Membrane filtration for the recovery of polyphenols from distillery stillage

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Introduction

The distillery industry contributes significantly to environmental pollution. For every 1 liter of alcohol produced, up to 15 liters of waste (distillery stillage) are generated. The stillage has low pH, high content of organics and nitrogen, and dark brown color. In line with the waste valorization approach, the recovery of value-added compounds with commercial potential from waste is a promising concept to reduce pollution and promote the economic competitiveness of the industry.

Distillery stillage is a source of polyphenols, including phenolic acids and flavonoids. Phenolic acids are derivatives of benzoic or cinnamic acids; they differ in the number and position of hydroxylated and methoxylated substituents on the aromatic rings, which affects their bioactive nature and antioxidant properties. Due to these properties, phenolic acids can be used in the pharmaceutical, cosmetic, and food industries.

Figure 1: Distillery stillage

To recover polyphenols from waste materials providing high yields and preserving the antioxidant activity of the recovered product, membrane technologies can be used because of high efficiency, simple equipment, low energy consumption, high selectivity, rapid separation, ease of scaling, and low recovery costs. The disadvantages of membrane filtration are the low chemical and mechanical strength of the membranes and the lower efficiency caused by fouling. However, fouling of membranes can improve the separation of compounds by size exclusion, reducing the effective pore size.

The objective was to investigate the possibility of using membrane pressure technique to recover polyphenols from distillery stillage and distillery stillage extracts. The effect of membrane pore size on total polyphenol content (TPC), total flavonoid content (TFC), phenolic acid species and contents, and antioxidant activity of the recovered compounds was investigated.

Results & Discussion

Distillery stillage, with the characteristics given in Table 1, was generated during the production of concentrated raw ethyl alcohol from cereals, mainly wheat and rye.

Table 1: Concentrations of pollutants in distillery stillage

Parameter	Concentration ± standard deviation (mg/L)
COD	48600 ± 1294
Total Nitrogen	4345 ± 386
Ammonium Nitrogen	8.4 ± 2.7
Total Phosphorus	280 ± 76
Volatile Fatty Acids	788.6 ± 137.0

For filtration of distillery stillage, membranes (Amicon Ultra-15 Centrifugal Filter Devices, MERCK) characterized by *cut-offs* of 100, 30, 10, and 3 kDa were used.

Membrane filtration was performed in two variants. In variant 1, the stillage supernatant (from stillage centrifugation at 8,000 rpm for 10 min) was filtered directly. In variant 2, membrane filtration was used to separate polyphenols from extracts formed during microwave-assisted extraction (MAE) of stillage using ethanol as solvent.
Antioxidant activity was measured by ABTS (2,2-azinobis (3-ethylbenzothiazoline-6-sulfonic acid)), DPPH (2,2-diphenyl-1-picrylhydrazyl) and FRAP (iron-reducing antioxidant activity) assays.

The highest TPC (4.57 mg GAE (gallic acid equivalent)/g d.m. (dry mass)) (Figure 2) and TFC (1.08 mg QUE (quercetine equivalent)/g d.m.) (Figure 3) were obtained in permeates from a membrane with a *cut-off* of 100 kDa. Reducing the pore size of the membrane to 3 kDa resulted in a decrease in TPC and TFC in permeates and an increase in retentates.

In permeates obtained at 100 kDa, total phenolic acid content (3.86 µg/g d.m.) and antioxidant activity (DPPH, FRAP and ABTS of 5.1, 3.4 and 25.1 µmol/g d.m., respectively) were also the highest. Antioxidant activity was positively correlated with phenolic acid content. Hydroxybenzoic acids (p-OH benzoic, vanillic, and syringic) and hydroxycinnamic acids (p-coumaric, ferulic and sinapic) were detected in permeates (Figure 4). Ferulic acid accounted for the largest proportion (42%) of the total phenolic acid content.

