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Development of a Diafiltration-Pervaporation Process for Beer Dealcoholisation

Paola Di Matteo[a], Marco Stoller[a], Rita Petrucci[b], Paola Russo[a]*

[a] Department of Chemical Engineering Materials Environment, Sapienza University of Rome, Via Eudossiana 18, 00184 Rome, Italy
[b] Department of Basic and Applied Sciences for Engineering, Sapienza University of Rome, Via del Castro Laurenziano 7, 00161 Rome, Italy
paola.russo@uniroma1.it

Nowadays, worldwide low-alcohol and alcohol-free beer markets are growing rapidly, and this leads to a strong demand of improved technologies for their production.
Among the various membrane-based processes, a dialysis in diafiltration mode, with no transmembrane pressure difference, has been chosen as first step of a combined process for beer dealcoholisation which includes a pervaporation stage to recover aroma compounds which are then integrated to the final low-alcohol beer. The results of experimental tests for the optimization of beer diafiltration process using a bench scale unit and two different membranes of cellulose and polyacrylonitrile are shown in this work.
A commercial lager beer has been dealcoholized, in a discontinuous diafiltration mode, interweaving concentration and dilution stages, up to an alcohol content lower than 1.2 %vol., which is the residual alcohol content for low alcohol beverages in European countries. Various dialyzing solutions and operating parameters (e.g., temperature, flow rate, volumetric concentration ratio) were tested in order to improve the ethanol removal from the beer. The physical-chemical characteristics of the beer such as pH, electrical conductivity, density and colour and free-phenolic profile, before and after the dealcoholisation process were evaluated. Results showed no substantial differences between the membranes tested for the dealcoholisation process and small differences in the physical and chemical characteristics of beer before and after the treatment.

1. Introduction

Beer is one of the most widely consumed and popular alcoholic beverages in the world (Lehnert et al., 2008), because of its delightful organoleptic characteristics and moreover for its healthy nutritional properties when assumed moderately.
The beer consumption is increasing globally and will reach USD 750 billion by 2022 (Zion market Research, 2017). In addition, alcohol-free and low-alcohol beer market is a fast-growing segment propelled by costumer preference for a healthier lifestyle, by the legislative restrictions on the alcohol consumption, and religious concerns (Kunal and Amit, 2019). The alcohol content in a low or non-alcoholic beer depends on regulations and varies with countries. According to the European Union legislation, non-alcoholic beer has an alcohol content below 0.5 % vol. and low-alcoholic beer from 0.6 to 1.2 % vol. (Direttiva 87/250/CEE).
One of the main objectives in the production of low alcohol beers (LABs) is to obtain a product very similar to regular beer (Sohrabvandi et al., 2010) in terms of organoleptic properties. In fact, as reported in literature, all the technologies used for dealcoholisation lead to marked losses of volatiles and provide beers with different characteristics (Ambrosi et al. 2014; Brányik et al. 2012; Liguori et al., 2015a,b). Among the physical dealcoholisation methods, membrane separation processes, like reverse osmosis, dialysis (DI), osmotic distillation and pervaporation (PV), provide several advantages compared to thermal treatments, because of low energy consumption, mild temperatures and reduced operating costs (Ambrosi et al. 2014). The main advantages of DI technology are the low operating temperatures and pressure, the consequent no worthy off-flavour formation and no thermal damage. On the other hand, the removal of ethanol is not selective, the process lead to the loss of volatile compounds and carbonation is necessary at the end of dealcoholisation

