

EFFECT OF ACID AND ULTRASONICATION PRE-TREATMENTS ON THE LIPID EXTRACTION FROM PETROCHEMICAL INDUSTRY AND MUNICIPAL WASTEWATER SLUDGES

D. Atik Alper*, E. Babayigit, A. Erdinciler

Boğaziçi University, Institute of Environmental Sciences

Hisar Campus, 34342, Bebek, İstanbul, Turkey

*Corresponding author: Tel: +90 535 015 3076

Fax: +90 212 257 5033

E-mail: atikdilek2@gmail.com

ABSTRACT

Energy is considered as a significant factor for economic and industrial growth. With the increasing use of fossil fuels and its environmental problems there is an urgent need for alternative energy source. Biodiesel is accepted to be the best alternative to the fossil fuels because of environmental benefits. Municipal and especially oily petrochemical industry wastewater sludges have high lipid content and can be used as feedstocks for biodiesel production. The biodiesel production process mainly consists of three steps: drying of sludge, extraction of lipids, and transesterification. The aim of this study was to explore the use of novel direct liquid-liquid lipid extraction technique, eliminating costly dewatering and drying steps, to obtain high lipid yields from the municipal and oily petrochemical industry wastewater sludges. The study also comparatively investigated the effects of acid and ultrasonic pre-treatments on the lipid extraction from municipal and petrochemical industry WWTP sludges by novel direct liquid-liquid lipid extraction and standard reference drying methods. The results of the study showed that acid pre-treatment increased the lipid yields of both sludge samples. The highest lipid yield was obtained by application of combined acidification/ultrasonication pre-treatment to the petrochemical industry WWTP sludge and using the liquid-liquid lipid extraction method. Compared to standard drying method, direct liquid-liquid lipid extraction is found to be more efficient for petrochemical industry WWTP sludge samples.

Keywords: biodiesel, lipid extraction, liquid-liquid extraction, municipal sewage sludge, petrochemical industry sludge

1. INTRODUCTION

Energy has a significant role in maintaining the modern economy and society. Energy consumption has increased with population growth, urbanisation and economic development. Currently, most of the energy demand is satisfied from fossil fuel sources which are non-renewable, and will be run out in near future [1]. Excessive use of these energy sources has caused important environmental problems such as air pollution and global warming. In order to overcome these problems the use of renewable energy resources is the best solution. Among the alternative fuel sources such as biodiesel, alcohol, biomass, biogas, synthetic fuels, biodiesel represents a better alternative to conventional diesel [2]. The reasons behind choosing biodiesel as the best candidate for diesel fuels are several. Its primary advantage is that it does not require new refuelling station. Biodiesel is also environmentally friendly, renewable, biodegradable, less toxic, safer for storage and handling and has low emission profiles [3]. Currently, biodiesel is produced from a variety of feedstock such as sunflower, soybean, canola, palm, rapeseed, and coconut oils. As the costs of pure vegetable oil and seed oils constitute between 70% and 85% of the total biodiesel production cost use of them as biodiesel feedstock is limited. Therefore, alternative sources of oils and fats such as waste frying oil, jatropha oil, microalgae, and sewage sludge draw attention in recent years [4]. Among these sources municipal wastewater sludge (sewage sludge) is gaining traction around the world as a lipid feedstock for biodiesel production due to its high lipid content. The sludge can be considered as a practically no cost, readily available, and plentiful lipid feedstock, which can make the biodiesel production profitable along with helping solve some environmental issues associated with sludge treatment and disposal. The lipid fraction of municipal sewage sludge consisting of triglycerides, diglycerides, monoglycerides, phospholipids, and free fatty acids originates from the direct adsorption of lipids sourced from fats and oils in wastewater onto the sludge solids and the phospholipids in the cell membranes of microorganisms, their metabolites, and by-products of cell lysis. [4,5,6]. A considerable amount of oily sludge generated from the petroleum industry during its crude oil exploration, production, transportation, storage, and refining processes can be used as a suitable feedstock for biodiesel [7]. It contains a high concentration of petroleum hydrocarbons (PHCs), phospholipids, free fatty acids (FFA), neutral lipids and water [8,9]. The improper disposal or insufficient treatment of petrochemical sludge can pose serious threats to the environment and human health due to its carcinogenic and immuno-toxic composition [10]. Because of its hazardous composition and population growth around the world, the effective treatment of oily sludge has gained importance in recent years. Consequently, biodiesel production from this sludge as an effective option to common sludge treatment methods will be a solution to the energy and environmental problems.

The use of these sludges as feedstock for biodiesel production can be considered as one of the recycling technologies. Extraction of lipids from sludge is the important step of biodiesel production process. In literature, there are many studies on lipid extraction to produce biodiesel from wastewater sludges utilizing different methods.

