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CHARACTERIZATION OF OIL EXTRACTED FROM ACTIVATED SLUDGE OF WASTEWATER TREATMENT PLANTS IN CHETUMAL, QUINTANA ROO

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Abstract: Oil was extracted from samples of activated sludge from the activated sludge reactors of the Fovissste V Etapa, Xul-Ha and Centenario wastewater treatment plants. Oil content, fatty acid composition and free fatty acid percentage were analyzed for these samples. The Gravimetric Oil Yields of the samples from the three plants had a significant variation with an interval of 3.12 to 11.09 %. Palmitic, stearic and oleic acids predominated in all the samples analyzed. Additionally, the oil had a composition of around 60% saturated fatty acids, 40% unsaturated fatty acids and an average content of 4.45% free fatty acids. The oil content of the activated sludge from these plants can be transesterified for biodiesel production.

INTRODUCTION

In the municipality of Othón P. Blanco there are three wastewater treatment plants that use activated sludge systems for the secondary treatment of wastewater. The El Centenario treatment plant has the capacity to treat: 120 l s^{-1} wastewater and the Fovissste V Etapa and Xul-Ha plants were designed to treat 5 l s^{-1} of waste water. In these plants, activated sludge appears as a potentially interesting option to produce biodiesel. Various studies have shown that activated sludge can be used as raw material to produce biodiesel because it contains a considerable amount of lipids (Dufreche, et al., 2007, Ede et al, 2021, Mondala, et al., 2012, Revellame, et al., 2010, Siddique, et al., 2011, Xie, et al, 2016). Activated sludge from municipal wastewater treatment plants contain considerable concentrations of lipids derived from direct adsorption of lipids on the sludge. These lipids, energy sources include triglycerides, diglycerides, monoglycerides and phospholipids in addition to free fatty acids contained in the fats and oils of the activated sludge. In addition, the cell membrane of the bacteria present in the activated sludge contains phospholipids with values between 24 and 25% of the total dry mass of the bacteria (Dufreche, et al., 2007). Regarding the content of fatty acids, this may vary depending on the wastewater treatment plant; however, various studies have shown that up to 36.8% of the dry sludge can be composed of steroids and fatty acids, with fatty acids predominantly between 10 and 18 carbons (Jardé et al., 2005). However, the presence of free fatty acids has a negative effect on biodiesel production, since free fatty acids have to be esterified to produce biodiesel and in the esterification reaction, in addition to requiring a greater amount of catalyst with respect to the transesterification reaction (Siddique, et al., 2011), water is formed as a by-product and in biodiesel production this represents a problem since the presence of water can stop the esterification reaction. Hence, the main objective of this work is to quantify the content of free fatty acids in three treatment plants in the municipality of Othon P. Blanco.

MATERIALS AND METHODS

EXTRACTION OF LIPIDS FROM THE SLUDGE

Activated sludge from the Fovissste V Etapa, Xul-Ha and Centenario plants were collected every third day directly from the activated sludge reactors and were allowed to settle for 24 hours at 4 °C. The supernatant was discarded and the dewatered sludge was spread on a tray and placed in a fume hood to dry under vacuum at room temperature. The dried sludge was pulverized in a mortar and subsequently stored under refrigeration. The oil was extracted from the dried sludge using a mixture of solvents which consisted of 60% hexane, 20% methanol and 20% acetone, because according to what was reported by Dufreche et al (2007), this mixture of solvents produces a high oil yield compared to other solvents. The dry sludge was weighed in a distillation flask previously dried at 100 °C for one hour. The solvent mixture was added and the resulting mixture was heated at reflux at 80 °C and ambient pressure for two hours, using a condenser with water at 20 °C to avoid solvent loss. After extraction, the resulting suspension was filtered with a Buchner funnel connected to vacuum and 70mm filter paper. The solvent mixture was removed using a Buchi R-200 rotary evaporator at 60 °C and the resulting lipid was stored refrigerated for further analysis.

