

Fouling in microfiltration of wine: The influence of the membrane polymer on adsorption of polyphenols and polysaccharides

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Abstract

Microfiltration (MF) is a frequently used to clarify wine, but the fouling of the membranes is the main limiting factor for the overall process capacity. In this work, data from MF clarification of a white wine are presented which show that membranes made from polypropylene (PP) yield significantly higher fluxes and through-put than membranes made from polyarylsulfone, both having the same cut-off pore size (0.2 µm). The aim of this study was then to pursue the hypothesis that different membranes (based on PP or polyethersulfone, PES) exhibit different levels of adsorption of typical foulants in wine such as polyphenols and polysaccharides, to link the level of adsorption to polymer characteristics and to correlate membrane fluxes with these findings. A model solution for wine ("synthetic red wine") has been established by using a commercial red grape marc extract (from grapes after fermentation). It was found that polyphenols and polysaccharides are only marginally adsorbed by PP but strongly adsorbed by PES membranes. Comparison between data for individual model substances for polyphenol or polysaccharide and their mixtures with data for "synthetic red wine" support the hypothesis that aggregates of polyphenols and polysaccharides present in red wine have a strong contribution to adsorptive fouling, and that the interaction between polyphenols and the membrane surface is the main driving force. In consequence, the low adsorption tendency of wine ingredients to PP membranes results in higher fluxes and longer service life of the respective filtration modules in wine clarification.

Keywords:

Adsorption, Fouling, Polyphenol, Filtration Performance, Wine Filtration

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1. Introduction

Membranes and their use in the filtration of beverages are well accepted today [1]. The clarification of juices by microfiltration (MF) has already a relatively long history and is widely applied in the industry; the analogous process for wine is rapidly growing in the recent decade. However, it is well-known from most of the applications of membranes in fluid filtration that fouling of the membrane surface is the reason for a major loss of membrane permeability and, therefore, of volume through-put. In addition, backflush procedures and chemical cleaning steps are time consuming and adding up mechanical and chemical stress to the filtration devices resulting in a loss of capacity and efficiency of such equipment. Despite the fact of being applied in field applications for the filtration of wine with different membranes (materials, geometries) and varying module concepts (dead end, cross flow), there is still relatively little fundamental knowledge of the method. Important contributions have been made by Moutounet, Vernhet and coworkers [2-7], and a few other groups [8-11]. Nevertheless, the mechanisms causing the fouling and the contributions of the properties of the membranes being used are still not resolved. It is accepted that dissolved substances like proteins, polysaccharides and polyphenols are involved in the fouling process, but typically with unclear individual impact on the level and the consequences of membrane blockage. In addition, particle fouling can play a major role, but the impact seems to depend on particle size; cake formation could even partially protect the membrane from internal pore blocking. The possible influence of fouling on the product quality (taste, colour) is even more complex and unpredictable.

Membrane fouling by proteins can lead to very large and almost irreversible flux decline, and the related mechanisms have been extensively investigated over the last three decades; the scenario leading to the strongest fouling are hydrophobic interactions between protein and membrane material in combination with conditions where protein-protein interactions are also facilitated [12-14]. In comparison to proteins, the fouling tendency of polysaccharides is less strong, but can still lead to significant flux reductions; the hydrophilic macromolecular solutes can bind to less hydrophilic membrane surfaces via "surface dehydration" [15,16]. Polyphenols, a diverse group of naturally occurring compounds, are secondary plant metabolites found in all fruits and vegetables [17]. Their antioxidant activity is typically related to health-promoting effects. However, in other cases, there is also the need to reduce polyphenol content in food and beverages in order to keep consistent quality [18]. In few studies, membrane filtration of various polyphenol containing streams had been investigated [19-21], but there is not yet sufficient systematic understanding of the underlying fouling mechanisms.

Recent research had provided evidence that the adsorption of foulants on the membrane surface (even without any flux through the membrane) can lead to significant fouling effects, and that correlations can be made between adsorptive fouling and the dynamic fouling in membrane filtration [22]. In addition to proteins as very well-known foulants, the significant role of polysaccharides, humic acids or polyphenols had also been identified, but these studies had been focussed on ultrafiltration (UF) [23-25].

There were also attempts in literature to examine the respective effects of polyphenols and polysaccharides contained in wine, also in combination with various membrane materials [3,4,8-11]. For instance, UF and MF membranes from poly(vinylidene fluoride) (PVDF) had been compared [10],

or 0.2 μm MF membranes from cellulose acetate, PVDF and track-etched polycarbonate had been evaluated under similar conditions [9]. It had been concluded that the pore size and pore size distribution of the membrane seem to have the main effect on fouling. In addition, differences in the amount of adsorbed polyphenols and polysaccharides were observed for different membrane materials (e.g., polyethersulfone, PES, vs. polyvinylchloride, PVC) [3]. It was found that accumulated amounts of polysaccharides in the pores result in an elevated loss of permeability but also that the adsorbed amount of polyphenols exhibits some influence. A more recent detailed study had focussed on the adsorption of individual polyphenols to PES MF membranes with different contents of polyvinylpyrrolidone (PVP), and dominant polar interactions leading to high levels of adsorption have been identified [6]. Overall, the results of these studies imply that the attractive interactions of wine components with the membrane surface may indeed play a major role in membrane fouling.

