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Innovative regenerable polyamide particles as new filter aids for wine lees filtration

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ABSTRACT

In oenology, the conventional dead-end filtration with filter aids, used for the processing of wine lees, consumes a high quantity of diatomaceous earth and brings serious environmental, sanitary and economic implications. In a real concern to improve wine quality and to decrease pollution, the "ecological filtration" concept based on the utilisation of a regenerative filter aid is proposed in this study. Polyamide particles were investigated as innovative filter aids for wine lees filtration. Trials were performed with two grades of polyamide particles D80 (D_{50} = 91.8 µm) and D100 (D_{50} = 111 µm). Filtration was carried out with wine added with two concentrations of lees (10.8 % and 20.2 %). The impact on wine quality was determined with oenological analyses, showing that the filtration made with polyamide particles did not modify wine organoleptic characteristics, improved turbidity and the filtrate fluxes are higher in comparison to the usual precoat filtration. Then, polyamide particle regeneration experiments proved that these particles could be reused as filter aids several times after cleaning.

KEYWORDS

filtration, wine lees, polyamide particles, regenerable

INTRODUCTION

Filtration is a key step in the elaboration of many agro-food products such as fruit juices, beer or wine. In oenology, filtration could be performed using a filter media using diatomaceous earth (DE), perlite and cellulose called filtration aids. DE is usually employed to clarify and represent the second source of pollution in the wine industry. Pollutant content reaches 100 g to 2000 g of residue per hectolitre of filtered wine (11,000 tonnes/year in France) (Fillaudreau *et al.*, 2008) mainly during wine lees filtration. Moreover, the crystal structure of aids, associated with their powdery nature, generates eco-toxicological risks through their use. Diatomaceous earth is made from the fossilised remains of tiny, aquatic organisms called diatoms. Their skeletons are made of a natural substance called silica. Rice *et al.,* 2001 proved that there is a significant risk of mortality from lung cancer that increased with cumulative exposure to respirable crystalline silica dust. There are different types of filtration such as (i) sterilising filtration, which retains yeast and decreasing bacteria population (ii) clarifying filtration which maintains particles larger than 10 µm and (iii) coarse filtration to reduce suspended matter content. Coarse filtration consists of eliminating coarser particles (from 100 µm to 10 mm), often carried out at flow rates comprising between 10 and 15 $hL.h^{-1}.m^{-2}$ under 2 or 12 bars of pressure (Ribéreau-Gayon *et al.,* 2012). Coarse filtration is mainly intended for filtration of wine lees, pre-filtration, clarification of young wines or for wines with a low filterability.

Wine lees are suspended solids present in wine after fermentation (Fornairon-Bonnefond *et al.,* 2001) and represent about 2 to 4 % of wine volume and could contain 20 % by weight of dry residue including plant particles, agglomerates of tartar crystals, colloidal materials, precipitated polyphenols, yeast, bacteria or other micro-organisms (Ribéreau-Gayon *et al*., 2012). Wine lees could contain more than 100 g of suspended materials per litter which can lead to fouling during filtration. Clogging phenomena could also be explained by the physico-chemical nature of the molecules existing in wine lees (Yammine *et al*., 2019a; Yammine *et al*., 2019b; El Rayess *et al*., 2016). Indeed, they are composed of a high number of proteins, glucans, polysaccharides and tannins (Blackfort, 2017; Ghidossi *et al*., 2018). It has been proved that glucans increase significatively the viscosity which induces lower permeability (El Rayess *et al*., 2016). There is either a link between the particles size involved in the clogging and the fouling behaviour of the porous media. These parameters are essential to consider avoiding rapid pore blocking (Rouquié, 2018). Grape seed tannins can also form interactions with polysaccharides increasing the colloid formation (Vernhet and Moutounet, 2002) which are retained during filtration inducing fouling mechanism and wine organoleptic modifications. Besides, the retention of particles could also correspond to electrical phenomena which are very difficult to predict. The good adequacy between filter material and particles must be considered both for filtration and cleaning efficiency. Traditionally, lees filtration is performed with vacuum rotary filters or press filters. Filtration aids are needed and added in the liquid to form a growing but permeable filter cake enclosing the suspended particles. During filtration, a continuously metered amount of aids called body feed is introduced into the liquid throughout the service cycle. This method maintains the cake channels open as suspended materials and the filtrate continues to percolate through the filter cake without clogging phenomenon. Using aids leads to high wine molecules adsorption phenomena and the regeneration of aids is not possible. Furthermore, after filtration, the DE used must be upgraded or eliminated in specific facilities resulting in higher filtration costs (incineration, co-composting, spreading) according to the Environment Code of France, Articles L. 541-1 to 50.

Recent research has led to the design and development of new filter media called Rilsans®, also known as polyamide 11 (PA11) (Boitelle *et al*., 2008 and 2009; Blackford, 2017). They are derivatives of grains of ricin through a series of physico-chemical reactions and are formerly known as Castor oil. The specificity of ricin oil comes from its high content of ricinoleic acid (up to 85 %) composed of a double bond and a hydroxyl function at the heart of a linear chain of 18 carbons. PA11 particles are resistant to acid and basic solutions and are available in different grades covering the entire particle size distribution of filtration aids with a range comprised between 10 µm and 140 µm (Boittelle *et al*., 2009). Comparative studies of Rilsans® and aids indicate that Rilsans® particles are dense unlike aids which are porous (Blackford, 2017). Besides they also studied the potential of these materials for an oenological application and they proved that a mixture of several grades of Rilsan® allowed performing clarifying filtration. The particle size employed was a mix of polyamide particles with size distribution close to 30 µm (D30) and 80 µm

(D80). The mix of these two grades of Rilsan® for pre-coat filtration compared to the commercialised aids for fine filtration (Diatomyl® P2) have the same efficiency in terms of reduction of turbidity (> 80 %), yeast (2 log CFU/mL reduction) and bacteria (1 log CFU/mL reduction). On the other hand, polyphenol and tannin concentrations as wine colour were modified after filtration in the same proportions for Diatomyl® P2 and Rilsan® (mix of D30/D80 grades). The sensory analysis of wines realised before, and after filtration has not shown significant differences. Moreover, the authors studied Rilsan® regeneration both with chemical products and physical processes. They proved that chemical regeneration by washing with sodium hydroxide and hydrochloric acid are efficient to clean Rilsan® and to recover initial characteristics (size distribution, permeability and form).

