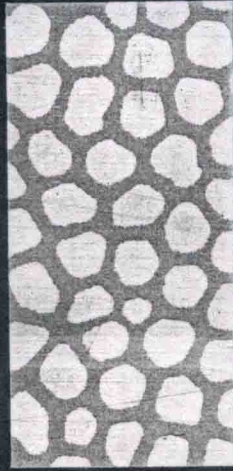

ULTRAFILTRATION *and* **MICROFILTRATION**

HANDBOOK



Munir Cheryan

ULTRAFILTRATION *and* **MICROFILTRATION**

HANDBOOK

Munir Cheryan, Ph.D.

University of Illinois
Urbana, Illinois, USA



LANCASTER • BASEL

Ultrafiltration and Microfiltration Handbook

a **TECHNOMIC** publication

Published in the Western Hemisphere by
Technomic Publishing Company, Inc.
851 New Holland Avenue, Box 3535
Lancaster, Pennsylvania 17604 U.S.A.

Distributed in the Rest of the World by
Technomic Publishing AG
Missionsstrasse 44
CH-4055 Basel, Switzerland

Copyright © 1998 by Technomic Publishing Company, Inc.
All rights reserved

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Main entry under title:
Ultrafiltration and Microfiltration Handbook

A Technomic Publishing Company book
Bibliography: p.
Includes index p. 517

Library of Congress Catalog Card No. 97-62251
ISBN No. 1-56676-598-6

ULTRAFILTRATION and MICROFILTRATION
HANDBOOK

2

HOW TO ORDER THIS BOOK

BY PHONE: 800-233-9936 or 717-291-5609, 8AM-5PM Eastern Time

BY FAX: 717-295-4538

BY MAIL: Order Department
Technomic Publishing Company, Inc.
851 New Holland Avenue, Box 3535
Lancaster, PA 17604, U.S.A.

BY CREDIT CARD: American Express, VISA, MasterCard

BY WWW SITE: <http://www.techpub.com>

PERMISSION TO PHOTOCOPY-POLICY STATEMENT

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by Technomic Publishing Co., Inc. provided that the base fee of US \$3.00 per copy, plus US \$.25 per page is paid directly to Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, USA. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is 1-56676/98 \$5.00 + \$.25.

PREFACE

Going back over the events in the membrane world since the first edition of *Ultrafiltration Handbook*, one cannot help being pleasantly surprised at the remarkable progress in many aspects of this ubiquitous technology. The development of the Sourirajan-Loeb synthetic membrane in 1960 provided a valuable separation tool to the process industries, but it faced considerable resistance in its early days. The situation is different today: membranes are more robust, modules and equipment are better designed (if the feedstream can be pumped, the chances are one or more of the modules available today will be able to handle it), and we have a better understanding of the fouling phenomenon and how to minimize its effects. Most important, costs have come down significantly, partly because of maturing of the technology and partly because of competition from an increasing number of membrane suppliers and original equipment manufacturers (OEM). Simultaneously, several company mergers and marketing alliances occurred that should provide a firmer footing from a business viewpoint. Developments in nanofiltration, gas separations, pervaporation, and bipolar membrane electrodialysis have widened the applicability of membranes, thus attracting even more attention. This revision of the *Ultrafiltration Handbook* is an attempt to catch up with these developments. The main themes remain the same and familiar to readers of the previous edition, but each chapter has been updated and revised while keeping the “handbook” flavor intact.

One major change in this edition starts with its title: *microfiltration* has been added to recognize it as an important member of the family of membrane technologies. Purists may argue that microfiltration (MF) is essentially the same as ultrafiltration (UF), with the difference being only in pore size. On the other hand, end users and membrane manufacturers tend to view them as distinct enough to justify separate treatment. I have tried to merge the two views since both are correct, but for different reasons. The scientific principles and much of the equipment may be the same, but these two sister technologies differ in operating strategies, mathematical modeling, and applications. A unified approach has been taken in earlier chapters, and distinctions are drawn in later chapters, especially when describing specific applications.

