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# ULTRAFILTRATION HANDBOOK



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# *Ultrafiltration Handbook*

## FOREWORD

The publication of a "handbook" on a new technology is generally regarded as evidence that the technology has achieved maturity in the eyes of its practitioners. Speaking as one who has had both the pleasure (and agony) of involvement with the science and practice of ultrafiltration since its early evolution (as a feasible separation technique) in the early 1960's through its present state of development, the arrival of this book as a benchmark of adulthood of the field leaves me with conflicting emotions—gratification that the immense potential of this technology is now being recognized and tapped, and sadness that much of the excitement of surprise and discovery which gripped those of us involved with its early growth may now become but fond recollection.

I find it now difficult to believe that my first brush with the concept of ultrafiltration was as an undergraduate student in Ernst Hauser's course in colloid chemistry at M.I.T. in the mid-forties, where Bechhold's work early in this century was described. The technique at that time was still little more than a laboratory curiosity with membranes then available. The possibility that membranes of sufficiently high permeability and adequate ruggedness to be useful as practical laboratory (let alone industrial) ultrafilters seemed beyond reach. It was perhaps that challenge which in part motivated our research program in molecular transport in polymers at M.I.T. in the 50's and 60's.

As Dr. Cheryan properly points out in his preface, it was the aggressive and well-funded federally sponsored research program on water-desalination which commenced in the mid-50's which really spawned the development of reverse-osmosis specifically, as well as all membrane separation processes generally. Our M.I.T. group was fortunate to be among the first to participate in this program—and it was out of this research that emerged the first promising candidate ultrafiltration membrane. Unfortunately, it wasn't at the time recognized for what it was—rather, it was just a high-water-permeability, poorly salt-retentive membrane with little prospect for use in water desalting.

When Amicon was founded in 1962, membranes and membrane separation

rations were not the highest priority items on the company's list of objectives. This situation rapidly changed, however, when we were approached by Dorr-Oliver to try to develop a membrane to remove organic solutes from secondary sewage effluent. Not only did the "salt-leaky" polyion complex membrane prove up to this task—the need sparked the development of the first asymmetric ultramicroporous membranes, which have since proved to be the workhorse of the ultrafiltration business. It is curious—and possibly significant—that the very industrial application which spawned the development of ultrafiltration as a practical separation process has been one of the last to enter industrial practice.

The very membranes developed initially for sewage treatment found a ready home in the life science research community; indeed, if there was a cradle of UF process development, it was the molecular biology laboratory. The rapidity with which UF was adopted and adapted to serve the special needs of life science research during the '60's and '70's was nothing short of astonishing—seldom has a new separations technology been pulled into service by its customers, particularly when those customers are sophisticated and resourceful scientists. Our preoccupation with satisfying the needs of the research laboratory community for membranes and equipment necessarily delayed efforts to develop UF as an industrial process and bona fide unit operation, although the opportunities for large scale application were beckoning. The membranes were in hand, but not the proper modules and supporting hardware and systems. We began to hear comments like, "When are you going to stop talking about industrial UF and *do* something about it?"

The decade of the '70's was the turning point—the period when engineering ingenuity and sound engineering design techniques were applied to ultrafiltration, and out of which emerged economic and reliable equipment and systems for large scale separations service. This developmental phase is not yet complete, but today there are available from many suppliers around the world well-engineered, high-performance equipment, membranes, and systems suitable for a wide variety of purification/separation functions—and with excellent field technical service as well. This is surely the major sign of maturity of the field.

Today, ultrafiltration (and crossflow filtration, which is its twin) stands at the threshold of a major penetration into the food, drug, and chemical industries as an efficient, energy-sparing, and economic separation process for liquid systems. Perhaps its greatest beneficiary is proving to be industrial biotechnology, where UF and CFF are uniquely effective in biologicals concentration, purification, and fractionation operations. The food and beverage industries are increasingly turning to these membrane methods for such functions as clarification, sterilization, dewatering, and waste treatment. Even the minerals and metals

processing industries are looking to UF and CFF for metals recovery, slurry dewatering, and water reclamation. For these industries, and the engineers which serve them, this handbook could hardly appear at a more appropriate time.

