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

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Introduction

Sewage sludge is an urban waste biomass that is generated in large quantities by water treatment plants. This waste has been considered as an interesting source to recovery components that can be used to obtain high added value products. In particular, the sewage sludge contains a significant amount of lipids that can be converted into biofuels. The lipids recovery from this biomass implies different challenges and is a fundamental stage to determine the feasibility and costs of biofuel production using this feedstock. Lipids recovery via extraction processes is mainly affected by the physicochemical properties of the solvent applied. Therefore, this study reports the analysis of lipids extraction from sewage sludge using ethyl esters of volatile fatty acids as green solvents. 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 obtained from a municipal wastewater treatment plant.

Materials and Methods

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. 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. 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. FTIR spectroscopy was utilized to characterize the 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 heptadecane 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 sewage sludge. These samples were collected from a municipal wastewater treatment plant

located at the city of Aguascalientes, México. This treatment plant has a capacity of 2000 L/s. The sludge was dehydrated and the amount of lipids, total solids and ash was determined. 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.

Results

Figure 1 shows the phase diagrams for the extraction of calcium soaps with the four solvents, which are reported in mass fractions *w*. 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) 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.

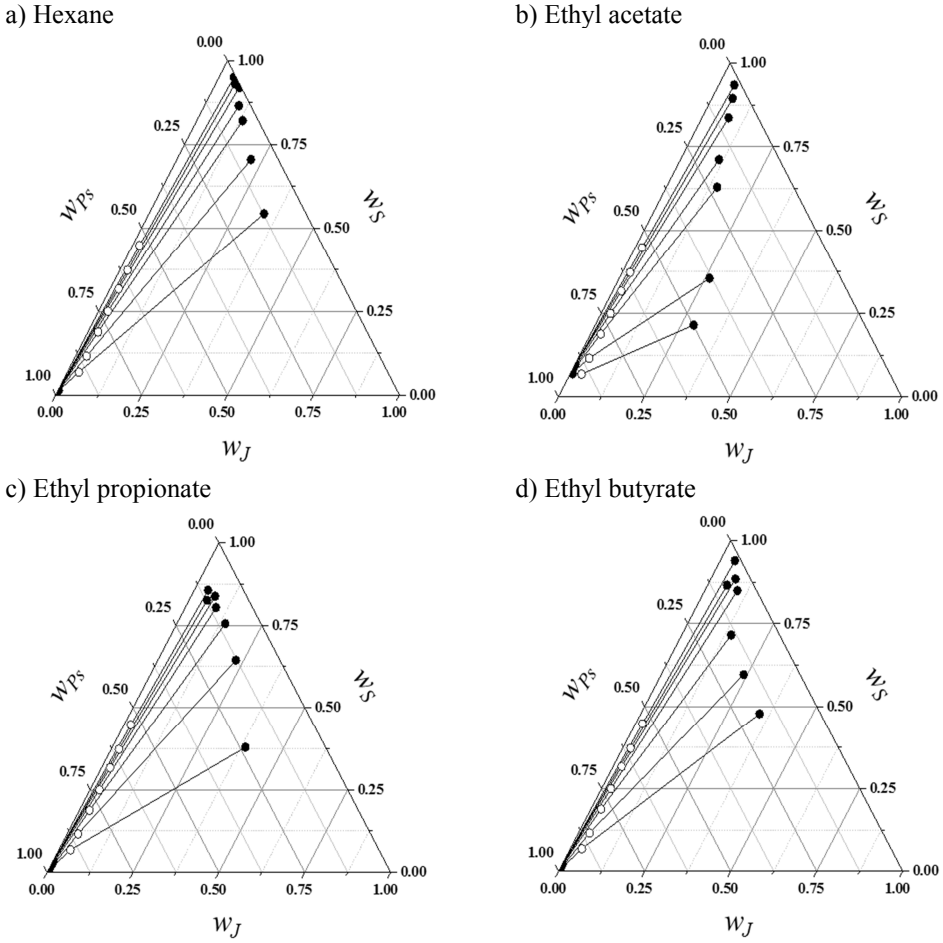

Fig 1. Phase diagrams for the extraction of calcium soaps using hexane and green solvents.

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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