Ultrafiltration for fractionation of polymer solutions

1. Introduction

In nature a variety of complex mixtures of polymers are known to exist and they include, for example, polysaccharides, proteins, celluloses and lignin type materials.

To separate these mixtures of macromolecules most commonly precipitation, GPC or ultrafiltration (UF) are used. Of the various membrane processes, ultrafiltration provides the right membrane with its pore size to separate macromolecules on molecular weight (molecular weight cut off).

Today ultrafiltration provides an efficient and environmentally friendly process for a variety of industries.(1,2) It is encountered on production scale for example in the dairy industry (cheese whey ultrafiltration), waste treatment (removal of higher molecular weight materials), textile industry (recovery of size warping agents like PVA and CMC), pulp and paper industry (concentration and recycling of effluents), food industry (clarification of juices) and biotechnology.(1,2) One of the most important issues in ultrafiltration is fouling of the membrane, a process in which the membrane is irreversibly blocked by macromolecules. Several methods have been developed to avoid or diminish the fouling effect.(1,2)

Literature provides several hundreds of publications each year dealing with the ultrafiltration in the aforementioned industries.

In addition, ultrafiltration can be used in a more refined way to isolate materials or narrow ranges of materials from polymer solution of synthetic or natural origin. As a consequence of the common synthetic polymerization processes, chain size polydispersity plays an important role in polymer chemistry. The chain size polydispersity can greatly influence the properties of the polymer specimens, i.e. changing the molecular mass distribution can affect properties like viscosity, density, volatility, crystallinity and even permeability through the skin. Especially in fields like medicine, cosmetics and chemical industry the molecular mass distribution plays an important role in determining the performances of the polymers.

As an example ultrafiltration is used to prepare a more monodisperse dextran (Figure 1). In this case the high molecular weight dextran, being toxic for the human body, can be removed,

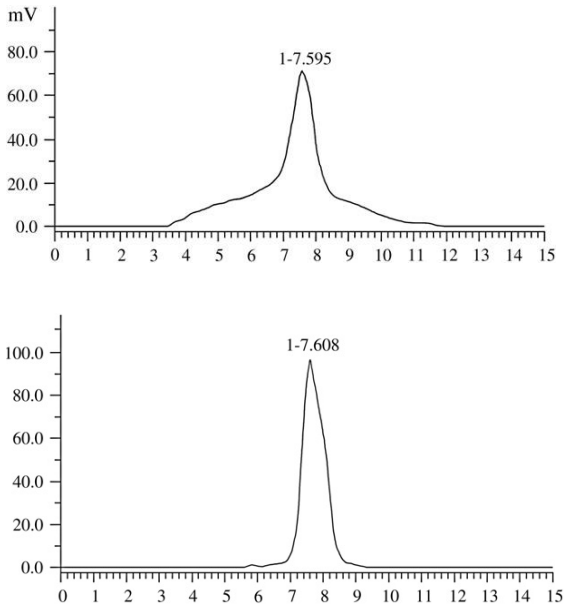

Figure 1. HPLC diagrams of dextran D20 before and after ultrafiltration and crystallization. Reproduced from ref 3. Copyright C.R.Chimie (2008).

The purpose of this colloquium is to explain the basic principles of ultrafiltration, followed by types, properties and recent developments in membranes. Finally, a review of the literature of the last decade on the fractionation of polymers is given.

2. General principle of the Ultrafiltration process

Ultrafiltration has a wide application in industry as a method to concentrate solutions and to purify water.(2)

For ultrafiltration to be effective, depending on the type of material that has to be concentrated, separated or purified, the properties of the membrane are essential. In literature, several articles are dealing with the type and characteristics of the membrane, which consists most of the time of an organic polymer and occasionally of a ceramic material. New membranes are and have been developed to solve the disadvantages of the existing polymer membranes.

Ultrafiltration is a separation method for substances in which a solution under high pressure is pushed through a membrane. A variety of membrane types with different pore sizes exist for which different pressures can be applied.

