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OBTAINING AND ANALYSIS OF YIELD FOR EXTRACTION OF OILS AND EXTRACTS FROM HOP (*HUMULUS LUPULUS L.)* VIA SOLVENT EXTRACTION AND ULTRASOUND PRE-TREATMENT

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Abstract: Hops (Humulus lupulus L.), a plant that belongs to the Cannabaceae family, has played an important role in the brewing industry, being an essential component in the production of beer, as it contributes to the chemical and sensorial qualities of the drink, imparting the aroma, bitterness, in addition to having antioxidant, anti-inflammatory, antifungal activities and other applications that can be associated with the insertion of the oily extract of this plant applied in different food products. In turn, extraction techniques are fundamental processes used to isolate specific constituents, primarily used to extract oils and essences that find applications in various fields, such as hops. The objective of this work was to comparatively analyze the yields obtained from the extraction of oils and extracts from Humulus lupulus L., using the solvent extraction technique with the application of ultrasound pre-treatment, aiming to optimize and improve these processes. For the three-hour extraction, 10 g of hops of the Citra® variety were used in T90 pellet format, previously crushed with particle size > 40 mesh, into 300 mL of solvent, hexane and ethanol being chosen for this work. And for the parameters used in ultrasound pretreatment, a duration of 20 minutes, a 12 mm tip and a power rate of 50% were defined. At the end of the extractions, the average yield results obtained for extractions with hexane and ethanol without pre-treatment were, respectively, 32.35% and 43.02% and with pre-treatment they were 25.27 % and 43.34%. From these results it was possible to conclude that the extraction of oil and essences from Humulus lupulus L. by solvent proved to be efficient, especially ethanol, and the use of ultrasound pre-treatment did not significantly influence the yield.

Keywords: Humulus lupulus L.; Oils and essences; Extraction methods; Solvent extraction; Ultrasound.

INTRODUCTION

Humulus lupulus L., belonging to the Cannabaceae family, is a plant widely cultivated for commercial purposes, being predominantly used in the brewing industry (DURELLO, 2019). This occurs due to the presence of compounds of interest, such as resins, polyphenols and, mainly, essential oils, which are volatile and valuable compounds. Due to their chemical properties, these oils and extracts add benefits and stability to the drink (ALMAGUER, GASTL, SCHÖNBERGER, et al., 2014); (DURELLO, 2019); (SILVA, 2018). In addition to its great role as a raw material for beer production, hops are also used for various applications in other sectors, from the pharmaceutical industry to cosmetics, leading to interest in different research due to their beneficial health properties (SIQUARA, 2020).

Germany and the United States are the countries that stand out most for hop production and Brazil is in third place as the largest beer producer in the world (RODRIGUES et al., 2015); (CARVALHO et al., 2018).

Hops in pellet format are one of the most common forms of commercialization and use in the manufacture of beer, mainly due to their conservation (RODRIGUES et al., 2015). In this work, T90 pellets were used, which contain around 90% of natural hops (RODRIGUES et al., 2015).

The main part of interest of *Humulus lupulus* L. are the cones of the female plant, which have a greater quantity of lupulin glands, responsible for the production of resins and essential oils, than male plants (SPÓSITO et al., 2019).

To obtain the volatile components of hops, the solvent extraction method was adopted, which consists of placing the solvent in contact with plant matter, which were selected based on their solubility properties and after a period of interaction between the solvent and the vegetable matrix, the oil is obtained by evaporation of the solvent (SILVEIRA et al, 2012).

As highlighted by Biendl (2009), α-Acids and β-Acids, present in hop essential oils, in addition to playing a fundamental role in contributing to the aroma and bitterness of beer, are also linked to metabolic functions and have anti-inflammatory properties. inflammatory and antifungal. Furthermore, xanthohumol, another compound present in the oil, has been shown to have anti-cancer activities, adding to the other benefits present in hop compounds (Biendl, 2009).