Recent experience from technical applications of MF in clarification of red and white wine had indicated that membranes with the same pore structure according to their specifications but made from different membrane polymer had shown quite different filtration performance. From field tests we will present results from a direct comparison of two MF membranes with 0.2 μm cut-off pore size made from either polyarylsulfone based polymers or polypropylene (PP) in the filtration of the same white wine without any pre-treatment; which revealed a much higher through-put and service life in case of PP-based modules. Triggered by these, at first glance, unexpected results, the aim of this study was therefore to pursue the hypothesis that different membrane materials exhibit different levels of adsorption of polyphenols and polysaccharides, to link the level of adsorption to polymer characteristics and to correlate membrane fluxes (service life of modules) with these findings. To follow the route to compare polyarylsulfone based polymers with polyolefin based types, the focus of this work was on two technically most relevant capillary MF membranes, either from PP or from PES. This comparison is new because in the only related previous study, PES and PP membranes with completely different pore sizes and structure had been used [11]. Additionally capillary and flat-sheet PP membranes from different manufacturing processes and with different pore structure were used for comparison. For the adsorption studies, a model system based on a solution of red grape marc extract was established. The adsorbed amounts were compared with those for individual model substances for polysaccharides and polyphenols and their mixtures. The levels of adsorption for polysaccharide and polyphenol, relative to the specific surface area of the membrane, were much lower for PP than for PES. The most important implication of this study is that aggregates of polysaccharides with polyphenols, having a higher affinity to the polar PES, seem to be a very critical component leading to severe fouling by pore narrowing and blocking under MF conditions.

2. Experimental

2.1 Materials

Membranes. The following PP membranes from Membrana GmbH, Wuppertal, Germany, have been used: capillary membrane Accurel® PP 300/1200 (types a and b; from different PP raw materials; both with 0.2 μm cut-off pore size), capillary membrane Celgard® X-30, and flat-sheet membranes Celgard® 2400 and 2500. The Celgard® membranes have been used only in some of the experiments

in order to consider effects of membrane preparation and pore structure. One PES capillary membrane (0.2 μm cut-off pore size), used in the field for wine filtration, was used throughout the experiments (for more data on pore structure see section 3.2.).

Filtration units. One cross-flow unit with 19 m^2 membrane area (2 devices of 9.5 m^2 ; LiquiFlux® B22, Accurel® PP 300/1200, 2400 capillaries, module length 1092 mm, module diameter 125 mm, housing material polysulfone) and one cross-flow unit with 42 m^2 membrane area (6 devices of 7 m^2 ; polyarylsulfone capillary membranes, cut-off pore diameter 0.2 μm , inner diameter 1.1 mm, 2000 capillaries, module length 1092 mm, module diameter 125 mm, housing material polysulfone) have been used for the field tests.

Chemicals. The following substances have been used for adsorption experiments or as reference material: tannic acid (CAS 1401-55-4; Sigma Aldrich), D-galactose (Sigma), arabinogalactan (>80%, from larch wood, Sigma; mean M_w ~80 kg/mol; PDI >4; from HP-GPC; free of protein according to MicroBCA assay), dextran (Fluka; mean M_w ~70 kg/mol; PDI ~2; from HP-GPC), arabic gum (Sigma), and commercial red grape marc extract (from grapes after fermentation; PROTEKUM, Oranienburg, Germany) [26].

Solutions. “Synthetic wine” was composed of 12.7% ethanol (Merck), 6 g/l citric acid (Fluka), 3 g/l maleic acid (Fluka), 100 mL/L acetic acid, 367 mg/L calcium chloride, 100 mg/L potassium sulphate, 42 mg/L magnesium chloride, all adjusted to pH = 3.5 with 5 N potassium hydroxide solution (cf. [3,4]). The following solutions were used for the adsorption experiments: i) tannic acid in “synthetic wine” as model for polyphenols, ii) arabinogalactan in “synthetic wine” as model for wine polysaccharides, iii) dextran in “synthetic wine” as model for an “bioinert” polysaccharide, iv) “synthetic red wine” consisting of red grape marc extract in “synthetic wine” (2.5 g in 250 mL for several hours on a shaker, then filtered with a Sartorius 0.45 μm cellulose acetate membrane, revealing an insoluble fraction of about 1 wt%; and then diluted to 4 g/L).

Wine. A white wine Kerner, vintage 2007 (winery Eckhardt, Aspisheim, Germany), was used for the filtration experiments.

2.2 Procedures

Measurement of membrane specific surface area and pore size distribution. Membranes were analysed using the Surface Area Analyser SA 3100 (Beckman-Coulter) according to the method of nitrogen adsorption and desorption. First, membrane samples (about 100 mg) were extracted with ethanol (p.a.) over night and then dried at 40°C to constant weight. By means of the data of the adsorption isotherm, the specific surface area of the membranes was determined using the method of Brunauer, Emmet and Teller (BET). Additionally, the pore size distributions (up to a maximum pore size of 80 nm) were quantified via the BJH method and the Kelvin equation.

Size exclusion chromatography for characterization of the polysaccharides (cf. section 2.1) had been performed as described earlier [15,16].

Measurements of the amounts of polysaccharides, polyphenols and tannic acid. The quantification of the polysaccharides was carried out as a sum parameter according to the method of Dubois [27]: To 0.5 mL of the respective sample solution, 0.5 mL of a solution of phenol (5 wt%) and 2.5 mL of sulphuric acid (conc.) were added, the mixture was agitated and kept for 30 min at room temperature.