Ultrafiltration is part of a range of filtration types. Membranes which have a relatively large pore size compared to ultrafiltration are used for Micro filtration (MF).(Figure 1) The MF membranes have a pore size of 0.1-10.0 µm, where a pressure of 1-5 bar is applied during filtration. These membranes are used for the sterile filtration and clarification.

Membranes with a relatively smaller pore size compared to ultrafiltration are used for Nano filtration (NF). The pore size lies in the order of 1 nm with an applied pressure during filtration of 1-10 bar. An application of NF is removal of Ca^{2+} ions (softening of water) and desalination.

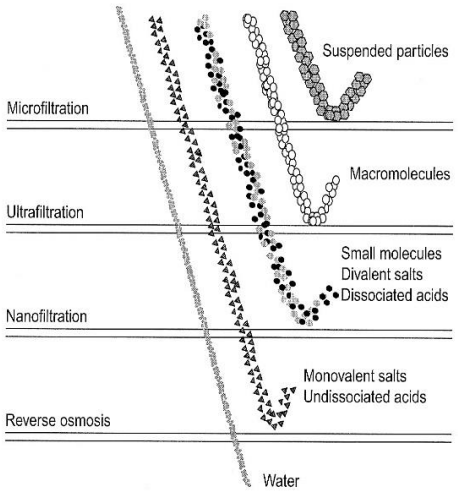

Figure 2. Microfiltration, ultrafiltration and nanofiltration. Reproduced from ref. 4. Copyright Elsevier 2010.

In the case of UF the pore size is in the range of 1-10 nm and applying a pressure of 10-30 bar. UF is primarily used in separation of macromolecular solutions.(4)

There are two distinct processes for UF: 1) the dead-end and 2) the cross-flow ultrafiltration. In the dead-end process the direction of the flow of the solution is perpendicular to the membrane surface, one stream flows towards the membrane and one stream leaves through the membrane. In the case of cross-flow UF the flow is along with the membrane surface and two streams are leaving the membrane unit; retentate and permeate flow.(Figure 3) In most applications the accumulation of rejected particles is so severe that dead-end UF becomes impractical.(4)

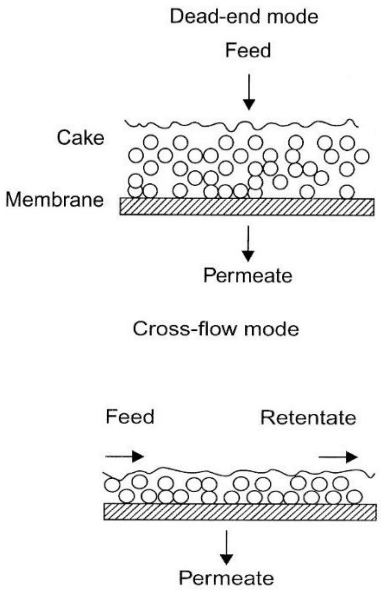

Figure 3. Dead-end filtration vs cross-flow filtration. Reproduced from ref. 4. Copyright Elsevier 2010.

As to the size of the separation process, UF can be used both on a small scale, for example by using laboratory centrifugation and GPC and on a larger scale in production processes, be it batch wise or continuous.(2)

2.1. Advantages and drawbacks of UF

The main advantages of the ultrafiltration process are:

- a low energy consumption/high energy efficiency in comparison with other processes where, for instance, water has to be evaporated
- ease of operation (5)
- ease of scale-up (4)

UF can also help to recycle valuable materials and create less waste. For example, for electrocoat paint the drag-out paint is collected from the waste by UF and reused in the paint process.(2) Its non-destructive character is an advantage for food industry when dealing with thermally labile ingredients or flavours.(1,6,7) UF can also be used to concentrate suspensions or solutions. In the dairy industry UF has been used for decades to pre-concentrate milk for cheese manufacture. Moreover, it is widely used for the fractionation of whey.(2)

One of the potential disadvantages of ultrafiltration can be the reduction of the membrane flux during operation. This can be either a reversible or irreversible process. The phenomenon of membrane flux reduction can occur in various ways. (Figure 4) First there is the reversible effect of concentration polarization, i.e. the retentate becoming increasingly concentrated in the proximity of the membrane (R_{cp}). The concentrated retentate can, with time, form a gel layer or a cake (R_g) that can reduce the flux further. Another possibility of reduction of membrane flux can be the adsorption of the solutes on the membrane itself (R_a). Moreover the efficiency of the membrane can be significantly reduced by deposition and pore blocking (R_p).