Considering these promising results, this work aims to evaluate Rilsan® capacity to filtrate the most problematic and charged liquids as wine lees. Filtrations were realised by using a continuous accretion filter with aids or Rilsan®. Different suspensions of lees (10.8 and 20.2 %) and two grades of polyamide 11 particles (D80 and D100) were used. Filters are composed of a complex network of interconnected pores each with tortuous paths. The filter performances are considered in terms of flux and particle removal efficiency. The regeneration method is also studied. The filtration capacities will be compared with commercialised adjuvant (P00) for coarse filtration in oenology.

MATERIALS AND METHODS

1. Aids Characteristics

The granulometry of the filter aids is an essential parameter because this parameter plays an important part in the relationship of tortuosity, filterability, retention capacities and porosity. Particles size distribution was determined by laser diffraction using a Mastersizer (model 3000, Malvern Instruments) in a range between 10 nm and 3500 µm. The measurements are based on the theory of diffraction by Fraunhofer, which states that the intensity of scattered light by a particle is directly proportional to the particle size.

The measurements were done in dry mode using an Aero S dry powder dispersion accessory. Particles disperse and travel through the detection cell by means of airflow with settings of 0.5 bar pressure, 3 mm of hopper gap and a feed rate of 20 % using a vibrational feeder. For each measurement, size distributions (mean diameter in volume) were provided (calculated from equation 1) and statistical volume diameters, D_{10}, D_{50} and D_{90} were given (D_x indicates a particle size for which x % of the particles are below that size).

$$(1)\ The\ volume\ mean\ diameter = D[4.3] = \frac{\sum_i N_i D_i^4}{\sum_i N_i D_i^3}$$

where N_i is the number of drops with a diameter D_i.

2. Initial permeability

Classical aids used in this study were Diatomyl® P00 and were provided by Laffort Oenologie. These aids are commonly used to filter the most charged liquids (wine lees) and represents appreciatively 80 % of the total production. The tested polyamide particles (Rilsan®) were D80 (80 µm) and D100 (100 µm), which were provided by Arkema. The filtration capacity and the characterisation of the powders (permeability before filtration and after regeneration) will be measured using the same device. The experimental permeameter was used to evaluate water permeability, filtration capacity and regenerable possibilities of the precoat layer expressed in the Darcy unit. The laboratory pilot used is presented in Figure 1.

The first step consists of creating the first precoat with about 1 kg.m^{-2} of filtration aids on the sintered stainless-steel sheet (22.4 × 10^{-4} cm²-40 µm pore size). The filtration aids were suspended and placed in the liquid chamber. Diatomyl® P00 is suspended in water, and Rilsan® in a mixture of water with 12 % of ethanol because Rilsan® are hydrophobic and require ethanol to be suspended. Agitation in body feed is maintained to ensure the mixing of filtration aids (200 rpm) and the device is pressurised to 0.4 bars. First, 200 ml of water is passed through the filter cell to form the cake. In a second step, the filtration time of 200 ml of water through the cake is measured. The cell is dismantled to measure the thickness of the cake with a calliper. The definition of the permeability for a filter aid results from Darcy's Law.

Permeability is the volume of a fluid passing through a unit cross-section of the medium in unit time under the action of a unit pressure gradient. These data were used to calculate the permeability according to Equation 2:

$$(2)\ Q = \frac{B\Delta P}{\mu e}$$

With Q, the flow rate expressed in m³/s per filtration surface unit (m²), B the permeability in m², µ the dynamic viscosity in Pa.s, ΔP the

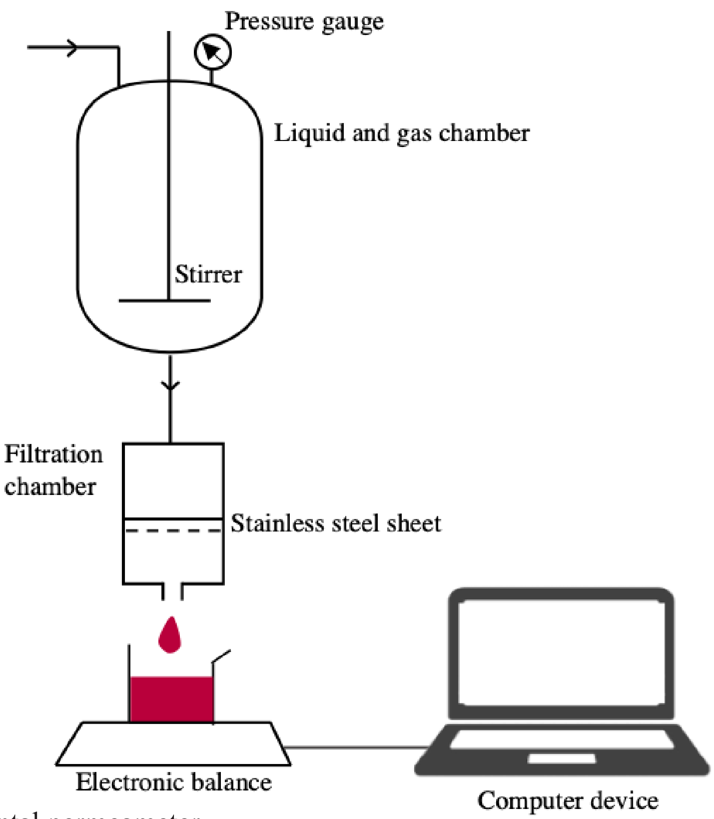

FIGURE 1. Experimental permeameter.

pressure gradient in Pa and e the thickness of the cake in m. The result is expressed in Darcy.

