Fouling Study in Ultrafiltration:
Mechanism and Control via Membrane Surface Modification

(Untersuchung zum Fouling in der Ultrafiltration:
Mechanismen und Kontrolle durch Oberflächenmodifizierung von Membranen)

by
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ABSTRACT

Two important issues in application of ultrafiltration (UF) membrane, i.e. study of fouling mechanism and synthesis of low fouling membrane have been performed. Study on fouling mechanism was done by investigation of membrane–solute interactions (static adsorption) and membrane–solute–solute interactions (UF) using dextran and myoglobin as the model for polysaccharide and protein, respectively. Low fouling UF membranes have been synthesized by photograft copolymerization of water soluble monomers, poly(ethylene glycol) methacrylate (PEGMA) and N,N-dimethyl-N-(2-methacryloyloxyethyl-N-(3-sulfopropyl) ammonium betaine (SPE), onto polyethersulfone (PES) membrane with and without cross-linker monomer N,N'-methylene bisacrylamide (MBAA). Commercial polyethersulfone (PES) and cellulose–based UF membranes were used during fouling mechanism study whereas two commercial PES UF membranes with different nominal cut–off were used as the base membrane upon surface modification.

In both studies, the membranes were characterized with respect to the membrane chemistry (by IR–ATR spectroscopy and elemental analysis), surface wettability (by contact angle), surface charge (by zeta potential) and pure water permeability, pore structure and surface morphology (by hydraulic permeability and rejection measurements, scanning electron microscopy, and atomic force microscopy). In addition, in the fouling mechanism study, quantification of solute attached on the membrane surface was performed by simultaneously diffusion adsorption measurements (SDAM).

The results obtained from fouling mechanism study showed that significant changes in membrane characteristics and water permeability were observed for PES membranes after static adsorption using dextran. However, such changes were not observed for cellulose–based membrane. Good correlations were obtained between the water flux reduction (RFR) caused by dextran adsorption and the quantitative data for bound dextran on the PES membranes. Further, a pronounced effect of dextran size on adsorptive membrane fouling was identified. Contact angle and zeta potential measurements with non–porous films, where solute entrapment in pores can be ruled out, gave additional clear evidence for dextran binding on the PES surface. Complementary data for adsorption and fouling of PES membranes and non–porous films by the protein myoglobin indicate that the larger fouling tendency for protein than for dextran is due to a higher surface coverage of PES by the adsorbed biomacromolecule layer. Data for UF confirmed the conclusions from the static contact experiments because significant fouling was observed for PES membranes (more severe for myoglobin than for dextrans), while no fouling was observed for a cellulose–based UF membrane with the same nominal cut–off. Finally, two mechanisms for the attractive PES–dextran interaction – multiple hydrogen bonding involving the SO_2 groups of PES and "surface dehydration" of the relatively hydrophobic PES – are discussed. Study on the synthesis of low fouling UF membrane suggests that PEGMA/SPE–modified membranes showed much higher fouling resistance evaluated by using protein, sugarcane juice, dextran and humic acid solutions than unmodified membranes having similar and larger nominal cut–off. However, contribution of membrane pore structure on membrane–solute interactions was still clearly observed. In some cases, the presence of cross-linker could improve both flux permeate and rejection during ultrafiltration. Modified membranes prepared using "period 2" for the first batch and PEGMA–modified membrane (PES-g-PEGMA) and PEGMA–modified with low concentration of cross-linker (PES-g-PEGMA/MBAA) for the second batch showed the best performance during evaluation. Furthermore, modified membranes prepared with an "old generation" non fouling material, PEGMA, showed better performances than modified membrane prepared with a "new generation" non fouling material, zwitterionic SPE. The surface chemistry as well as surface wettability of modified membranes did not change after incubating in sodium hypochlorite solution for a period of 8 days. Finally, their combined high fouling resistance and high rejection supported by chemical stability by cleaning suggest that those modified membranes were very attractive as new generation of thin layer composite low fouling UF membranes.

This thesis is dedicated with love to my wife (Titik) and my children (Qori and Ihdina) both for the support, love and tolerance provided over three years during my doctorate study.

PREFACE

All the praises and thanks be to Allah. This work would not have finished without help from him. This work was performed in the time from April 2004 up to March 2007 to fulfill the requirements of doctoral program (Dr. rer. net) at the Institute of Technical Chemistry (Lehrstuhl für Technische Chemie II), Department of Chemistry, Universität Duisburg-Essen under the supervision of Prof. Dr. Mathias Ulbricht. Basically, this work concerns on fouling study of ultrafiltration membranes and surface modification via photograft copolymerization for control of fouling.

This thesis is composed of six chapters. Chapter 1 focuses on the background and state of the research problem. Chapter 2 provides briefly the fundamental theories for ultrafiltration and surface modification. Further, recent developments in surface modification for control of fouling are also described. Material and method used during experimental works are written in Chapter 3. Chapter 4 presents the results obtained from this study. The results are classified into four main parts, i.e. (i) commercial membrane characterization, (ii) study on dextran fouling of UF membrane, (iii) membrane surface modification, and (iv) evaluation of modified membranes performance. Chapter 5 discusses the phenomena behind the obtained results and tries to correlate each other. Chapter 6 presents the conclusions of this work.

Upon finishing this work I would like to take the chance to thank many people who have supported and helped me to perform this project. First of all, I would like to express my hearty thank for the supervision and the support provided by my advisor Prof. Dr. Mathias Ulbricht. He has supervised me not only to think critically and to conduct a comprehensive research but also to trust with my own opinion. Moreover, he also paid attention to my private life where I lived in Germany with my family during the study. I would like to thank my reviewer Prof. Dr. Axel Schönbucher for his advice and support.

I would like to give special thanks to DAAD (Deutscher Akademischer Austauschdienst) for providing my doctoral scholarship. I am grateful to the all members of membrane research group at Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, i.e. Mehmet, Inge, Danuta, Halim, Abdus, Christian, Dongming, Melvy, Claudia, Frank, Alex, Jun, Uwe, Dimitrios, Rafael, Frau Steffens and Frau Nordmann for good discussion and environment. In particular I would thank Diete Jacobi for his contribution in GPC analysis, Tim Leimer for conducting the ATR−IR analysis, Dr. Stefen Franzka for

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The main parts of this thesis have been published in the following publications:

H. Susanto, M. Ulbricht, Photo-grafted thin polymer hydrogel layers on PES ultrafiltration membranes: Characterization, stability and influence on separation performance, Langmuir 2007, 23, 7818.

H. Susanto, S. Franzka, M. Ulbricht, Dextran fouling of polyethersulfone ultrafiltration membranes–Causes, extent and consequences, J. Membr. Sci. 296 (2007) 147.

H. Susanto, M. Balakrishnan, M. Ulbricht, Via surface functionalization by photograft copolymerization to low-fouling polyethersulfone-based ultrafiltration membranes, J. Membr. Sci. 288 (2007) 157.

H. Susanto, M. Ulbricht, Influence of ultrafiltration membrane characteristics on adsorptive fouling with dextrans, J. Membr. Sci. 266 (2005) 132.

Other publications including submitted and conference papers during doctoral study are attached in Appendix-1.

CONTENTS