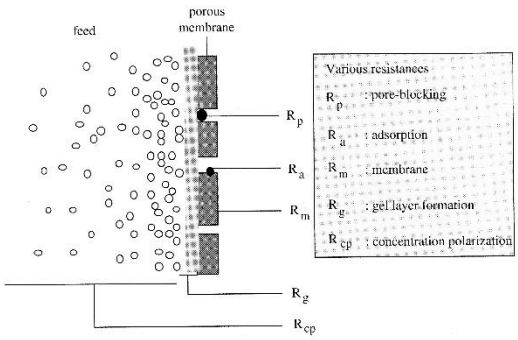

Figure 4. Schematic representation of the possible mechanisms for reduction of the membrane flux. Reproduced from ref. 8. Copyright Kluwer academic publishers 1996.

Fouling, a term often encountered in literature on UF, is used for indicating the irreversible loss of membrane permeability. Fouling can be caused by different mechanisms such as adsorption, chemical interactions, pore blocking and cake formation.(5)

Fouling can be controlled and minimized by surface modification of the membrane i.e. by inserting hydrophilic groups making it less prone to organic fouling (see 2.2). The membrane flux can be kept higher by performing a pretreatment or an ethanol precipitation step of the polymer solution prior to the UF process in order to remove insoluble materials. Use of turbulence or ultrasound above the surface of the membrane, pulsed or reversed flow, rotating or vibrating membranes are all techniques which might prevent the fouling process.

Application of an electric field can be an effective method to reduce a gel layer. Despite the above cleaning methods, a gradual irreversible fouling will occur which at a certain moment needs to be dealt with. Usually chemical cleaning will than take place, for organic polymer based membranes with the potential drawback that the membrane might be gradually chemically degraded. Membranes based on inorganic/ceramic materials do generally not present this disadvantage.(1)

2.2 Membranes

The membranes commonly used for UF are prepared from polymeric materials by a phase inversion process.(2) Usually, the polymer is deposited by evaporation of a solvent or by immersing the polymer dispersed in an organic solvent into water. The substrate in general is a microfiltration membrane.

Some of the most commonly used organic type of membranes consist of polyethersulphone, polysulphone, poly(vinylidene fluoride), polyacrylonitrile, cellulose (e.g. regenerated cellulose or celluloseacetate), polyimide/poly(ether imide), aliphatic polyamides and polyetheretherketone.(7, 8)

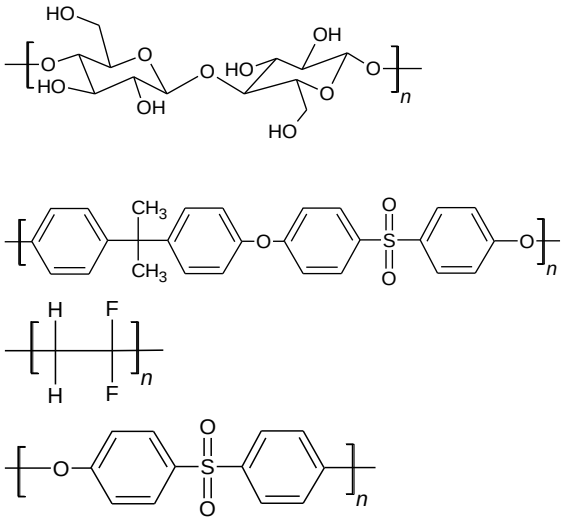

Figure 5. Examples of the most common used organic membrane polymers; cellulose, polysulphone, poly(vinylidene fluoride) and polyethersulphone.

In Table 1 several of the aforementioned membrane types are listed with their properties for application regarding pH range, maximum operating temperature and chemical stability.

Table 1: General application range of membranes (2,14).