A Darcy is defined as 1 mL/(sec.cm^2) of a liquid with 1 centipoise viscosity (water) passing through a 1 cm thick cake at a 1-atmosphere pressure differential. In the practice of wine filtration, the permeability of the layer depends on the permeability of the filter aid, but also the retention of suspended particles. To recover the initial characteristics of polyamide aids, the initial permeability must be recovered after cleaning.

Filtration curves express the variations in the filtered volume (V) as a function of time (t). These curves are not linear, as the flow rate decreases over time, while the cake of filtration increases in thickness due to the continuous alluvium. They are therefore not extrapolable. However, it is possible to obtain linear filtration curves, per extrapolating the results using a logarithmic form, expressing the variations of log V as a function of log t (Dubourdieu *et al.*, 1976). The curves become straight lines that can be extended to predict the volumes that could be filtrated over time. In this case, the slope is closed to 0.5. We can demonstrate, from Darcy's law, this linearity of the filter curves in logarithmic coordinates and the value 0.5 of their slopes when there is no clogging phenomenon.

If S is the filtering surface, the volume filtered at the end of time (t) is written:

$$(3)\ V = S\int_0^t q\,(t)\,dt$$

On the other hand, S the filtration surface (m^2), the thickness (e) of the filter layer at time (t) is proportional to the filtered volume (V) and the dose the alluvium per unit of surface C (in g) and δ as a constant; therefore

$$(4)\ e = \delta \frac{C}{S} V$$

Within these equations, we could consider that:

$$(5)\ Q = \frac{1}{\sqrt{2Lt}}$$

with

$$(6)\ L = \frac{n\,\delta\,C}{B\,\Delta P} = constant$$

so,

$$(7)\ V = S\int_0^t \frac{1}{\sqrt{2Lt}}dt = S\sqrt{\frac{2t}{L}}$$

then,

$$(8)\ V = S\sqrt{\frac{2B\,\Delta P}{n\,C\,\delta}}\ x\sqrt{t}$$

this equation could be written as follows

$$(9)\ \log V = 0.5\log t + \log S\sqrt{\frac{2B\,\Delta P}{n\,C\,\delta}}$$

$$(10)\ logV = 0.5logt + constant$$

We can notice that the liquid viscosity differential pressure also affected the ordinate at the origin of the straight line, but not its slope. The filtration of coarse liquid containing high content of suspended particles is tough; however, it can be interpreted from the previous simple model. Clogging results in a decreased value of this slope. Hence, obtaining a linear filtration curve in logarithmic coordinates is a condition to maintain good filtration.

The prediction of the volume filtered after 8 h will be represented by a specific graph. Thus, thanks to the directing coefficient of the lines (noted k), it is possible to estimate the volume filtered after 8 h. With these results, we can therefore forecast the possibilities for an industrial filtration system.

3. Filtration test

The first step is to form the precoat with water in the experimental setup presented in Figure 1, which ensure initial clarity. Then, a mix is made with wine lees and filter aid to reproduce the wine filtration step in continuous alluvium mode. In both cases, 1 $kg.m^{-2}$ of filtration aids will be used for creating the first precoat on the sintered stainless-steel sheet (22.4 × 10^{-4} cm^2 - 40 µm pore size). Once the filter cake is created, the water in the feed flask is replaced by 2 L of the liquid to be filtered (in our case the wine lees). The addition of filtration aids into the liquid to be filtered is realised and called body feed. The wine lees are mixed with P00, D80 and D100 with a content equal to 2 kg/hL. Agitation in body feed is maintained to ensure the mixing of wine lees and aids (200 rpm). If the alluvium is enough and well-adapted, no rapid clogging will appear and the filtration will be subjected to the law of cake filtration.

The experiments are carried out at constant pressure (2 bars) supplied by a compressed nitrogen source. We note the volumes of filtrate collected during the time. The filtration test was carried out at 20 °C with the experimental permeameter for the three aids studied: P00 (as reference), D80 and D100.

4. Wine lees – dried matters

Real lees with a dry matter content of 10.8 % and 20.2 % have been used to compare Rilsan® D80, D100 and Diatomyl® P00. Dried matters were estimated by weighing after removing the water by heating a sample. The sample was dried for 48 h in an oven at 100 °C and weighed after membrane filtration (membrane Whatman 0,45 µm). The dry matter (DM) was expressed in g/100 g of products.

5. Physico-chemical analyses

Filtration efficiency was estimated by measurement turbidity with a nephelometer (HACH 2100Q with an accuracy of 0.2 NTU). A pH meter (Labomat H128 brand, precision 0.1) was used. The chromatic characteristics of the wines were measured using a Perkin Elmer LAMBDA 850 spectrophotometer. The absorbance of the wine sample was measured by placing an aliquot of each sample in a quartz cuvette with 1 cm light path at a wavelength of 420 nm detects yellow tones (Optical Density OD_{420}), 520 nm detects red tones (OD_{520}) and 620 nm detects purple tones (OD_{620}). The colour index (CI) was obtained from the sum of the absorbance of the samples for the three wavelengths. The Total Polyphenols Index (TPI) or OD_{280} were determined according to the OIV methods (2018). Current analyses in oenology (tannins, anthocyanin, total acidity, volatile acidity) were carried out using a sequential enzymatic analyser, Y15 from BioSystems. The Y15 equipment was calibrated with the external standards that are provided in every kit by BioSystems.

6. Regeneration, cleaning in place

The two regeneration procedures consisted of an immersion of the filter cake in 1 % of an alkaline detergent chlorinated (Divos 120CL) during 3 min or in 12 % of Divos 120CL for 3 weeks followed by at least three rinses with water (up to a neutral pH).

7. Statistical analyses

All the analyses were realised in triplicate. Statistical analyses were performed using the R software and the Kruskal–Wallis test (α = 0.05).