I have followed the same format as the first edition. Chapter 1 is a brief history of membranes, definitions, and basic thermodynamic principles. Chapter 2 reviews membrane chemistry and materials. The objective is not to teach membrane manufacture or design, but what membranes are designed to do. Unlike the early days when most membrane development was done by a few companies, there are numerous public and private institutions, universities, and independent research organizations involved today. This has lifted the veil of secrecy and improved manufacturing techniques to the extent that membranes are now considered to be a commodity. The trend today is towards specialization: many companies offer only membranes and/or modules of a certain type while relying on OEMs to provide system design and engineering. This is why Chapter 3 assumes even greater importance. Quality control and properties of membranes, inasmuch as they affect their potential use, are now the shared responsibility of the end user. Chapter 4 reviews mathematical models that will be useful in understanding the effect of process parameters on system performance. Here also, the emphasis is on factors the end user will need to consider when designing a membrane process.

Listing all the changes that have occurred over the past decade in equipment and module design (Chapter 5) has been a daunting task. Some of the companies that were major players a decade ago have ceased to exist or have been merged out of existence. This is part of the risk in a technology that is rapidly changing, not only to users of the equipment (where will they get replacement parts and support from?), but to authors of books targeted at the end user. Rather than attempt to describe each manufacturer's equipment in detail, the approach in this book has been to describe general operating principles of each type of equipment, with commercial examples being used to illustrate selected design features. Chapter 6 deals with an area of crucial importance: membrane fouling. A more general approach has been taken instead of the case study approach of the first edition. This is partly because of a better understanding of this vexing problem and also in order to be useful in as many applications as possible. Cleaning has been discussed in greater detail in this edition. Chapter 7 focuses on process design aspects, with expanded coverage of system design and cost calculations.

Like the previous edition, Chapter 8 forms the bulk of this book. At that time, I noted that the bias towards citing biologically oriented examples was probably because of the special interests of the author, rather than a reflection of actual usage of ultrafiltration. Although the range of applications of MF and UF has widened, it now appears that these bio-industries did indeed constitute the major market for UF and MF and will continue to be important for the foreseeable future. In contrast, chemical and petroleum industry applications are few. It is likely that water treatment and environmental applications will see the greatest growth in the next decade.

In order to serve readers with a variety of backgrounds and to keep this book as practical as possible, I have not delved too deeply into the theoretical aspects of the technology. Appendix C contains a list of books that provide greater depth in these areas. I have also minimized the use of jargon in order to be readily comprehensible to the novice, but sometimes it is unavoidable. A list of abbreviations at the beginning of the book and the glossary of terms at the end should be useful in this regard. Appendix A provides names and addresses of some membrane manufacturers (with the caveat that inclusion in this list should not be interpreted as an endorsement nor should omission be taken to mean otherwise). Appendix B contains conversion factors (to help translate English engineering units to the metric and vice versa).

Numerous individuals working for membrane manufacturers, engineering companies, and end users have continued to educate me in this exciting technology. Interacting with them has expanded my knowledge and appreciation of what it takes for this technology to succeed in the marketplace as much as scholarly papers from academic institutions helped elucidate the scientific principles. This subject has long ceased to be a “laboratory curiosity” or an “emerging technology.” This, in turn, has generated vast numbers of papers and books over the past decade. I may have summarized, simplified, or omitted contributions of several distinguished workers in this area and perhaps not cited them individually. It should not be construed as ignoring or minimizing their contributions or those of the legions of scientists, engineers, and marketing people who may not publish papers but have done much to move this technology forward.

I am once again indebted to my graduate students and research associates for their enthusiasm and doing much of the experimental work while we were learning the art of membrane technology. Technomic Publishing Company did a magnificent job of converting essentially classroom notes into a widely used reference book with the first edition. They were extraordinarily patient waiting for this long-overdue revision. Needless to say, the most important element has been my family. This book is dedicated to them in appreciation for their support and for sharing the joys and tribulations that accompanied my professional life and the writing of this book.