The yellow-orange coloured complex was measured by means of UV-VIS spectroscopy at 490 nm (spectrophotometer Cary 50, Varian). Calibration was performed using a mixture of Arabic gum and galactose (ratio 7:3) in “synthetic wine”. This is mimicking the monosaccharide composition of the pectic polysaccharides contained in red wine especially with respect to the concentrations of arabinose, rhamnose and galactose (cf. [3,4]). The measurement of polyphenol was also performed as a sum parameter using the UV-VIS spectroscopy. Tannic acid as the model substance was dissolved in “synthetic wine”. The photometric determination was performed at 280 nm. To quantify the polyphenols in “synthetic red wine”, tannic acid in “synthetic wine” was used as the reference substance.

Adsorption experiments on membranes out of “synthetic wine” and out of “synthetic red wine”. For all adsorption experiments, the adsorbed amounts on the membrane were quantified measuring the reduction of the concentration in the solution used as the contact medium (difference between start concentration and the concentration at equilibrium). For proper quantification of the substances, a complete wetting of the membrane samples and an exact knowledge of all volumes (adsorption solution and wetting solution in the membrane, i.e. in the lumen and in the membrane pores) are mandatory. The sum of specific lumen and pore volume (normalized to membrane mass) of the capillary membranes was determined gravimetrically from the difference between dry and wet membrane. The treatment of the membrane samples in order to ensure complete wetting of all pores was always performed as follows: weighing of a defined piece of membrane (between 120 and 150 mg), wetting with ethanol, solution exchange facilitated by rinsing the capillary lumen with help of a syringe and then wetting with “synthetic wine” to equilibrium (4 hours), weighing of the filled membrane, transfer of the membranes to the adsorption solution (15 mL), facilitation of liquid exchange by rinsing the capillary lumen with help of a syringe and 5 days of adsorption in a closed vessel (20 mL polyethylene beaker), and thereafter analysis of the concentrations of the supernatant.

Wine filtration. The LiquiFlux® B22 modules with PP membranes had been assembled in a RS2 CS unit (ROMFIL GmbH, Wolfsheim, Germany) for two modules; backwashing was performed after every 7 min. for 8 sec. into a separate tank; the accumulated backwash volume was concentrated at the end of the filtration. The modules with the polyarylsulfone membranes had been assembled in a ROMFIL RS6 CS unit including a 400 L feed recycling tank; backwashing was performed after every 6 min. for 20 sec. into the recycling tank.

3. Results and Discussion

3.1. Wine microfiltration with two different membranes

In field filtration employment with a typical white wine (type Kerner, 2007 vintage) we surprisingly measured a much higher initial flux and also a higher filtrate volume flow over time with a 19 m² filtration unit containing PP membranes compared to a 42 m² unit containing polyarylsulfone membranes. Details are presented in **Figure 1**. Taking into account that the membrane area of the PP modules was about half of the area of the polyarylsulfone modules and that the filtrate volume flow was about twofold after 4 hours of filtration, the superiority of the PP membranes is obvious. The mean transmembrane pressures were about 1.3 bar for the PP modules and about 2 bar for the polyarylsulfone modules.

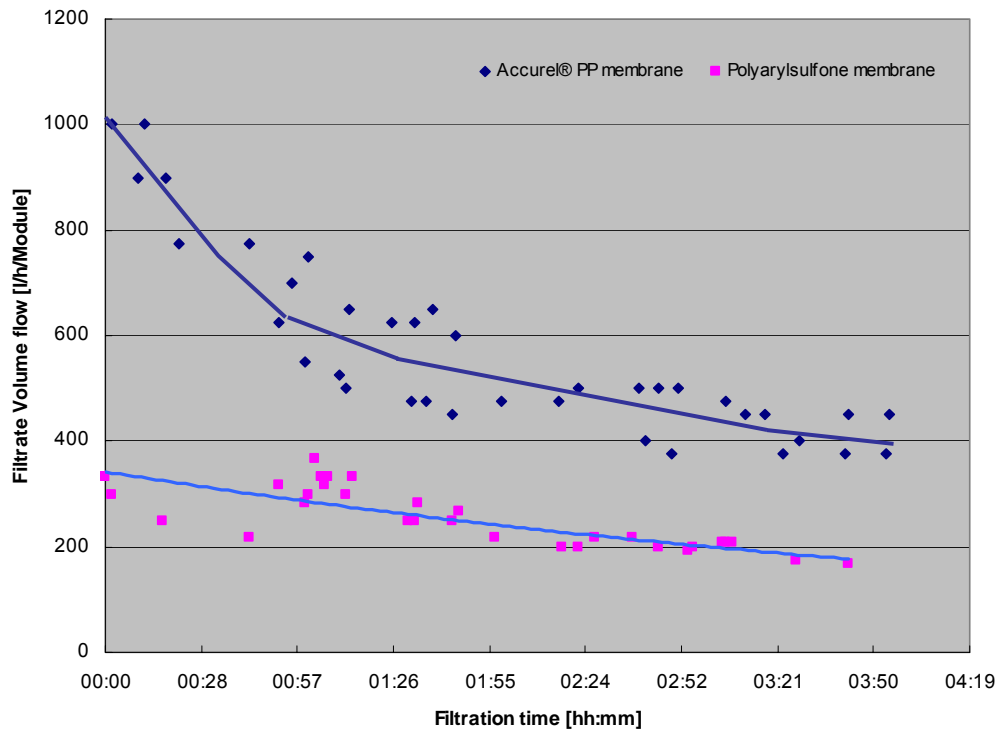


Figure 1: Filtration of White Wine, Type Kerner, 2007 vintage (for details see section 2).