Membrane	pH range	Max T(°C)	Chemical stability
Cellulose acetate	3-8	30	Protic solvents
PVDF	4-8	75	Good
Regenerate cellulose	2-13	75	Protic solvents
Polysulphone	1-13	75	Hydrocarbons, protic solvents
Polyimide	2-7	360	Good
Ceramics	0.5-13	130	Good/excellent

The organic polymer based membranes as to their nature are susceptible to specific organic solvents. As polymers are usually soluble in organic solvents, this limits the use of the type of membranes. For example, regenerated cellulose is incompatible with acetone, toluene or chloroform.(9) The organic membranes are usually stable in water, although care has to be taken

regarding acidity and alkalinity. In literature, the organic polymer based membranes are mostly applied for fractionation and purification of polymers which can be dissolved/suspended in water, for example polysaccharides, cellulose derivatives etc.(2)

The maximum temperature for UF membranes is important for those cases where a high viscosity of the polymer solution makes ultrafiltration process at room temperature impossible. By raising temperature and selecting the proper UF membrane a feasible processing can be achieved.

The pH range (next to solvent resistance) of UF membrane is relevant for cleaning purposes. In addition, there are a variety of biopolymers which only dissolve in strongly alkaline or acidic media and therefore a specific membrane has to be selected.

Each type of membrane has its characteristics. For example, polysulphone has the advantage of good mechanical properties, strong chemical stability and a wide pH operating range from 1 to 13, however is susceptible to concentration polarization and fouling by deposition of polymers due to its hydrophobic profile by repulsion of water and hydrophilic compounds. In order to prevent fouling the hydrophobicity of the membrane can be changed e.g. the surface of the membrane can be made more hydrophilic by for example grafting with PEG.(10) Alternately polysulphone membranes can be embedded with graphene oxide. Testing with bovine serum albumin (BSA) showed improvement of the antifouling properties.(11)

Also the incorporation of an inorganic component can improve the hydrophilicity.(12) Treating the membranes with TiO_2/TiO_2-g-HEMA nanoparticles improves the properties of the polysulphone membrane considerably. The used molecules to test the separation capabilities of the membranes were BSA and EPS (Extracellular polymeric substance).

Also using polyethyleneimine as an additive (0.3%) for polyethersulphone UF membrane improved permeability and selectivity. The performance of the membrane was tested with both BSA and PEG. The membrane gave a better eluent (water) flux and a molecular weight cut off (MWCO).(13)

Although polyimide membranes show a very high temperature resistance (up to 360°C) and a good resistance to aggressive solvents (membrane does not swell or dissolve in aggressive/organic solvents) (14), almost no applications of these type of membranes have been found in the last 5 years.

The aforementioned membranes can be produced with different pore sizes which consequently will afford the membrane to act as a screen for different polymer sizes. In essence the membrane will block 90% of polymer up to a certain size. This is called the molecular weight cut off (MWCO). The MWCO gives an indication of the molecular weight the retentate and the filtrate will contain. It is a rough indication, because if the polymer is branched, a globular protein or a linear polymer the MWCO will significantly differ for the same membrane, whilst the macromolecules have the same molecular weight. Other parameters are more important like shape and flexibility of the macromolecule, but also the interaction with the membrane and concentration polarisation. Another factor is the presence of a higher molecular weight molecule, which can block the pores of the membrane. Also the radius of the macromolecule is influenced by other factors like type of solvent and temperature. For flexible polymers the intramolecular interactions are

low, but proteins have strong interactions and have a stable globular structure. So for the choice of a membrane also other factors should be taken into account like the molecule that is fractionated.(8)

Stimuli responsive membranes are of increasing interest because a reversible change of the membrane properties is possible. Thermo-responsive membranes alter their pore diameter and surface properties by a temperature change thereby tuning the permeability and selectivity of the membrane between two different states. Silica of distinct sizes could or could not pass the polyethyleneterephtalate track-etched membrane depending of the temperature of the membrane. This membrane is investigated to be used for nanoparticles/protein mixtures.(15)

Apart from the organic polymer based membranes occasionally inorganic (ceramic) membranes especially alumina (Al_2O_3) and zirconia (ZrO_2) are used.(8) Compared to organic polymer based membranes, the ceramic membranes are inert and do not dissolve in solvents or water. Furthermore the temperature range in which ceramic membranes can be used goes much higher (Table 1) than for almost all organic polymer based membranes.(2)

The high temperature stability up to 130°C is relevant for sterilization at 121°C in UF for biotechnology and fermentation.

