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Valorisation of spent *Calendula Officinalis* by Ionic Liquids

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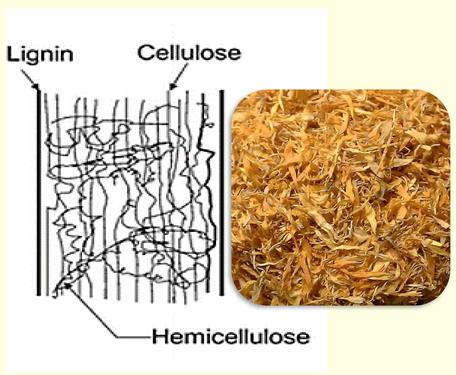
INTRODUCTION

Calendula officinalis is cultivated to produce bioactive extracts with added-value in cosmetic and pharmacy industry [1]. After its extraction, the spent *Calendula officinalis* (SCO) is a biomass residue that can be valorized. Recently, some studies have revealed that ionic liquids (IL) can easily dissolve carbohydrates, wood, and lignin by their interaction with the hydroxyl groups of cellulose breaking the hydrogen bonds, which link cellulose, hemicellulose and lignin. Therefore, ILs can be considered as a promising method for lignocellulosic biomass pretreatment for fermentation or biofuel production [2]. We investigated the feasibility of a high biomass load (10% w/v) in the hydrolysis of SCO with 1-Ethyl-3-methylimidazolium chloride (Emim[Cl]) at different IL to biomass (ILB) ratios.

MATERIALS AND METHODS



Spent *Calendula officinalis (SCO)*

Biomass Pretreatment with Ionic liquid

T= 80, 100, and 120 ºC; t= 2 h
Water load= 20 mL. Biomass concentration 10 % w/v.
Blank assay (hydrothermal): 2 g biomass and 20 mL water
ILB ratios (w/w): 1, 3, 5 (g ionic liquid/g dried biomass)

Ionic liquid and product recovery

Filtration → **Solid product** → **Wash-up** → Deionized water ↓ byproducts

Liquid product ↓

Separation ← Isopropanol

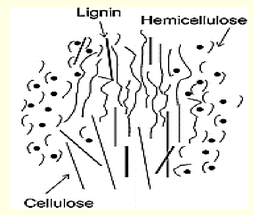
IL Recovery yield of 70% ↓

Vacuum distillation → Isopropanol water

Recirculation ← Ionic liquid recovered

Characterization of solid and liquid products

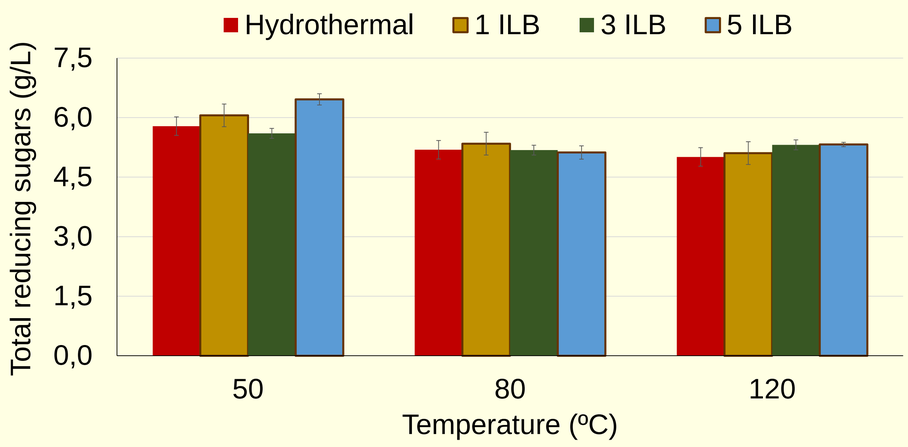
Final solid product



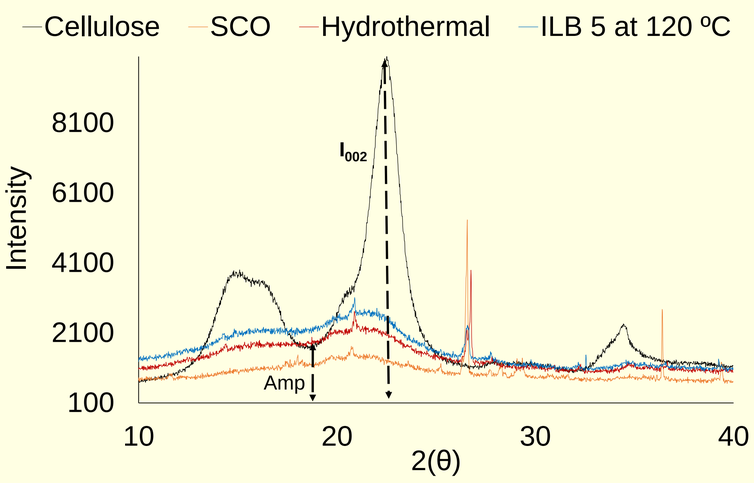
Solid product:
- ❑ Elemental composition
- ❑ X-ray powder diffraction
- ❑ Fourier-transform infrared spectroscopy