Boocock et al. studied two different lipid extraction methods; Soxhlet extraction and boiling solvent extraction methods by using chloroform and toluene as solvent. They found the lipid yields to be about 12%wt dry matter (DM) and 17-18%wt DM for both of the solvents by using Soxhlet extraction and boiling solvent extraction methods, respectively. Although both solvents gave similar lipid extraction yields, toluene was preferred for economic and environmental reasons [11].

Zhu et al. investigated the organic solvent extraction method by using different organic solvents to determine which solvent has the ability to extract the maximum lipid yield from sewage sludge. They concluded that mixed solvent has higher extraction efficiency than the single solvent [6].

In the study by Olkiewicz et al., Soxhlet extraction method was used to extract lipids from municipal wastewater sludges. They compared four different types of sludges (primary, secondary, blended and stabilized) in terms of lipid content. The results indicated that among four sludge tested, primary sludge gave the highest lipid yield to be 25.3%, on the basis of dry sludge [3].

Another study by Olkiewicz et al., the effect of acid pre-treatment, ultrasonic and mechanical disintegration on the lipid extraction by using Soxhlet apparatus was investigated. The results showed that the pre-treatment methods did not increase remarkably the amount of extracted lipid [12].

Zhu et al. investigated the performance of three different extraction methods (acid hydrolysis extraction, soxhlet extraction, and the water bath shaking extraction) and compared the lipid yields obtained from sewage sludge. They also studied the effects of different organic solvents on extraction efficiency. They concluded that Soxhlet extraction gave the best lipid yield compared to other methods [13].

In aforementioned investigations, dry sludge was used directly as a raw material for biodiesel production from waste sludges. As municipal wastewater sludge has higher water content of 95-98% by weight, the energy cost of sludge dewatering and drying processes almost 50% of the total biodiesel production cost making the process very expensive and difficult the scale up [3, 14]. In order to eliminate the expensive preliminary step of sludge drying Pastore et al. used dewatered sludge as raw material for extraction of lipidic compounds. However, the energy necessary for water elimination still constitutes 14% of the total biodiesel production cost [14, 15].

Olkiewicz et al. developed a new method for extraction of lipids from municipal wastewater sludges different from the methods used by other researchers. They used the sludge samples directly in liquid form without dewatering and drying. They explored the novel direct liquid-liquid lipid extraction method and compared that method with standard reference method in terms of lipid extraction efficiency. In this method, hexane was used as an organic solvent and extraction was performed in batch mixer settler reactor at room temperature. The results of this study demonstrated that higher lipid yield (27%wt, dry sludge) was obtained from primary sewage sludge via direct liquid-liquid extraction technique, whereas 25%wt (dry sludge) of lipid was produced by using the standard method. They concluded that direct liquid-liquid lipid extraction method can be used effectively for primary sludges; however it is not efficient for secondary sewage sludges [16].

Kech et al. improved the direct liquid-liquid extraction method proposed by Olkiewicz and co-workers. They obtained 32.8% (on the basis of dry sludge) of lipid yield from wet primary sewage sludge by using hexane as solvent [17].

The proposed alternative, direct liquid-liquid extraction method has rather limited information on the biodiesel production from wastewater sludges. Surprisingly, the direct liquid-liquid extraction of lipid from petroleum refinery oily sludge has neither been reported, so the sludge drying and dewatering can thus become unnecessary and the yield of biodiesel can increase due to the high concentration of fatty acids and lipids in petroleum sludge through this extraction method. Additionally, it has been demonstrated that ultrasonic pre-treatment is able to

increase the lipid extraction yield from sewage sludges but their utilization to improve lipid extraction from petrochemical oily sludge in the direct liquid-liquid extraction process has not been reported.

The aim of this study was to explore the use of novel direct liquid-liquid lipid extraction technique, eliminating dewatering and drying steps, to obtain high lipid yields from the petrochemical industry WWTP sludge (oily sludge) and sewage sludge. The study also comparatively investigated the effects of acid and ultrasonic pretreatments on the lipid extraction from sewage and petrochemical industry WWTP sludges by novel direct liquid-liquid lipid extraction and standard reference drying methods.

2. MATERIALS AND METHODS

2.1. Sludge Characterization

In the study, the primary sewage sludge samples were collected at the bottom of the primary clarifier of a municipal wastewater treatment plant located in İstanbul; whereas the oily sludge samples were obtained from thickening unit of a petrochemical industry wastewater treatment plant (WWTP) in Turkey. The sludge thickening unit contains waste activated sludge from secondary clarifier and the sludges from primary clarifier and oil separators. Sludge samples were characterized by measuring their total solid (TS), volatile solid (VS), chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD) concentrations, viscosity and pH. All of the analyses were conducted according to the Standard Methods of the Examination of Water and Wastewaters [18].