Based on the above, conducting scientific studies aimed at obtaining and characterizing these compounds becomes extremely important. In the present work, we used the extraction technique using organic solvents via soxhlet, valuing a choice of less aggressive solvents, to obtain the oils and extracts from *Humulus lupulus L.*

METHODOLOGY

GRANULOMETRIC ANALYSIS

To carry out the extractions, the samples were previously crushed and subjected to a granulometric analysis, in which the samples were placed on sieves and shaken by the granulometer to be separated by their dimensions, with a mesh > 40 being chosen.

EXTRACTION WITHOUT ULTRASOUND PRETREATMENT

The extractions were carried out in duplicate, using 10g of Citra® hops, in T90 pellet form, produced by Barth-Haas Group and packaged by LND Latino Americana. The procedure consisted of 3 hours of extraction, in which 300 mL of solvent (ethanol or hexane) were added to volumetric flasks, previously weighed, for each sample. Then, the flask containing the solvent and oily compounds was subjected to rotary evaporation to separate them. For future analyzes and quantification of yields, the samples were properly weighed and stored in a Falcon tube containing 25 mL of the respective solvent in a refrigerator.

EXTRACTION WITH ULTRASOUND PRETREATMENT

After weighing 10g of hop sample and carrying out the granulometric analysis, pre-treatment by ultrasound (US) was carried out. The parameters determined were as follows: 20 minutes of procedure, power rate: 50%, tip size 12 mm, pulse on: 2.0s and pulse off: 4.0s. After pre-treatment, the samples were subjected to the extraction process following the same procedures mentioned previously in item 2.2.

CHARACTERIZATION OF BIOACTIVE COMPOUNDS

To characterize the samples that were previously stored in the Falcon tube, they were subjected to analysis using Fourier transform infrared spectroscopy (FTIR), which will provide the absorption bands that correspond to the vibration of functional groups present, using a relationship between the radiation transmittance by the wavenumber.

DATA ANALYSIS

From the data collected, the yields obtained were quantified using the equations demonstrated in Formulas 1 and 2. And after submitting the samples to FTIR, the transmittance bands obtained were analyzed and compared for a characterization of the compounds of interest present.

$$\text{Flask mass after rotary evaporation (g)} - \text{Initial flask mass (g)} = \text{Extraction obtained (g)}$$

Formula 1.

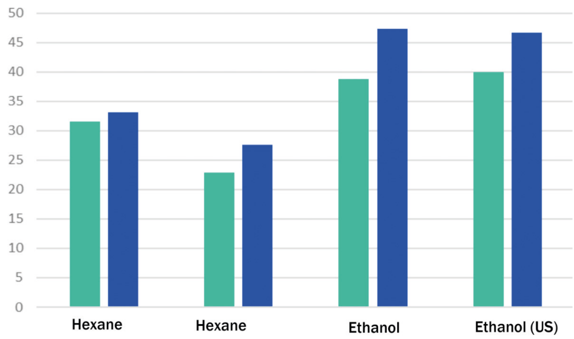
$$\text{Yield (\%)} = \frac{\text{Extraction obtained (g)} \times 100}{\text{Initial hop mass (g)}}$$

Formula 2.

RESULTS

SOLVENT EXTRACTION OF HUMULUS LUPULUS L. VIA SOXHLET

The results obtained in solvent extraction (hexane and ethanol) with and without the application of ultrasound pretreatment were expressed in Graph 1 and Table 1.



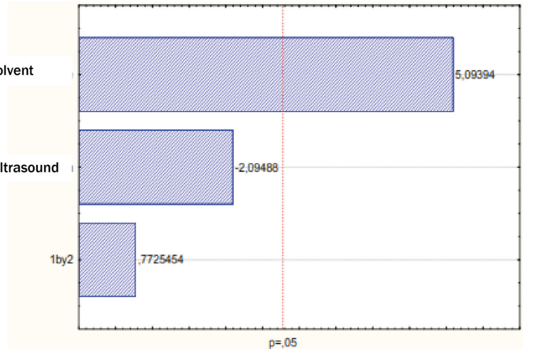
Graphic 1: Comparison of yields obtained from *Humulus lupulus* L. via Soxhlet.

