Inamuddin · Mohammad Luqman
Editors

Ion Exchange Technology I

Theory and Materials

Springer

Ion Exchange Technology I

Inamuddin • Mohammad Luqman
Editors

Ion Exchange Technology I

Theory and Materials

Springer

Editors

Inamuddin
Assistant Professor
Department of Applied Chemistry
Faculty of Engineering & Technology
Aligarh Muslim University
Aligarh, India

Mohammad Luqman
Assistant Professor
Chemical Engineering Department
College of Engineering
King Saud University
Riyadh, Kingdom of Saudi Arabia

ISBN 978-94-007-1699-5 ISBN 978-94-007-1700-8 (eBook)
DOI 10.1007/978-94-007-1700-8
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2012938478

© Springer Science+Business Media B.V. 2012
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Ion exchange is a process of exchanging ions between stationary and mobile phases. It is a natural process and has been in practice for ages. Since commercial development took place in the last century, both academic and industrial research have been improving technology to find new applications.

This edition covers the introduction, principle, instrumental and theoretical fundamentals, structure, synthesis and characterization, kinetic and equilibrium, simulation and computer modeling studies of ion exchange materials in addition to the preparation and properties of ion exchange membranes for electrodialysis and fuel cells.

Chapter 1 covers the basic fundamentals of ion exchange kinetics and equilibrium and discusses the various applications that utilize ion exchange processes. Chapter 2 reviews the selectivity coefficient as well as the exchange isotherm diffusion and transport in terms of thermodynamics, equilibria and ion exchange kinetics. Chapter 3 examines the various conditions of ion exchange equilibrium with important theories developed in literature and reviews ion exchange kinetics and mass transport processes based on semi empirical models, Fick's law and derived expressions. Chap. 4, presents fundamentals of ion exchange fixed bed operations. Chapter 5 deals with the performance of ion exchange membrane electrodialysis for saline water desalination. The desalination performance of a practical-scale electrodialyzer is discussed using computer simulation. Chapter 6 is devoted to the structure, synthesis and properties of organic ion exchange materials. Preparation, properties and application of ion exchange membranes are discussed in Chap. 7. Chapter 8 focuses on the synthesis, structure, properties and applications of synthetic ion exchange materials. Chapter 9 reviews the most important aspects such as: synthesis, physical and chemical properties, equilibria and kinetics, as well as of sorption processes, possible and real field applications of fibrous ion exchangers. Fibrous catalysts, color-changing sorbents and hybrid fibrous sorbents impregnated with nanoparticles of inorganic substances are also described. The structure, coordination chemistry and applications of most commonly employed chelating ion exchangers are discussed in Chap. 10. Chapter 11 focuses on the recent advances in the field of ion exchanger–based voltammetric sensors, whose widespread use has instigated a new electroanalytical technique named ion exchange voltammetry. Chapter 12 discusses the properties of sulfonated poly(ether ether ketone) (SPEEK) as a promising membrane material for polymer electrolyte fuel cell. Chapter 13 reviews the preparation and use of organic–inorganic hybrid ion exchangers in organic reaction catalysis. An introduction to the ion exchange technique in solid matter, mainly optical glasses, to fabricate wave guides telecommunications is reviewed in Chap. 14. Network simulation of electrical response using Nernst–Planck and Poisson equations is used to describe the ionic transport processes through a cation-exchange membrane and two diffusion boundary layers on both sides of the membrane in Chap. 15. Chapter 16 reviews the authors' work on the mathematical and computer modeling of ion exchangers on styrene–divinylbenzene matrix, a mathematical model based on the concept of the influence of neighbouring exchange sites on the properties of each other. Such a model allowed to explain the dependence of selectivity and additive properties of the ion exchange system on the degree of ion exchange.

Acknowledgments

We are most indebted to the grace of the Almighty “One Universal Being,” who inspires entire Humanity to knowledge, and who blessed us with the needed favor to complete this work.

This book gathers the remarkable contributions from international leading experts in the field of ion exchange technology and provides a comprehensive review and research work. We are thankful to all the authors for their esteemed contribution to this book. We would also like to thank all the publishers and authors who granted us permission to use their copyright material. Although sincere efforts were made to obtain copyright permissions from the respective owners and to include citations with the reproduced materials, we would like to offer our sincere apologies to any copyright holder whose rights may have been unknowingly infringed.

Dr. Inamuddin would like to express his deep sense of gratitude to Profs. Syed Ashfaq Nabi, Ishtiyaq Ahmad, Rakesh Kumar Mahaja, Seon Jeon Kim, Kenneth I. Ozoemena, Saleem-ur-Rahman, S.M.J. Zaidi, Gaber E. Eldesoky, Zeid A. AL-Othman, Sheikh Raisuddin, Byong-Hun Jeon, and A.I. Yahya, and to Drs. B.D. Malhotra and Raju Khan for their valuable suggestions, guidance, and constant inspiration.