Liquid product:
- ❑ Total reducing sugars

RESULTS



Effect of treatment temperature on sugar production at different IL:biomass ratio



$$Crl(\%) = \frac{I_{002} - I_{amp}}{I_{002}} \times 100$$

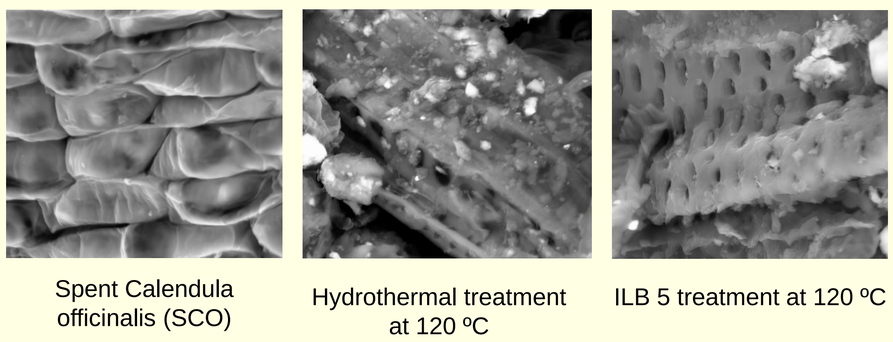
Crl= Crystallinity Index

I_{002} = Intensity of the highest pick in the plane (002) at the diffraction angle 2 (ɵ) =22.4º

I_{amp} = Intensity of the highest pick for amorphous cellulose at the diffraction angle 2(ɵ) =16º

Sample	I_{002}	I_{total}	CrI (%)
SCO	1938	9667	20.1
Hydrothermal	2330	10030	23.2
ILB 5 at 120 ºC	2654	11393	23.3

X-Ray powder diffraction: Reduction in cellulose crystallinity of SCO by ionic liquid treatment

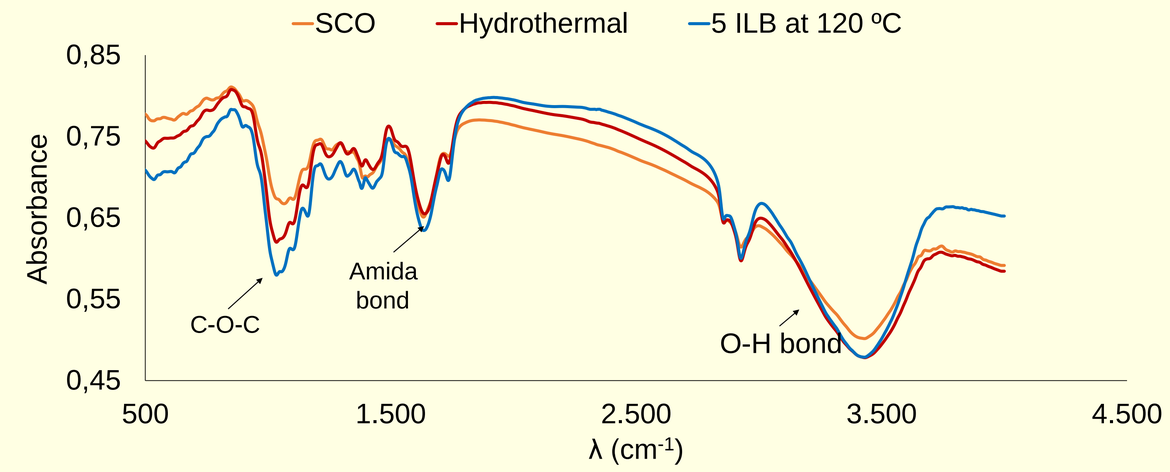


Spent Calendula officinalis (SCO)

Hydrothermal treatment at 120 ºC

ILB 5 treatment at 120 ºC

SEM analysis: Changes in superficial area in Calendula officinalis by ionic liquid treatment



FTIR analysis: Changes in lignocellulosic polymer bonds in SCO by ionic liquid treatment

CONCLUSSIONS

- EmimCl could effectively dissolve a high load of *Calendula officinalis* (10 % w/v) into sugars. Although, increase in treatment temperature did not improve the sugar recovery from liquid fractions, due to sugar hydrolysis at high temperature; increase in treatment temperature boosted structural changes in lignocellulosic matrix of solid products.
- The SEM analysis confirmed that IL treatment drained away organic compounds adsorbed in the SCO. Then, a spongy solid product with characteristics of porous material was produced.
- The X-ray diffraction and FTIR analysis showed changes in polymeric matrix structure of SCO by means to EmimCl pretreatment. SCO presented poor crystallinity index which indicated that a significant percentage of cellulose in the feedstock had already changed into amorphous cellulose during extraction of bioactive compounds. Then, the IL treatment boosted re-crystallization of cellulose despite the treatment conditions (ILB of 5, t=2 h, T=120 ºC) used, which have been reported elsewhere to be effective conditions for IL treatments to loads below 5% (w/v).

References

[1] López-Padilla, A., Ruiz-Rodriguez, A., Reglero, G., Fornari, T. (2017) Supercritical carbon dioxide extraction of Calendula officinalis: Kinetic modeling and scaling up study. The Journal of Supercritical Fluids 130, 292–300.

[2] Aung A.U., Endo T., Fujiia, S., Kuroda, K., Ninomiyad, K. (2018) Efficient pretreatment of bagasse at high loading in an ionic liquid. Industrial Crops & Products 119, 243–248.

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