RESULTS AND DISCUSSION

1. Aids characteristics

The complexity to understand the phenomenon that occurs inside filtration aids are involved in limited information such as packing porosity, particle shape and tortuosity. Filters are composed of a complex network of interconnected pores each with tortuous paths. For either porous material, high permeability is dependent on low tortuosity. It is important to note that tortuosity will increase during filtration and the path travelled by the fluid will be longer as the pores will be clogged. Aids particles may be plates or needle-shaped, with small circular perforations. For a large distribution of particles, tortuosity is low and this packing

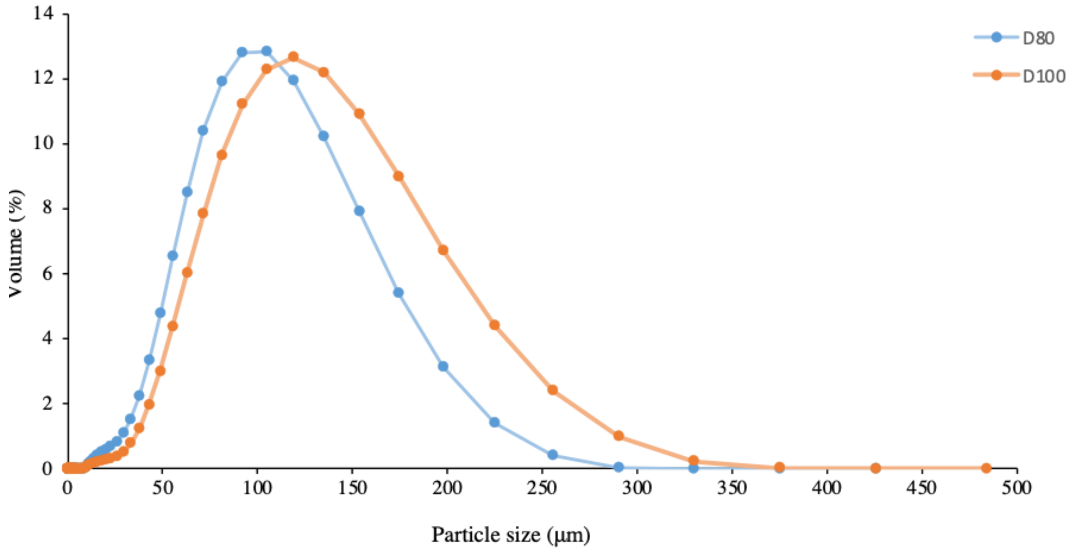

FIGURE 2. Particle size distribution for Rilsan® D80 and D100.

modifies permeability and retention capacities. A compromise has to be identified between all these parameters but we first verify that there is a potential difference in granulometry between our polyamide particles (D80 and D100). Figure 2 indicates the particle size distributions of the two grades of Rilsan® and Table 1 summarise statistical diameters and mean diameter in volume

TABLE 1. Statistical diameters (D_{10}, D_{50} and D_{90}) and mean diameter in the volume of Rilsan® D80 and D100.

	D80	D100
D_{10} (µm)	46.0	56.5
D_{50} (µm)	91.8	111.0
D_{90} (µm)	159.0	195.0
D[4.3] (µm)	97.7	119.0

For all parameters, the given values are the average of three trials and all standard deviation values are inferior to 5 % of the average value.

This is a monomodal distribution with a positive skew. The D_{50} referring to the median value is 91.8 µm for D80 Rilsan® and 111 µm for D100. The mode value that is the peak frequency distribution is 92.0 µm for D80 and 118.8 µm for D100. The volume mean diameter D[4.3] for D80 is equal to 97.7 µm. This diameter differs from those measured for the D100 equal to 119.0 µm. We observe a D[4.3] larger than D_{50} for both Rilsan® particles. These results are fairly typical because D[4.3] emphasise the detection of large particles. The particle sizes vary from 8 µm to 290 µm for the D80, and from 8 µm to 425 µm for the D100. We observe a positive skew in the particle distribution where the mean, the median and the mode are three different values. Concerning D80 and D100, the particles are also far from spherical and the diameter based on the real volume of the particles cannot give sufficient information. However, the long path those particles must take through the filter leads to an increase in the possibility that a particle may be trapped. The large distribution size with the smallest particles started at 8 µm could be locked in the inner space formed by the largest particles in both cases of Rilsan® (> 200 µm). This improves the probability of a particle being removed by the filter aids rather than passing through.

2. Initial permeability

Considering the dispersion of the potential particles, tortuosity will be modified and will impact permeability (Griffiths *et al.*, 2020). This is the reason why permeability must be characterised and represents a very important characteristic to consider in our work. Table 2 indicates the initial permeability measured for P00, D80 and D100.

TABLE 2. Comparison of the initial permeability obtained for the different adjuvants (P00, D80 and D100).

	P00	D80	D100
Darcy	3.68 ± 0.3	2.51 ± 0.2	3.93 ± 0.3

To realise these experiments 6 g for P00 and 10 g for Rilsan® were added to form the precoat cake thickness (1 cm) and flux were measured for 20 min. The thickness of the cake layer must be the same in both cases (1 cm) and the weight is different because the initial density of Diatomyl® and Rilsan® are 2.3 ± 0.1 g.cm-3 and 1.24 ± 0.1 g.cm-3, respectively.

First, we can notice that our system permits having reproducible values (low dispersion). These values will be used as a reference and cleaning protocols must ensure to recover the initial permeability.

Diatomyl® P00, which has permeability closed to 4 Darcy and these aids are usually used for coarse filtration in wineries. We can notice that these values are very close to D100 (3.93 Darcy). These results obtained confirm the potential utilisation of polyamide particles especially D100 for coarse filtration.