2.2. Sludge Pretreatment (Disintegration)

Sludge samples were disintegrated by acid pretreatment by adding hydrochloric acid (0.1N HCl) into the samples to decrease their pH to 2 and by ultrasonic pretreatment by using an ultrasonic homogenizer before the lipid extraction step. Ultrasonic pretreatment experiments was performed by using an ultrasonic homogenizer (Bandelin-Sonopuls HD 3400). The ultrasonic homogenizer is equipped with a generator (GM 3400), an ultrasonic converter (UW 3400), a booster horn (SH 3425) and a probe (VS 200 T). The ultrasonic unit with had a constant frequency of 20 kHz. Subsequent to optimization studies, the amplitude was set to 70% and the energy-output was 200 W.

In ultrasonication pretreatment of the sludge samples, the specific energy input was adjusted to 15000 kJ/kg TS. Specific supplied energy has been calculated using the equation below; Specific energy (E_s), ultrasonic power (P), ultrasonic time (t), sample volume (v) and total solid concentration (TS):

$$E_s = \frac{(P \times t)}{(v \times TS)}$$

2.3. Lipid Extraction

2.3.1. Extraction of lipids from dried sludge

The extraction procedure after drying was carried out in a Soxhlet apparatus using solvent according to standard method 5520E [16]. For the Soxhlet extraction, the sample was homogenous as possible. The homogenous sample was placed in a cellulose thimble and top of the thimble was blocked by using glass wool to prevent lipid loss with the scattering of the solids. After the lipids extraction, the solvent was removed from the flask and recovered to use for the further steps. Then, the remnant lipids were stored in a desiccator overnight and weighed the next day to determine the extraction yield. After the determination of the yield, the lipids were kept frozen and dissolved in the solvent until next analyses.

2.3.2. Liquid-liquid extraction of lipids from sludge samples

Liquid-liquid extraction of lipids was performed using the mixing and settling batch reactor set to understand its feasibility. Firstly, sludge samples were acidified to pH=2 by the addition of 0.1N HCl to the samples to understand the effect of previous acidification. After each consecutive extraction stage, samples was extracted

again with additional solvent and then the solvent phase was filtered using a filter paper. Later, the solvent was recovered using Soxhlet apparatus and reused for the sequential step. Selection of suitable variables provided the optimisation of liquid-liquid extraction. After the extraction process, solvent was removed and lipids will be weighed to determine the extraction yield.

3. RESULTS AND DISCUSSION

3.1. Sludge Characterization

The sewage sludge samples were collected from a municipal wastewater treatment plant located in İstanbul; whereas the petrochemical industry WWTP sludge samples were collected from a petrochemical refinery wastewater treatment system in Turkey. Sludge samples were analysed for TS and VS (Standard Methods 2540 B and 2540 E, respectively), COD and sCOD (Hach Method 8000), viscosity (ASTM D445) and pH (Standard Methods E9040 C). The initial characteristics of the sludge samples are given in the Table 1.

Table 1. Characteristics of sludge samples

| Parameter | Unit | Primary sewage sludge | Petrochemical industry WWTP sludge |
|-----------|-------|-----------------------|------------------------------------|
| TS | % | 4.2 | 3.4 |
| VS | % | 2.4 | 2.1 |
| COD | mg/L | 40280 | 63220 |
| sCOD | mg/L | 3090 | 10800 |
| Viscosity | mPa.s | 8.0 | 52.8 |
| pH | - | 6.2 | 6.8 |

3.2. Effect of Extraction and Pretreatment Methods on the Lipid Yields

The lipid yields from primary sewage sludge and petrochemical industry WWTP sludge using standard drying and direct liquid-liquid extraction methods are presented in Table 2. The values represent the average of at least three different samples collected in WWTP during several months.

The results of the study showed that, in both of the lipid extraction methods, acid pretreatment (pre-acidification) improved the lipid yields obtained from both sewage and petrochemical industry wastewater treatment plant sludge samples. In the direct liquid-liquid lipid extraction method, acid pre-treatment increased the lipid yields by 86% for primary sewage sludge. However, the improvement was just 14% for the petrochemical industry WWTP sludge. In the standard drying method, the increase in lipid yields remained in a range of 6% to 11% for all of the sludge samples.

