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Green solvent extraction of lipids from sewage sludge of wastewater treatment plants

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This study reports the analysis of lipids extraction from sewage sludge using ethyl esters of volatile fatty acids (EEVFA). EEVFA are naturally occurring compounds, representing ones of the main constituents of flavour of fruits. They can be considered bioderivable solvents, since industrially obtainable through direct esterification of ethanol and VFAs, which can be both produced through fermentation of dedicated or exhausted feedstocks. In addition, they are easily hydrolysable in an aqueous environment, by regenerating species of origin which are completely biodegradable. For all these reasons, the use of EEVFA as extracting solvents would minimize the environmental impact respect with conventional solvents (hexane is typically used). A theoretical thermodynamic study of the lipids extraction was performed with an experimental matrix that emulated the chemical characteristics of a sewage sludge. This theoretical study was performed to obtain the phase diagrams for the lipids extraction and to identify the optimum operating conditions. A comparison of the lipids extraction using these green solvents and hexane was also performed. Then, the optimum conditions were tested and validated on real samples of sewage sludge, sampled from different municipal wastewater treatment plants. Theoretical thermodynamic studies, as well as experimental evidences confirmed that ethyl butyrate was an alternative and effective green solvent to extract lipids from sewage sludge.

Key words: Calcium soaps, sewage sludge, green extraction, volatile fatty acids, ethyl esters.

INTRODUCTION

Sewage sludge is an urban waste biomass that is generated in large quantities by water treatment plants [1]. This waste has been considered as an interesting source to recovery components that can be used to obtain high added value products [2]. In particular, the sewage sludge contains a significant amount of lipids that can be converted into biofuels [3]. The lipids recovery from this biomass implies different challenges and is a fundamental stage to determine the feasibility, costs of biofuel production and environmental impact using this feedstock [4]. Lipids recovery via extraction processes is mainly affected by the physicochemical properties of the organic solvent applied [5-7]. Hexane is the most preferred organic solvent adopted for extracting lipids from biomasses, but it has a huge impact and several drawbacks [8]. Therefore, this study reports the analysis of lipids extraction from sewage sludge using ethyl esters of volatile fatty acids as green solvents. Ethyl esters of volatile fatty acids are natural occurring compounds, whose use in industry has been growing for the relevant biodegradability and bioderivability [9]. First, a theoretical thermodynamic study of the lipids extraction was performed with an experimental matrix that emulated the characteristics of a sewage sludge where calcium soaps were used as the lipid phase. This theoretical study was performed to obtain the phase diagrams for the lipids extraction and to identify the optimum operating conditions. A comparison of the lipids extraction using these green solvents and hexane was performed. In a second stage, the optimum conditions were tested and validated with a real sample of sewage sludge.

MATERIALS AND METHODS

Composition of an urban primary sewage sludge

Samples of urban primary sewage sludge (2-4 % wt of total solid) were monthly up-taken from the WWTP of Aguascalientes (México), which has a treatment capacity of 2000 $l.s^{-1}$ raw wastewater. The sludge was dewatered through filtration and/or centrifugation up to 8-10 % wt of total solids and fully characterized by adopting analytical procedures reported in literature [10]. 20-25 $\%_{TS}$, 10-15 $\%_{TS}$, 20-30 $\%_{TS}$ and 15-20$\%_{TS}$ were determined for lipids, cellulose, proteins and ashes respectively.

Preparation of calcium soaps from palm oil

Calcium soaps were synthesized from palm oil (food grade) via a saponification reaction. The reaction system included 10 g of palm oil, 3 g of potassium hydroxide and 100 mL of ethanol.

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Saponification reaction was performed at 373 K for 1 h. The potassium salts of fatty acids were used in a second reaction for transforming these potassium soaps into calcium soaps. This reaction was performed with an aqueous solution of calcium chloride at room temperature and atmospheric pressure under constant stirring at 300 rpm for 3 h. Calcium soaps were stored at 277 K for 15 h and the solids were washed with deionized water and dried at 373 K for 24 h.

Determination of phase diagrams for the lipids extraction with green solvents

Phase equilibrium data of the lipids extraction were recorded using an experimental matrix that emulated the composition of a sewage sludge obtained from a municipal wastewater treatment plant. This matrix was composed of 50 mL of deionized water, 1 g of cellulose, 2 g of protein (food grade, brand Isopure) and 2 g of calcium soaps. Hexane, ethyl acetate, ethyl propionate and ethyl butyrate were the solvents employed in the extraction studies of calcium soaps. Phase diagrams were obtained by varying the amount of the solvent where the extraction data were obtained at 297 K and pH of 6.4 ± 0.1. The solvent and the aqueous solution containing the calcium soaps were mixed for 1 h under constant stirring of 250 rpm. The organic and aqueous phases were separated, weighted and dried where the mass loss was quantified. Results of the material balance of drying process was used to calculate the amounts of hexane and ethyl acetate in the extractions studies, while gas chromatography was utilized to quantify ethyl propionate and ethyl butyrate. The dehydrated solids from extraction studies were grounded and used in a reaction with a solution of 2 g/L of heptadecanoate in methanol at 273 K for 2 h. The content of the methyl esters of fatty acids in the solution was quantified with gas chromatography. All the experiments were performed in duplicate and the average value was used for data analysis. Tie-lines for the extraction phase diagrams were calculated with material balances. A ternary system was considered for data analysis, which implied the mass composition (g) of the calcium soaps *J*, solvent *S* and a pseudo-component *Ps* formed by the aqueous solution containing the protein and cellulose. This approach allowed to visualize and analyze the thermodynamic data in a ternary diagram. Thermodynamic consistency of phase diagrams was verified using the Othmer-Tobias and Hand models. The modeling of theoretical phase diagrams for the calcium soap extraction was performed using an artificial neural network. Recovery of calcium soaps with different solvents was calculated and the optimum conditions for the extraction was identified.

