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Effect of sludge features and extraction-esterification technology on the synthesis of biodiesel from secondary wastewater treatment sludges

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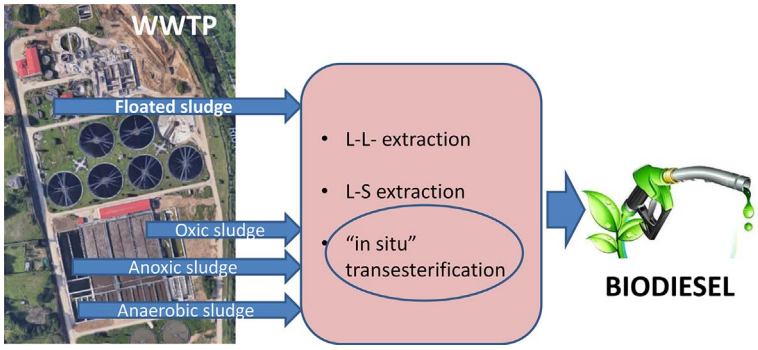
GRAPHICAL ABSTRACT



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ABSTRACT

Secondary sludge from municipal wastewater treatment plant is proposed as a promising alternative lipid feedstock for biodiesel production. A deep study combining different type of raw materials (sludge coming from the oxic, anoxic and anaerobic steps of the biological treatment) with different technologies (liquid–liquid and solid–liquid extractions followed by acid catalysed transesterification and *in situ* extraction-transesterification procedure) allows a complete comparison of available technologies. Different parameters – contact time, catalyst concentration, pretreatments – were considered, obtaining more than 17% FAMEs yield after 50 min of sonication with the *in situ* procedure and 5% of H_2SO_4. This result corresponds to an increment of more than 65% respect to the best results reported at typical conditions. Experimental data were used to propose a mathematical model for this process, demonstrating that the mass transfer of lipids from the sludge to the liquid is the limiting step.

1. Introduction

The rise in oil price, the fossil fuels depletion, and, even more markedly, the environmental and climate problems associated with their combustion, are promoting the development of renewable fuels. Among the different alternatives currently available, biodiesel highlights as one of the most promising ones since it is biodegradable, less toxic than fossil fuels and provides similar energy density than the mineral one, but improving its lubricating properties (Revellame et al., 2010; Xue et al., 2006). In addition, its ignition point is considerable higher than the diesel one, making it easy and safe to manipulate it (Anuar and Abdullah, 2016; Shahid and Jamal, 2011).

Chemically, biodiesel is a mixture of monoalkyl esters of long chain fatty acids, commonly called fatty acid methyl esters (FAME).

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Industrially, it is currently obtained by transesterification of vegetable oils or animal fats with methanol, obtaining a product known as "first generation" biofuel (Atabani et al., 2012; Shahid and Jamal, 2011). However, the competitive potential of biodiesel is limited due to the high cost of these lipid feedstocks. This fact, as well as ethical issues related to the competition between energy and food industry, have triggered the search for inedible, inexpensive and, if possible, residual raw materials, making up the "second generation" biodiesel (Hajjari et al., 2017). The use of oleaginous microorganisms, those that accumulate lipid droplets in their cells, reaching dry lipid percentages up to 25 % (Koutb and Morsy, 2011), is an attractive alternative. However, the high consumption nutrients and the specific needs of their growth (light, temperature) can discourage its cultivation for this specific aim. On the other hand, the microorganisms used in biological treatments of a wastewater treatment plants (WWTPs) have relevant concentration of triglycerides, and constitute the solid phase of sludge streams usually considered as a waste (Kumar et al., 2016; Mondala et al., 2009).

Due to the urbanisation and industrialisation, quantities of sewage sludge produced increase year on year, being considered as the main waste of these plants. It is forecasted that approximately 13 million tonnes of sludge will be produced in the European Union in 2020 (Comission, 2010). Its treatment and disposal implies an important cost, in both, economic and environmental terms (Dufreche et al., 2007). Therefore, sewage sludge is an available and cheap feedstock that has attracted attention during the last decade (Dufreche et al., 2007; Kumar et al., 2016; Olkiewicz et al., 2014). Particular characteristics of these sewage sludge (high humidity, heterogeneous and few reproducible composition, etc.), makes difficult its fast commercialisation, being no possible the direct application of conditions previously optimised for the first generation biofuels. Thus, many efforts are nowadays focused on the study and standardisation of this process.

