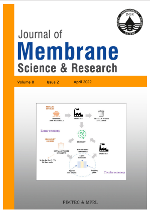
Journal of Membrane Science and Research 8 (2022) 529429

Journal of Membrane Science & Research

journal homepage: www.msrjournal.com



Research Paper

Vacuum Membrane Dryers: From Basic Principles to Applications

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Article info

Received 2021-04-30
Revised 2021-06-10
Accepted 2021-06-30
Available online 2021-06-30

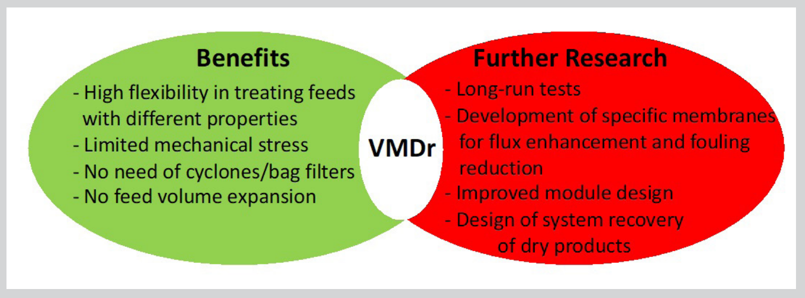
Keywords

Vacuum Membrane Dryers
Vacuum Membrane Distillation
Polystyrene microparticles
Caffeine
Dehydration

Highlights

- VMDrs development and application were reviewed and discussed.
- Aqueous feeds of polystyrene and of caffeine were efficiently treated.
- Benefits of VMDrs and further research needed were presented.

Graphical abstract



Abstract

Vacuum Membrane Dryers (VMDrs) are new membrane operations designed for the recovery of dry compounds from aqueous feeds. In this work, VMDrs development and application were reviewed and discussed. Flat and capillary membrane modules with feed recirculation and in static configuration (feed in contact with one side of the membrane without recirculation) were compared. VMDRs in static configuration were applied to the treatment of aqueous suspensions of 10 wt.% polystyrene microparticles (size ranging from 0.3 µm to 7 µm) at 30°C and 4 mbar, and to the treatment of aqueous solutions of caffeine (concentration ranging from 0.1 wt.% to 0.3 wt.%) at 45°C and 4 mbar. In both cases, a 0.2 µm polypropylene flat membrane was used. Dry solids (polystyrene) and crystals (caffeine) were obtained, together with distillates free of solids and crystals. For the two case studies, the drying efficiency and main differences were underlined. Finally, benefits of VMDrs and further research needed were presented.

1. Introduction

The production of food powders, catalysts, pills, pigments, etc., always passes through a drying step which is essential for obtaining a product with high stability and processability. Dryers are, therefore, present in many industries, like food, chemical, pharmaceutical, cosmetic, plastic and paint ones. Among the different dryers, those most used are spray-dryers, fluidised beds, vacuum dryers and freeze dryers. Each one presents some specific drawbacks, as summarised in Table 1. Fluidized beds and spray-dryers, for example, can only be applied to specific particle sizes and lead to particles deformation because of the high mechanical stress. Furthermore, to reduce the particles loss in the air stream used in the processes, cyclones/bag filters are required at the exit of the units. Finally, the evaporated liquid is not recovered. The need of cyclones/bag filters is also present for the vacuum dryers when fine particles have to be dried. This is because in vacuum dryers the feed is directly exposed to vacuum and the removed vapor can entrain some particles, if they are too small in size. For the same principle (vacuum directly applied to the feed), the feed volume can expand during the drying process affecting the final product structure. Finally, a high energy consumption is required for freeze dryers.