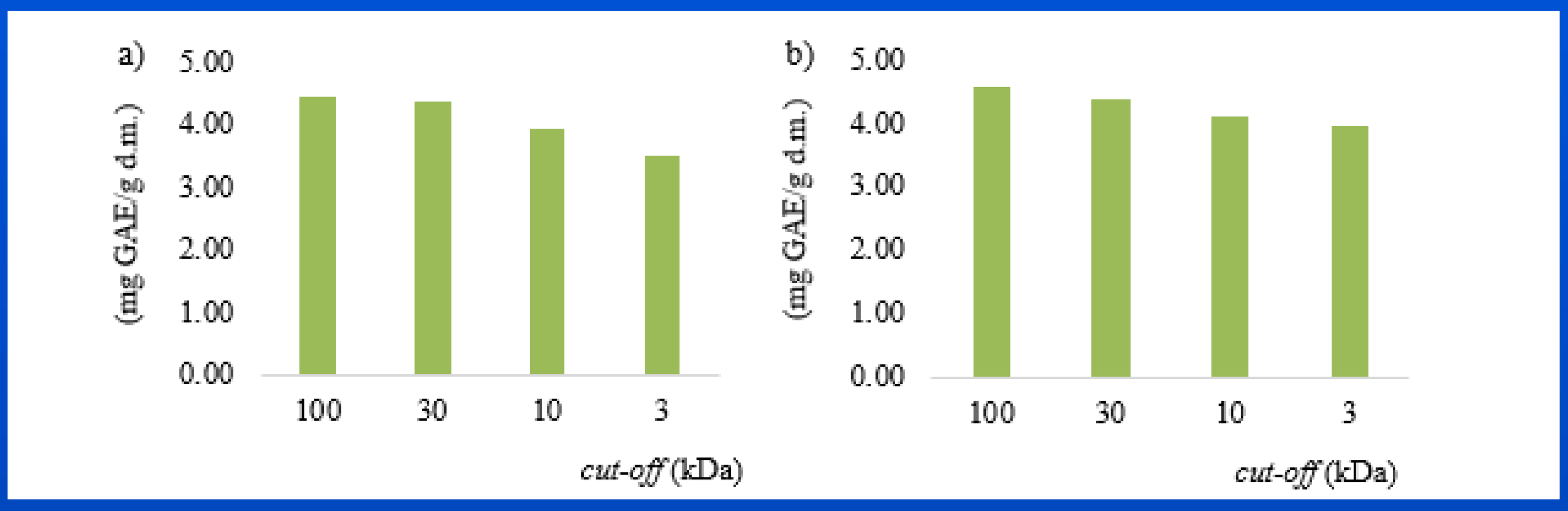

Figure 2: TPC in permeates after membrane filtration (variant 1) (a), and after MAE and membrane filtration (variant 2) (b)