ANALYSIS OF FREE FATTY ACIDS

The amount of free fatty acids was measured as the difference of the hydrolyzed lipids and the transesterified lipids. The hydrolysis reaction was carried out to determine the total fatty acids, for this 1ml of Methanol:Chloroform (1:1) solution was added to one gram of oil, to this mixture 0.5g of NaOH was added, 20 ml of methanol and 3 ml of water. This mixture was placed on a grill at 78 °C for one hour and allowed to cool to room temperature. Subsequently, 20 ml of methanol and 3 ml of HCl were added and it was placed back on the grill at 78 °C for 1 hour. Subsequently, 20 ml of hexane was added and this mixture was placed in 50 ml separatory funnels. The hexane phase was separated and placed in the fume hood to remove the hexane, the remaining solution was resuspended in 500 µl hexane and analyzed by gas chromatography.

The transesterification reaction was carried out using the lipid fraction extracted from the sludge by adding 3 ml of hexane. Subsequently, an aliquot equivalent to 10 mg was taken and placed in a 10 ml test tube and placed in the extraction hood to evaporate the hexane. Subsequently, 3 ml of a mixture of solvents Methanol:HCl:Chloroform (10:1:1) was added, stirring in a vortex for 5 min. The tube was placed in a Buchi R-200 rotary evaporator in a water bath at 90 °C for 2 hours and 2 ml of deionized water was added and extractions were carried out with 2 ml of a mixture of hexane: chloroform (4:1). The upper phase (hexane) was recovered and 0.5g of anhydrous Na2SO4 was added to maintain moisture-free conditions. The hexane was removed in a Buchi R-200 rotary evaporator at 60°C. The dried sample was resuspended in 100 µL hexane, placed in 300 µL vials, brought to dryness and resuspended in 50 µL and analyzed by gas chromatography.

CHROMATOGRAPHIC ANALYSIS

A Perkin Elmer 9000 series gas chromatograph equipped with an ionized flame detector and a 30 m × 0.25 mm × 0.25 µm Omegawax TM-250 fused silica capillary column were used. The temperature in the column oven was programmed to be kept at 150°C for one minute and then increased from 150 to 250°C at 5°C min-1 and finally kept at 250°C for 35 minutes. Helium was used as carrier and 2 µl of sample was injected with a split ratio of 80:1. A mixture of 37 methylated fatty acids (47885-U, 37 Component FAME Mix; Supelco, Bellefonte, PA, USA) was used as standard.

RESULTS AND DISCUSSION

Figure 1 shows the Gravimetric Yields obtained in the Xul-Ha, Centenario and Fovissste treatment plants. The Figure shows that the highest average Yield was obtained at the Centenario plant with a value of 8.96% ± 0.91. The Fovissste plant presented an average value of 5.10% ± 0.87 and the Xul-Ha plant of 3.87% ± 0.58. These yields are below the Gravimetric Yields reported by Dufreche et al (2007), where they determined an oil content of approximately 28 % in dry secondary activated sludge