Finally, the inorganic membranes have usually extended operating lifetimes as they are able to withstand the cleaning agents better. There are a few articles dealing with the fractionation of polymers through ceramic membranes. The extreme conditions which can be used for ceramic membranes is highlighted for UF on a kraft lignin solution which is strongly alkaline i.e. pH>13.(16)

3. Fractionation of polymers by ultrafiltration

UF can be used to separate relatively large (natural) molecules like proteins, starch cellulose, but also colloidally dispersed substances like clays, paints, pigments and latex particles.(2) Chapter 3 deals with the research done in the last decade on the latter subject. In view of the vast amount of developments on the application UF for protein fractionation this subject will be omitted.

3.1 UF involving polysaccharides and celluloses

Polymers that are fractionated in order to obtain a more monodisperse polymer are mostly biopolymers and/or polymers that dissolve in water. In many articles a polymer is harvested from the water based waste of a production process. Hemicelluloses from lignocellulosic materials can be used to produce polymer films. These renewable films have properties that make them interesting as barrier materials for food packaging.(17,18)

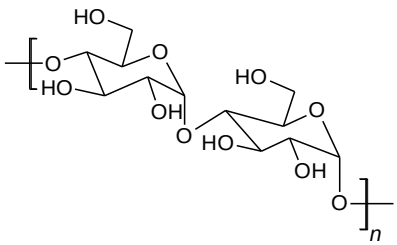

Figure 6. Polysaccharide (n glycose units)

For example, hemicellulose can be harvested from the waste of corn. In the separation and purification process the waste is hydrolysed and then fractionated by ultrafiltration with membranes with a MWCO of 1, 5 or 10 kDa. By taking the retentate of the 10 kDa ultrafiltration the physicochemical characteristics of the hemicellulose were improved.(17)

UF with a 1 kDa regenerated cellulose membrane was used for separation of a noncellulosic polysaccharide-rich wood hydrolysate. Three separations methods were used: ultrafiltration, ultrafiltration/ diafiltration combination and ethanol precipitation. For the purpose of a film on a substrate the unseparated fraction is already good by having the lowest OP (oxygen permeability). Although the fractionated samples have a lower OP, they do have better mechanical properties in conjunction with a different composition.(18)

For clinical use dextran with an extremely narrow molecular weight distribution is required.(5) Normal UF with membrane cut-offs of 100, 30, 5 and 1 kDa provided dextrans with a wide molecular weight distribution with a polydispersity index between 2.2 and 5.4. The polydispersity index could be further enhanced to 1.2 by applying water washings during the UF process. Another point that is brought up by the authors is that because dextran is branched the MWCO's do not correspond to the obtained molecular mass. This was checked with a HPGPC.

UF can also be used to purify polysaccharide based vaccines. Using polyethersulphone based UF membranes with MWCO between 30 and 1000 kDa the vaccines were purified from the unreacted polysaccharides.(19)

Polysaccharides are often fractionated to simulate industrial production. In the work of by Xie *et al.* (20) the polysaccharide was extracted from *C. paliurus* (commonly called sweet tea tree). The ultrafiltration through a polysulphone membrane is used as a possible replacement for conventional process based on the combination of ethanol precipitation and gel permeation chromatography. By applying UF the removal of lower molecular weight polysaccharides improved the quality of the polysaccharide. Three membranes are used in sequence with a MWCO of 300, 100 and 6 kDa. The ultrafiltration afforded four fractions each showing two to three peaks in the GPC chromatograms, indicating that the ultrafiltration did not work perfectly.(20)

Fractionation of polysaccharides and protein from rapeseed was carried out with a PVDF (500 kDa) membrane.(21) UF was performed using a polyethersulphone membrane with a MWCO of 3, 8 and 12 kDa and tested for the influence of temperature, pH and ionic strength. Temperature has generally a positive effect, as well as high pH. On the contrary, higher ionic strength has generally a negative influence. Sun *et al.*(21) succeeded in fractionation of the polysaccharides, obtaining the highest yield of polysaccharides using a 3 kDa membrane. However, no clear conclusions are drawn regarding exclusion of the anti-nutritional and toxic components.