MUNIR CHERYAN
Urbana, Illinois

LIST OF ABBREVIATIONS

ACFF	affinity cross-flow filtration
AFM	atomic force microscopy
ATD	antitelescoping device
ATP	adenosine 5'-triphosphate
BOD	biochemical oxygen demand
BSA	bovine serum albumin
Btu	British thermal units
CA	cellulose acetate
CD	continuous diafiltration
cfu	colony forming units
CGM	corn gluten meal
CIP	clean-in-place
CMC	carboxymethyl cellulose (Section 8.E)
CMC	critical micelle concentration (Section 8.D.7)
CMP	caseinomacropptide
Co-A	coenzyme A
COD	chemical oxygen demand
CPF	co-current permeate flow
CR	cross-rotating
CSTR	continuous, stirred-tank reactor
CTA	cellulose triacetate
DAF	dissolved air flotation
d.b.	dry basis
DBP	disinfection by-product
DD	discontinuous diafiltration
DE	dextrose equivalent or diatomaceous earth
DESC	dead-end stirred cell
DF	diafiltration
DMF	dimethylformamide
DS	degree of substitution
E-coat	electrocoat
ED	electrodialysis

EDTA	ethylenediaminetetraacetic acid
FESEM	field emission scanning electron microscopy
FFA	free fatty acid
FIP	formed-in-place
FOG	fats, oils, and greases
FRP	fiberglass reinforced plastic
GFD	gallons per square foot per day
gpd	gallons per day
gpm	gallons per minute
HFF	hollow fiber fermenter
HFER	hollow fiber enzyme reactor
HIMA	Health Industry Manufacturers Association
IgG	immunoglobulin G
IPA	isopropyl alcohol
IPC	isophthaloyl chloride
JTU	Jackson Turbidity Units
LMH	liters per square meter per hour
LRV	log reduction value
LWC	low-weight cardboard
MEUF	micellar-enhanced ultrafiltration
MF	microfiltration
MJ	Megajoule
MPD	<i>m</i> -phenylene diamine
MRB	membrane recycle bioreactor
MW	molecular weight
MWCO	molecular weight cut-off
NAD	nicotinamide adenine dinucleotide
NADP	nicotinamide adenine dinucleotide phosphate
NF	nanofiltration
NMWCO	nominal molecular weight cut-off
NMWL	nominal molecular weight limit
NTU	nephelometric turbidity unit
OEM	original equipment manufacturer
ONPG	<i>o</i> -nitrophenyl- β -D-galactopyranoside
PA	polyamide
PAC	powdered activated carbon
PAN	polyacrylonitrile
PBW	periodic backwash
PEG	polyethylene glycol
PEI	polyethylenimine
PES	polyethersulfone
PI	polyimide
PLC	programmable logic controller

PP	polypropylene
PS	polysulfone
PTFE	polytetrafluoroethylene
PV	pervaporation
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
PVP	polyvinylpyrrolidone
QAC	quaternary ammonium compound
RBC	red blood cells
RC	regenerated cellulose
RO	reverse osmosis
RPM	revolutions per minute
RVPF	rotary vacuum precoat filter
SBR	styrene butadiene rubber
SCR	solute concentration ratio
SDS	sodium dodecylbenzene sulfonate
SEC	size exclusion chromatography
SEM	scanning electron microscope
SS	stainless steel
SS	suspended solids
SSL	spent sulfite liquor
TDI	toluene 2,4 diisocyanate
TDS	total dissolved solids
TEM	transmission electron microscope
TFC	thin-film composite
THM	trihalomethane
TMC	trimesoyl chloride
TMP	transmembrane pressure
TOC	total organic carbon
TPH	total petroleum hydrocarbon
TS	total solids
UF	ultrafiltration
UPW	ultra-pure water
UTP	uniform transmembrane pressure
VCR	volume concentration ratio
V-SEP	vibratory shear enhanced processing
WCR	weight concentration ratio
WPC	whey protein concentrate