While I indicated at the outset my concern that the maturation of ultrafiltration technology might signal the end to the excitement of discovery in this field, I am reassured by recent events that this is unlikely to happen. As is characteristic of every broadly-useful new technology, the development of one important application stimulates interest in adapting that technology to new and untested needs. This is already happening to UF: Much work is afoot to develop enzymatic and catalytic reactors containing membranes; to develop highly efficient membrane-modulated fermentors and tissue culture devices; and to develop hybrid artificial organs based on membranes for important biomedical uses. Thus, I suspect that, within a few years, Dr. Cheryan will be confronted with the even more formidable challenge of writing a revision to his chef d'oeuvre which does justice to the new concepts, products, and applications that will by then have appeared on the scene.

As a final note, I call attention with considerable personal pride and pleasure to the observation that a significant fraction of the experts in membrane separations and ultrafiltration who are cited in Dr. Cheryan's monograph are former members (or students of former members) of our core research team at M.I.T. between 1950 and 1965. It is for me particularly gratifying to have been associated with such a distinguished group of colleagues, and to have shared vicariously in their success.

ALAN S. MICHAELS

## PREFACE

Membrane separations technology, in its modern incarnation, was born from a single landmark event: the development of the synthetic asymmetric membrane in 1960 at the University of California, Los Angeles, by Sourirajan and Loeb. Since then it has spawned a vast array of applications ranging in diversity almost unmatched by any other separation process. Desalination and water treatment by reverse osmosis is probably the earliest and best-known application. In its ideal definition, reverse osmosis is essentially a dewatering operation, while ultrafiltration is a fractionation technique that can simultaneously concentrate macromolecules or colloidal substances in process streams. The major boost to ultrafiltration occurred in the late 1960s with the development of asymmetric non-cellulosic ultrafiltration membranes that overcame some of the limitations of cellulosic ultrafiltration membranes.

Today, ultrafiltration is applied in a wide variety of fields, from the chemical industry (such as electrocoat paint recovery, latex processing, textile size recovery and recovery of lubricating oils) to medical applications, such as kidney dialysis operations. Most industrial applications to date have been secondary operations, i.e., in waste treatment or recovery of valuable products from plant effluents (such as cheese whey). However, the scientific and trade literature indicates a number of applications where ultrafiltration is also considered a primary unit operation. Among them are cheesemaking by ultrafiltration, vegetable protein isolates and concentrates, and the biotechnology-oriented applications, such as the harvesting of microbial cells, fractionation of fermentation broths, and high-performance membrane bioreactors for enzymatic and fermentation processes. What is remarkable is that this technology is now only 25 years old, and yet it has more than 50 companies around the world (most are listed in the appendix) actively participating in the marketing, manufacturing or research into synthetic membrane technologies. The world-wide market for membranes, less than \$US 10 million prior to 1960, is now variously estimated at \$400-



600 million per year. Few other technologies have moved so rapidly into the marketplace nor have had such an impact.

Despite the obviously growing importance of membrane separations and ultrafiltration, there are few educational institutions that include this topic in their regular curricula, apart perhaps from a token few lectures in a broader unit operations course. One problem I have faced in my graduate course on membrane separations has been the lack of a good comprehensive text-book. I have also observed, at national and international conferences and corporate seminars, especially those that are commodity- or product-oriented, that few in the audience know enough of the basics of synthetic membrane technology to appreciate its potential and limitations. Few have the time or background to learn it the hard way like those of us who have been working in membrane separations all of our professional lives.

The impetus for writing this book arose from these twin needs. There are several books related to membrane separations that have been published since the early sixties; most of them are listed in the appendix. Almost all that deal with the technology and applications have been edited by reputable scientists. Those that are not proceedings of conferences have chapters written by different authors who have reviewed material in their area of expertise. Although they serve as valuable reference texts, with rare exceptions they are not for the novice, but for the advanced student and experienced researcher. Most also deal primarily with either reverse osmosis or microfiltration. Few, if any, deal exclusively or primarily with ultrafiltration. Those books that are proceedings of conferences are of necessity written as scientific papers dealing with a specific and narrow problem. Thus they are rarely used by students or workers in microbiology, biology, food technology, environmental sciences, chemical technology or biotechnology, who wish to learn the basics, the criteria for selection of membranes and equipment, how to optimize the operating parameters and the potential and limitations of ultrafiltration.

Although this book focuses on *ultrafiltration* (which in itself is considered a misnomer by some experts), a certain amount of overlap with the operations on either side of the size scale (*reverse osmosis* or *microfiltration*) is unavoidable. Chapter 1 is a brief introduction to the history of membranes, definitions and classification of membrane processes and some basic thermodynamic principles. Chapter 2 reviews membrane chemistry and materials. As with most young technologies, much of the work on membrane development has been done by membrane companies or individual entrepreneurs, who jealously guard their secrets. This veil of secrecy is being lifted, albeit slowly, and there will probably soon be no real secrets left in this business.

