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A wide range and high resolution one-filtration molecular weight cut-off method for aqueous based nanofiltration and ultrafiltration membranes

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ABSTRACT

A new and superior one-filtration method for the determination of the molecular weight cut-off (MWCO) of aqueous based nanofiltration and ultrafiltration membranes has been developed using the widest range of polyethylene glycol oligomers as MWCO probes of any MWCO method so far. This method was enabled by a new, high resolution oligomer separation and detection using high performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD). The refined method can determine the MWCO of membranes over a MW range from 678 to 4594 g mol^{-1} with a molecular weight difference of just 44 g mol^{-1} and a bonus further one point extension to 6000 g mol^{-1} – giving the widest range and most precise difference of MWs that can be resolved of any single filtration MWCO method that exists. MWCO determination of five commercial membranes from GE Osmonics™ and Millipore showed good agreement with manufacturer and literature values, confirming the accuracy of the method. As this new method has significant advantages over all other existing aqueous MWCO determinations (i.e. single filtration, higher resolution over a wider MW range, low cost MWCO molecular probes), it is suggested that it could be adopted as the new standard for determining aqueous MWCO over a MW range from 678 to 6000 g mol^{-1}.

1. Introduction

Pressure driven membrane separations have been widely applied in many industries as they enable separations to become more energy efficient and environmental friendly [1,2]. Membranes are selective semi-permeable barriers that are used to produce purified streams and therefore the worth of a membrane is in its productivity (normally quantified as flux) and selectivity. Selectivity for pressure driven membrane processes such as nanofiltration (NF) and ultrafiltration (UF) is typically quantified and benchmarked as the molecular weight cut-off (MWCO), [3] which is defined as the molecular weight (MW; also known as molecular mass) that a 90% rejection of the filtered solutes is obtained. A reliable technique for measuring MWCO values is crucial for end users to make an appropriate choice of membrane in order to buy, test and apply over the wide range of applications, solvents and solutes that are wanted for a particular membrane [4,5].

A range of methods and MWCO molecular probes currently are used, including styrene oligomers [4,6,7], polyethylene glycols (PEGs) [1,2,2,8–10], dextrans [11–16], alkanes [17,18], sugars [19,20], dyes [21], acids [9], and others [20,22–24]. The MWCO of UF membranes can also be determined by liquid–liquid displacement porometry (LLDP) method [25]. A literature comparison of MWCO probes for aqueous filtrations can be found in Rohani et al.[1,2] and so will not be repeated here. Of importance are the limitations of these existing methods so these can be addressed:

(1) The detection of multiple compounds in a single filtration is difficult to accomplish, thus most of the methods require multiple and repetitive test filtrations of individual solutes to obtain the MWCO curve, which is both time consuming and costly compared to a single filtration method [2,4,24,26].
(2) Of the available MWCO molecular probes, pure alkanes and dextrans are only commercially available with MWs of below 400 g mol^{-1} and above 1000 g mol^{-1}, respectively. Styrene oligomers are expensive in comparison to all other molecules used and therefore this limits their application at a larger scale. Dyes are mainly charged molecules and therefore will also potentially be rejected by Donnan Exclusion, which does not reflect the MW

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(size/mass) based separation that MWCO should primarily reflect. Furthermore, it is not easy to source a suitable variety of dyes with similar molecular structures that have a similar interaction with the membrane. Other solutes, like alkane and polypropylene glycol, have limited solubility in water, especially at higher MWs, which limits their use [1,21].

(3) Other methods, such as liquid–liquid displacement porometry is used for UF membranes and was examined for MWCOs between 5 and 100 kDa [25]. However the method is less accurate in the low UF range that is aimed for in this paper and has not been extended accurately into the NF range. Therefore an alternative method is still needed.

(4) Some of the methods are for organic solvent based separations and limited to the NF (200–2000 g mol^{-1}) range and due to limited water solubility cannot be directly employed in aqueous systems [2,4,26].

(5) For aqueous systems, many of the methods that have been developed only have a limited range of MWs that can be probed, with many mainly focused on and/or just above the NF range [1,27,28]. This limits the potential membranes that can be screened and characterised, for example low MWCO UF membranes have attracted considerable attention as they are widely used in oil/organic solvent separation [29], the food industry for sweetener purification [30], metal removal [31] and drinking water treatment [32]. Moreover, when a new membrane is synthesised and the MWCO is unknown, a method that allows a wide range of MWs to be tested with relative precision and resolution would allow a faster characterisation time, which in turn provides faster feedback in order to speed up development time – something needed for high throughput synthesis of membranes for example [33]. Consequently, it is of importance to develop an approach for the MWCO determination of both NF and low UF membranes over the widest possible MW range with the highest possible resolution between adjacent MWs.