3. Filtration

To assess filtration capacities in the case of coarse wine, two matrices (10.8 and 20.2 % DM) were studied. The results obtained using filter P00, D80 and D100 aids were compared. The filterability was evaluated thanks to filtrate accumulation curves. Figure 3 represents respectively the evolution of the permeability along the time for a solution at 10.8% DM (case a) and 20.2 % DM (case b).

The performance of each filter aids can be compared and results tend to prove that Rilsan® D80, D100 and Diatomyl® P00 have similar filtration capacities in case of 10.8 % of DM (Figure 3, case a). Concerning the experiments realised with high concentration for dried matters with 20.2 % (Figure 3, case b), D100 permeability is still 30 % higher after 45 min of filtration (146 $L.h^{-1}.m^{-2}.bar^{-1}$ for D100 compared to 110 $L.h^{-1}.m^{-2}.bar^{-1}$ and 113 $L.h^{-1}.m^{-2}.bar^{-1}$ for P00). In that way, D100 are more suitable to perform wine lees filtration when DM is around 20.2 % compared to D80 and P00.

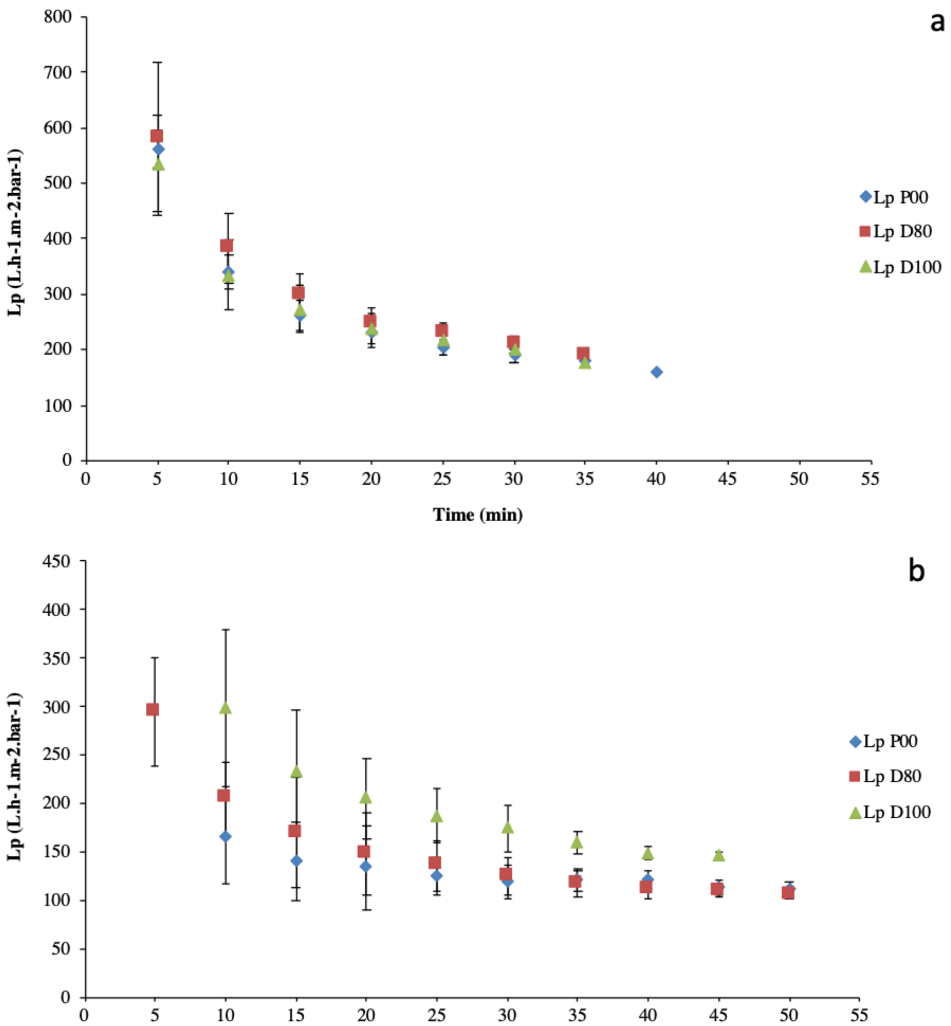

FIGURE 3. Evolution of the permeability (Lp) along the time for a solution at 10.8 % DM (case a) and 20.2 % DM (case b) for Diatomyl® P00, Rilsan® D80 and Rilsan® D100.

This difference could be caused by a higher dense structure of the filter cake during the filtration stage for D80 and P00. The compressibility is higher for aids when pressure and tortuosity increase. Considering D80 and D100, polyamide is not impacted within this pressure and cake structure is conserved during filtration. As shown above in Figure 2, the particle size distribution implies that D80 is composed of the finest particles, in comparison with the other D100. It means that internal fouling can occur and limit the flux for matrices that have a high content of dried matter. Concerning D100, the inner flow is facilitated per the low tortuosity and higher fluxes are maintained. Within these values, we could also if alluvium is well realised and if a rapid clogging occurs by plotting log V and log t (Figure 4a and 4b).

First, the linearity of these filter curves in logarithmic coordinates and the slope value close to 0.5 indicate there is no clogging and the model cake law filtration without clogging is respected (equation 9). It means that the filter does not contain particles that can change the permeability of the porous layer (case of pure water). We can then consider that the flow is only managed by the aid's tortuosity and, consequently, it is constant throughout the filtration. Rilsan® D100 could also realise good filtration for solutions with higher suspended matters (20.2 % DM). Within this representation and by considering the slope equation, it is possible to evaluate the volume that could be filtered after 8 h. In the case of 20.2 % DM filtration, this means that in the case of a 10 m² filter press, the volume of lees filtered after an 8 h of filtration cycle would be 74 hL,