An extract in water obtained of primary cell wall polysaccharides from buriti fruit pulp (*Mauritius flexuosa*, a tropical palm) was fractionated over regenerated cellulose membranes of 300 kDa, 100 kDa and 30 kDa.(22) The retentates of the 100 kDa (100R) and 30 kDa (30R) membranes contained homogeneous polysaccharides with an Mw of 126 kDa and 20 kDa respectively. The 100R fraction was mainly composed by arabinose and uronic acid, indicating the presence of arabinan-rich pectic polysaccharide. For the 30R fraction the content of arabinose was half of the 100R fraction, balanced by uronic acids.

Mixtures of cyclodextrins (CD_6 to CD_{60}), produced from synthetic amylose by the enzyme cyclodextrin glycosyltransferase have been fractionated and purified using UF and NF membranes.(23) CD6, CD_7 and CD_8 can already be fractionated by other techniques, however with larger ring CDs this purification does not work. Three membranes with a MWCO of 0.15-0.3, 1

and 2 kDa were tested with PEG and used. The determined MWCO were 0.5, 1.8 and 4.1 kDa. The diafiltration process was modelled using simulation. The difference between the model and the results lies in glucose which was found in the retentate of the last filtration step. The authors gave the explanation that with CD molecules with a higher MW could form some host-guest compounds.

Arabinoxylans can be extracted from destarched wheat bran**.** The extract is fractionated by three methods, the first one is with NaOH and diafiltration with a UF MWCO of 100 kDa. The second method is a hydrothermal method followed by a filtration. The third method is using the enzyme endoxylanase. In the latter case the solid is also treated like the first method, but filtrate is fractionated by UF with a MWCO of 10 kDa and 100 kDa. This method led to low extraction yields. The processes that were tested were up scalable processes. The three different methods gave different composition and different properties. Both ultrafiltration and ethanol precipitation are efficient and the choice of which one should be used, should be based on the basis of financial and environmental arguments.(24)

3.2 UF involving Lignin polymers

Lignin is considered a waste product of which only 1.5% is commercialized. However lignin can be applied as dispersant in the cement industry, as emulsifier or chelating agent for removing heavy metal from effluents.(25) Therefore it is of interest to isolate lignin from waste materials.

Molecular mass is the key parameter affecting the reactivity and thermo-mechanical behaviour of lignin, therefore fractionation is a key step to obtain a lignin with a narrow distribution of properties.(16)

The alkaline hydrolysis of wood pulp affords a complex lignin mixture (black liquor), which can be separated by UF in different MW fractions using TiO_2 (ceramic) based membranes with cut-offs of 5, 10 and 15 kDa.(25) In comparison with alternative methods like successive extraction with organic solvents and selective precipitation, UF gives the best results as the lignin obtained is less contaminated with hemicelluloses. Although the obtained fractions have a glass transition of T_g = 105-110°C, they differ in M_n being 940, 946, 1891 and 2032 Da at MWCO of 5, 10, 15 and >15 kDa respectively.(25)

Another study by Sevastyanova *et al.* (16) using ceramic membranes of TiO_2 and ZrO_2 with MWCO of 1 and 5 kDa and a regenerated cellulose membrane (used for the retentate of the 5 kDa UF) with a MWCO of 10 kDa showed different results. The obtained fractions had a T_g ranging from 70 to 170°C. The M_n for the various fractions ranges from 1200-9500 Da. The kraft lignin hydrolysate of pH >13 was used as such, in the temperature range 40-65°C, such alkalinity and temperatures only being possible with ceramic membranes.