Although the quality of the filtered wine is only slightly different (see **Table 1**) there are hints that the adsorptive behaviour of the two types of membranes might be different with respect to some ingredients. In particular, this can be discussed for the amount of the sugar free extract which is different for both types of membranes used for the filtration. From this result it could be argued that the polyarylsulfone membranes show higher adsorptive capacity for the sum of the non sugar components. However, it also has to be taken into account that the area of the polyarylsulfone membranes was much higher (see description of the filtration units; section 2). Due to this fact, a conclusion for the reason of the difference can not be drawn from the field experiments. To be able to differentiate among these two possible effects or even to find a different explanation it is necessary to perform experiments under more controlled conditions in the lab. Therefore, we performed the study described in this paper.

Table 1: Typical data* obtained for the White Wine, Type Kerner, 2007 vintage, before and after MF with the two different membranes.

| Parameter** | Unfiltered wine | Filtered wine, PP | Filtered wine, polyarylsulfone |
|--------------------------|-----------------|----------------------|-----------------------------------|
| Turbidity, NTU | 7.0 | 0.8 | 0.66 |
| Total alcohol (%) | 12.6 | 12.6 | 12.5 |
| Sugar free extract (g/L) | 22.2 | 22.2 | 21.4 |
| pH value (-) | 3.2 | 3.2 | 3.3 |
| Total acid, pH = 7 (g/L) | 7.7 | 7.7 | 7.0 |
| Carbon dioxide (g/L) | 0.07 | 0.35 | 0.29 |

* measurements were performed by the accredited external lab Chemisches Labor Dr. Merten GmbH, Freiburg, Germany.

** sugars were enzymatically measured, sugar free extract was calculated from that; carbon dioxide was measured according to VO (EWG), No. 267690/37; turbidity was measured according to DIN EN ISO 7027; all other parameters were measured with FTIR spectroscopy.

It is also interesting to note that in a very recent study, Boissier et al. [7] had observed very stable fluxes during wine filtration with PP membranes, and they stated – without further explanation – that this was different from results of their previous work with other membranes (PES, PES with different contents of PVP, and PVC) [3,4].

3.2. Pore structure of the membranes used for adsorption studies

The main aim of this work was to elucidate the influence of the membrane polymer and adsorptive fouling. This has been done with two groups of materials:

- a) two capillary membranes, from PP and PES, already used for wine filtration and focus of the adsorption tests,
- b) three other capillary or flat-sheet membranes from PP (in order to elucidate the effect of the membrane material).

In order to take into account the different porosity, the adsorbed amount had to be related to the specific surface area of the membranes. In addition, the fraction of smaller pores may also have influence onto the adsorbed amounts, especially for high-molar mass solutes. Both kinds of information can be retrieved from gas adsorption measurements, and an overview on pore structure data for the membranes is given in **Table 2**.

Table 2: Specific surface area (BET model) and pore volume (BJH model)*

| | Membrane | Specific surface area (m ² /g) | Pore volume (d _p < 80 nm) (mL/g) |
|----|--|--|--|
| #1 | PES | 3.6 | 0.010 |
| #2 | Accurel® PP 300/1200; type a ^a | 13.4 | 0.018 |
| #3 | Accurel® PP 300/1200; type b ^a | 17.3 | 0.036 |
| #4 | Celgard® X30 ^b | 26.4 | 0.118 |
| #5 | Celgard® 24 (flat-sheet) ^b | 37.3 | 0.232 |
| #6 | Celgard® 25 (flat-sheet) ^b | 48.2 | 0.192 |

* 3 independent determinations had been performed; variation coefficients were <2% for specific surface area and <5% for pore volume.

^a prepared via the TIPS process

^b prepared via film extrusion and stretching

Both capillary membranes, from PES (#1) and PP (#2) have markedly different pore structure: the specific surface area of the PP membrane, as of all other PP membranes investigated in this study, was significantly larger than for the PES membrane. This is mainly due to the larger fraction of pores with diameters in the range of 20 to about 180 nm for the PP membranes (as seen from pore size distribution obtained via the BJH model; data not shown in detail). The three membranes (#4 to #6), made by a stretching process and having completely different pore morphology, had consistently larger specific surface area and pore volume in the diameter range, $d < 80$ nm.

3.3. Model system for red wine

A commercial extract from red grape marc (from grapes after fermentation) had been selected as model system because it contains large amounts of substances which are “typical” for red wine, and because this material could be obtained in larger quantity. Fluctuations of compositions, typical for trials with original wine, could thus be reduced. On the other hand, the detailed composition of the extract will depend very much on the raw material, the processing (here fermentation to wine), and, especially, on the extraction process; an overview on previous work in the literature along with original experiments toward overcoming the empiric character of the extraction process has been reported recently [28]. The aim of those preparations is to maximize “purity” and anti-oxidant activity of extracts, but the complete characterization of extract composition or an efficient further purification of extracts are still not established.

Solutions of the commercial extract were made up in “synthetic wine”, a buffer containing all main matrix constituents of wine. The UV absorption spectrum of this “reconstituted” (synthetic) red wine is shown in **Figure 2**.