Chapter 3 is a discussion of quality control aspects and properties of membranes inasmuch as they affect the potential use of membranes. Chapter 4 is a review of the mathematical models used to describe ultrafiltration processes and optimize process parameters.

Chapter 5 is a survey of membrane modules and equipment. No attempt has been made to be comprehensive and describe each manufacturer's equipment in detail. Rather the approach has been to describe the general operating principles behind each *type* of equipment, using specific examples from selected companies. Chapter 6 covers an area of crucial importance in membrane processing and ultrafiltration in particular: fouling. Since fouling in its true sense is due to specific membrane-solute interactions, a case study approach has been used: the fouling of UF membranes by cheese whey, a notorious foulant. The lessons learnt from this one case should be useful in attacking fouling problems in other applications. Process design aspects are presented in Chapter 7, such as methods to determine process time, membrane area, energy consumption, and economics.

Chapter 8 forms the bulk of this book. A variety of applications has been selected covering several broad categories of industries. In this chapter, and throughout the book in fact, the reader will notice a bias towards citing examples from the bio-processing industries, such as food and biotechnology. This not only reflects the special area of expertise of the author, but also a feeling that these are the areas that will see the greatest growth in the immediate future. Chapter 8 is followed by the appendices, containing names and addresses of membrane manufacturers, conversion factors, and a listing of journals, books, and other publications related to ultrafiltration. A glossary of terms and the index are found after the appendices.

Much of the material in the book is a synthesis of information from a variety of sources, including my own personal experiences. I have relied on informal discussions with personnel from several companies in the U.S.A., Japan, and Europe to keep abreast of developments in this rapidly changing—and highly competitive—field. In order to keep this book as simple as possible so that readers with a variety of backgrounds will be able to understand the basics and appreciate the potential of ultrafiltration, I may have omitted, summarized, or simplified contributions of several distinguished workers in this area. If I have not cited them individually, it should not be construed as ignoring or minimizing their contributions. Indeed, in some cases involving company personnel, some of these individuals do not wish to be publicly acknowledged.

In researching materials for the book, I became aware that much of the development work in membranes in general, and ultrafiltration in particular, have been done by membrane/equipment manufacturers. I

have thus freely used material from manufacturers' catalogs and bulletins. I have attempted to provide as much up-to-date information as possible, but in such a dynamic area of research, I wouldn't be surprised if at least half of the specifications change significantly a few years after the first edition of this book appears.

My thanks go to Dr. Norman W. Desrosier for his initial interest in this book, to several of my graduate research assistants for sharing my enthusiasm and doing much of the experimental work while we were learning the art of ultrafiltration, and to participants in my courses on membrane separations at the University of Illinois and other locations for suggestions and feedback. I especially wish to acknowledge my wife, Leela, for her constant encouragement and many sacrifices during the writing of this book. This book is dedicated to her in appreciation for understanding why I had to spend so many weekends and nights with my PC working on the book instead of being with her and my children.

MUNIR CHERYAN

## TABLE OF CONTENTS

<i>Foreword</i>	ix
<i>Preface</i>	xiii
<b>1. INTRODUCTION</b>	<b>1</b>
1.A. Definitions and Classification of . . . . .	1
Membrane Separation Processes	
1.B. Historical Developments . . . . .	8
1.C. Physical Chemistry of Membrane Separations . . . . .	13
1.C.1. <i>Chemical Potential and Osmosis</i>	13
1.C.2. <i>Vapor Pressure</i>	17
1.C.3. <i>Derivation of Relationships between Osmotic                 Pressure and Chemical Potential</i>	17
References . . . . .	25
<b>2. MEMBRANE CHEMISTRY, STRUCTURE, AND FUNCTION</b>	<b>27</b>
2.A. Definitions and Classification . . . . .	27
2.A.1. <i>Depth vs. Screen Filters</i>	27
2.A.2. <i>Microporous vs. Asymmetric Membranes</i>	27
2.B. General Method of Manufacture of Membranes . . . . .	31
2.C. Phase Inversion Process of Membrane Manufacture . . . . .	32
2.D. Polymers Used in Membrane Manufacture . . . . .	35
2.D.1. <i>Cellulose Acetate</i>	35
2.D.2. <i>Polyamide Membranes</i>	39
2.D.3. <i>Polysulfone Membranes</i>	39
2.D.4. <i>Other Polymeric Materials</i>	43
2.D.5. <i>Composite Membranes</i>	44
2.D.6. <i>Mineral or Ceramic Membranes</i>	46
2.D.7. <i>Track-Etch Membranes</i>	48
References . . . . .	50
<b>3. MEMBRANE PROPERTIES</b>	<b>53</b>
3.A. Bubble Point Technique . . . . .	53
3.B. Direct Microscopic Observation . . . . .	56