(Bandel et al., 1986; Zufall and Wackerbauer, 2000). In this perspective, it is reasonable to optimize the process for beer dealcoholisation by DI.
Besides dealcoholisation, pervaporation can also be used to extract and concentrate volatile aroma compounds from beer and subsequently add them to the final dealcoholized beer (Salanta et al. 2020). At present, several methods for the production of LABs are reported in literature, but the cascade process proposed in this study has not yet been investigated, and it looks promising in order to achieve a beer with very similar aroma and taste to the original beverage.
Among volatile aroma compounds, phenolic compounds are always present in beer. They mainly come from malt and hops, and their quantitative and qualitative profile in the beverage depends on raw starting materials. Several studies reported that active compounds as polyphenols in beer produce health beneficial effects. They have good antioxidant activity and in the case of low alcoholic beers, there is the simultaneous effect of the lower energy intake and of the minor content of alcohol and of its related negative effects. Polyphenols are important also from a technological point of view, because they are involved in foam maintenance, physical and chemical stability and shelf life and they are considered as quality indicators for beer processing (Montanari et al., 1999).
Several flavour components, including alcohols, esters, acids, ketones, aldehydes, contribute to the beer aroma and taste. Due to the higher concentrations and threshold in beer, the most important compounds for the aroma characterization are propanol, isobutanol, isoamyl alcohol, ethyl acetate, isoamyl acetate and acetaldehyde.
In this study, a combined diafiltration-pervaporation process for beer dealcoholisation was developed. In the first step, ethanol was removed from a commercial beer through a dialysis process, in diafiltration mode; in the second step, the obtained dialysate was pervaporated to recover the main aroma compounds lost during the dealcoholisation step. The physical and chemical characteristics, the free polyphenols profile and the aroma compounds content of the low-alcohol beer before and after the aroma compounds addition were evaluated and compared to those of the original beer before dealcoholisation.

2. Experimental

2.1 Materials

Chemicals and reagents: chemicals were of analytical grade, purchased from Sigma-Aldrich and used as received.
Beer: Commercial lager beer, with an alcohol content of 4.7 % vol., from the same batch, was bought locally and stored at 4 °C. The bottle was opened the day before the dealcoholisation stage and it was kept semi-opened at 5 °C to decarbonate, in order to avoid the rapid release of CO_2 and the stripping of aromatic compounds from the sample (Martins et al., 2015).
Membrane: A commercial cellulose triacetate (CTA) membrane for diafiltration tests was purchased from Carlo Erba, and a PAN 3651 (polyacrilonitrile, thickness of 30 µm and a pore size of 20 nm) membrane from Deltamem ®. Flat sheet membrane samples, with an effective area of 44.17 cm^2, were cut, rinsed, and soaked in deionized water for conditioning. For pervaporation, a flat-sheet hydrophobic membrane in PDMS (PERVAP® 4060) from Deltamem, with a surface area of 44.17 cm^2, was used.

2.2 Diafiltration

The diafiltration bench-scale unit comprises a flat sheet membrane module, a peristaltic pump with one pump head, a water-cooled jacket feed tank and a vessel for the dialysing solution. The feed flows tangentially to the membrane and the retentate was recycled to the top of the tank by a pump. The dealcoholisation was conducted in a discontinuous diafiltration mode, interweaving eight concentration and nine dilution stages, and lasted 190 and 210 min for PAN and Cellulose membrane, respectively. Tap water or a 0.05 M solution of $MgCl_2$, buffered to pH 4.50 with sodium citrate and citric acid were used as dialysing medium. The dialysing solution flow rate was in the range 1 – 3 L/h and the volumetric concentration ratio ($VCR=V_i / V_f$, V_i and V_f initial and final volume, respectively) was equal to 1.13 and 1.33. Tests were performed at 25 °C and 5 °C, the feed and dialysing solution volume was 400 mL and 1 L, respectively.