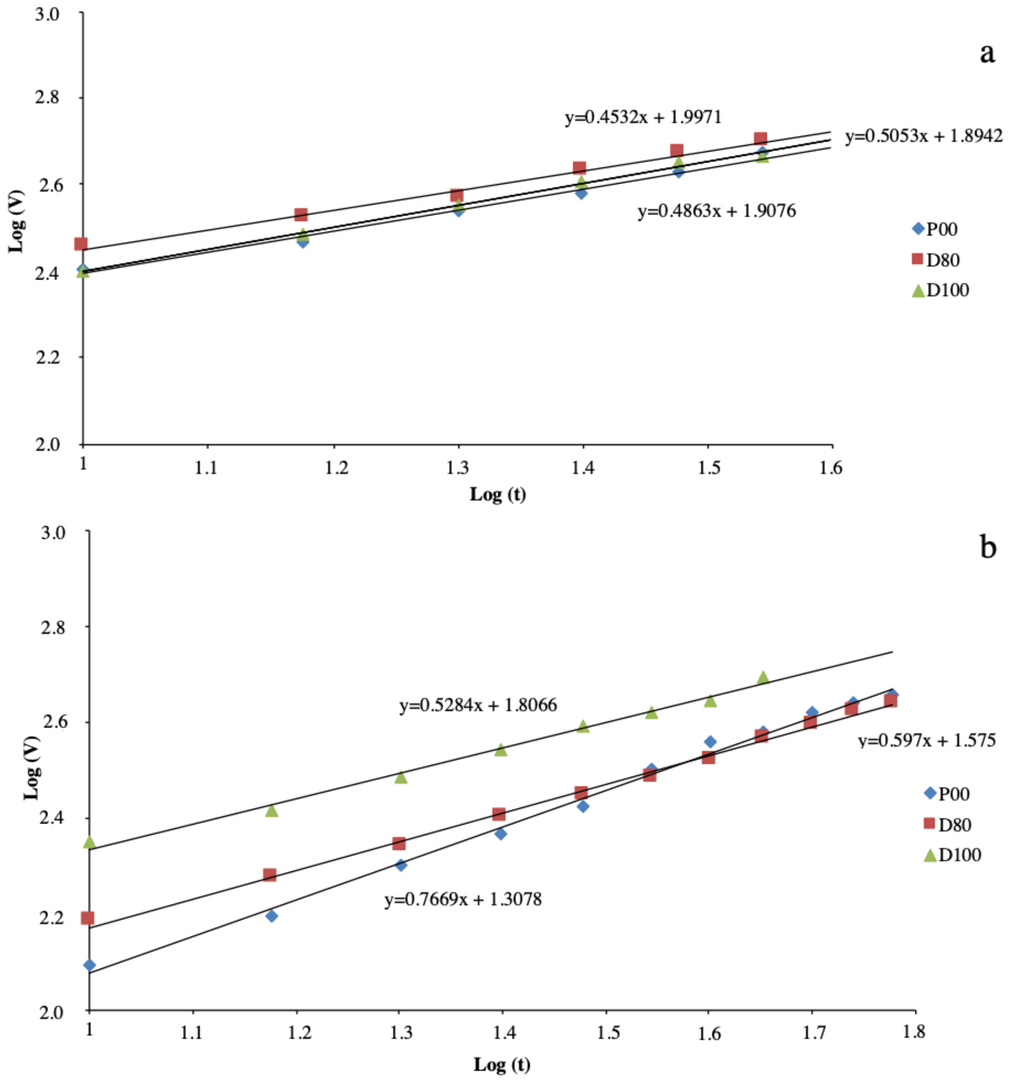

FIGURE 4. Evolution in logarithmic coordinates of the volume as a function of time of the filtration realised with Diatomyl® P00, Rilsan® D80 and Rilsan® D100 using the matrices 10.3 % DM (case a) 20.2 % DM (case b).

66 hL and 102 hL, respectively, for P00, D80 and D100. In the case of D100, the filtered volume after 8 h is 1.37 higher in comparison to P00. Considering D80, this volume is 1.12 lower in comparison to P00. The retention capacities must also be considered for this filtration and physical-chemical characterisation must be done.

4. Physico-chemical characterisation of the wine after filtration

To determine if the new filter aids modified wine characteristics after filtration, chemical and usual oenological analyses were performed before and after filtration. These analyses were supplemented by considering turbidity (Table 3). These analyses were realised in the case of filtration of wine lees with 20.2 % DM.

TABLE 3. Turbidity measurement after filtration realised with Diatomyl® P00, Rilsan® D80 and Rilsan® D100 using the matrix 20.2 % DM.

	P00	D80	D100
After filtration	5.1 ± 0.3	6.0 ± 0.4	7.5 ± 0.2

These turbidities are comparable and represent a significative diminution. Before filtration, turbidity cannot be determined (> 2000 NTU). These values are consistent and in line with the expectations of winemakers. At this stage, it is necessary to reduce the turbidity of the wines; however, the objective is not to obtain a brilliant wine or a wine with low levels of micro-organisms. Several other physicochemical parameters were measured to ensure that the main components of the wines are not modified (Table 4).

No difference is remarkable concerning pH, total acidity, volatile acidity, polyphenols and anthocyanins after filtration for each aid. Total tannins and anthocyanin contents are not impacted which means that the polyphenolic compounds are not retained by the porous media by steric retention or specific adhesion phenomena to polyamide particles. Chromatic characteristics were also measured to validate these results (Table 5).

The absorbance was measured at 280 nm for the TPI and the sum of OD 420, 520, and 620 for the colour index. These results do not indicate significant differences. These outcomes correlate with the previous ones and we can consider that only the particulate fraction is stopped by the filter media. However, it should be noted that D100 allowed faster filtration than P00. Besides, analysis results showed that the polyamide particles did not affect wine characteristics.

5. Cleaning-in-place

The last part of this work was to evaluate if Rilsan® could be reused after filtration. Cleaning-in-place

TABLE 4. Physicochemical characteristics of wines before and after filtration with Diatomyl® P00, Rilsan® D80 and Rilsan® D100 using the matrix 20.2 % DM.