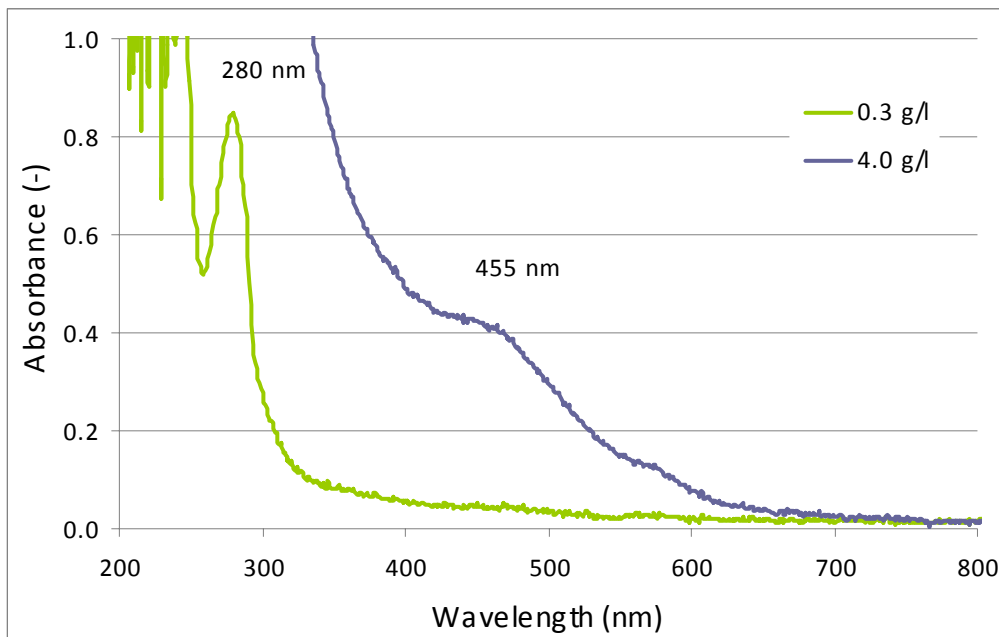


Figure 2: UV-Vis spectrum of „synthetic red wine“ (two different concentrations, cuvette thickness 1 cm).

The solutions had an intense absorbance in a wide range of the UV-Vis spectrum with a maximum around 280 nm. The turbidity was negligible (as indicated by no significant absorbance at 700 nm), what can be explained by the pre-filtration through a 0.45 μm MF membrane (cf. section 2.1). The relatively strong additional bands beyond 400 nm (intensity at 455 nm / intensity at 280 nm was 0.038) are a clear indication that a significant fraction of flavonoids, including anthocyanines, are contained in the „synthetic red wine“. In contrast, the UV-Vis spectrum of tannic acid was markedly different because no significant band was observed beyond 400 nm (intensity at 455 nm / intensity at 280 nm was ≤ 0.001).

Since the intensity at 280 nm was about 4 times higher than the highest values observed for proteins (due to their content in aromatic amino acids) at the same concentration, this is a confirmation of the relatively high content of polyphenols. By using the calibration for the model substance tannic acid, the content of polyphenol in the solutions extract was determined to be 0.075 g/g per dry mass. According to the manufacturer of the extract, the polyphenol content should be 0.444 g/g gallic acid equivalents per dry mass [29]. Therefore, it is most probable that the polyphenol content has been determined systematically too low with tannic acid as reference substance.

The content of polysaccharides was determined using a standard method (cf. section 2.2) to be 0.3 g/g per dry mass. Consequently, the “synthetic red wine”, made up with a solid content of 4 g/L, contained ~0.3 g/L polyphenol (in tannic acid equivalents) and ~1.6 g/L polysaccharide. Vernhet und Moutounet [4] had in their study tried to „reconstitute“ the composition of original red wine from a polysaccharide (1.2 g/L) and a polyphenol fraction (3.4 g/L); both fractions had been isolated from the wine by adsorption. Hence, in our work the concentrations of polysaccharides were very similar while the concentrations of polyphenols were significantly lower. Possible reasons, besides a systematically too low value (cf. above), are a different source (grape marc after fermentation, a wine-making waste, instead of red wine) as well as another processing method (solvent extraction instead of adsorption) in

order to obtain the material used in our work. Recent results in the literature demonstrate that for tannins (flavane-3-ol oligomers and polymers) with higher molar mass and PES, the plateau values of the adsorption isotherm are already reached at solution concentrations of 100 mg/L [6]. Therefore, the model system „synthetic red wine“ established here, should, irrespective of a somewhat lower content of polyphenol than in real wine, be very well suited for the intended adsorptive fouling studies.

3.4. Adsorption studies

All adsorption experiments were performed in a 12% ethanol/water buffer (pH 3.4) to ensure “wine-like” conditions. Flavane-3-ols, from monomers to oligomers with a molar mass of about 3.8 kg/mol, had been used also in other studies as relatively well-defined model substances for polyphenols [6]. Arabinogalactan is an important polysaccharide occurring in wine [4], while dextran has a completely different structure but had already been used in other studies of adsorptive fouling [15,16]. Both substances used in this work had similar average molar mass, in the range of 70 to 80 kg/mol, as determined by HP-GPC (cf. sections 2.1. and 2.2.). In wine, the polyphenol and polysaccharide composition is obviously more complex, and aggregates between both substances constitute high molar mass polysaccharide fractions containing polyphenol units. In order to identify effects of the more complex composition of the “synthetic red wine”, the following experiments were performed: adsorption of the individual model

Figure 4 shows the adsorption of tannic acid on the two capillary membranes normalized to the specific surface areas: More than ten times higher bound amounts were observed for PES relative to PP. The adsorbed amounts are in the range of what had been interpreted as monolayer coverage of PES with flavan-3-ols (0.6 to 2.0 mg/m², depending on the orientation of the molecules) [6]. This is also in agreement with previous results, indicating that almost complete surface coverage has been achieved at a solute concentration of 100 mg/L [6]. All these arguments point to a relatively high affinity due to the attractive polar interactions. Consequently, the affinity of PP for this polyphenol under the adsorption conditions was much lower; this can well be explained by the matrix, especially ethanol, which will not favour attractive interactions between the polar solute and the non-polar surface. In addition, hydrogen bonding between polyphenol and PES likely also contribute to the driving force for adsorption; PP does not support the formation of hydrogen bonds to the surface. From **Figure 4**, it can also be seen that the amounts of adsorbed tannic acid did not change much in mixture with a ten-fold excess of polysaccharide; for PES a reduction of about 10% was observed while the data for PP were very low anyway.