In this context, the optimisation of lipid extraction is a major challenge that determines the economy of the process (Kargbo, 2010). Thus, several researchers have proposed different alternatives, such as the liquid–liquid extraction, the solid–liquid extraction and the *in situ* transesterification (Dufreche et al., 2007; Kwon et al., 2012; Mondala et al., 2009; Olkiewicz et al., 2014; Pokoo-Aikins et al., 2010; Revellame et al., 2010; Siddiquee and Rohani, 2011; Willson et al., 2010). The two first ones, liquid–liquid and solid–liquid extractions, require the use of organic solvents, without agreement about the optimum ones, although interesting results using toluene, chloroform, hexane, methanol and ethanol are published (Dufreche et al., 2007; Kwon et al., 2012; Pokoo-Aikins et al., 2010; Siddiquee and Rohani, 2011). However, reported results are difficult to compare because many different conditions were tested and, to the best of our knowledge, there is not a systematic study comparing the different available techniques. Consequently, general conclusions are difficult to withdraw, being difficult to predict the behaviour of other sludges.

As to the transesterification, acid catalysis is the most frequently used procedure, mainly using sulphuric acid, obtaining higher biodiesel yields in comparison with results with basic catalyst (Olkiewicz et al., 2016). Despite that classical transesterification of pure oils is industrially carried out using basic materials, when the raw material is a waste, the presence of free fatty acids in a basic medium promotes the saponification, obtaining a non-desired product that hinders the separation and purification of the biodiesel fraction. Recent studies also propose the enzymatic catalysis or the non–catalytic transesterification, when reaction is done under subcritical conditions (Kwon et al., 2012; Pourzolfaghar et al., 2016).

Analysing all these previous results, one of the main conclusion is that acid transesterification is very efficient, and results are mainly conditioned by the lipid extraction step. As consequence, some authors propose different alternatives to enhance this step, being the sonication one of the most promising pretreatment. Sonication technology is based on the introduction of high intensity sound waves in the sludge, creating bubbles that implode, breaking the cell walls and releasing the intracellular content, including the lipids, into the medium. This technology has been previously used for obtaining biodiesel from algae or biogas from sludge (Ruffino et al., 2015; Tran et al., 2012; Wolski, 2012). However, the few studies applied to this aim are not conclusive enough (Olkiewicz et al., 2015; Olkiewicz et al., 2012) Taking into account this entire context, biodiesel yields reported in the literature using secondary sludge as raw material vary greatly from one study to another. Therefore, we consider that a systematic comparison of the results obtained applying the three lipid extraction techniques to a specific secondary sewage sludge is of key interest for both understanding the process and being able to propose efficient technologies for this purpose. Once the raw material is the same for all the treatments, and after the transesterification of the obtained lipids, tracking down conclusions would be easy and useful.

The main aim of this work is to present a deep comparison among biodiesel yields obtained by applying the three different techniques – liquid–liquid extraction, solid–liquid extraction, and *in situ* transesterification – to the same type of secondary sludge. Three different raw materials were used, from oxic, anoxic and anaerobic zone (sampled directly from the corresponding reactor) and results were compared with those obtained from the floating sludge (common pretreatment for these sludges). Industrially, only floating sludge adds up (taking samples directly from the reactors before being concentrated by decantation or floating is economically and technically unviable). However, the individual study of each sludge fraction allows analysing if the sludge nature has any effect in the final efficiency, suggesting an independent pre-concentration of the most interesting fraction to maximize the biodiesel yield. The effect of catalyst concentration as well as the role of sludge pretreatment by sonication was also analysed.

2. Materials and methods

2.1. Chemicals

n-Hexane (97%) and sulphuric acid (96%) were purchased from Sigma-Aldrich. Sodium chloride (99.5%) and methanol (≥99.8) were purchased from Panreac. A mixture of 37 reference fatty acid methyl esters (FAMEs) was supplied by Supelco (Ref. 47885-U), and it was used for identification and quantification purposes (in the GC–MS and GC-FID analyses).

2.2. Sample collection and preparation

Secondary sludge samples were collected from the municipal wastewater treatment plant (WWTP) in Villapérez-Oviedo (Asturias, NW Spain). The block diagram of this plant, which has a capacity to process 8500 L/s, is summarized in Fig. 1, indicating the steps where the four different types of secondary sludge (oxic, anoxic, anaerobic and floating ones) are sampled. Considering the global process of this WWTP, primary sludge was discarded because of their low potential capacity (this sludge mainly correspond to solid particles, inorganic chemicals and free fatty acids that can suffer saponification). Samples were taken weekly during one month (4 batches) and stored at 4 °C prior to use.

The sludge from the oxic, anoxic and anaerobic zones were individually pre-treated following with the aim to reduce the water content and to prepare the samples for the extraction and transesterification. Sludges were settled for 24 h, after which the supernatant was removed. The resulting sludge was centrifuged at 3000 rpm for 10 min using a Kubota 6500 centrifuge. Dewatered sludge was dried at 100 °C for 24 h and the desiccated sludge was crushed into a fine powder (with particle size ranging from 150 to 255 μm) in order to prepare a homogeneous suspension for the following steps. These dried sludge samples were used to the solid–liquid extraction and *in situ* transesterification studies. In the case of liquid–liquid extraction, the sludges were only subjected to the settling process. This procedure has been previously reported in the literature, observing a relevant decrease in