2.3 Pervaporation

A lab-scale pervaporation equipment was used in the experiments for aroma recovery. The operating pressure of the feed was controlled at 2.5 bar and the temperature was maintained at 35 ± 1 °C. The liquid circulates tangentially to the membrane for minimizing the effects of concentration-polarization. Permeate pressure was set at 25 mbar. A Pyrex trap cooled at - 1 °C was used to condensate and collect permeate vapor stream. Samples of retentate and permeate were collected at intervals of two hours and weighted by a digital balance. The run lasted 7 h and all the samples were frozen at -18 °C until further analysis for the content of aroma

compounds by GC. The pervaporation performance was expressed in terms of permeate flux and mass enrichment factor for each aroma compound. The permeate flux J_p is obtained from the equation:

$$J_p = \frac{m_P}{A\,t} \quad (1)$$

where m_p is the condensed permeate mass, A is the effective membrane area and t is the permeation time.
The mass concentration enrichment factor for the i-component is defined as follows:

$$\beta_i = \frac{C_i(permeate)}{C_i(feed)} \quad (2)$$

where C_i (permeate) is the mass concentration of compound i in the permeate and C_i (feed) is that one in the feed.

2.4 Beer physical-chemical properties

Measurements of pH, electrical conductivity, density and colour of the beer before and after dealcoholisation were carried out using a pH meter (Crison GLP 21), a digital conductivity meter (Amel 2131), a picnometer and a UV/Vis spectrometer, respectively.
Ethanol (Et) and aroma compounds concentration in the permeate were determined by gas-chromatography using a Perkin Elmer GC Clarus 500 equipped with a flame ionization detector (FID) and a capillary Stabilwax-Da column (30 m, 0.25 µm Restek). The temperature program used was reported by Catarino et. al (2009), the carrier gas was helium at 2 mL/min, FID and injector temperatures were 250 °C and 110 °C, respectively.
The free polyphenols profile of the beer, that includes gallic acid (GA), p-hydroxybenzoic acid (pHBA), m-hydroxybenzoic acid (mHBA), 3,4-dihydroxybenzoic acid (PCA, protocathecuic acid), vanillic acid (VA), syringic acid (SyA), p-coumaric acid (CoA), caffeic acid (CA), ferulic acid (FA), sinapic acid (SA), 5-caffeoylquinic acid (CQA), quercetin (Q), kampferol (K) and rutin (Ru), before and after the treatments, was evaluated according to the protocol reported by Petrucci et al. (2020). All the analyses were performed in triplicate.

2.5 Statistical analysis

The measurements in Table 1 and the amounts of phenolic and aroma compounds quantified in the original lager beer and in the LABs have been reported in Table 3 and 4 as mean values ± standard deviation. The comparison between the values of three samples was carried out using one-way analysis of variance ANOVA. The significance of differences ($P < 0.05$) among samples was determined by the Tukey test.

3. Results and Discussion

Beer was diafiltered at different temperatures, dialysing solution flow rates, dialysing solution type and volumetric concentration ratios, in order to optimize the dealcoholisation process. Preliminary tests for both membranes and at different temperatures indicated that the retentate changed the original color, from 4.3 to 6.1 EBC when the process was carried out at 25 °C, while it decreased slightly at 5 °C, from 4.3 to 3.9 EBC. For this reason, the latter temperature was chosen for the further tests. With the increase of volumetric concentration ratio (VCR) from 1.13 to 1.33 the removal of ethanol from beer was lower for both PAN 3651 (2.10 Vol. %) and cellulose (2.50 Vol. %) membranes. A similar result was obtained when the dialysing flow rate was decreased from 3 to 1 L/h. Once the best conditions for dealcoholisation were defined, the process led to a final retentate at the concentration of ethanol 1.1 %vol. after eight concentration and eight dilution steps.
The total permeate flux for PAN and Cellulose membrane was reported in Figure 1. The total flux was practically constant during the experiment and varied in the range 8.00 ± 0.30 – 8.70 ± 0.90 L/m^2 h for cellulose membrane and from 7.50 ± 0.40 – 7.80 ± 0.70 L/m^2 h for PAN membrane. This can be explained by the constant osmotic pressure difference between feed and dialysing solutions due to the dilution of the feed, during the process.
The concentration profile of ethanol in the retentate for both membranes tested was similar (data not shown). During the process, the rejection coefficient for ethanol was quite constant in each concentration step; the average rejection coefficient for ethanol was 24% and 29% for cellulose and PAN membrane, respectively. To investigate the influence of dialysing solution, the process was carried out with a solution of $MgCl_2$ at pH 4.5 and using a PAN membrane. In this case the permeate flux was lower (from 5.30 ± 0.50 to 6.12 ± 0.6 L/ m^2 h) and the ethanol concentration reached in the retentate, at the same conditions, was 1.65 %vol., higher than the acceptable value for a LAB.

