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# pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation

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## ABSTRACT

In this work polyamine membranes are presented that are prepared by the interfacial polymerisation of polyethylenimine and cyanuric chloride on porous polyethersulfone supports. The thin film composite polyamine membranes have superior pH stability as compared to conventional polyamide membranes that are derived from polyethylenimine and trimesoyl chloride. The polyamine membranes show exceptionally strong resistance towards nucleophilic attack induced by extreme pH conditions. This is verified by the stable salt rejection and molecular weight cut off performance after five weeks of treatments at pH=1 and pH=13. The polyamine membranes exhibit a persisting separation performance over this entire pH range, whereas hydrolysis of the conventional polyamide membranes at high pH conditions causes a tremendous drop in their salt rejection. Their isoelectric points of both the polyamide and polyamine membranes are around pH=7.5. The polyamine membrane is tighter. It has a fivefold lower permeance as compared to the polyamide membrane, and a sodium chloride rejection of 65%, exceeding that of the polyamide by ~10%.

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## 1. Introduction

Nanofiltration (NF) is a useful technique for the separation of small molecules ( $< 1000 \text{ g mol}^{-1}$ ) and multi-valent ions from a liquid. It is widely used in wastewater treatment, water purification, water softening, food processing, and bio-separation [1]. At present the use of NF is often limited to processes with moderate operating conditions, due to limited stability of the available membrane materials. Many separation processes in the chemical industry involve extreme conditions, due to the presence of aggressive solvents and/or low or high pH. In the past two decades the development of advanced solvent resistant NF membranes has received considerable attention [2]. The development of pH resistant NF membranes has gained less momentum, despite the wide range of potential applications. Examples of such applications include the filtration and reuse of Cleaning In Place (CIP) solutions in the dairy industry [3], the production of sodium

sulphate crystals from mother liquor obtained from salt production [4], the treatment of effluents from the pulp and paper [5] and the textile industry [6], and the separation of hemicellulose from concentrated alkaline process liquors [7]. Applications involving very low pH conditions include the purification of acids [8], the recovery of phosphorus from sewage sludge [9], the removal of metals like copper and gold from process streams with a high sulphuric acid concentration [10], and the removal of sulphate ions from effluents in the mining industry [11].

Table 1 summarises the properties of various NF and reverse osmosis (RO) membranes, including commercially available products. Most prevalent are the thin film composite (TFC) polyamide membranes, due to their high flux and good selectivity or salt rejection [12]. However, the amide bonds in these membranes are inherently susceptible to hydrolysis under alkaline conditions, via direct nucleophilic addition of  $\text{OH}^-$  to the carbonyl group [13]. The hydrolysis is manifested by a severe reduction in membrane performance. For example, poly(piperazine amide) membranes show a strongly reduced selectivity after exposure to  $\text{pH} > 11$  [14]. For extreme pH applications, there are a number of commercially available NF membranes. These include the NF series from

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**Table 1**  
Commercially available and previously studied NF membranes.

Materials	Polyamide		Polyethersulfone	Proprietary		Melamine-polyamine	SPEEK [15]	Ceramic	
Examples	NF-270	Desal 5DK	Nadir NP030	Koch MPF-34	GE Duracid	AMS A3014	AMS B4022	–	Inopor <sup>®</sup> nano
Permeance (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	10.6	5.4	1.7	1.5	~8.0	~2.4	~2.2	1.3–4.5 [15]	3.4 [18]
MWCO (Da)	200–400	200	520 [19]	200	400	400	180	500 [15]	450
pH range	2–11		0–14	0–14	0–9	0–12	3–14	1–13 [15]	0–14
Drawbacks	Only for mild pH condition		Low flux and high MWCO	Low flux	Only for acidic pH		–	High MWCO	Expensive & low packing density

Note: If not specified, the data is extracted from product specification.