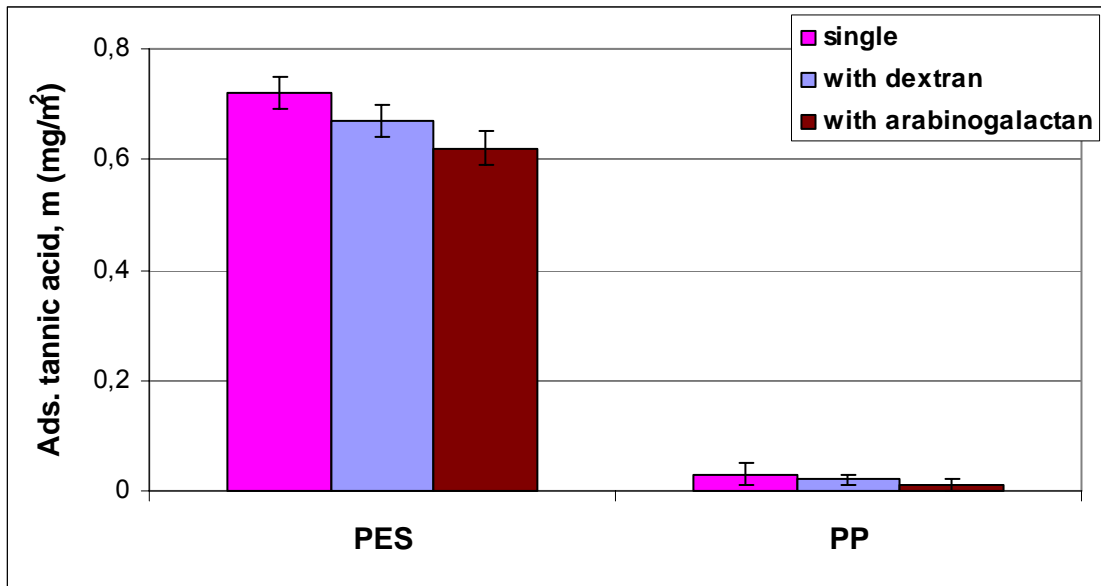


Figure 4: Adsorption of tannic acid (0.1 g/L) from single solute solution and mixtures with arabinogalactan or dextran (1 g/L; in “synthetic wine”) to PES and PP membranes (#1 and #2), relative to the membrane specific surface area.

The amounts of adsorbed polysaccharide in the same experiments with solute mixtures are shown in **Figure 5**. It is clear, that the low data for PP were not changed within the range of error, while the values for PES were lower than in the single polysaccharide adsorption experiments (due to the large error, the difference was only significant for dextran; cf. **Figure 3**). This reduction can well be explained by the saturation of most binding sites on the surface with tannic acid (cf. **Figure 4**). Overall, the amounts of adsorbed polysaccharide on PES were somewhat higher than for tannic acid but this is mainly due to the much higher molar mass and not because a dense monolayer would have been formed. Also, those higher values are only reached at ten-fold higher polysaccharide concentration than for tannic acid, and the smaller polyphenol model substance can well displace the polysaccharide from the surface.

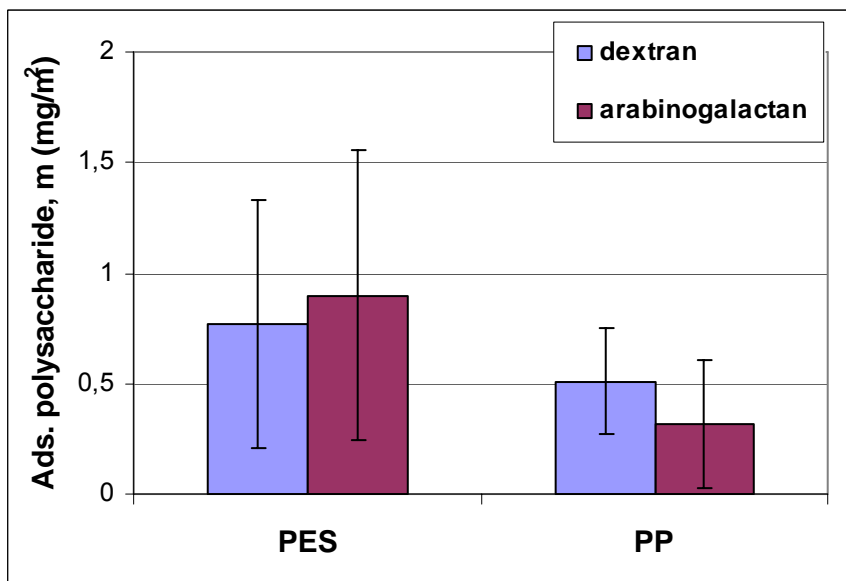


Figure 5: Adsorption of arabinogalactan or dextran (1 g/L) from solutions of mixtures with tannic acid (0.1 g/L; in “synthetic wine”) to PES and PP membranes (#1 and #2), relative to the membrane specific surface area.

