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Optimization of direct liquid-liquid extraction of lipids from wet urban sewage sludge for biodiesel production

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ABSTRACT

Efficient lipid extraction is one of the main remaining challenges for full-scale production of biodiesel from urban sewage sludge, a low-cost feedstock. The common approach is to extract lipids from dewatered or dry sludge by means of organic solvents. However, sludge dewatering and drying are energy-consuming and represent more than 50% of the total production cost. Direct liquid-liquid extraction of lipids has been poorly explored; only extraction using hexane as solvent is described in the literature. This study focuses on the optimization of the extraction of lipids from wet raw urban sewage sludge at room temperature. This optimization is conducted varying solvent, pre-treatment, number of extraction steps, contact time and ratio sludge to solvent. The optimized method gives larger lipid amount (34.5%wt dry matter (DM)) than using hexane extraction (32.8%wt DM). Finally, the potential of lipid fractions extracted from eight sludge samples for biodiesel production was evaluated through the determination of acid value and free fatty acid (FFA) content, saponification number and fatty acid composition.

1. Introduction

The third target of the 2020 climate change and energy package adopted by the European Union (EU) is to reach a share of 20% of renewable fuels in the gross final consumption of energy in the EU in 2020. In that context, the Directive 2009/28/CE establishes a mandatory target of at least 10% of renewable fuel in the transport sector in 2020 [1]. Biodiesel is one of the most promising renewable fuels. It mainly consists of a mixture of fatty acid alkyl esters obtained through esterification/transesterification of lipid sources with alcohol and in the presence of a catalyst. At present, the main obstacle to a widespread production and commercialization of biodiesel is the need to use costly edible oil (like soybean, rapeseed, sunflower, palm, cottonseed and peanuts oil) as feedstock, representing between 70% and 85% of the total production cost. Furthermore, the cultivation of crop-for-fuel competes with human food production [2–4].

Urban sewage sludge generated in wastewater treatment plants (WTTPs) is a low-cost lipid feedstock available in large quantities. In Belgium, Walloon urban WWTPs produced around 49,000 tons dry matter (DM) of sludge in 2014 [5]. Moreover, sludge management represents a major cost in WWTPs operation (between 50% and 60% of the total operating costs). The advantage of using urban sewage sludge for the production of biodiesel is thus twofold: it is in line with EU Directive 2009/28/CE and its associated targets on renewable fuels, and it provides new valorisation options for urban sewage sludge generated as waste in WTTPs.

The main challenge associated to the production of biodiesel from sludge is an efficient lipid extraction. Sludge water content can account for up to 95–98%wt. Dewatering and drying involve high energy inputs, potentially representing more than 50% of the total biodiesel production costs [6]. In addition, water removal by thermal drying results in the loss of valuable organic compounds. It probably causes the loss of lipids, decreasing biodiesel production yield [7]. Hence, other extraction methods need to be identified in order to be able to efficiently produce biodiesel from wet sludge.

The common approach for extracting lipids from sludge is to use organic solvents, usually in mixtures. The Bligh and Dyer method (chloroform/methanol/water) is the most popular method for lipid extraction from several materials [8]. This method uses the properties of ternary mixtures: when solvents are mixed in an appropriate ratio, they form a monophasic solution improving contact between lipids and the organic solvent where lipids are soluble. Addition of more water and/or chloroform produces a biphasic system from which it is easy to isolate the lipids-containing chloroform layer. The advantage of the

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Bligh and Dyer method is the presence of water, avoiding the need for prior sludge drying. However, the maximum ratio of water allowed in the sludge in order to reach a monophasic solution is 80%wt, implying that the sludge has to be at least partially dewatered [3]. In addition, the use of a chlorinated solvent results in the production of large amounts of chemical hazardous waste that is highly toxic to the environment.

Smedes and co-workers studied the possibility of replacing chloroform by a non-chlorinated solvent for the determination of total lipid in marine tissues [9]. They tried several solvent combinations and the mixture of cyclohexane/isopropyl alcohol/water (Smedes mixture) gave the best results. Pastore and co-workers describe the extraction of lipids from a dewatered primary sludge (dry matter content (DMC) 14.4%wt) with hexane (ratio 1:1) under acid media (sulphuric acid) at 38 °C for 1 h (three consecutive extractions). These conditions gave a lipid yield of 20.0%wt (on the basis of DM) [10]. Only one reference reports the direct liquid-liquid extraction of lipids from wet primary sludge (DMC 3.4%wt) by mean of hexane [7]. The extraction under acid media (hydrochloric acid) at room temperature for 1 h using a 2:1 sludge/hexane ratio (three consecutive extractions) gave 26.7%wt of lipids (on the basis of DM). The advantage of this method is that sludge drying or dewatering was unnecessary. Other solvents were not tested.