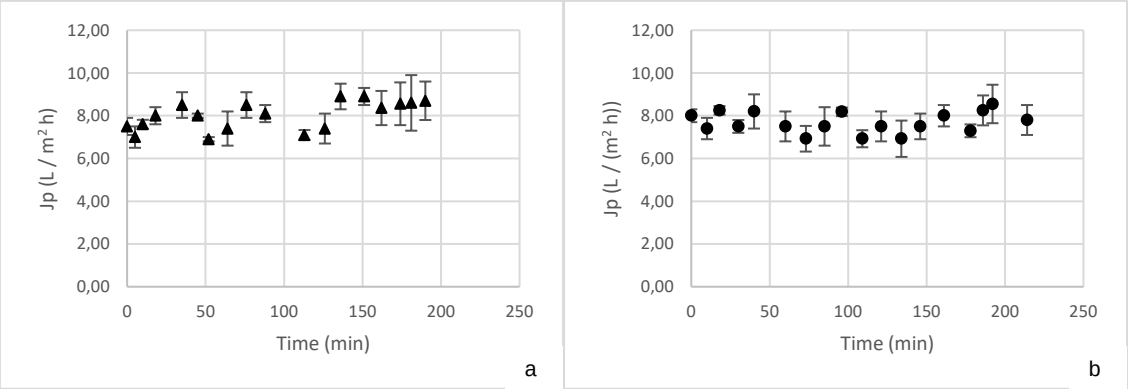

Figure 1. Total permeate flux during dealcoholisation of a commercial lager beer using diafiltration, at 5 °C and VCR 1.33 and dialysing solution rate at 3 L/h. Points represent the average between three independent experiments (a: PAN membrane; b: Cellulose membrane).

The main characteristics of the original beer and of the beer at the end of the dealcoholisation process, for both membranes tested, are presented in Table 1. pH of beer slightly increased after the dealcoholisation process, but in an acceptable range. This behaviour is due to the presence of salts and weak acids in the beer that avoid pH alterations like a buffer (Preedy, 2009). The electrical conductivity decreased in LAB samples, probably for the loss of salts that passed through the membranes in the dialysate. Also, the colour of beer decreased because of the loss of pigment in the dialysate, but the variation was minimal while the density remained constant.
Data of the quantification of free polyphenols identified in all the beer samples were reported in Table 2.

Table 1. Main characteristics of original lager beer and LAB obtained after the diafiltration-pervaporation process using different membranes. Mean values ± SD from triplicate analysis. Values with different letters within rows are significantly different (p<0.05).

Property	Original Beer	LAB (PAN 3651)	LAB (Cellulose)
Ethanol (%Vol)	4.71±0.05^{a}	1.11±0.05^{b}	1.14±0.05^{b}
pH	4.53±0.05^{a}	4.71±0.05^{a}	4.65±0.02^{a}
Electrical conductivity (mS cm^{-1} , 25°C)	1.51±0.10^{a}	1.32±0.15^{b}	1.25±0.05^{b}
Density (g mL^{-1})	1.01±0.05^{a}	1.00±0.05^{a}	1.04±0.05^{a}
Colour (EBC)	4.3±0.1^{a}	3.9±0.1^{b}	3.8±0.1^{b}

Table 2. Amounts of free phenolic compounds (mg/L) quantified by HPLC-ESI-MS/MS in the original beer and in the LABs. Mean values ± SD from triplicate analysis. Values with different letters within rows are significantly different at p < 0.05 (ANOVA). $^{\#}$ LOQ and LOD values previously reported. nd = not detected; nq = not quantified.