In this scenario, an alternative membrane process for drying, based on the principle of Vacuum Membrane Distillation (VMD) was recently proposed, and was named Vacuum Membrane Dryer [1]. The fact that in VMD the heat loss by conduction through the membrane can be neglected and that high trans-membrane fluxes can be achieved already at low operating temperatures, increased the interest for this membrane distillation configuration in different fields [2-11]. VMD is based on the use of a microporous hydrophobic membrane, one side of which is in contact with the feed to be distilled the other side being under vacuum. At the feed-membrane interface, in correspondence of each micropore, the evaporation occurs: water vapor moves from the interface through the micropores thanks to the applied vacuum and is condensed outside the membrane module in a condenser. Figure 1 shows how VMD works.

Theoretically, all non-volatiles contained in the feed cannot permeate the membrane and a high-purity distillate can be produced. When solid microparticles are present into the feed, the same concept applies, thus they are blocked at the retentate side. Their possible entrainment by the vapor flux is further avoided if their size is higher than the membrane pore size. Therefore, with respect to vacuum dryers, in VMDrs the membrane acts as a barrier and avoids the feed to be directly exposed to vacuum, preventing both particles entrainment and feed volume expansion. In this work, main results obtained with VMDrs in recently published papers are reviewed and

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DOI: 10.22079/JMSR.2021.529429.1465

discussed [1,12,13]. In particular, the most appropriate module design and configuration, as well as a comparison of the performance of VMDrs for two different applications, are presented. Specifically, VMDrs were applied for drying solid microparticles of polystyrene and caffeine. In the latter case, the caffeine extraction from coffee beans by supercritical CO_2 was considered. Once the CO_2 with caffeine exits the extraction column, it is sent to another column where the caffeine is removed from CO_2 by a water stream. The caffeine content of the water stream ranges from 0.1 wt.% to 0.3 wt.%, and a distillation step followed by a crystallization one is employed to recover dry caffeine. Therefore, a high energy input is required. Figure 2 depicts the traditional and the proposed caffeine drying processes.

In particular, the VMDr unit was tested as alternative process to recover in a single unit dry caffeine, starting from the aqueous solution produced in the water extraction step. It is evident that the two investigated applications are significantly different: polystyrene microparticles are hydrophobic solids and the feed to be treated is an aqueous suspension, while caffeine is solubilized into water and the feed to be processed is an aqueous solution. Nevertheless, the application of the VMDr to such different feeds had the aim of studying the potential and flexibility of this new membrane operation in various industrial sectors.

2. Materials and methods

2.1. Feeds

Four samples containing microparticles (0.3 μm, 0.5 μm, 1 μm, 7 μm) were tested. Each sample was of 100 ml and only one sample per particle size was purchased, except for the 7 μm sample, for which 200 ml were bought (Magsphere Inc. USA). Each sample had a solid content of 10 wt.%.

Typical concentrations of aqueous streams containing caffeine (0.1 wt.% - 0.3 wt.%) were obtained by dissolving pure caffeine (supplied by Verwerkaf, Italy) in distilled water.

2.2. Investigated membranes and VMDr configurations

Both commercial flat and capillary membranes (i.d., 1.8 mm; o.d., 2.6 mm) made of polypropylene (0.2 μm) were tested in two different VMDr configurations: one with aqueous feed recirculation and one with aqueous feed loaded in the membrane module (static configuration). Experiments were carried out on the aqueous suspension of 7 μm polystyrene at 30°C and 4 mbar. Figure 3 summarizes main differences of the investigated configurations. When the feed was recirculated, it was warmed up to the operating temperature outside the module, while in the static configuration, the module-self was thermostated. In the module with the capillary membranes and the feed recirculation, the feed flowed inside the fibers (n_f, 3; l_f, 16.5 cm), whereas it was loaded at the shell side in the static configuration (n_f, 3; l_f, 6 cm). The recirculation of the feed inside the capillaries rather than at the shell side, was preferred to work at higher feed velocities and, then, to reduce the resistance to the mass and heat transport.

Table 1
Main drawbacks of conventional dryers.