Extraction from sludge may be influenced by many variables such as sludge composition, type and amount of solvent, extraction time, temperature, stirring rate, type of micro-organisms present in the sludge, etc. [11]. As a preliminary research for the development of a feasible and economical biodiesel production method using wet sewage sludge, this paper aims at improving the liquid-liquid extraction method at room temperature proposed by Olkiewicz and co-workers, as described above [7]. Different solvents or combination of solvents for lipid extraction from a wet sludge (DMC < 5%wt) were explored, and the method was optimized varying (i) sludge pre-treatment, (ii) number of consecutive extraction steps, (iii) contact time, and (iv) sludge to solvent ratio. In a second step, the most favourable conditions were applied to compare lipid content before and after sludge drying. In a third step, the lipid content of eight sludge samples (four primary sludge samples and four secondary sludge samples) was determined. Finally, in order to verify the potential of the extracted lipids for biodiesel conversion, the lipid fractions obtained from all eight sludge samples were characterized for acid value and free fatty acid (FFA) content, saponification number, and fatty acid composition.

It must be noted that lipid content is not strictly measured in this study. Instead, groups of substances with similar physical characteristics and that are not volatilized during the test, are determined quantitatively on the basis of their common solubility in the organic solvent used for extraction. They should thus be referred to as “extractable oil and grease”. However, for the sake of brevity, the term “lipid content” will be used throughout this paper.

2. Materials and methods

2.1. Reagents and instruments

2.1.1. Reagents

Experiments were conducted using methanol, ethanol, isopropyl alcohol, hexane, cyclohexane, diethyl ether, *tert*-butyl methyl ether, standardized potassium hydroxide 0.1 N in methanol, standardized hydrochloric acid 0.1 N, sodium methoxide 10% in methanol, fuming hydrochloric acid, sulphuric acid, phenolphthalein, thymolphthalein, anhydrous sodium sulphate and sodium chloride (all of analytical-reagent grade).

The standard used for calibration of Karl Fisher coulometric titrator was supplied by Riedel-de Haën (Hydranal®-Water Standard 1.00).

The standard used for identification of fatty acid methyl esters was supplied by Supelco (37 Component FAME Mix).

All chemicals were used as received.

Water was obtained with a MilliQ Advantage A10 (Millipore).

2.1.2. Instruments

Three-dimensional shaker mixer T2C (WAB), Multi Reax Vortex Mixer (Heidolph™), 870 KF Titrino plus (Metrohm), 8510 Ultrasonic Cleaner MTH (Branson), centrifuge BR4-I (Jouan), automated evaporation system TurboVap®II (Zymark), oven EU53 (Jouan), oven FD240 (Binder), analog dry block heater (VWR®), ThermoQuest Trace GC 2000 equipped with a Trace MS analyzer (Interscience), BP5-MS capillary column (30 m × 0.25 mm I.D., 0.25 µm film thickness, SGE Analytical Science), Software Xcalibur (Thermo Scientific).

2.2. Sludge sampling and handling

Four primary and four secondary sludge samples were collected before (raw sludge) or after partial dewatering at the urban WWTP located in Wegnez (Liège, Belgium, population equivalent of 110,000) from August 2015 to October 2016. This facility uses an activated sludge process that produces three sludge types: greasy, primary and secondary sludges.

Sludges were poured into 5000 mL plastic buckets, transported in a refrigerated car to the laboratory and stored at 4 °C prior to subsampling (maximum storage time 2 days). The manual subsampling was realized in 250, 500 and 1000 mL plastic bottles (HDPE). The homogeneity of the subsampling was checked by comparing lipid content values obtained from four 250 mL bottles of the same primary sludge sample using the optimized method described in this paper (RSD = 9.7%).

All the bottles were frozen to prevent degradation of biological material and modification of sludge properties. The bottles were unfrozen one at a time at 4 °C for direct analysis avoiding long time of conservation (maximum shelf life: 15 days at 4 °C).

2.3. Sludge characterization

Prior to optimization of the liquid-liquid extraction, sludge samples were analyzed in order to determine DMC and water content. After optimization, the liquid-liquid extraction method was used to determine lipid content of the sludge samples.

2.3.1. Dry matter content (DMC)

DMC was determined according to a drying method described in ISO 11465 [12]. The results were expressed as weight of residual solid after thermal treatment per unit weight of initial wet sludge.

2.3.2. Water content

Water content W_S (%) was determined according to Karl-Fisher titration (external dilution method). Each sample was measured in triplicate.

2.3.3. Lipid content

The initial sludge sample must contain maximum 5% of lipids because high lipid concentrations may affect the nature of the organic phase and have a measurable effect on the result [9]. 5 g of wet sludge previously treated 30 min in an ultrasonic bath (in order to improve extraction efficiency), was weighed in a 50 mL PE centrifugation tube and acidified until pH 2 by the addition of 1 mL of fuming hydrochloric acid. The mixture was then shaken for 2 min at room temperature (1900 rpm). 8 mL of isopropyl alcohol and 10 mL of cyclohexane (ratio of 1:1.6:2) were added and accounting for the amount of water in the sample, V_{WATER} mL of water was added to obtain a total of 11 g of water. V_{WATER} is calculated with Eq. (1):

$$V_{WATER} = 11 - m_{HCl} - (m_S \times W_S)/100 \quad (1)$$

where m_S (g) is the mass of the sludge sample, m_{HCl} (g) is the mass of hydrochloric acid (≅hydrochloric acid volume (mL)) and W_S (%) is the