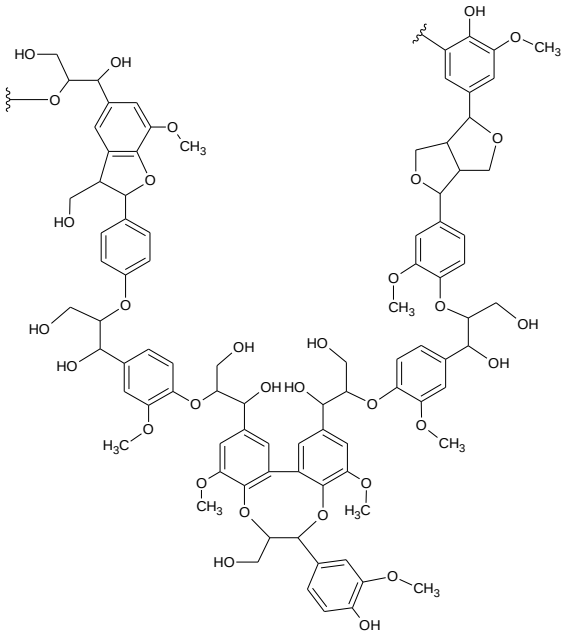

Figure 7. Segment of lignin polymer

Wang *et al.*(26) obtained through the prehydrolysis kraft-based process on wood pulp a high grade dissolving pulp. In this case however with UF the oligosaccharides, lignin and monosaccharides components could not be separated. Four filters were used with the MWCO of 30, 10, 3 and 1 kDa, yet remarkably almost all fractions still contain oligosaccharide with a MW of 32 kDa. The explanation of the authors is that the oligosaccharide is linear and will go through the membranes.(26)

A disadvantage of the alkaline or kraft hydrolysis is that more material is dissolved due to the hydrolysis and partial hydrolysis of the original lignin and oligosaccharides occurs. By applying the organosolv treatment, an alcohol/water based extraction process of biomass (non-woody fibres, *Miscanthus sinensis L.*) at 160°C, more of the original lignin is retained and less cellulose is hydrolysed/dissolved. On a semi-production scale using ceramic membranes with MWCO's of 5, 10 and 15 kDa four fractions were isolated with M_n of 1050, 1270, 1260 and 1500 g/mol with a polydispersity index ranging from 1,3 to 1.6, whereas the starting material showed a M_n of 1150 and a polydispersity index of 1.9.(Table 2)

Table 2: Results from the analysis of the lignin fractions by GPC.

Lignin fraction	Yield fraction	M_w	M_n	M_w/M_n
Rough	0.138	2180	1150	1.9
Lignin > 15 kDa	0.087	2390	1500	1.6
10 kDa < Lignin < 15 kDa	0.028	1900	1260	1.5
5 kDa < Lignin < 10 kDa	0.015	1780	1270	1.4
Lignin < 5 kDa	0.008	1357	1050	1.3

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A higher cost than for the kraft lignin fractionation was calculated, however the high quality and purity in conjunction with the low polydispersity make the lignin produced via organosolv treatment a potentially high added value product.(27)

A similar organosolv treatment on wheat straw applied a combination of UF (polysulphone and hydrophylized polyethersulphon) and NF to fractionate the lignins. Fractions ranging from larger than 150 kDa down to less than 200 Da were isolated indicating much higher Mw than in the study on *Miscanthus sinensis*.(27) Results have to be regarded with care as the authors mention insufficient conditioning time for the 150 kDa membrane.(28)

An alternative to the alkaline and organosolv treatment is the acidic sulphite process, carried out at 135-140°C and a pH of 1.2-1.5. In contrast to the alkaline process in the acidic sulphite process the hemicellulose is hydrolysed into monomers, therefore not contaminating the UF lignin fractions. In particular using a TiO_2 ceramic membrane of 15 kDa affords a higher concentration of lignin in the retentate, although the polydispersity index is higher. The permeate affords a somewhat improved polydispersity index, but has a lower lignin concentration.(29)

3.3 UF involving miscellaneous polymers

Olive oil by-products present a large waste hazard, however contain high molecular polymers that, if isolated, could afford added value. Hydrothermal treatment, chemical treatment and precipitation techniques afford a solution which gives two fractions by UF. The first fraction below 10 kDa rich of pectic polymers and between 3 and 1 kDa rich of polysaccharides. The first fraction could be used as it is, for example as gelling agent. In addition the second fraction got chemical and enzymatic hydrolyses to get oligomers with different uses.(30)

Second cheese whey, a by-product of whey cheeses still contains valuable compounds like proteins, peptides and oligosaccharides.

