Adsorption of phenolics isolated from agricultural byproducts on solid sorbents.

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Introduction

Agricultural by-products contain substantial amounts of phenolic compounds characterized for their antioxidant properties. In this work, a method to recover and isolate high concentrated fractions of phenolic substances was developed. Extracts from olive leaves was used as a typical agricultural by-product, which was further fractionized in a cascade of membrane modules. The NF concentrate stream which was rich in phenolics was the tested sample in experimental process. Phenolic substances were isolated by extraction using various environmentally friendly solvents such as water, ethyl alcohol and water-alcohol mixtures. Then the extracts were fractionated on a membrane array, Ultrafiltration-Nanofiltration-Reverse Osmosis. The NF concentrate fraction, which contained the low molecular weight organics (simple phenols, carbohydrates) was further treated by a sorption/desorption process in a cylindrical column packed with XAD16N resin.

Figure 1: Experimental set-up for the adsorption/desorption processes. A 30-cm height column packed with XAD -16N resin (non-ionic, cross-linked polymer)

The aim of the present experimental study was to optimize the isolation and enrichment of phenolic compounds through their selective adsorption on resin. In the first series of experiments, standard compounds such as gallic acid (phenolic compound) and glucose (carbohydrates) were tested to find the optimal sorption and desorption times of the phenol and carbohydrate families and the sorption parameters were estimated using mathematical models. Next, experiments were performed with the NF fraction.

Results & Discussion

ADSORPTION EXPERIMENTS

Adsorption experiments, of a rich in phenols sample (4500mg/L of total phenolics) were performed, in a column packed with XAD 16N resin grains. Samples were collected at different time intervals (arrows in Fig. 2) to check the physicochemical characteristics of the extract, at the outlet of the bed and to arrive to safe conclusions for the compounds that are being adsorbed on the resin grains within the bed.

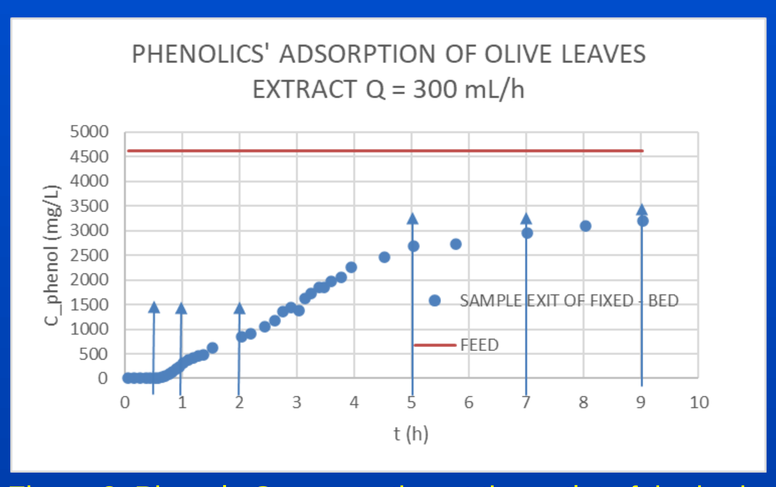

Figure 2: Phenols Concentration at the outlet of the bed versus time.

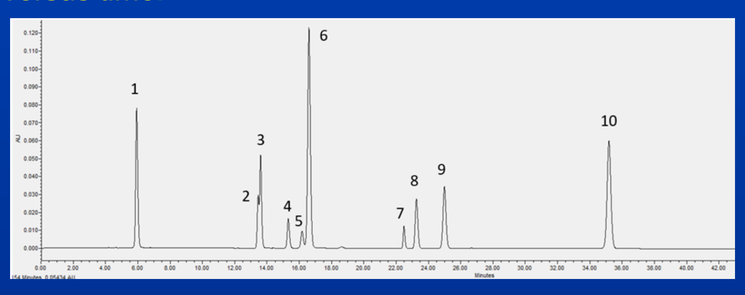

Figure 3: HPLC analysis for ten standard solutions versus time.

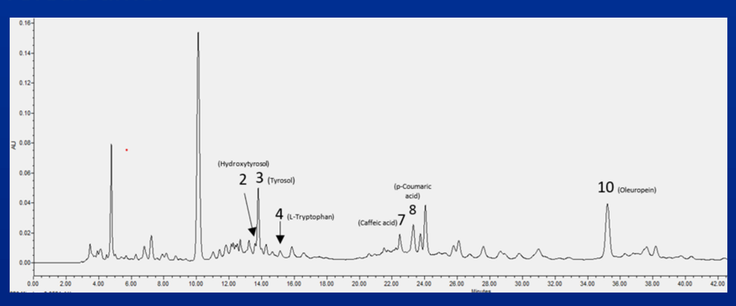

Figure 4: HPLC analysis for the phenolic compounds in the feed solution.

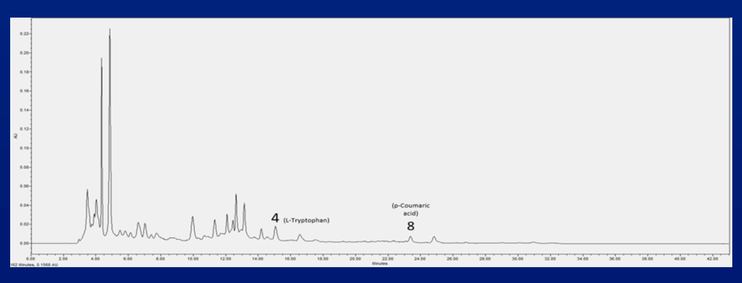

Figure 5: HPLC analysis for the sample collected at the outlet at 2 h.

