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# Influence of ultrafiltration membrane characteristics on adsorptive fouling with dextrans

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## Abstract

This paper presents a detailed investigation of fouling mechanisms for ultrafiltration membranes with polysaccharides obtained by studying membrane–solute (static adsorption) and membrane–solute–solute interactions (ultrafiltration (UF)). Two polyethersulfone (PES) membranes and one stabilized cellulose (cellulosic) membrane with a nominal cut-off of 10 kg/mol and dextrans with average molar mass (*M*) of 4, 10 and 15 kg/mol were used. The membranes before and after static adsorption of dextran were characterized by captive bubble contact angle and tangential streaming potential measurements as well as ultrafiltration sieving curves for polyethylene glycols. Significant water flux reductions (4–15%), which also correlated with dextran molar mass, and changes of the other membrane characteristics occurred after static dextran adsorption for the PES membranes. An empirical model to describe the correlation between the relative water flux reduction and the concentration of solute had also been proposed. In contrast, no significant changes could be detected for the cellulosic membrane. Significant membrane–solute interactions had also been confirmed in the ultrafiltration experiments with dextrans where irreversible fouling had been observed for the PES but not for the cellulosic membranes. The results provide fundamental information for a better understanding of fouling by polysaccharides. In particular, it had been confirmed that hydrophilic and neutral dextrans can significantly foul PES membranes via adsorption to the surface of the membrane polymer. On this basis, methods for control of this fouling can be properly developed.

*Keywords:* Ultrafiltration; Fouling; Polysaccharides; Dextran; Surface characterization

## 1. Introduction

In the last decade, ultrafiltration (UF) has been successfully developed from a useful laboratory tool to an industrial process. The application areas of UF include the production of pure water, fractionation or concentration steps in the food, pharmaceutical and biotechnological industries, and the treatment of waste water [1–3]. Nevertheless, in the use of UF processes, the decline of flux over time due to the concentration polarization and membrane fouling is the major limitation. This limitation prevents a more widespread commercial applicability of UF. Many studies have been conducted to elucidate the fouling mechanisms [3–11]. Membrane fouling is affected by three major factors namely the membrane material properties, the feed characteristics and the operating parameters. The concentration polarization can facilitate irreversible membrane fouling by altering interactions among solvent, solute and membrane. In particular, membrane surface chemistry, membrane–solute interactions and solute–solute interactions are the key to understanding the fouling phenomena. Membrane–solute interactions will determine fouling through adsorption of solute on the membrane surface. This interaction had been proposed as the important parameter in a fouling study by Mathiasson [4] using bovine serum albumin as a model solute. Furthermore, this interaction will enhance or modify the particle deposition and the pore blocking processes whereas the solute–solute interactions will facilitate fouling by solute aggregation in solution and/or on the surface preadsorbed with solutes [12].

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Most of the fouling studies in UF had been concerned with fouling caused by proteins. Much less attention has been devoted to fouling caused by polysaccharides. However, in real applications, e.g. in the sugar industry, polysaccharides as potential foulant components are found, often in very high concentrations.

This paper presents the first part of a comprehensive study towards a better understanding of the characteristics and mechanisms of polysaccharide fouling obtained by studying membrane–solute and membrane–solute–solute interactions. Considering dextran as a model polysaccharide, it turned out that dextran does play also a major role in real feed streams, for example in sugar beet or sugar cane processing [13,14] and in medical applications [15]. Furthermore, dextrans are extensively used for the characterization of the rejection of UF membranes including the nominal cut-off [16–20]. However, specific studies on membrane fouling by dextran had not been clearly conducted yet. In fact, there had been some uncertainty regarding the extent of membrane–dextran interactions. Nobrega et al. [16,17] showed that dextran molecules did not foul the membrane. Different results were reported by Gekas et al. [18]. They observed that the water flux decreased after UF of dextran for both polysulfone and cellulose triacetate 20 kg/mol nominal cut-off membranes. Furthermore, under some conditions, dextran can form a deposit on the upper surface of the membrane, as had been reported by Mochizuki and Zydney [19]. Mulherkar and van Reis [20] showed recently that there were significant interactions between a neutral composite regenerated cellulose (CRC) membrane and a positively charged fluorescent-labeled dextran and between a modified positively charged CRC membrane and a neutral fluorescent-labeled dextran, with a reduced permeability and a changed retention of the membranes as consequences. However, these authors had not clearly reported the causes of these interactions, i.e. whether fouling was caused by the dextran macromolecular structure or by the hydrophobicity of the conjugated fluorescent dye molecule or by the charge associated with the dye-label.