Dryer	Main drawbacks
Spray-dryer	1. Limited to particle size in the range of 10-100 μm; 2. Particles subjected to mechanical stress; 3. Need of cyclones/bag filters; 4. No recovery of the liquid.
Fluidised bed	1. Limited to optimal ranges of particle size and feed concentration; 2. Particles subjected to mechanical stress; 3. Need of cyclones/bag filters; 4. No recovery of the liquid.
Vacuum dryer	1. Feed volume expansion; 2. Need of cyclones/bag filters (1-5 μm mesh size) when drying fine particles.
Freeze dryer	1. High energy consumption.

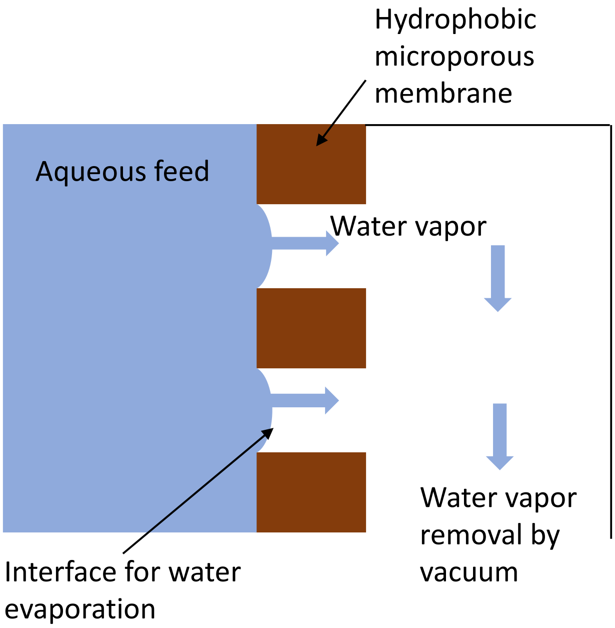

Fig. 1. Water vapor removal in VMD.

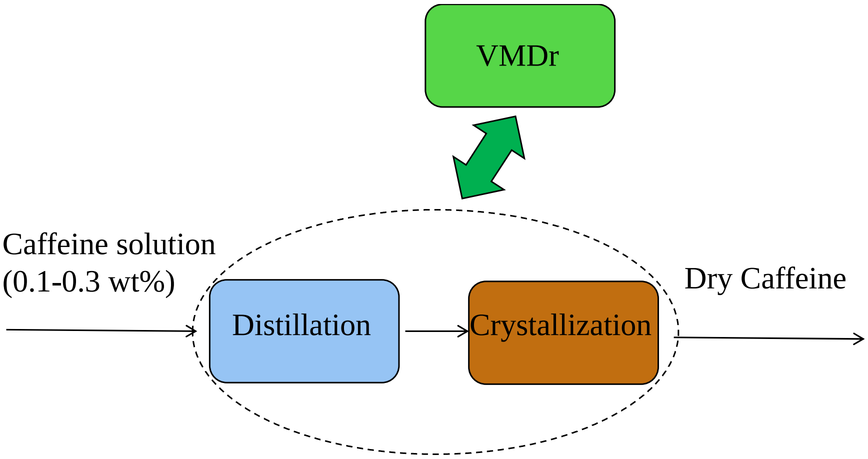

Fig. 2. VMDr as alternative process to recover dry caffeine from a caffeine solution.