During the adsorption, up to 2 hr only p-coumaric acid appeared at the outlet while at longer time tyrosol, hydroxytyrosol and caffeic acid appeared.

Oleuropein, the prevalent phenolic compound, did not appear. Thus, it is possible to isolate it, since it is trapped within the bed.

DESORPTION EXPERIMENTS

Desorption experiments took place in two steps; in the first step, clean water was injected in the resin bed for the removal of carbohydrates and in the second step, a mixture of alcohol and water was injected. Thus, at the second step phenolic compounds were eluted.

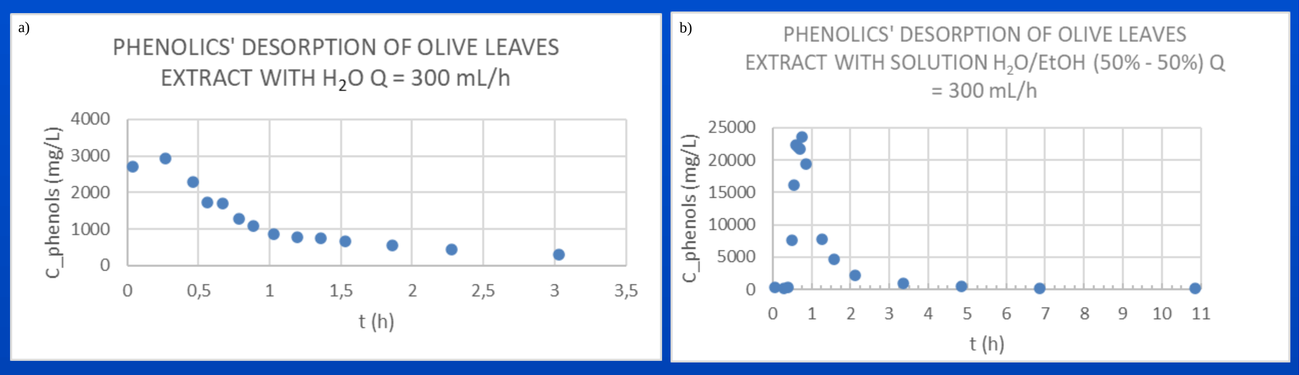

Figure 6: Concentration of phenolic compounds during a) the first stage of desorption with pure water and b) during the second stage of desorption with a mixture of ethanol and water

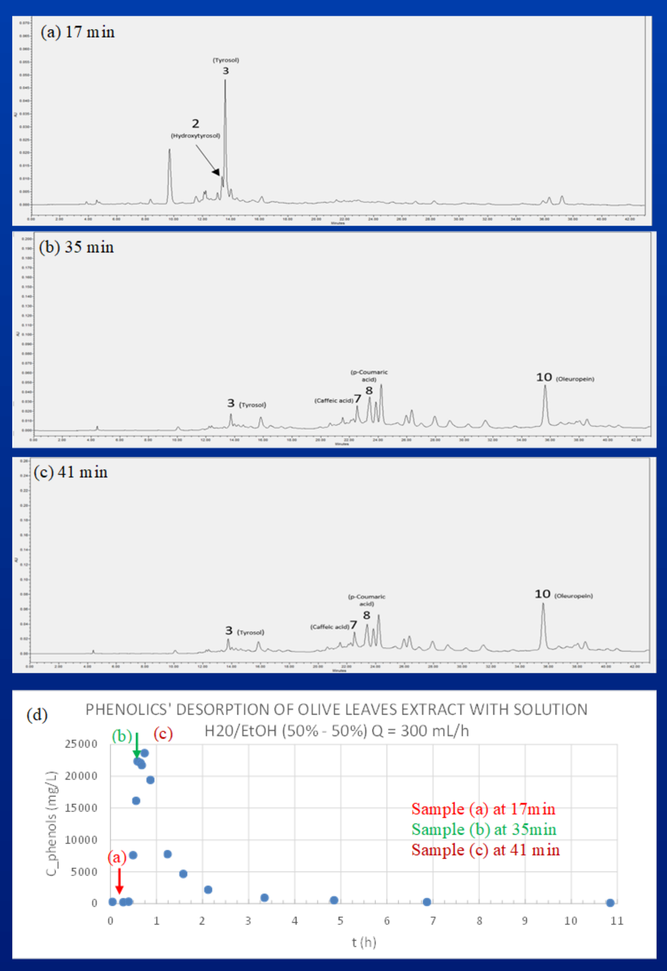

Figure 7: HPLC analysis for the samples collected the outlet of resin bed during the 2nd stage desorption process at a) 17min b) 35 min and c) 41min. d) Concentration of phenolics during the 2nd stage of desorption.

At the end of the first step of desorption and in the beginning of the second step, tyrosol and hydroxytyrosol appeared at the outlet. During the second step, caffeic acid and coumaric acid were eluted while oleuropein was eluted at longer times.

Conclusions

The HPLC analysis showed that the NF fraction contained hydroxytyrosol, tyrosol, caffeic acid, p-coumaric acid and oleuropein which was the prevalent compound. During the desorption process, the phenolic compounds were eluted progressively. A design of sorption and desorption experiments is possible to be done to isolate the main phenolics at high purities and to scale up at pilot and industrial scale.

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