	DM (g/100 g)	pH	Total acidity (g H_2SO_4/L)	Volatile acidity (g of acetic acid/L)	Total Anthocyanins (mg/L)	Total Tannins (mg/L)
Before filtration	20.2 ± 0.3	3.80 ± 0.02	4.0 ± 0.2	0.47 ± 0.02	524 ± 12	2444 ± 20
After filtration P00	2.0 ± 0.1	3.77 ± 0.01	3.9 ± 0.4	0.50 ± 0.01	530 ± 15	2506 ± 23
After filtration D80	1.1 ± 0.1	3.78 ± 0.02	3.9 ± 0.5	0.50 ± 0.02	559 ± 11	2439 ± 18
After filtration D100	1.6 ± 0.2	3.79 ± 0.01	3.9 ± 0.2	0.51 ± 0.01	484 ± 18	2490 ± 26

TABLE 5. Chromatic characteristics of wines before and after filtration with Diatomyl® P00, Rilsan® D80 and Rilsan® D100 using the matrix 20.2 % DM.

	Before filtration	After P00	After D80	After D100
OD_{420}	0.517 ± 0.010	0.402 ± 0.007	0.444 ± 0.015	0.489 ± 0.018
OD_{520}	1.199 ± 0.023	1.205 ± 0.041	1.156 ± 0.088	1.129 ± 0.059
OD_{620}	0.235 ± 0.015	0.235 ± 0.009	0.205 ± 0.021	0.206 ± 0.027
Colour Index (CI)	1.951 ± 0.058	1.842 ± 0.073	1.805 ± 0.067	1.824 ± 0.056
Total polyphenol Index (TPI)	47.6 ± 0.011	44.9 ± 0.029	45.0 ± 0.017	44.1 ± 0.031

systems were developed using the circulation of chemicals and water. To ensure the viability of this CIP, it seemed essential to focus primarily on classical cleaning products already existing in the winery.

Regarding the particles retained inside the filter mainly composed of organic matters and we decide to retain a chlorinated alkaline detergent (Divos 120CL). The second concern was to validate that the polyamide was not impacted by this product after a long contact time. We have decided to leave the polyamide immersed in a concentrated solution (10 %) of Divos 120CL for a long time (3 weeks) then to check that the permeability remained unchanged. In the literature, polyamide membranes are known to swell in alkaline conditions, because the dissociation of carboxylic groups in polymer chains leads to a negative charge of the chains and they repel each other (Huang *et al*., 2021). Swelling expands the membrane matrix, increases the average pore size of the membrane and changes the membrane surface morphology (Dalwani *et al*., 2011). In our case, we have powder but the modification of permeability must be considered by measuring the permeability after various CIP. The results for D100 are presented in Figure 5.

In this case, the solid fraction retained inside the porous material is mostly a combination of yeast, organic acids (mainly tartaric acid), insoluble carbohydrates (such as cellulosic or hemicellulosic materials), inorganic salts, lignin, proteins, phenolic compounds, pulp and other parts of the grape. The caustics act through the solubilisation, swelling, and degradation of organic matters and detergent improve wetting and degradation. Within this CIP, initial permeability is at the same level after filtration and after a long exposition to the alkaline agent. The initial permeability is regained after cleaning and prolonged contact does not modify its characteristics. Rilsan® could be employed in the case of wine lees filtration and could be regenerable.

CONCLUSIONS AND PERSPECTIVES

The main objective of this project was to evaluate the potential use of a new reusable filter aid, Rilsan®, which can be adapted to devices already in use for coarse filtration. The results permit drawing several conclusions. Filtration of wine lees on a laboratory scale with polyamide particles is feasible comparable with conventional diatomaceous earth filtration already commercialised. The use of D100 filter aids appears relevant in coarse filtration and is an interesting alternative. Fluxes with wine less (20.2 % dried matters) were higher than those classically obtained in wineries (+ 37 %).

No impact has been noticed within the filtration realised at the laboratory scale. The Rilsan® powder made of organic sourced polyamide 11 could be an alternative to diatomaceous earth mainly used for wine lees filtration. The particle size distribution, the granular bed deposition and the filtration efficiency are very interesting and could be compared to commercialised aids. The fouling mechanisms follow an intermediate pore blocking law and alluvium quantity allowed to

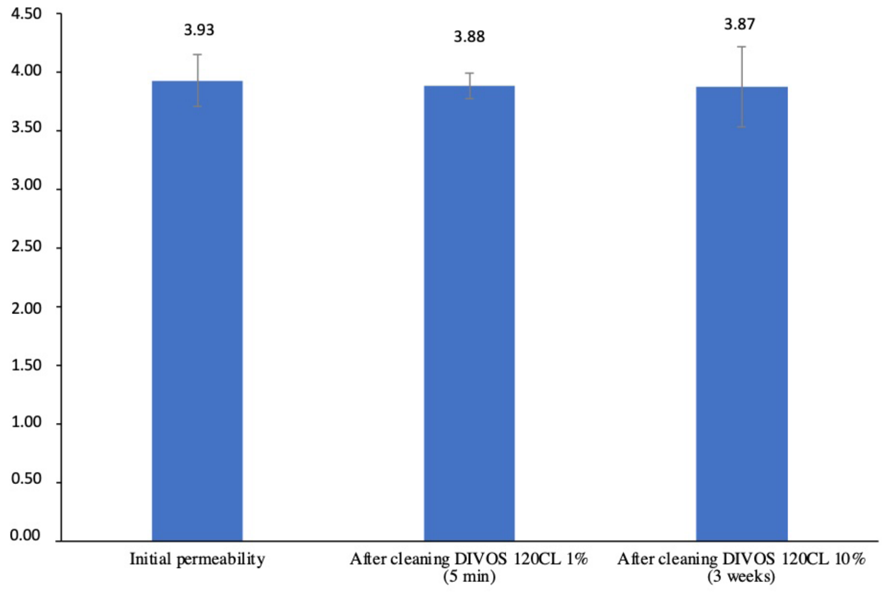

FIGURE 5. Permeabilities for Rilsan® D100 after various CIP (Divos 1 %-5 min and Divos 10 %/3 weeks).

avoid clogging (1 $kg.hL^{-1}$). According to their non-porous structure compared to diatomite, these particles are cleanable by using a chlorinated alkaline detergent and their regeneration is possible by a chemical agent. Rilsan® D80 and more specifically Rilsan® D100 appear to be an alternative to diatomite in terms of filtration efficiency. The use of Rilsan® as filtration aids would allow a reduction in the quantity of waste and improvement in the health risks associated with the use of silica-based additives. Further trials on different types of wine lees are still needed to validate their use on an industrial scale as well as a sensorial study.