Therefore, this research aims to develop a reliable, cost effective, high resolution, single filtration MWCO evaluation method covering a wider MW range than any other MWCO method for aqueous based NF and low MWCO UF membranes.

2. Materials and methods

2.1. Materials

Table 1 gives the MWs and suppliers for the commercial PEG and purer PEG standard used in the method. The properties of commercial membranes used as well as the filtration pressures are provided in Table 2. GE Osmonics™ (GE, GK, GH) and TriSep UA60 were purchased from Sterlitech (US). Millipore disc membranes (Ultracel PLAC04310, Ultracel PLBC04310) were purchased from Sigma-Aldrich (UK). GE Osmonics™ GE and Millipore Ultracel PLAC04310 are NF membranes while GE Osmonics™ GH, GE Osmonics™ GK, TriSep UA60 and Millipore Ultracel PLBC04310 are UF membranes. Acetonitrile (HPLC grade) and Rose Bengal (dye content 95%) were obtained from Sigma-Aldrich (UK). All solutions were prepared with deionised (DI) water produced from an ELGA deioniser (PURELAB Option).

Commercial grade PEGs were selected as MWCO molecular probes since they are available in a wide range of MWs from a number of different manufacturers, are low price compared to other MWCO molecules (e.g. styrenes), are electrically neutral, are soluble in water over a wide range of concentrations and have minimum chemical interactions with membranes compared to more polar and charged molecules [1,2]. These commercial grade PEGs were dissolved in deionised water to obtain a PEG oligomer mixture solution with a wide MW range. Two different PEG mixture solutions were prepared:

(1) The 'feed solution' was used in the filtrations and was: 600 mg L^{-1} for PEG 1000 and 2400 mg L^{-1} for PEGs 1500–6000. Note that the concentration of the PEG 1000 was three times lower than the other PEGs used in the mixtures since its peak response in the DAD detector was 3 times higher when comparable concentrations and so was used at this lower concentration to ensure peak heights and areas were similar across the entire HPLC chromatogram.

(2) A stock solution that is used to produce the calibration curves, had double the concentration of the feed solution as this is the maximum concentration the retentate can reach if there is 100% rejection of any of the oligomers (since only 50% of the feed volume is filtered in the method used). This stock solution was diluted to produce the different concentrations needed in the external calibration need to determine the concentrations of each oligomer in the resolved HPLC peaks – this is referred to as 'diluted stock solution'. The lowest concentration the stock solution was diluted to for the calibration curve was: 75 mg L^{-1} for PEG 1000 and 300 mg L^{-1} for PEGs 1500–6000 as below this concentration, the detector baseline appeared to drift and showed excessive noise. The feed concentration used for the MWCO determination of commercial membranes was 600 mg L^{-1} for PEG 1000 and 2400 mg L^{-1} for PEG 1500–6000. Feed concentration was expected to be as low as possible to prevent or at the very least minimise possible concentration polarisation which could affect the MWCO curves and value determined and so the feed concentration applied in the study was comparable to previous publications [2,43].

2.2. MWCO Analysis method

High performance liquid chromatography (HPLC) coupled with an evaporative light scattering detector (ELSD) was used for the identification of individual PEG oligomers. An ELSD was used since previous work in this research group and elsewhere has demonstrated that it is the most robust, reliable and sensitive detector for clear detection of different MW PEG oligomers at close MWs if coupled with an appropriate gradient elution [1,2,44]. The HPLC apparatus (Agilent 1260 infinity series, Agilent Corporation, USA) consisted of an autosampler (G1329B), a Colcom column oven (G1316A), a Quat pump (G1311B), a degasser and an Agilent data interface. The detection was performed utilising an Agilent ELSD (Agilent 1260 infinity G4260B,

Table 1
Supplier and MW of the commercial grade PEGs and purer grade PEG standard used.

Chemical	Supplier	Manufacturer specified average MW (g mol^{-1})
PEG 1000 (Commercial grade)	Alfa Aesar (UK)	950–1050
PEG 1000 (Purer grade)	Fluka (Switzerland)	950–1050
PEG 1500 (Commercial grade)	Alfa Aesar (UK)	1450–1500
PEG 2000 (Commercial grade)	Alfa Aesar (UK)	1800–2200
PEG 3000 (Commercial grade)	EMD Millipore (UK)	3000
PEG 4000 (Commercial grade)	Alfa Aesar (UK)	3600–4400
PEG 6000 (Commercial grade)	Alfa Aesar (UK)	5400–6600