The application of ultrasonication pretreatment did not improve the lipid yields obtained from non-acidified primary sewage sludge samples by both of the drying and liquid-liquid lipid extraction methods. However, combined acidification/ultrasonication pretreatment improved the lipid yields of non-acidified primary sewage sludges for both extraction methods. While the lipid yield was increasing by 10.6% in standard drying method, the lipid yield increased by 2 folds in the direct liquid-liquid lipid extraction method by the effect of combined acidification/ultrasonication pretreatment. Compared to acidification pretreatment, only slight increases of 4-8 % were observed in the lipid and yields.

Table 2. Lipid, yields obtained from sludge samples pretreated with different methods

| Sludge type | Extraction method | Lipid Yield (%) ^(a) | | | |
|---|---------------------------------|--------------------------------|------|-----------------|---------|
| | | Pre-treatment method | | | |
| | | No-pretreatment | Acid | US (Ultrasonic) | Acid+US |
| Primary sewage sludge | Standard drying ^(b) | 22.6 | 24.0 | 20.5 | 25.0 |
| | Direct liquid-liquid extraction | 10.3 | 19.2 | 9.0 | 20.8 |
| Petrochemical industry WWTP sludge | Standard drying ^(b) | 21.4 | 23.7 | 29.1 | 33.1 |
| | Direct liquid-liquid extraction | 30.5 | 34.8 | 30.9 | 45.2 |
| ^(a) All transesterification experiments were performed at least twice. | | | | | |
| ^(b) Extraction according to standard MgSO ₄ .H ₂ O method, lipid yield on the basis of dry sludge. | | | | | |

The combined acidification/ultrasonication pretreatment increased the lipid yields of petrochemical industry WWTP sludge samples by 48% and 54.6% for the direct liquid-liquid lipid extraction method and standard drying method, respectively. As it can be seen, the effect of combined acidification/ultrasonication pretreatment on the direct liquid-liquid lipid extraction method was much smaller compared the standard drying method was used for lipid extraction.

It seems that in lipid extraction, acidification itself is enough for the pretreatment of primary sewage sludge. Application of combined acidification/ultrasonication pretreatment to domestic wastewater sludge samples is not beneficial due to the high cost and low benefit.

In the direct liquid-liquid lipid extraction method, while the application of ultrasonication pretreatment itself did not cause to an important change in the lipid yields of petrochemical industry WWTP sludge samples, in the standard drying method the improvement was about 36%. Combined acidification/ultrasonication pretreatments increased the lipid yields obtained from petrochemical industry WWTP sludge samples in both of the extraction methods. The highest lipid yield was achieved by the application of combined acidification/ultrasonication pretreatment to the petrochemical industry WWTP sludge samples and using the liquid-liquid lipid extraction method. Compared to standard drying method, direct liquid-liquid lipid extraction method is found to be more efficient for petrochemical industry WWTP sludge samples in terms of both lipid extraction.

Agreeing with the literature, the results of this study showed that the direct liquid-liquid method is more efficient for lipid extraction from materials having high lipid and low biological content. However, for the for materials having lower lipid and high biological content, the standard drying lipid extraction method was found to be more efficient. Accordingly, Speight [19] obtained low lipid yields from sludge samples having low lipid content through the standard drying method chemically drying the wet sludge samples and then extracting the lipids by using a Soxhlet apparatus. Speight [19] reported that this method is more suitable for biological lipids and mineral hydrocarbons.

The results of this study revealed that for the petrochemical industry WWTP sludges the direct liquid-liquid extraction method resulted with higher lipid extraction yields, while the standard drying lipid extraction method performed better for the municipal wastewater sludges.

4. CONCLUSIONS

The oily petrochemical industry WWTP sludges were found to be an efficient source of lipids that can be used for biodiesel production.

Compared to standard drying method, direct liquid-liquid lipid extraction method was found to be more efficient for petrochemical industry WWTP sludge samples. The direct liquid-liquid lipid extraction method, which does not require expensive sludge drying or dewatering steps, resulted with 50% higher lipid yield for petrochemical industry WWTP sludge samples than the standard drying method. However, standard drying method was found to be more effective in lipid extraction from the primary sewage sludge samples.

Acid pretreatment caused to an increase in the lipid yields obtained from both primary sewage and petrochemical industry WWTP sludges by using direct liquid-liquid and standard drying lipid extraction methods. The ultrasonication pretreatment did not cause to an important change in the lipid yield obtained from primary sewage sludge. The combined acidification/ultrasonication pretreatment considerably increased the lipid yields for both sludge types.

The highest lipid yield was obtained from combined acidification/ultrasonication pretreated petrochemical industry WWTP sludge by using liquid-liquid lipid extraction method. .

Additionally, the reuse of wastewater sludges in biodiesel production is an energy and cost efficient way of sludge management.

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