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REFERENCES

Blackford, M. (2017). Étude de nouveaux media granulaires et non tissés pour la filtration du vin (Doctoral dissertation, Université de Bordeaux).

Boitelle, C., Poupot, C., Milisic, V., & Mietton-Peuchot, M. (2008). Advances in the Precoat Filtration Process. *Separation Science and Technology*, 43(7), 1701-1712. https://doi.org/10.1080/01496390801974563

Boittelle, C., Milisic, V., & Mietton-Peuchot, M. (2009). New filter aids for wine filtration, *OENO One*, 43(4), 231–238. https://doi.org/10.20870/oeno-one.2009.43.4.789

Dalwani, M., Benes, N. E., Bargeman, G., Stamatialis, D., Wessling, M. (2011) Effect of pH on the performance of polyamide/polyacrylonitrile based thin film composite membranes, *Journal of Membrane Science,* 372(1–2), 228-238. https://doi.org/10.1016/j.memsci.2011.02.012

Dubourdieu, D., Lefebvre, A., & Ribéreau-Gayon, P. (1976). Influence d'un traitement physique d'ultra-dispersion sur la filtration des vins, *Connaissance Vigne Vin*, 7392. https://doi.org/10.20870/oeno-one.1976.10.1.1646

Fillaudreau, L., Bories, A., & Decloux, M. (2008). Brewing, winemaking and distilling: an overview of wastewater treatment and utilization schemes in In Woodhead Publishing Series in Food Science, Technology and Nutrition, *Handbook of Water and Energy Management in Food Processing*. 929-995. https://doi.org/10.1533/9781845694678.6.929.

Fornairon-Bonnefond, C., Camarasa, C., Moutounet, M., & Salmon, J. M. (2001) New trends on yeast autolysis and wine ageing on lees: a bibliographic review, *OENO one,* 35(2), 57-78. https://doi.org/10.20870/oeno-one.2001.35.2.990

Ghidossi, R., Qiu, Y., Lacampagne, S., Mirabel, M., Renouf, V., & Mietton-Peuchot, M. (2018). Oxygen desorption and oxygen transfer through oak staves and oak stave gaps: an innovative permeameter, *OENO One*, *52*(1), 1-14. https://doi.org/10.20870/oeno-one.2018.52.1.909

Griffiths, I. M., Mitevski, I., Vujkovac, I., Illingworth, M. R., & Stewart, P. S. (2020). The role of tortuosity in filtration efficiency: A general network model for filtration. Journal of Membrane Science, 598, 117664. https://doi.org/10.1016/j.memsci.2019.117664

Huang, J., Luo, J., Chen, X., Feng, S., Wan, Y. (2021). New insights into effect of alkaline cleaning on fouling behavior of polyamide nanofiltration membrane for wastewater treatment, *Science of The Total Environment,* 780, 146632, https://doi.org/10.1016/j.scitotenv.2021.146632

OIV- Recueil des méthodes internationales d'analyse des boissons spiritueuses d'origine viticole. Edition 2018. *Office Internationale de la Vigne et du Vin*, Paris.

El Rayess, Y., Manon, Y., Jitariouk, N., Albasi, C., Peuchot, M. M., Devatine, A., & Fillaudeau, L. (2016). Wine clarification with Rotating and Vibrating Filtration (RVF): Investigation of the impact of membrane material, wine composition and operating conditions, *Journal of Membrane Science*, *513*, 47-57. https://doi.org/10.1016/j.memsci.2016.03.058

Ribéreau-Gayon, P., Glories, Y., Maujean, A., & Dubourdieu, D. (2012). Traité d'œnologie - Tome 2 - 6e éd. - Chimie du vin. Stabilisation et traitements (Vol. 5). Dunod. 624.

Rice, Fl., Park, R., Stayner, L., Smith, R., Gilbert, S., & Checkoway, H. (2001) Crystalline silica exposure and lung cancer mortality in diatomaceous earth industry workers: a quantitative risk assessment. *Occupational and environmental medicine*, 58(1), 38-45. https://doi.org/10.1136/oem.58.1.38

Rouquié, C. (2018). Microfiltration de jus de fruits et suspensions à base de fruits: faisabilité et performances d'une filtration par membranes immergées (Doctoral dissertation, Université de Bordeaux).

Vernhet, A. & Moutounet, M. (2002). Fouling of organic microfiltration membranes by wine constituents: importance, relative impact of wine polysaccharides and polyphenols and incidence of membrane properties, *Journal of Membrane Science*, 201(12), 103122. https://doi.org/10.1016/S0376-7388(01)00723-2

Yammine, S., Rabagliato, R., Vitrac, X., Peuchot, M. M., & Ghidossi, R. (2019a). Selecting ultrafiltration membranes for fractionation of high added value compounds from grape pomace extracts, *OENO One*, *53*(3), 487-497. https://doi.org/10.20870/oeno-one.2019.53.3.2343

Yammine, S., Rabagliato, R., Vitrac, X., Mietton-Peuchot, M., & Ghidossi, R. (2019b). The use of nanofiltration membranes for the fractionation of polyphenols from grape pomace extracts, *OENO One*, *53*(1), 11-26. https://doi.org/10.20870/oeno-one.2019.53.1.2342.