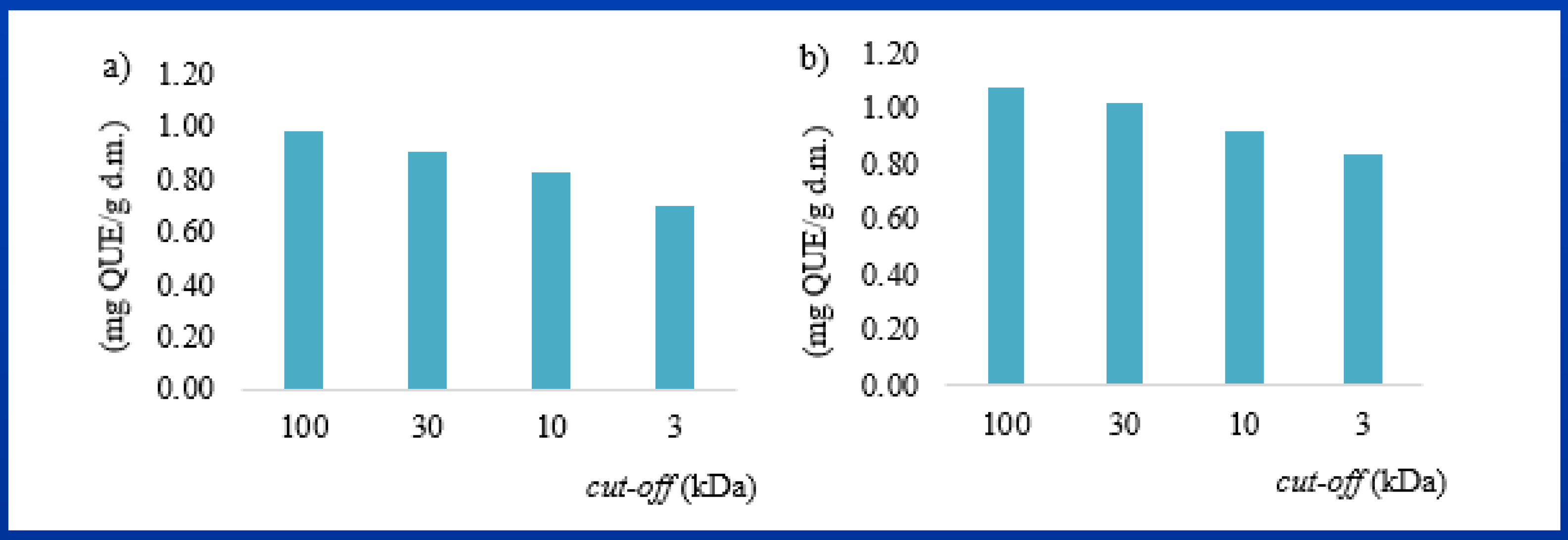

Figure 3: TFC in permeates after membrane filtration (variant 1) (a), and after MAE and membrane filtration (variant 2) (b)

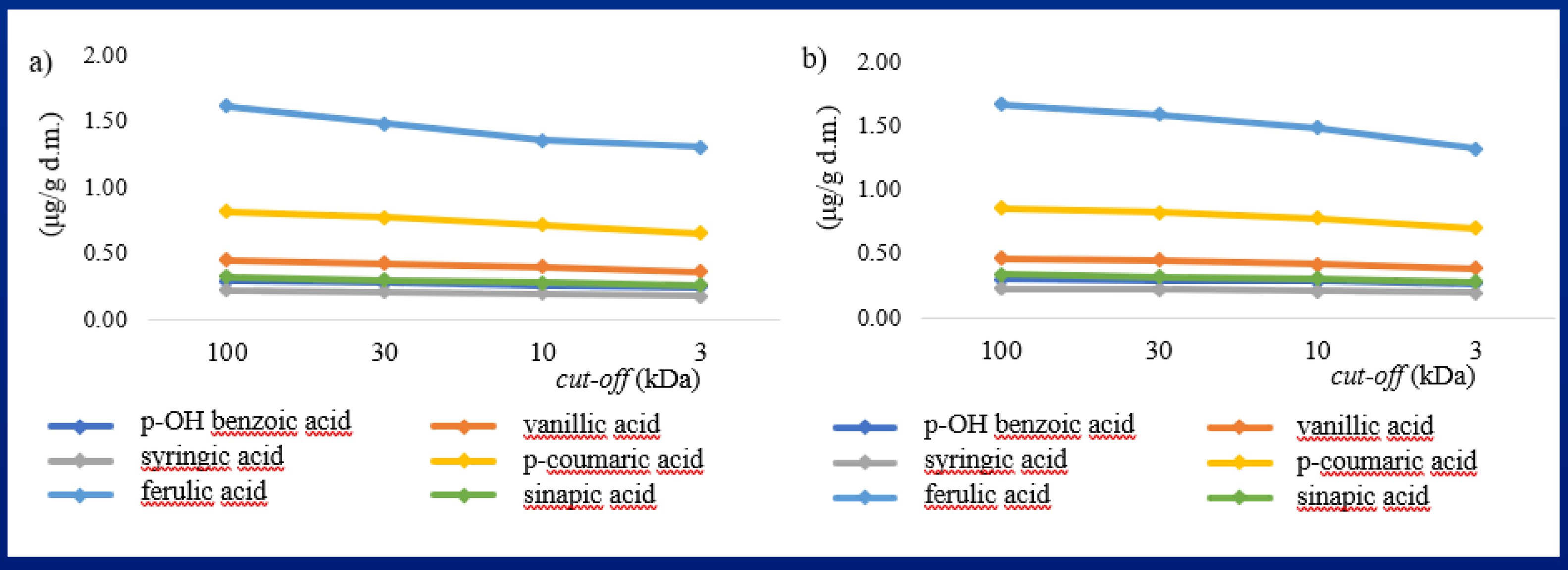

Figure 4: Phenolic acids in permeates after membrane filtration (variant 1) (a), and after MAE and membrane filtration (variant 2) (b)

Conclusions

Distillery stillage is a source of valuable polyphenols. Membrane filtration can be used to concentrate polyphenols, and the method of recovery from retentates should be developed to improve the yield.

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