Compounds	Original Beer	LAB (PAN 3651)	LAB (Cellulose)
Gallic acid	0.30±0.05^{a}	0.22±0.05^{b}	0.18±0.02^{b}
Protocathecuic acid	0.14±0.03^{a}	0.08±0.01^{a}	0.11±0.02^{a}
5-caffeoylquinic acid	< 0.24$^{\#}$	< 0.24$^{\#}$	< 0.24$^{\#}$
p-hydroxybenzoic acid	1.27±0.05^{a}	1.15±0.05^{b}	0.94±0.06^{b}
Vannilic acid	0.79±0.01^{a}	0.76±0.06^{a}	0.80±0.03^{a}
Caffeic acid	nd	nd	nd
Syringic acid	nq	nq	nq
p-coumaric acid	0.84±0.02^{a}	0.67±0.04^{b}	0.61±0.04^{b}
Sinapic acid	0.59±0.05^{a}	0.43±0.03^{b}	0.42±0.06^{b}
Ferulic acid	2.12±0.05^{a}	1.77±0.10^{b}	1.69±0.10^{c}
Rutin	< 0.29$^{\#}$	< 0.29$^{\#}$	< 0.29$^{\#}$
Quercetin	< 0.23$^{\#}$	< 0.23$^{\#}$	< 0.23$^{\#}$
Kempferol	< 0.06$^{\#}$	< 0.06$^{\#}$	< 0.06$^{\#}$

SyA was identified but not quantified because of the co-elution with another compound; CQA, Q, Ru and K resulted under the limit of quantification (LOQ). In general, the free polyphenols content of the dealcoholized beers was found significantly different ($p < 0.05$) from the corresponding alcoholic samples, with decreasing values as a general trend (see GA, pHBA, FA, CuA, in Table 2). This was an expected result because free polyphenols have small size and could be lost during the membrane process. The major loss was observed for FA and p-HBA both for PAN and Cellulose membranes. However, the diafiltration process had not shown a strong effect on the content of free polyphenols.
In the second step of the process the aroma compounds lost through diafiltration were recovered. The feed of PV process is the dialysate obtained by dealcoholisation step using PAN membrane. The analysis was focused on ethanol (Et), isobutanol (IB), isoamyl alcohol (IAOH), isoamyl acetate (IAA) and acetaldehyde (AA), as they were found in the dialysing solution coming from the previous diafiltration step. As reported in Table 3, the original beer contained also ethyl acetate (EA), and isopropanol (IP): the first remained in the retentate coming from the diafiltration process while the second was totally lost. The quantified aroma compounds concentrations were in the range found in the literature (Catarino, 2010).

Table 3. Amounts of aroma compounds (mg/L) quantified by GC-FID in the original beer and in the LABs; mean values ± SD from triplicate analysis. Values with different letters within rows are significantly different at $p < 0.05$. nd = not detected. Isopropanol (IP), isobutanol (IB), isoamyl alcohol (IAOH), ethyl acetate (EA), isoamyl acetate (IAA) and acetaldehyde (AA).

Compounds	Original Beer	LAB (PAN 3651)	Dyalisate(DI) / Feed(PV)	Enriched LAB (PAN 3651)
EA	59.00 ± 1.10^{a}	49.70 ± 1.21^{b}	nd	47.00 ± 1.11^{b}
AA	54.00 ± 1.02^{a}	40.17 ± 1.36^{b}	8.12 ± 1.16^{d}	45.39 ± 1.23^{c}
IAOH	65.25 ± 2.17^{a}	15.14 ± 3.20^{b}	42.13 ± 1.74^{d}	55.20 ± 1.14^{c}
IB	55.40 ± 1.30^{a}	35.30 ± 1.14^{b}	12.00 ± 1.65^{d}	42.13 ± 1.30^{c}
IP	< 10.00	nd	nd	nd
IAA	30.14 ±1.14^{a}	10.10 ±1.18^{b}	10.23 ± 2.04^{d}	21.34 ± 1.58^{c}
Et	4.71 ± 0.05^{a}	1.11 ± 0.03^{b}	1.19 ± 0.01^{d}	1.13 ± 0.05^{c}