3.C. Predicting Flux from Pore Statistics .....	59
3.D. Solute Passage Testing .....	62
3.E. Factors Affecting Retentivity of UF Membranes .....	65
References .....	70
<b>4. MODELLING OF ULTRAFILTRATION PROCESSES</b> .....	<b>73</b>
4.A. The Velocity Boundary Layer .....	73
4.B. The Concentration Boundary Layer .....	74
4.C. Models for Predicting Flux .....	76
4.D. Models to Predict Limiting Flux .....	82
4.D.1. <i>Mass Transfer (Film Theory) Model</i> .....	84
4.D.2. <i>The Resistance Model</i> .....	89
4.E. Osmotic Pressure Model for Limiting Flux .....	91
4.F. Factors Affecting Flux: Operating Parameters .....	93
4.F.1. <i>Feed Concentration</i> .....	93
4.F.2. <i>Temperature</i> .....	100
4.F.3. <i>Flow Rate and Turbulence</i> .....	102
4.G. Physical Properties of the Liquid Feed Stream .....	109
4.G.1. <i>Density</i> .....	111
4.G.2. <i>Viscosity</i> .....	111
4.G.3. <i>Diffusion Coefficients</i> .....	114
4.H. Experiment vs. Theory: The "Flux Paradox" .....	117
4.H.1. <i>The Tubular Pinch Effect</i> .....	118
4.I. Design Factors Affecting Flux .....	119
References .....	123
<b>5. ULTRAFILTRATION EQUIPMENT</b> .....	<b>127</b>
5.A. Laboratory Scale Apparatus for Ultrafiltration .....	127
5.B. Industrial Ultrafiltration Equipment: Tubular Modules .....	128
5.B.1. <i>Processing Characteristics of Tubular Membranes</i> .....	142
5.C. Hollow Fibers .....	144
5.C.1. <i>Characteristics of Hollow Fiber Modules</i> .....	146
5.D. Plate Units .....	151
5.D.1. <i>Characteristics of the DDS Plate Unit</i> .....	159
5.E. Spiral-Wound .....	160
5.E.1. <i>Characteristics of Spiral-Wound Modules</i> .....	166
5.F. Summary .....	168
References .....	169
<b>6. FOULING OF ULTRAFILTRATION MEMBRANES</b> .....	<b>171</b>
6.A. Characteristics of Fouling .....	171
6.B. Consequences of Fouling .....	173
6.C. Mathematical Models of Fouling .....	173

6.D. Physico-Chemical Factors Affecting Fouling .....	174
6.D.1. <i>Proteins</i> .....	175
6.D.2. <i>Salts</i> .....	182
6.D.3. <i>pH and Heat Treatment</i> .....	185
6.D.4. <i>Lipids and Other Components</i> .....	187
6.E. Processing Factors Affecting Fouling .....	187
6.E.1. <i>Temperature</i> .....	187
6.E.2. <i>Flow Rate and Turbulence</i> .....	188
6.E.3. <i>Pressure Effects</i> .....	190
6.E.4. <i>Feed Concentration</i> .....	192
6.F. Summary: Fouling .....	192
6.G. Cleaning .....	193
References .....	194
 7. PROCESS DESIGN .....	 197
7.A. Physics of the Ultrafiltration Process .....	197
7.B. Modes of Operation .....	205
7.B.1. <i>Discontinuous Diafiltration (DD)</i> .....	206
7.B.2. <i>Continuous Diafiltration (CD)</i> .....	208
7.C. Batch vs. Continuous Operation .....	210
7.C.1. <i>Batch Operation</i> .....	210
7.C.2. <i>Single-Pass Processing</i> .....	210
7.C.3. <i>Feed-and-Bleed</i> .....	212
7.C.4. <i>Multistage Operations</i> .....	213
7.D. Minimum Process Time .....	217
7.E. Fractionation of Macromolecules .....	218
7.F. Energy Requirements for Ultrafiltration .....	221
7.G. Process Economics .....	225
References .....	229
 8. ULTRAFILTRATION APPLICATIONS .....	 231
8.A. Electrocoat Paint Recovery .....	231
8.B. The Dairy Industry .....	235
8.B.1. <i>Cheesemaking by Ultrafiltration</i> .....	235
8.B.2. <i>Fractionation of Cheese Whey</i> .....	242
8.C. Water Treatment .....	245
8.D. Oily Wastewaters .....	250
8.E. Sugar Refining .....	256
8.F. Vegetable Protein Processing .....	258
8.G. Textile Industry .....	263
8.H. Latex Emulsions .....	264
8.I. Egg Processing .....	268
8.J. Pulp and Paper Industry .....	269