For this study, two state-of-the-art commercial UF membranes made from the high performance membrane polymer PES had been selected because the consistency of membrane properties of membranes manufactured industrially is typically much better than for lab-made membranes and the obtained data should therefore have a larger fundamental and (potentially) practical relevance. A novel commercial cellulosic UF membrane had been included in the study based on the same arguments and because cellulosic membranes are expected to be advantageous in applications where changes of selectivity and product loss due to fouling may not be tolerated [3,20]. The experimental results of this work show that significant water flux reductions and changes of other important membrane surface and separation characteristics changed after static adsorption for the PES membranes whereas no significant changes could be detected for the cellulosic membrane. On that basis, this work provides fundamental information for a better understanding of polysaccharide fouling and its effect on membrane characteristics, and it will facilitate both further detailed mechanistic investigations and the development of methods for controlling such fouling.

## 2. Experimental

### 2.1. Materials and analyses

In these experiments, two polyethersulfone (PES) membranes obtained from DSS (Alva Laval), Denmark (*GR*81PP), and from Sartorius, Germany (*SG*124.39), and one stabilized cellulose (cellulosic) membrane from Sartorius (*SC*, “Hydrosart”) were used. All membranes had a nominal cut-off of 10 kg/mol. Before all experiments, the membranes were soaked overnight in water to remove impurities left over from the manufacturing process or additives used for stabilization. Dextran T-4 and T-15 from Serva Feinbiochemica GmbH&Co., Heidelberg, Germany) and dextran T-10 from Pharmacia Fine Chemicals, Uppsala, Sweden) were used as model polysaccharides. The characteristics of the dextrans as given by the manufacturer and obtained from gel permeation chromatography (cf. below) are summarized in Table 1. Polyethylene glycols (PEG 1.5, PEG 3, PEG 6, PEG 12, PEG 35; the numbers indicating M) were purchased from Fluka Chemica GmbH. Nitrogen gas purchased from Messer Griesheim GmbH, Krefeld, Germany, was of ultrahigh purity. KCl, KOH and HCl, all of p.a. quality, were purchased from Bernd Kraft GmbH, Duisburg, Germany. Sulfuric acid was from J.T. Baker, Holland. Potassium acid phthalate and ferroin indicator solution were purchased from Acros Organics, Geel, Belgium. Potassium dichromate was reagent grade. Ferrous ammonium sulfate (FAS) was purchased from Fluka Chemica GmbH. Water purified with a Milli-Q system from Millipore was used for all experiments.

Gel permeation chromatography (GPC) was used to analyze the molar mass distribution of PEGs and dextrans in solution. PEGs were analyzed using a MZ Hema Bio column (MZ Analytik, Mainz, Germany) coupled with a Waters refractive index detector. Calibration curves for the correlation of retention volume and molar mass were obtained using different PEG molar mass standards. A PSS Suprema (PSS, Mainz, Germany) and a MZ Hema 40 (MZ Analytik, Mainz Germany) column in series were used to analyze dextran.

Table 1
Characteristics of dextrans used in this study

| Dextran type | $M^a$ (kg/mol) | $M_n{}^b$ (kg/mol) | $M_w{}^b$ (kg/mol) | $D = M_w/M_n{}^b$ |
|---|---|---|---|---|
| T-4 | 4–6 | 1.95 | 4.5 | 2.31 |
| T-10 | ∼10 | 4 | 9.4 | 2.35 |
| T-15 | 15–17 | 8.75 | 16 | 1.83 |

[a] Given by manufacturer.

[b] Data were obtained from GPC method using PSS Suprema column-MZ HEMA 40.