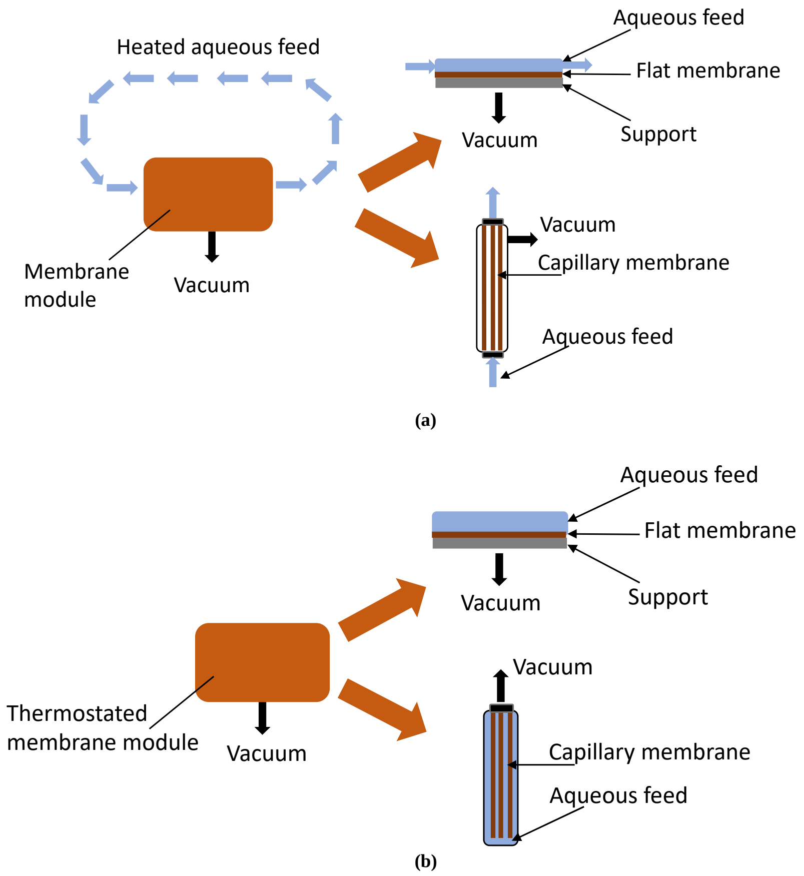

Fig. 3. (a) Configuration with feed recirculation, and (b) configuration with static feed.

2.3. Membrane and VMDr set-up for the two case studies

The static flat VMDr configuration was tested in the two case studies and a microporous hydrophobic membrane (polypropylene, 0.2 µm pore size, 91 µm thickness, 70% porosity) purchased from Membrana, Germany (now 3M) was used. The VMDr was heated at the desired temperature by sending hot water into the module jacket (thermostated membrane module). Table 2 shows main operating conditions of the carried-out experiments.

Besides the different types of feed and the initial concentration values, differences in operating temperature, membrane area and mixing procedure must also be noticed. A higher temperature for the treatment of aqueous feeds of caffeine was needed to solubilize the caffeine in water. The lower membrane area of the module employed for the dehydration of polystyrene microparticles was due to the limited volumes of feed available. Concerning the different mixing procedure, a timed-mixing was applied for the feed containing polystyrene to limit particles deformation, while ensuring a constant vapor flux through the membrane. The timed-mixing procedure consisted in mixing the feed for 1 minute, each 20 minutes of test. In the case of caffeine solutions, a continuous mixing was preferred, to guarantee a more uniform distribution of the temperature into the feed and, then, to avoid any early formation of caffeine crystals inside the liquid.

2.4. Flux calculation and streams analysis

The water vapor permeating the membrane was condensed outside the module and its weight was registered. Then, the trans-membrane flux J (kg/m^2h) was obtained by considering the mass of distillate (kg), the membrane area (m^2) and the experiment duration (h). Each test was repeated at least three times and the average flux value was calculated. For all tests, the collected distillates, as well as the feeds and concentrates, were characterized in terms of solid content by using a moisture analyser (Ohaus-MB 45).

3. Results and discussion

3.1. Choice of the VMDr configuration and membrane geometry

Both flat and capillary VMDrs with feed recirculation led to higher trans-membrane fluxes than the corresponding static configurations, due to the lower heat and mass transfer resistance in the feed boundary layer. However, experiments were stopped already at 50 wt.% feed concentration, due to the difficulty in pumping the concentrated feed, as well as its deposition in the set-up. On the contrary, by using the static configurations, the drying was successfully carried out. Concerning the membrane geometry, the flat one resulted to perform better, because the feed was in contact with all the membrane surface throughout the experiments, while with the capillary module part of the membranes was not in contact with the feed as its volume decreased and, therefore, not all the membrane area was effectively used. Moreover, the recovery of the dried particles was more difficult and some of them were also deposited on the module shell. Based on these results, the static flat VMDr configuration was chosen for the two case studies.