TABLE OF CONTENTS

Preface xi

List of Abbreviations xv

1. INTRODUCTION 1

1.A. Definition and Classification of Membrane Separation Processes 1

1.B. Historical Developments 9

1.C. Physical Chemistry of Membrane Separations 13

1.C.1. *Chemical Potential and Osmosis* 13

1.C.2. *Vapor Pressure* 16

1.C.3. *Osmotic Pressure and Chemical Potential* 16

References 28

2. MEMBRANE CHEMISTRY, STRUCTURE, AND FUNCTION 31

2.A. Definitions and Classification 31

2.A.1. *Depth Versus Screen Filters* 31

2.A.2. *Microporous Versus Asymmetric Membranes* 32

2.B. General Methods of Membrane Manufacture 38

2.B.1. *Phase-Inversion Process of Membrane Manufacture* 39

2.C. Polymers Used in Membrane Manufacture 41

2.C.1. *Cellulose Acetate* 42

2.C.2. *Polyamide Membranes* 45

2.C.3. *Polysulfone Membranes* 45

2.C.4. *Other Polymeric Materials* 50

2.D. Composite Membranes 53

2.E. Inorganic Membranes 57

2.E.1. *Properties of Inorganic Membranes* 65

References 69

3. MEMBRANE PROPERTIES 71

3.A. Pore Size 71

3.A.1.	<i>Bubble Point and Pressure Techniques</i>	72
3.A.2.	<i>Direct Microscopic Observation</i>	78
3.B.	Predicting Flux from Pore Statistics	83
3.B.1.	<i>Example</i>	84
3.C.	Passage (Challenge) Tests	85
3.C.1.	<i>Microfiltration Membranes</i>	85
3.C.2.	<i>Ultrafiltration Membranes</i>	89
3.D.	Factors Affecting Retentivity of Membranes	96
3.D.1.	<i>Size of the Molecule</i>	96
3.D.2.	<i>Shape of the Molecule</i>	98
3.D.3.	<i>Membrane Material</i>	98
3.D.4.	<i>Presence of Other Solutes</i>	100
3.D.5.	<i>Operating Parameters</i>	104
3.D.6.	<i>Lot-to-Lot Variability</i>	105
3.D.7.	<i>Membrane Configuration</i>	106
3.D.8.	<i>Fouling and Adsorption Effects</i>	106
3.D.9.	<i>The Microenvironment</i>	107
References	111
4.	PERFORMANCE AND ENGINEERING MODELS	113
4.A.	The Velocity Boundary Layer	113
4.B.	The Concentration Boundary Layer	114
4.C.	Models for Predicting Flux: The Pressure-Controlled Region	116
4.D.	Concentration Polarization	120
4.E.	Mass Transfer (Film Theory) Model	124
4.E.1.	<i>Determining the Mass Transfer Coefficient</i>	128
4.E.2.	<i>Example</i>	130
4.F.	The Resistance Model	132
4.G.	Osmotic Pressure Model for Limiting Flux	135
4.H.	Factors Affecting Flux: Operating Parameters	136
4.H.1.	<i>Feed Concentration</i>	136
4.H.2.	<i>Temperature</i>	146
4.H.3.	<i>Flow Rate and Turbulence</i>	147
4.I.	Physical Properties of Liquid Streams	155
4.I.1.	<i>Density</i>	157
4.I.2.	<i>Viscosity</i>	158
4.I.3.	<i>Diffusion Coefficients</i>	159
4.J.	Experiment versus Theory: The "Flux Paradox"	162
4.K.	Design Factors Affecting Flux	165
References	167
5.	EQUIPMENT	171
5.A.	Laboratory-Scale Devices	171