Macedo *et al.* fractionated the whey with three UF membranes (cellulose regenerated acetate, fluoropolymer and hydrophilic polysulphone) all with a MWCO of 10 kDa.(31) Comparing cellulose regenerated acetate membrane and a fluoropolymer membrane best results regarding the permeate flux were obtained using the cellulose acetate membrane. Regarding selectivity similar results were obtained with the aforementioned membranes. The higher flux for the cellulose acetate membrane was thought to be attributed to the higher hydrophilicity of the latter.(31)

The polyphenols, ellagitannins and anthocyanins, present in the tropical highland blackberry could play a role in human nutrition and health.(32) Authors were able to isolate the aforementioned materials through UF using 6 membranes with MWCO's ranging from 1 to 150 kDa achieving a purity of over 90%.

UF, as a non-destructive method, was also used in determining the tannin fraction in wine that causes the astringency, the in-mouth drying and a dry mouth after spitting effect.(33) The tannins were fractionated in four fractions with different DP (degree of polymerisation) range. The authors were able to establish that the largest tannins with a DP range >30 subunits were responsible for astringency effects.

A study from Galanakis *et al.* investigated the fractionation of wine sludge by UF and the separation of co-extended components.(6) The employed polysulfone membranes were not able to fractionate phenolic compounds, because separation was mainly affected by severe fouling phenomena on the membrane surface and less by a sieving mechanism. Non-polar fluoropolymer membranes (MWCO of 1 kDa) successfully separated different phenolic classes like hydroxycinnamic acids, flavonols and anthocyanins on the basis of polarity. The authors did not use the membranes sequentially.(6)

Over a decade ago research on UF with polyimide membrane with several polydisperse polystyrene solutions in ethylacetate was carried out.(34)

Ultrafiltration allows further identification of complex compositions. For example, coal tar pitch, after being fractionated by solvent solubility in 3 fractions can be further segmented by UF using various MWCO cellulose membranes. In this case NMP was used as solvent. (9)

Graphene quantum dots are of interest because of their photoluminescence at exactly confined and tuneable wavelengths.(35) It is of critical importance to control their size both in diameter and layer number. UF membranes of 3 kDa and 10 kDa have been shown to be able to isolate single layer polyethyleneimine graphene quantum dots and bilayer polyethyleneimine graphene quantum dots.

4. Critical conclusions

Although there is a continuous stream of publications about specific ultrafiltration subjects like desalination, waste water treatment and purification and concentrating in the food industry, there are much less articles that deal with the fractionation of polymers by using the ultrafiltration technique. Most of the articles on fractionation of polymers discuss naturally occurring substances which are extracted as a complex mixture from a certain type of biomass and through ultrafiltration natural polymers which have a distinct molecular weight range are isolated. In many articles on fractionating polymers the UF technique is used in combination with other purification steps like MF and water washing or other solvents. In particular for polymers of natural origin, researchers struggle with separating different types of polymers e.g. mixtures of cellulose, lignin and

polysaccharides. Only in a few references a proper way of choosing the right membrane (pore size) was observed, leading in many other articles to disappointing results.

Surprisingly there is virtually no literature in the last decade of the fractionation of synthetic polymers, although one would anticipate that ultrafiltration would be an efficient way to isolate fractions of polymers with a narrow chain length distribution.

Although UF has some nice advantages like simplicity, low cost, energy efficiency, application for sensitive materials and the possibility to concentrate a polymer solution, it has unfortunately also some disadvantages, fouling being the most severe one. However there are several options described in literature to decrease the fouling process. The literature concentrates both on new membranes and on new techniques to prevent fouling.

Looking at the development of new membranes it might be anticipated that in the coming years new ways will be found to solve the challenges of ultrafiltration and will allow ultrafiltration to be used in a broader field to purify and achieve more monodisperse polymers.

In view of the ongoing development of new types of membranes better selectivity and lower polydispersity of polymers might be expected.

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