Figure 6 shows the adsorbed amounts of polysaccharide and polyphenol from the “synthetic red wine”, both of them determined with the same methods as used for the model systems shown and discussed above, on the two capillary membranes normalized to the specific surface areas. The difference between the two membrane polymers was very pronounced for both solutes: Much higher values were observed for PES than for PP. It was even more remarkable that also the absolute values were very similar to the data for the model substances. Especially for polyphenol on PES the values were only about 10% higher, and this can be explained by a full surface coverage on the one hand and by the fact that the photometric method will give similar results independent of molar mass of the solute. The considerably higher bound amounts for polysaccharide on PES (when compared with the mixture of polysaccharide with tannic acid; cf. **Figure 5**) could then be related to a higher average molar mass of the adsorbed material in the “synthetic red wine” or to a higher adsorption tendency compared to the mixtures. Even for these polysaccharides, the adsorbed amounts on PP were almost 10 times lower. However, it should be noted that the data obtained here are significantly different from the results obtained with PES membranes and original red wine, where the level of adsorbed polyphenol had been in the same range (up to 1.3 mg/m²) while the level of bound total polysaccharide had been about one order of magnitude lower (up to 0.2 mg/m²) [4]. These differences are presumably because the model system “synthetic red wine” from an extract of fermented red grapes is different from a red wine, in terms of overall polysaccharide and polyphenol contents as well as the structure of these fractions. Changes of contents and structure can be linked to differences with respect to extraction or enzymatic and chemical conversions during the different processing, but a detailed discussion is not possible due to limited analytical data.

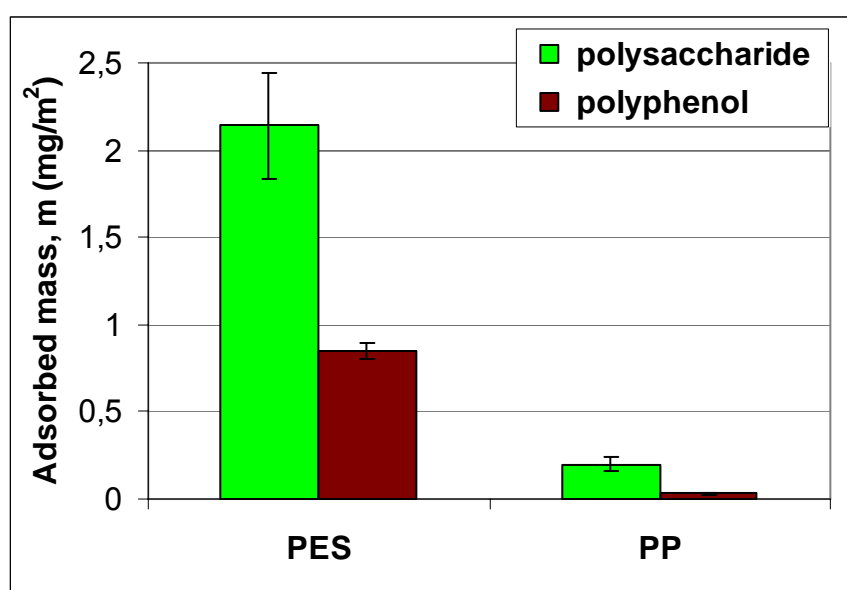


Figure 6: Adsorption of polysaccharide and of polyphenol from “synthetic red wine” (4 g/L) to PES and PP membranes (#1 and #2), relative to the membrane specific surface area.

More data for the other PP membranes are summarized along with the already discussed data in **Table 3**. The adsorbed amounts for both solutes relative to membrane mass were markedly different. However, after normalizing the values to the specific surface area (cf. **Table 2**), all data for polyphenol were similar on a very low level, and the polysaccharide values were all much lower than for the PES membrane. Further, a clear trend as function of pore structure could be identified: The membranes prepared by the stretching process had smaller values than those produced by the TIPS process. In addition, membrane #4 (Celgard® 24) with the highest porosity in the micro- and meso range had lower values than membrane #5 (Celgard® 25), and this would provide further support for the hypothesis that size exclusion of the polysaccharide from membranes pores does also play a role.

Table 3: Overview in adsorbed polyphenol and polysaccharide from “synthetic red wine” (4 g/L) for all membranes.

| | Membrane | Polyphenol | | Polysaccharide | |
|----|---------------------------------|---|-------------|----------------|-------------|
| | | Adsorbed amount, mean \pm standard deviation (mg/m ²) | | | |
| #1 | PES | 0.831 | \pm 0.147 | 1.558 | \pm 0.554 |
| #2 | Accurel® PP 300/1200; type a | 0.055 | \pm 0.018 | 0.566 | \pm 0.233 |
| #3 | Accurel® PP 300/1200; type b | 0.061 | \pm 0.014 | 0.524 | \pm 0.163 |
| #4 | Celgard® X30 | 0.000 | \pm 0.030 | 0.120 | \pm 0.031 |
| #5 | Celgard® 24 (flat-sheet) | 0.042 | \pm 0.020 | 0.250 | \pm 0.060 |
| #6 | Celgard® 25 (flat-sheet) | 0.052 | \pm 0.010 | 0.350 | \pm 0.200 |

All results can be discussed with the dominating polar interactions (van der Waals and electron donor / acceptor, both as function of the phenolic groups) during adsorption of polyphenols to surfaces as starting point. This is true for relatively small molar masses (here 1.7 kg/mol, for tannin). The resulting attractive forces, especially in presence of ethanol, are much stronger for PES than for PP. Further, with the additive PVP in PES, additional attractive interaction based on directed hydrogen bonds is likely to occur [18,30]. An increase of both adsorbed amount and affinity for polyphenol binding to PES with increasing PVP content had been confirmed before [6]. In this study we did not try to analyse the content of PVP in the commercial PES membrane (and the determination of the fraction of PVP exposed on the PES surface in the membrane pores is still an unsolved analytical challenge). However, in another parallel study it had been found that PES membranes prepared without any additive showed severe adsorptive fouling by polyphenols (from green tea), and the extent of fouling for the PES membrane prepared with PVP was only 10% higher [25].