Validation of the optimum conditions of the lipids extraction process using samples of sewage sludge

The optimum extraction conditions identified in the thermodynamic theoretical studies were tested and validated with samples of real sewage sludge. Extraction studies were performed with ethyl butyrate and results were compared with those obtained using hexane, which was used as a reference solvent. 55 g of the dehydrated sludge were used in extraction studies with different amounts of tested solvents.

ANALYSIS OF RESULTS

Characterization of urban sewage sludge carried out on samples up-taken from the urban WWTP of Aguascalientes (México), confirmed results already reported concerning the nature and the amount of the lipid phase [11]. In detail, lipids were always ranged among 20-25%TS and they were mainly constituted by calcium soaps per over 85%. For this reason, the optimization study of the extraction of lipids from sewage sludge has been carried out on a synthetic mixture, whose composition respected the typical profile in terms of lipids, cellulose and proteins of a primary sludge. Considering that lipid in primary sludge were principally calcium soaps with a high content of saturated fatty acids, Palm oil (food grade) was used for preparing synthetic calcium soaps. XRD and FTIR spectroscopy were utilized to characterize these calcium fatty soaps, whereas the profile of fatty acids was defined through gas-chromatographic determination (Figure 1).

FTIR analysis presents a high diagnostic power in identifying in the carbonyl region the asymmetric stretching of carbonyl which appears typically as a couple of bands at 1576 and 1540 cm^{-1} as already reported [12,13]. Once that "synthetic" fatty calcium soaps were prepared, synthetic sludge was further prepared by mixing to calcium soaps the right amount of cellulose and proteins. Then, optimization of extracting procedure was carried out. All phase diagrams can be classed as Type I where a two-phase region was present. Extraction phase diagrams indicated that the two-phase region obtained with hexane and ethyl butyrate was greater than those of ethyl acetate and ethyl propionate. Differences in the extraction phase diagrams can be associated to the polarity and water solubility of tested solvents. Determination coefficients (R^2)

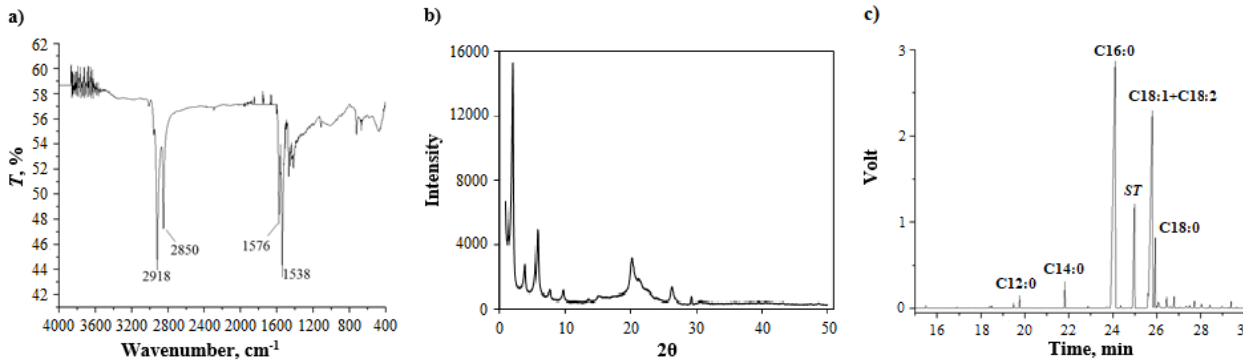

Fig. 1. a) FTIR spectrum, b) X-ray diffraction pattern of calcium soaps and c) GC spectra of the product obtained from the reaction of calcium soaps and methanol in presence of methyl heptadecanoate as internal standard.

higher than 0.82 were obtained for the thermodynamic consistency assessment with both Othmer-Tobias and Hand models. Recovery of calcium soaps ranged from 82 to 98 % using 4 – 44.5 g of tested solvents. Hexane and ethyl butyrate were the best solvents and showed the highest recoveries in the theoretical extraction studies of the calcium soaps. The artificial neural network model was reliable to correlate and predict these extraction phase diagrams. Finally, the performance of hexane and ethyl butyrate using samples of sewage sludge was confirmed where the lipids recoveries were higher than 90%. However, ethyl butyrate is a bioderivable solvent that can offer additional advantages, mainly in terms of environmental impacts, in comparison with hexane

CONCLUSION

The use of ethyl esters of volatile fatty acids for the recovery of lipids from sewage sludge has been analyzed and compared. Theoretical thermodynamic studies confirmed that ethyl butyrate was an alternative and effective green solvent to extract calcium soaps. This green solvent showed high lipids recoveries in experimental matrix and samples of sewage sludge.

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