the microalgae biomass and the utilisation of imidazolium-based ionic liquids. The high cost of imidazolium-based ionic liquids [15,24] could limit their availability and suitability for this purpose. On the other hand, phosphonium-based ionic liquid was recently used to extract lipids from microalgae, *Chlorella vulgaris* and *Nannochloropsis oculata* [25]. Furthermore, phosphonium-based ionic liquids offer the advantage of commercial availability (manufactured on a multi-ton scale) and low prices [24]. Nevertheless, the application of ionic liquids for the lipid extraction from sewage sludge as well as the use of phosphonium-based ionic liquids for this purpose have not yet been reported in literature.

Therefore, the aim of this study was to investigate for the first time the feasibility of ionic liquids to extract lipids from wet primary sewage sludge as a green and potentially energy saving system for the production of biodiesel. The comparison of performance between phosphonium and widely used imidazolium ionic liquids was evaluated and compared to the conventional Soxhlet method. The lipid extraction from wet (raw) sludge was evaluated and compared with that from dried sludge, in order to decide on the most economically favourable process. Additionally, the recovery of other valuable components from primary sludge (cellulose and proteins) was also investigated.

2. Materials and methods

2.1. Reagents

Ionic liquids, 1-butyl-3-methylimidazolium methyl sulfate (>95% purity, 1.21 g cm^{-3} density), [C_4mim][$MeSO_4$] and tetrakis(hydroxymethyl)phosphonium chloride (hydrated ionic liquid, 80% in water, 1.34 g cm^{-3} density), [P(CH_2OH)$_4$]Cl were supplied by Sigma–Aldrich. Transesterification experiments were carried out using anhydrous methanol and sulfuric acid from Sigma–Aldrich, at the highest purity available. Greater than 99% purity sodium chloride, sodium bicarbonate and sodium sulfate anhydrous were also provided by Sigma–Aldrich. Standards used for identification and quantification of fatty acid methyl esters (FAMEs) were supplied by Supelco (37 component FAMEs mix). All other solvents and reagents were high performance chromatography grade and analytical reagent grade provided by Sigma–Aldrich.

2.2. Sludge collection, handling and preparation

Primary sludge was collected from the municipal wastewater treatment plant (WWTP) in Reus (Tarragona, Spain) with a capacity to process near 25,000 m^3 of wastewater per day. The collected sludge was immediately delivered to the laboratory and stored at 4 °C prior to use. Depending on the experimental design, primary sludge was either used as received (raw sludge, 96% water content) or in dried form (dried sludge, 2% residual water content). The sludge was dried for 2 days at 105 °C [8].

2.3. Analysis of sludge composition by conventional methods

Total solids (TS), volatile solids (VS) and ash content were analysed according to standard methods 2540B and 2540E respectively [26].

Protein determination was carried out by the Lowry method [27], when the sludge sample was first pretreated by heating with 2 M sodium hydroxide at 100 °C for 10 min. The absorbance was measured at 750 nm.

The total carbohydrate amount was quantified by the phenol–sulfuric acid method of Dubois [28]. The absorbance was measured at 480 nm.

Lipid extraction was carried out in a Soxhlet apparatus using hexane as a solvent according to standard method 5520E [26]. After extraction, the hexane was removed using a rotary evaporator, the lipids were stored in a desiccator overnight and weighed the next day. The lipid yield was determined gravimetrically and expressed as gram of extractable lipids per gram of dry sludge.

2.4. Lipid extraction using ionic liquids

The primary sludge (dried or raw) and ionic liquid in ratio 1 g TS equivalent to 10 cm^3 ionic liquid were added to a round bottomed flask (50 cm^3) fitted with a condenser. The mixture was heated at 100 °C in an oil bath for 24 h under magnetic stirring, 500 rpm. After the reaction completed, further procedure was carried out according to our previous study [25]. The optimisation study using [P(CH_2OH)$_4$]Cl ionic liquid and raw sludge was carried out with varying extraction times (½, 1, 3, 6, 12 and 24 h), extraction temperatures (25, 40, 60, 80 and 100 °C) and sludge:IL ratios (1:5, 1:10, 1:20; g/TS: cm^3/IL).

2.5. Lipid transesterification and FAMEs analysis

The lipids were converted into FAMEs (biodiesel) through acid catalysis transesterification/esterification using 1 v% of sulfuric acid in methanol according to the procedure previously described [8]. Then, the FAMEs were analysed by GC–FID as described previously [8]. The results of GC–FID were used to estimate the amount of saponifiable (transesterifiable/esterifiable to FAMEs) material in the lipid fraction and hence the maximum mass of biodiesel (FAMEs) that could be yielded.

2.6. Recovery of precipitated solid

After lipid extraction from raw sludge by ionic liquid, the precipitated solid was recovered for further analysis from the IL/methanol/sludge's water solution by centrifugation (6000 rpm, 10 min) and subsequent removal of the aqueous supernatant. The recovered solid was washed with methanol (3 × 10 cm^3), followed