In Figure 2a the total permeate flux during pervaporation is shown. It was observed a higher flux at the initial stage of the process, while after five hours a slower decay was recorded. The fluxes of ethanol and aroma compounds were evaluated from the concentration data of samples collected during the pervaporation process and reported in terms of mass concentration enrichment factor [2] in Figure 2b. The Et flux was some order of magnitude higher than the aroma fluxes because of its higher concentration in the feed, but Et and IAA have much lower values of mass concentration enrichment factor [2] with respect to IB, which had the highest, followed by AA and IAOH. This can be explained by the hydrophobicity of the membrane used, that avoided the passage of polar species against less polar molecules like aldehydes. Among the alcohols, Et was the most polar compound while IAA have the highest molecular weight and its passage is avoided because of the interactions with the membrane.

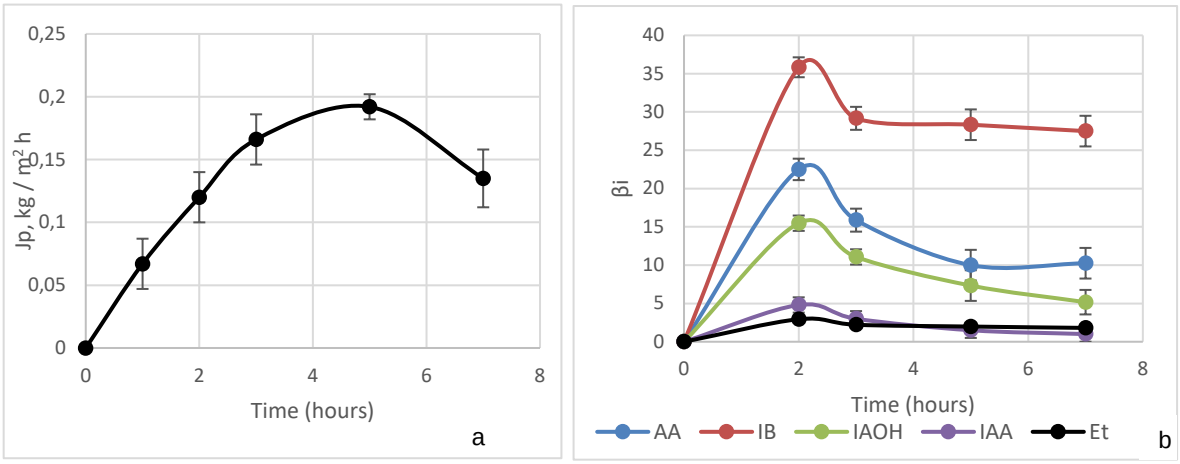

Figure 2. a) total permeate flux during pervaporation and b) mass concentration enrichment factor [2] for aroma compounds and ethanol. Each point is an average of triplicate analysis.

The aroma compounds recovered by PV, were incorporated into the LAB obtained using PAN membrane. The results of GC analysis (Table 3) showed an increase of aroma compounds in enriched beer, although the total process led to the loss of isopropanol and of carbon dioxide.

4. Conclusions

The diafiltration-pervaporation process has been studied to obtain a low-alcohol beer. Beer properties like pH, density, electrical conductivity, colour and free phenols content remained almost the same after the diafiltration step. The pervaporation step is useful for the recovery of aroma compounds of beer, lost in the first stage of diafiltration. The membrane used showed higher selectivity for IB, IIA, IAOH and AA than ethanol. The addition of these aroma compounds to the LAB enriched it aromatic profile, but the carbonation is necessary after the dealcoholisation process.

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