8.K. Tanning and Leather Industries .....	271
8.L. Animal Products Industry .....	272
8.M. Recovery of Printing Ink .....	278
8.N. Biotechnology Applications .....	278
8.N.1. <i>Separation and Harvesting of</i> <i>Enzymes and Microorganisms</i> 279	
8.N.2. <i>Membrane Bioreactors</i> 295	
8.N.3. <i>Tissue Culture with Membranes</i> 322	
8.O. Medical and Therapeutic Applications .....	332
8.P. Binding Analysis by Ultrafiltration .....	335
8.P.1. <i>The Direct Partition Method</i> 336	
8.P.2. <i>Deposition Ultrafiltration Method</i> 337	
8.P.3. <i>Continuous Ultrafiltration (Diafiltration)</i> 339	
8.Q. Fruit Juices and Other Beverages .....	340
APPENDIX A Manufacturers and Suppliers of .....	351
Membrane Systems	
APPENDIX B Conversion Factors .....	357
APPENDIX C Books, Journals, and General References on .....	360
Ultrafiltration	
<i>Glossary of Terms</i>	365
<i>Index</i>	369
<i>About the Author</i>	375

## 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. 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. Hwang and Kammermeyer (1975) have defined a membrane in its broadest sense as "a region of discontinuity interposed between two phases." Lakshminarayanaiah (1984) refers to a membrane 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." By this definition, a membrane can be gaseous, liquid or solid or combinations of these. Membranes can be further classified by (a) nature of the membrane—natural vs. synthetic, (b) structure of the membrane—porous vs. non-porous, 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 vs. 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*.



Figure 1.1 shows a classification of various separation processes based on particle or molecular size and the primary factor affecting the separation process. The five major membrane separation processes, reverse osmosis, ultrafiltration, microfiltration, dialysis and electrodialysis, cover a wide range of particle sizes, matched in versatility only by centrifugal processes. However, an absolute requirement for centrifugal processes is the existence of a suitable density difference between the two phases that are to be separated, in addition to the two phases being immiscible. Membrane separation processes have no such requirement, and indeed, the real value of ultrafiltration and reverse osmosis is that they permit separation of dissolved molecules down to the ionic range, provided the appropriate membrane is used.

Among membrane separation processes itself, the distinction between the various processes is somewhat arbitrary and has evolved with usage and convention. Table 1.1 shows the characteristics of various membrane processes. Osmosis (to be discussed in detail in Section 1.C.), is the transport of solvent through a semi-permeable membrane from the dilute solution side to the concentrated solution side of the membrane. It is driven by chemical potential differences between the water on either side of the membrane. With an ideal semi-permeable membrane, only water should permeate through the membrane. The common laboratory technique of dialysis, on the other hand, is primarily a technique for purifying macromolecules, such as desalting of proteins, and the primary driving force would be difference in concentration of the permeable species between the solution in the dialysis bag and on the outside of the bag. Electrodialysis relies primarily on voltage or electromotive force and ion-selective membranes to effect a separation between charged ionic species.

What distinguishes the more common membrane processes—microfiltration, ultrafiltration, and hyperfiltration (reverse osmosis)—is the application of hydraulic pressure to speed up the transport processes. However, the nature of the membrane itself controls which component permeates and which component is retained. In its ideal definition, reverse osmosis or hyperfiltration retains *all* components other than the solvent (water) itself, while ultrafiltration retains only macromolecules or particles larger than about 10–200 Å (about 0.001–0.02  $\mu\text{m}$ ). Microfiltration processes, on the other hand, are designed to retain particles in the “micron” range, that is, suspended particles in the range of 0.10  $\mu\text{m}$  to about 10  $\mu\text{m}$ . In conventional usage particles larger than 10  $\mu\text{m}$  are best handled by conventional filtration processes. Thus, in its broadest sense, reverse osmosis or hyperfiltration is essentially considered to be a dewatering technique, while ultrafiltration can be looked at as a method for simultaneously purifying, concentrating, and fractionating macro-