Extraction conditions	Averages (%)	Standard deviation
Hexane	32,35	± 1,17
Hexane (US)	25,27	± 3,34
Ethanol	43,02	± 6,01
Ethanol (US)	43,33	± 4,70

Table 1: Means and standard deviations of income obtained from *Humulus lupulus L.*

Graph 1 displays the results obtained through the use of the soxhlet extraction technique, in which the results are compared with and without the application of Ultrasound (US) pre-treatment. However, as shown in Table 1, the need to perform additional repetitions for each extraction was identified, given the high standard deviations. Such variations can be attributed to possible operational errors, contamination and other factors. It was observed that the most effective solvent was ethanol, but the yields obtained in both extraction conditions with and without US were similar.

In Graph 2 and Figure 1 there is a greater analysis of the most effective conditions for extractions.



Graph 2: Significance of the analyzed conditions.

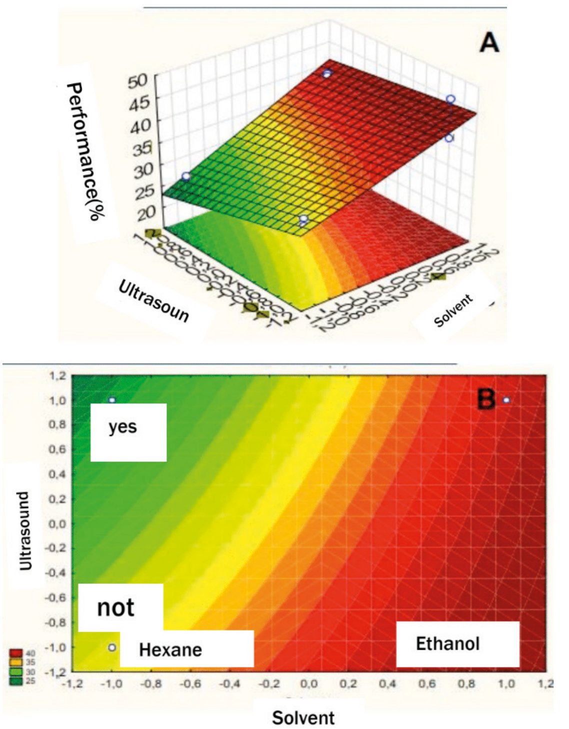


Figure 1: Response surface model (A) and extraction yield contour (B).

When analyzing the data present in Graph 2, it becomes evident that the yields obtained by the soxhlet solvent extraction method are influenced only by the solvents analyzed, with no influence from the ultrasound pretreatment or the interaction between the solvent and the ultrasound. And the response surface model together with the level curve (Figure 1) demonstrates where the point of highest yield obtained experimentally is directed, in this case, in extractions with ethanol.

TRANSMITTANCE SPECTRUM ANALYSIS IN FTIR

According to Almeida (2019) and comparing with the infrared spectra of hop extracts obtained by the same author (Figure 2), for Figures 3 and 4, it is observed that in bands of lengths between 790 and 840 cm^{-1} we can identify the C=C group of alkene compounds. In transmittance bands close to 1600 cm^{-1}, the frequencies of the C-C group present in aromatic compounds are characteristic. In transmittance bands close to 1390 cm^{-1}, the presence of C=O groups can be identified.

The frequencies between 2850 and 3000 cm^{-1} correspond to the C-H group present in alkane compounds, while in the bands of length close to 2900 cm^{-1}, there is the band referring to the aliphatic C-H groups.

For Figures 5 and 6, it is mainly noted at lengths between 1000 and 1100 cm^{-1}, where the bands related to the C-O group associated with phenols stand out. And in the broad bands present between the frequencies of 3100 and 3500 cm^{-1}, the O-H groups are present.