Table 2
Main operating conditions.

Aqueous feed	**T_{feed} (°C)**	**P_{vacuum} (mbar)**	**A_m (cm^2)**	**Mixing**
10 wt.% Polystyrene	30	4	7.1	Each 20’ for 1’
0.1-0.3 wt.% Caffeine	45	4	49	Until the stirrer was immersed into the feed

3.2. Main results of the two case studies

In all experiments, the VMDr was effective in producing dry solids (98 ± 0.5 wt.% polystyrene) and crystals (99.42 ± 0.5 wt.% caffeine) together with distillates free of solids and crystals. It is worthy to mention that the target in solid content for polystyrene was 98 wt.% and that the solid content measured in the produced crystals of caffeine was the same of that measured in the pure caffeine sample used for the preparation of the caffeine solution. Figure 4 shows a picture of caffeine crystals grouped on the membrane surface before their recovery. It is important to point out that for both feeds, no fouling issues were registered and, after each test, the membrane was simply washed with distilled water.

Main results are summarised and discussed hereinafter. The flexibility of the VMDr in handling variations of feed properties was proved for both case studies: the same performance in terms of drying efficiency (time needed and drying degree) was registered when treating caffeine streams with the typical concentrations of real decaffeination plants, as well as when treating feeds containing polystyrene microparticles of different size. In particular, the same efficiency was obtained for 10 wt.% feeds containing only 7 µm particles, only 0.5 µm particles and 0.3, 0.5, 1 and 7 µm particles (each one present in the same amount), without registering particles losses into the permeate. The significant difference in particles size is clearly evident in Figure 5.

The time needed to dry the two feeds as function of the height (thickness) of the liquid feed onto the membrane surface is reported in Figure 6. By increasing the height of the liquid, more water has to be evaporated and the time for drying increases. However, for the polystyrene feed, the increase is quite linear, whilst a different trend is observed for the caffeine feed. The difference in results can be attributed to the difference in the mixing procedure. In the case of polystyrene, the mixing time was fixed in order to work at an average constant flux. Then, at parity of trans-membrane flux, higher is the amount of water to remove, higher is the operating time. In the case of caffeine, the feed was continuously mixed until the stirrer was immersed into the liquid. Then, higher is the height of the liquid, higher is the time the feed is under stirring with a consequent more homogeneous temperature distribution and better storage of the accumulated heat. Therefore, in this case, by increasing the height of the liquid, two opposite phenomena occur: a higher amount of water to be removed (that means higher operating time) and a higher temperature inside the feed (that leads to higher trans-membrane flux). For this reason, the increase in the operating time at a higher height of liquid is lower than that registered for the polystyrene feed.

Finally, the lower times registered for the caffeine feed are due to the higher average flux (4.5 kg/m^{2}h for caffeine vs 2.3 kg/m^{2}h for polystyrene). The higher average flux can be attributed to the higher operating temperature as well as to the significantly lower concentration of the feed containing caffeine. When the operating conditions are fixed, the only way to improve the flux is to act on the membrane properties and module design. The effect of the membrane properties (porosity and thickness), at parity of pore size, was theoretically investigated for both case studies. In VMD, the trans-membrane flux can efficiently be described by the Knudsen mechanism [14]:

$$J = K_{Knudsen} \times (P_{fm} - P_{vacuum}) \qquad (1)$$

with

K$_{Knudsen}$, the Knudsen coefficient, kg/(m^2 s Pa)

P$_{fm}$, the water vapor pressure at the membrane-feed side, Pa

P$_{vacum}$, the vacuum pressure, Pa

The Knudsen coefficient includes the membrane properties grouped into the ratio:

$$Membrane\ properties\ ratio = \frac{r_p \times \varepsilon}{\delta \times \tau} \qquad (2)$$

with

r$_p$, the pore size, m

ε, the porosity, /

δ, the thickness, m

τ, the tortuosity, m. It can be calculated from porosity as 1/ε [15].