As already discussed above, the adsorption tendency of the model polysaccharides with much higher molar mass (70 to 80 kg/mol) was weaker, but leads still to relatively high values, especially for PES.

The differences between the adsorption of polysaccharide from “synthetic red wine” as compared to the synthetic model systems (exemplaric for arabinogalactan) are expressed in the ratios summarized in **Figure 7**. For PES, there is a clear increase of adsorption tendency (factor ≥ 2) while for PP the amounts are lower (factor 0.4 to 0.6). This enhancement can directly be related to the presence of aggregates between polyphenol and polysaccharide in the “synthetic red wine”: The polyphenol moieties as “sticking groups” (cf. above) draw also polysaccharide with high molar mass to the PES surface. That the opposite tendency is seen for PP may be related to the fact that the total amounts are much smaller and the experimental error larger, but also to hindrance by the small pores to the accumulation of high-molar mass polysaccharides on the entire PP surface (note that the fraction of small pores was much larger for PP than for PES, cf. above).

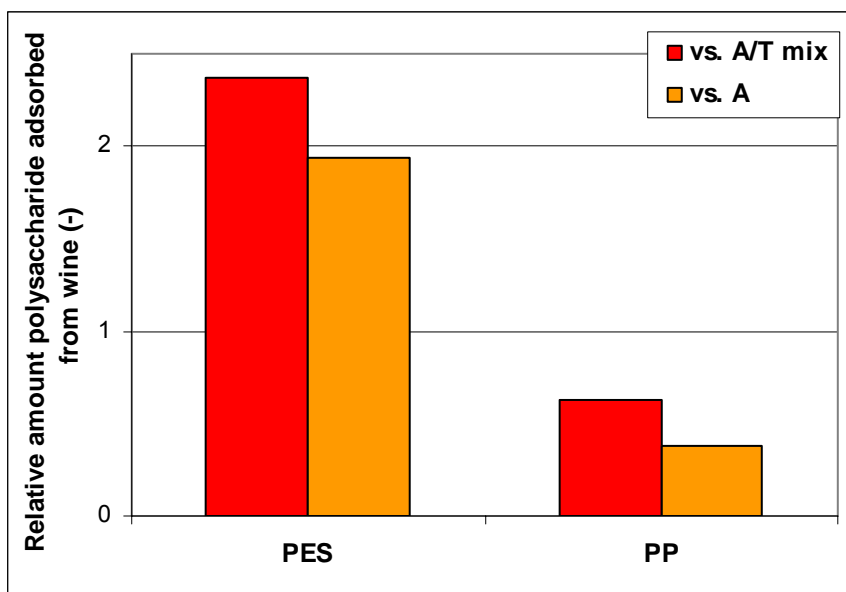


Figure 7: Relative amount of adsorbed polysaccharide from “synthetic red wine” (4 g/L) to PES and PP membranes (#1 and #2), in comparison to experiments with model solutions: “A/T mix” ... mixture of arabinogalactan (1 g/L) and tannic acid (0.1 g/L) in “synthetic wine”; “A” ... arabinogalactan (1 g/L) in “synthetic wine”.

We note that in previous studies, protein-polysaccharide conjugates, such as arabinogalactan-proteins or mannoproteins, have been found as the main adsorbed polysaccharides from wine [3,4]. Mannoprotein from white wine had been analysed, and a very wide molar mass distribution had been found, the largest fractions had molar masses >500 kg/mol [31]. We believe that the results from our model study provide more experimental data about consequences of the complex colloidal structure in polyphenol/polysaccharide mixtures in grape extracts, and we hypothesize that such colloidal effects could also be the “physico-chemical interactions likely to take place between wine constituents (especially polysaccharides and polyphenols)” [4]. And our results may help explaining why also in other experimental studies, PP capillary membranes have shown surprisingly stable flux in cross-flow MF of wine, what had not been observed with membranes from other materials [7].

4. Conclusions

Individual polyphenols and polysaccharides in “wine-like” ethanol-containing buffer are only marginally adsorbed by PP but strongly adsorbed by PES MF membranes. When relating the adsorbed amounts to the specific membrane surface areas, surface coverage for PP was much less than expected for a monolayer while monolayer coverage of PES had presumably already been achieved at relatively low solute concentration (here about 100 mg/L). The adsorption of polyphenols seems to be governed by two mechanisms, depending on the membrane polymer: Polar interactions (van der Waals interactions and electron donor-acceptor interactions) were much stronger with PES than with PP, and multiple hydrogen bonds towards the additive PVP in PES may further increase adsorption tendency. Adsorption of polysaccharides from the model “synthetic red wine” made from red grape marc extract is higher than from the buffer “synthetic wine” with model substances, and there is a correlation between the adsorbed amounts of polysaccharide and polyphenol from “synthetic red wine”; both findings support the hypothesis that aggregates of polyphenols and polysaccharides present in red wine have a major contribution to adsorptive fouling. This fouling is strong for PES, but very weak for PP membranes. The low adsorption tendency of wine ingredients to PP membranes results in higher fluxes and longer service life of the respective filtration modules in wine clarification.

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