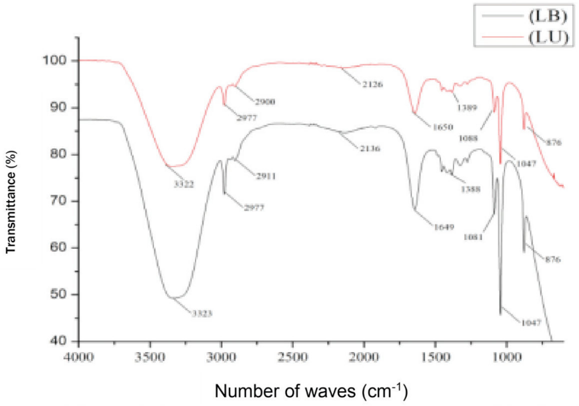


Figure 2: Comparison of Brazilian (LB) and US (LU) hop extraction curves (ALMEIDA, 2019).

In the following figures, it is possible to notice that for the transmittance spectra of the same solvent, but with conditions with and without ultrasound pretreatment, there is no significant variation, however, there is a difference in the bands presented with the change in extraction solvent.

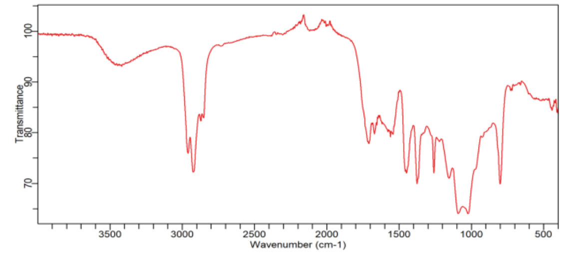


Figure 3: Transmittance curve using the solvent hexane without ultrasound pretreatment.

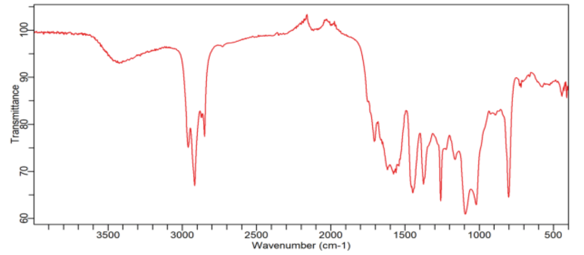


Figure 4: Transmittance curve using the solvent hexane with ultrasound pretreatment.

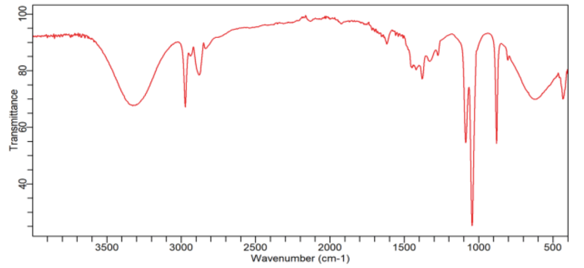


Figure 5: Transmittance curve using ethanol solvent without ultrasound pretreatment.

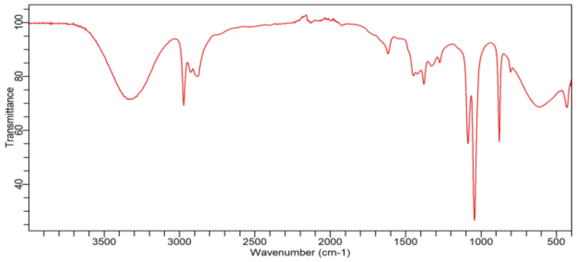


Figure 6: Transmittance curve using ethanol solvent with ultrasound pretreatment.

CONCLUSION

The method of extracting oils and extracts from *Humulus lupulus* L. using solvents proved to be efficient. Despite this, the use of ultrasound pretreatment did not have the expected impact, when compared to the solvent-free extraction method, without influencing the yields obtained. Highlighting, ethanol was the most effective solvent, obtaining higher yields throughout the extractions.

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