Starting from the experimental flux value obtained with the experimental membrane properties ratio of 0.54 ^{x} 10^{-3}, and assuming to work always at the experimental membrane temperature (optimized mixing conditions), the flux which might be achieved using membranes with different properties can be calculated by considering for the flux the same increment of the membrane properties ratio. Figure 7 shows the variations in porosity and thickness investigated with respect to the experimental ones, as well as the corresponding membrane properties ratios. It has to be pointed out that, while membranes with 75%-80% porosity and 70 µm thickness can be successfully employed in VMD, lower thickness values could lead to a decrease of mechanical resistance. In these cases, the use of supports is strongly requested. Figure 8 reports the increase of flux with the membrane properties ratio for the two case studies. A gain of 50% can be achieved already with a 75% porosity and 70 µm thickness membrane.

Fig. 4. Picture of the caffeine crystals grouped on the membrane surface.

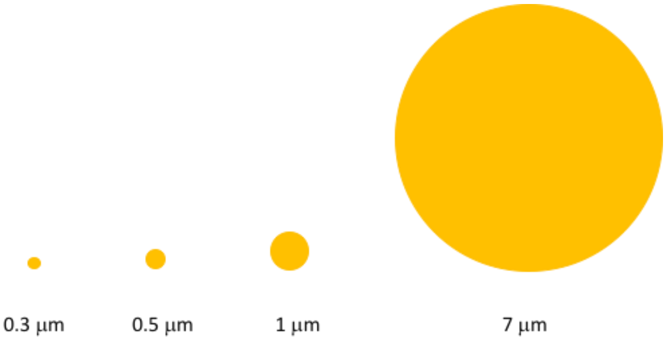

Fig. 5. Polystyrene particle sizes investigated.

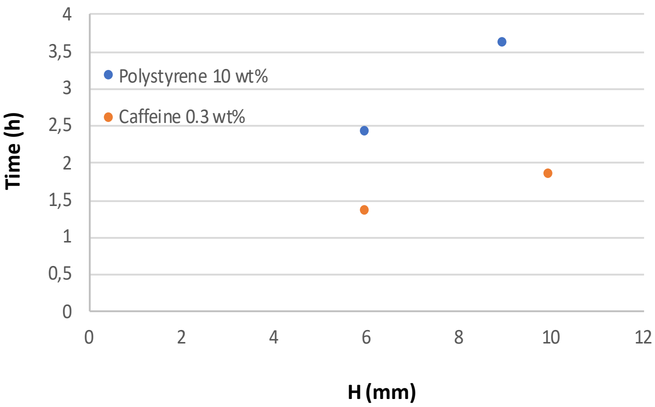

Fig. 6. Drying time as function of the height of liquid feed on the membrane surface.

4. Concluding remarks

The flat membrane geometry and the static module configuration resulted to be the optimal choice for the design of VMDrs. Loading the feed on the flat membrane surface allowed, in fact, an efficient use of all the membrane area for the water evaporation and an easier recovery of dried products. VMDrs were successfully applied to the drying of both solid polystyrene microparticles, starting from a 10 wt.% aqueous suspension, and of caffeine contained into high-diluted aqueous solutions. The positive results obtained in these so different fields clearly underline the versatility of the new proposed membrane operation. In both case studies, a high flexibility in handling variations of the feed stream was observed: the same efficiency was obtained for a quite large range of polystyrene size (from 0.3 μm to 7 μm) and for the two typical concentration values of caffeine in decaffeination plants (0.1 wt.% and 0.3 wt.%). The two aqueous feeds had different characteristics and needed different operating conditions, with a consequent difference in the trans-membrane fluxes achievable. The effect of membrane porosity and thickness on the flux was theoretically investigated, at parity of experimental conditions, and it was found that already with a 75% porosity and 70 μm thickness membrane a gain of 50% in flux can be obtained with respect to that measured during tests. Therefore, by acting on membrane features, as well as on the module design, the VMDRs performance can be enhanced. Moreover, the choice of membrane material must carefully be made based on the type of feed to be treated, to reduce fouling phenomena. Vacuum Membrane Dryers presents many benefits with respect to conventional dryers, as summarized in Figure 9. Nevertheless, as it is also reported in the figure, there are different aspects to further investigate in order to optimize the VMDRs efficiency and to promote their scale-up.