Microdyn-Nadir (e.g. NP030), and HYDRACoRe70pHT (based on the NTR 7470 membrane) from Hydranautics/Nitto Denko. These membranes are based on hydrophilised or sulfonated polyethersulfone (PESf) materials, and have a relatively low flux and limited molecular weight cut off (MWCO). Koch Membrane Systems (KMS) supply highly pH resistant membranes with a molecular weight cut-off of MWCO  $\approx$  200 Da (SelRO<sup>™</sup> MPF-34) and MWCO  $\approx$  1000 Da (SelRO<sup>™</sup> MPF-36). The membrane material for these membranes is proprietary. The permeance of MPF-34 is relatively low, making it less commercially attractive. Previously, TFC membranes based on the coating of sulfonated poly(ether ether ketone) (SPEEK) on a PESf ultrafiltration support have been proposed [15]. These membranes appear to be very stable in extreme pH environment and still have a relatively low MWCO of about 500. Their pure water permeance is slightly higher than that of MPF-34. Nevertheless, the complex fabrication method and the high material cost remain as the obstacles for commercialisation of these membranes. GE offers a series of acid stable membrane, Duracid<sup>®</sup>, that has impressively good permeance. However, it is not stable at alkaline conditions. On the other hand, Advanced Membrane System Technologies (AMS) specialises in membrane processes at critical conditions. They have acid stable membranes designated as the A3012 or A3014 series. Another base resistant membrane, B4022 is believed to be a melamine-polyamine membrane which was previously marketed as BPT-NF series. This membrane is claimed to be stable at highly acidic conditions, which is attributed to the stability of the conjugated bond structure of the triazine ring in melamine [16,17].

The search for membranes that combine high pH stability with high flux and low MWCO is on-going. In the past 50 years, interfacial polymerisation has been the prevalent technique to produce thin film composite membranes with high flux and high selectivity. Predominant chemistry for the reaction is based on the polycondensation of a polyfunctional amine and acyl halide, despite the lack of stability of the resulting polyamide. The most commonly used polyfunctional amines include piperazine, *m*-phenylene and diamines. Common acyl halides include trimesoyl chloride and isophthaloyl chloride. The amine is dissolved in an aqueous phase that is used for impregnating a porous support. The loaded support is then contacted with an organic phase containing the halide. The polymerisation reaction at the interface creates a  $\sim$ 100 nm thick polyamide layer on top of the porous support.

Apparent from Table 1, membranes offered by KMS and AMS show good stability at extreme pH conditions. The chemical structures of these membranes are not publicly disclosed. However, the patents filed by KMS and AMS suggest a melamine-polyamine structure that was fabricated from a reaction between an amine and cyanuric chloride (CC) [20,21]. KMS prepared the membrane based on a multi-step process, i.e., tandem offset gravure, slot die coating and ends with heat treatment. In a patent

assigned to AMS, more than one preparation method was described. One method was to graft the support membrane with amine groups before the subsequent reaction with CC in aqueous phase. The other method was first to prepare an oligomer based on CC with diaminopropane. The resulted oligomer can be made into an aqueous ethanol solution, which is subsequently used to react with polyethylenimine (PEI) coated on a support membrane [21]. An earlier patent filed by Aligena AG in 1987 that uses CC to make NF membranes [22]. One of the examples used hydroxylamine to wash a support membrane for half an hour. Then, it was soaked into an aqueous CC solution (water/acetone 4:1 mixture) before the final step of reacting with PEI for 10 min. The only report of using CC in the straight forward interfacial polymerisation method is given in a patent filed by Cadotte in 1977 [23]. In this patent, for a single membrane prepared via interfacial polymerisation of PEI and CC, values are given for the flux and NaCl retention. However, no further investigation was performed after that, especially for liquid filtration at extreme conditions.

In the current work, the authors revisit interfacial polymerisation based on PEI/CC for fabrication of membranes with superior resistance to hydrolysis, without compromising the flux and selectivity. In particular, it is aspired to avoid the presence of the carbonyl group in the amide bond. The performance of the thin film composite membrane based on PEI and CC investigated in extreme pH applications. Permeance, selectivity, and pH resistance are assessed and compared with membranes derived from the conventional interfacial polymerisation polyamide chemistry using PEI and trimesoyl chloride (TMC).

## 2. Experimental

### 2.1. Chemicals and materials

Branched polyethylenimine (PEI,  $\sim$ 25 kDa, >99% purity), cyanuric chloride (CC, 99% purity), and anhydrous grade *n*-hexane (95%) were acquired from Sigma Aldrich (Germany), and were used as received. Analytical grade sodium dodecyl sulphate (SDS), sodium nitrate (NaNO<sub>3</sub>), sodium azide (NaN<sub>3</sub>), ethylene glycol (EG), and synthesis quality polyethylene glycol (PEG) with average molecular weights of 200, 600 and 1500 g mol<sup>-1</sup> were acquired from Merck (Germany). Analytical grade sodium chloride (NaCl), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), and magnesium chloride (MgCl<sub>2</sub>) were acquired from Arcos Organics (Belgium) for salt rejection experiments. Analytical grade potassium chloride (KCl) for zeta potential measurements was obtained from Fluka (Germany). Standard volumetric solutions of 0.1 M nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Fluka (Germany). Deionised (DI) water was used to prepare all aqueous solutions. All chemicals were used without further purification.

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