5.B.	Industrial Equipment	178
5.B.1.	<i>Tubular Modules</i>	178
5.B.2.	<i>Hollow Fibers</i>	190
5.B.3.	<i>Plate Units</i>	205
5.B.4.	<i>Spiral-Wound</i>	211
5.C.	Special Modules	226
5.C.1.	<i>Rotary Modules</i>	227
5.C.2.	<i>Vibrating Modules</i>	230
5.C.3.	<i>Dean Vortices</i>	233
5.D.	Summary	234
References	235
6.	FOULING AND CLEANING	237
6.A.	Characteristics of Fouling	237
6.A.1.	<i>Water Flux</i>	239
6.B.	Consequences of Fouling	242
6.C.	Mathematical Models of Fouling	243
6.D.	Factors Affecting Fouling	245
6.D.1.	<i>Membrane Properties</i>	245
6.D.2.	<i>Solute Properties</i>	256
6.D.3.	<i>Process Engineering</i>	263
6.E.	Flux Enhancement	267
6.E.1.	<i>Turbulence Promoters/Inserts/Baffles</i>	267
6.E.2.	<i>Backflushing, -pulsing, -shocking, and -washing</i>	267
6.E.3.	<i>Uniform Transmembrane Pressure/Co-Current Permeate Flow</i>	267
6.E.4.	<i>Permeate Backpressure</i>	271
6.E.5.	<i>Intermittent Jets</i>	274
6.E.6.	<i>Pulsatile Flow</i>	274
6.E.7.	<i>Electrical Methods</i>	274
6.F.	Summary: Membrane Fouling	275
6.G.	Cleaning Membranes	276
6.G.1.	<i>Important Factors During Cleaning</i>	278
6.G.2.	<i>Typical Foulants and Soils</i>	281
6.G.3.	<i>Cleaning Chemicals</i>	282
6.G.4.	<i>Sanitizers</i>	285
References	288
7.	PROCESS DESIGN	293
7.A.	Physics of the Membrane Process	293
7.A.1.	<i>Example</i>	294
7.B.	Modes of Operation	298
7.B.1.	<i>Discontinuous Diafiltration</i>	299
7.B.2.	<i>Continuous Diafiltration</i>	302

7.B.3.	<i>Dialysis Ultrafiltration</i>	305
7.C.	Batch Versus Continuous Operation	307
7.C.1.	<i>Batch Operation</i>	308
7.C.2.	<i>Single Pass</i>	309
7.C.3.	<i>Feed-and-Bleed</i>	309
7.C.4.	<i>Multistage Operations</i>	311
7.C.5.	<i>Example</i>	313
7.C.6.	<i>Control Methods</i>	316
7.D.	Minimum Process Time	318
7.E.	Fractionation of Macromolecules	324
7.F.	Energy Requirements	326
7.F.1.	<i>Example</i>	330
7.G.	Costs and Process Economics	334
7.G.1.	<i>Arrays and Configurations</i>	334
7.G.2.	<i>System Cost</i>	339
7.H.	Summary	342
References	343
8.	APPLICATIONS	345
8.A.	Electrocoat Paint	345
8.B.	The Dairy Industry	349
8.B.1.	<i>Fluid Milk and Fermented Products</i>	352
8.B.2.	<i>Cheese Manufacture</i>	353
8.B.3.	<i>Milk Microfiltration</i>	360
8.B.4.	<i>Cheese Whey Ultrafiltration</i>	363
8.B.5.	<i>Microfiltration of Whey</i>	367
8.C.	Water Treatment	369
8.C.1.	<i>Process Water</i>	370
8.C.2.	<i>Drinking Water</i>	373
8.D.	Wastewaters	375
8.D.1.	<i>Oily Wastewater</i>	376
8.D.2.	<i>Stillage from Bioethanol Plants</i>	382
8.D.3.	<i>Caustic and Acid Recovery</i>	384
8.D.4.	<i>Brine Recovery</i>	384
8.D.5.	<i>Printing Ink</i>	385
8.D.6.	<i>Laundry Wastewater</i>	386
8.D.7.	<i>Micellar-Enhanced Ultrafiltration</i>	386
8.E.	Textile Industry	388
8.F.	Latex Emulsions	391
8.G.	Pulp and Paper Industry	393
8.H.	Tanning and Leather Industries	397
8.I.	Sugar Refining	399
8.J.	Soybean and Other Vegetable Proteins	402