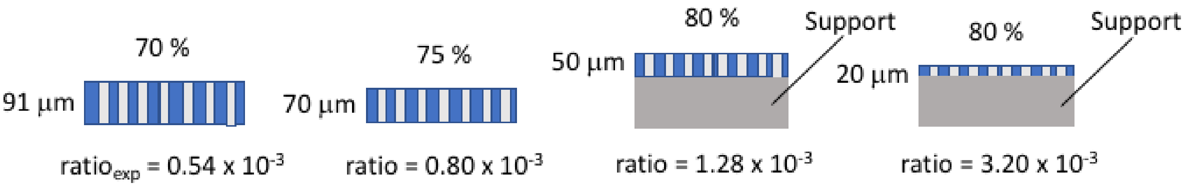

Fig. 7. The different membrane properties considered. First figure on the left side: experimental values.

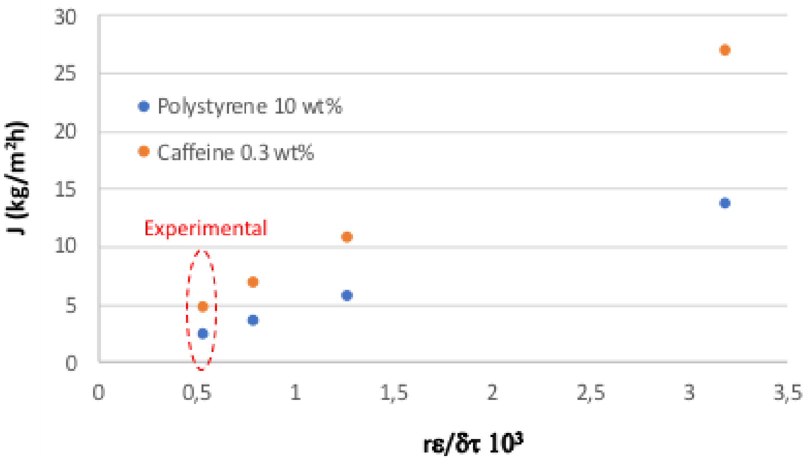

Fig. 8. Membrane flux as function of the membrane properties ratio.

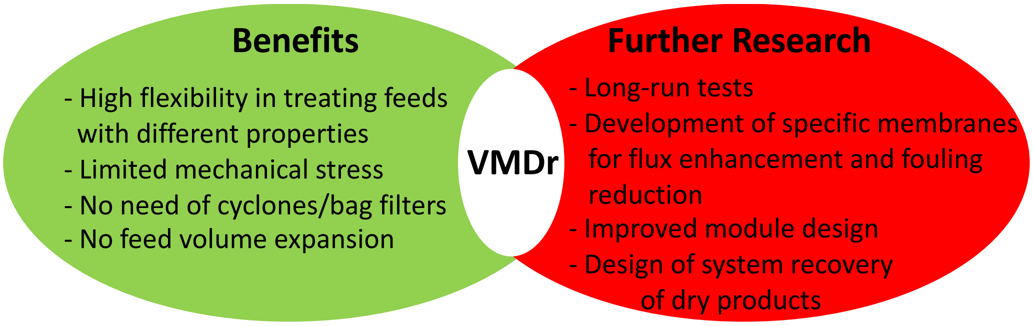

Fig. 9. Benefits of VMDr and future research.

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