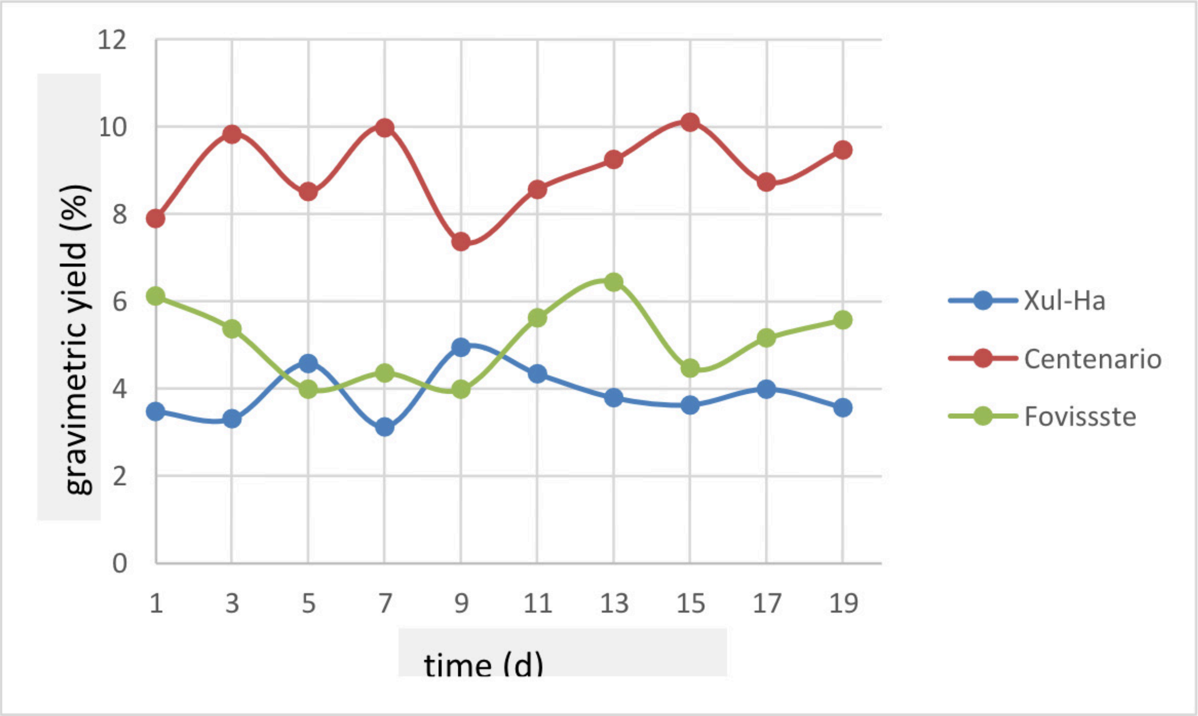

Figure 1. Gravimetric yields (grams of oil per gram of dry sludge) in three treatment plants.

Saturated Fatty Acid	Percentage	Unsaturated Fatty Acid	Percentage
lauric (C12:0)	0.38	oleic (C18:1)	13.93
myristic (C14:0)	3.41	linoleic (C18:2)	7.40
pentadecanoic (C15:0)	1.58	linoleic (C18:3)	2.66
palmitic (C16:0)	37.95	palmitoleic (C16:3)	7.43
heptadecanoic (C17:0)	1.62	Others	6.65
stearic (C18:0)	14.25		
arachidic (C20:0)	0.98		
Lignoceric (C24:0)	0.47		

Table 1. Percentages of saturated and unsaturated fatty acids in activated sludge oil from the Fovissste plant.

samples. The variation of the Yields obtained in the treatment plants studied, may be due to the amount of fats and oils present in the residual water. Table 1 presents the average percentages of saturated and unsaturated fatty acids in the activated sludge oil from the Fovissste plant. The percentages of myristic, palmitic, stearic and linoleic acids are within the range of percentages reported by Demirbas et al, (2017) with the exception of lauric, palmitoleic, oleic and linoleic fatty acids (18:3).

The percentages of free fatty acids quantified for the oil samples from the three plants were between 0.38 and 6.64% with an average value of 4.45%. this percentage is lower than the average percentage reported for jatropha curcas of 14% (Patil et al., 2009). It has been reported that in the specific case of jatropha curcas the presence of free fatty acids in the oil affects transesterification reactions when the content of free fatty acids in the oil exceeds 3% (Patil et al., 2009). Additionally, esterified free fatty acids produce water as a by-product and this also affects biodiesel production. The Centenario plant presented an average value of 5.4% of free fatty acids while the Fovissste V Etapa and Xul-Ha plants presented average values of 3.1% and 2.8% respectively. The low percentages of fatty acids in the oil from the sludge of these plants would allow a good transesterification of oil in the production of Biodiesel.

CONCLUSIONS

The oil extracted from activated sludge samples from the Fovissste V Etapa, Xul-Ha and El Centenario wastewater treatment plants was characterized. The gravimetric yields of oil from the El Centenario plant were higher than the other plants with an average value of 8.96% ± 0.91. the lowest yields were obtained in the Xul-Ha plant. These values are below the values reported by Dufreche et al, (2007). Through the chromatographic analysis of the oil samples, average values of free fatty acid percentages of 5.4 %, 3.1% and 2.7 % were determined for the Centenario, Fovissste V Etapa and Xul-Ha plants, respectively. Additionally, the oil was characterized to measure the percentages of saturated and unsaturated fatty acids where it was observed that palmitic and stearic acids were present in a greater proportion in the samples analyzed from the three plants. The oil extracted from the activated sludge generated in these plants can be transesterified for the production of biodiesel where the presence of free fatty acids is lower with respect to the oil extracted from jatropha curcas.

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