8.K. Vegetable Oils	406
8.K.1. <i>Degumming</i> 408	
8.K.2. <i>Deacidification</i> 408	
8.K.3. <i>Bleaching</i> 411	
8.K.4. <i>Removal of Metals</i> 411	
8.K.5. <i>Dewaxing</i> 412	
8.K.6. <i>Clarifying Frying Oils</i> 413	
8.L. Corn and Other Grains	413
8.L.1. <i>Dextrose Clarification</i> 415	
8.L.2. <i>Protein Processing</i> 418	
8.M. Animal Products	420
8.M.1. <i>Red Meat</i> 420	
8.M.2. <i>Gelatin</i> 421	
8.M.3. <i>Egg Processing</i> 425	
8.M.4. <i>Fish Processing</i> 427	
8.M.5. <i>Poultry Industry</i> 428	
8.N. Biotechnology Applications	429
8.N.1. <i>Separation and Harvesting of Microbial Cells</i> 432	
8.N.2. <i>Enzyme Recovery</i> 439	
8.N.3. <i>Affinity Ultrafiltration</i> 440	
8.N.4. <i>Membrane Bioreactors</i> 443	
8.O. Fruit Juices and Extracts	470
8.P. Alcoholic Beverages	480
8.P.1. <i>Wine</i> 480	
8.P.2. <i>Beer</i> 483	
References	484
APPENDIX A Manufacturers and Suppliers of Membrane Systems ...	495
APPENDIX B Conversion Factors	503
APPENDIX C Books and General References	507
<i>Glossary of Terms</i>	511
<i>Index</i>	517
<i>About the Author</i>	527

CHAPTER 1

Introduction

1.A.

DEFINITION AND CLASSIFICATION OF MEMBRANE SEPARATION PROCESSES

Filtration is defined as the separation of two or more components from a fluid stream based primarily on size differences. In conventional usage, it usually refers to the separation of solid immiscible particles from liquid or gaseous streams. Membrane filtration extends this application further to include the separation of dissolved solutes in liquid streams and for separation of gas mixtures.

The primary role of a membrane is to act as a selective barrier. It should permit passage of certain components and retain certain other components of a mixture. By implication, either the permeating stream or the retained phase should be enriched in one or more components. In its broadest sense a membrane could be defined as “a region of discontinuity interposed between two phases” (Hwang and Kammermeyer 1975), or as a “phase that acts as a barrier to prevent mass movement but allows restricted and/or regulated passage of one or more species through it” (Lakshminarayanaiah 1984). By these definitions, a membrane can be gaseous, liquid, or solid or combinations of these. Membranes can be further classified by (a) nature of the membrane—natural versus synthetic; (b) structure of the membrane—porous versus nonporous, its morphological characteristics, or as liquid membranes; (c) application of the membrane—gaseous phase separations, gas–liquid, liquid–liquid, etc.; (d) mechanism of membrane action—adsorptive versus diffusive, ion-exchange, osmotic, or nonselective (inert) membranes.

Membranes can also physically or chemically modify the permeating species (as with ion-exchange or biofunctional membranes), conduct electric current, prevent permeation (e.g., in packaging or coating applications), or regulate the rate of permeation (as in controlled release technology). Thus, membranes may be either passive or reactive, depending on the membrane’s ability to alter the chemical nature of the permeating species (Lloyd 1985). Ionogenic groups and pores in the membrane confer properties such as *permselectivity* and *semipermeability*.