He would also like to thank his departmental colleagues, Profs. M. Mobin, Asif Ali Khan, and R.A.K. Rao, and Drs. M.Z.A. Rafiqui, Abu Nasar, Rais Ahmad, and Yasser Azim. Without their continuous encouragement, this book would have not been brought to its final form. Dr. Inamuddin is at a loss of words to express his gratitude to his friends and colleagues, Drs. M.M. Alam, Amir-Al-Ahmad, Zafar Alam, Mu. Naushad, Salabh Jain, Hemendra Kumar Tiwari, Adesh Bhadana, Shakeel Ahmad Khan, Satish Singh, and others, for their timely help, good wishes, encouragement, and affection.

Dr. Luqman would like to acknowledge the lively environment provided by Samsung Cheil Industries during the time he spent with them. He is also very grateful to his colleagues, more specifically to the Chairman of the Chemical Engineering Department, King Saud University, and other departmental staff for their help, support, and encouragement throughout the preparation of this book.

Last but not least, we would like to express our heartfelt gratitude to our family members for their constant inspiration and gracious support.

Inamuddin
Mohammad Luqman
Editors

Editors' Bios

Dr. Inamuddin is currently working as Assistant Professor in the Department of Applied Chemistry, Aligarh Muslim University (AMU), India. He received his Master of Science degree in Organic Chemistry from Chaudhry Charan Singh (CCS) University, Meerut, India, in 2002 and his Master of Philosophy and Doctor of Philosophy degrees in Applied Chemistry from AMU in 2004 and 2007, respectively. He has extensive research experience in the multidisciplinary fields of Analytical Chemistry, Material Chemistry, and Electrochemistry and, more specifically, Renewable Energy and Environment. He has worked in different projects funded by the University Grants Commission (UGC), Government of India, and Council of Scientific and Industrial Research (CSIR), Government of India. He has received Fast Track Young Scientist Award of Science and Technology, Government of India, to work in the area of bending actuators and artificial muscles. He has published 30 research articles and 4 book chapters of international repute. Recently, he has edited the book entitled *Advanced Organic–inorganic Composites: Materials, Devices and Allied Applications* and co-edited the books entitled *Green Solvents I: Properties and Applications in Chemistry* and *Green Solvents II: Properties and Applications of Ionic Liquids* published by Nova Science Publishers, Inc, and Springer, United Kingdom, respectively. He is presently working as editor in chief of the Journal of Chemical and Environmental Research published from The Muslim Association for the Advancement of Science (MAAS), India. He has worked as a Postdoctoral Fellow, leading a research team at Creative Research Initiative Center for Bio-Artificial Muscle, Hanyang University, South Korea, in the field of renewable energy, especially biofuel cells. He has also worked as Postdoctoral Fellow at Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum and Minerals, Saudi Arabia, in the field of polymer electrolyte membrane fuel cells and computer fluid dynamics of polymer electrolyte membrane fuel cells. He is a life member of the *Journal of the Indian Chemical Society*.

Mohammad Luqman, Ph.D., is serving as an Assistant Professor in Chemical Engineering Department, King Saud University (KSU), Saudi Arabia. He teaches Polymer/Material Science and Engineering courses. Before joining the KSU, he served as an Assistant Manager in Samsung Cheil Industries, Korea. He worked on the development of heat-resistant polymers, organic glass, and block copolymers as impact modifiers and compatibilizers for engineering alloys. He served as a post-doctoral fellow at Artificial Muscle Research Center, Konkuk University, Korea, in the field of Ionic Polymer Metal Composites. He was awarded the Ph.D. degree in 2007, in the field of Ionomers, by Chosun University, Korea. Dr. Luqman has published numerous papers and book chapters in the field of Ionomers, Ion-exchange Polymers, and Polymer Nanocomposites. One of his papers, published in "*Polymer*", Elsevier, was Ranked the "first" among the "Top 25 Hottest Articles" in "all" chemistry journals during April–June 2008. Dr. Luqman is acting as a Regional (Middle East) Editor of the International Journal *Chemical and Environmental Research*, Published from MAAS, India. He also serves as a Section Editor of *Journal of Industrial Research & Technology* by HATAM Publishers, Malaysia. He has delivered few invited lectures at International podiums and very recently, has served as an Invited Editor of a reference book entitled *Recent Advances in Plasticizers*.

Contents

Contributors

Amir-Al-Ahmed Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

Simão P. Cardoso CICECO/Department of Chemistry, University of Aveiro, Aveiro, Portugal

Dilson Cardoso Chemical Engineering Department, Federal University of São Carlos – UFSCar, São Carlos, SP, Brazil

Vassilis J. Inglezakis SC European Focus Consulting srl, Bacau, Romania

Mahadevappa Y. Kariduraganavar P. G. Department of Studies in Chemistry, Karnatak University, Dharwad, KA, India

Arjumand A. Kittur Department of Chemistry, SDM College of Engineering & Technology, Dharwad, KA, India

E.G. Kosandrovich Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus, Minsk, Republic of Belarus

Srikant S. Kulkarni Department of Chemistry, JSS Degree College, Dharwad, KA, India

Patrícia F. Lito CICECO/Department of Chemistry, University of Aveiro, Aveiro, Portugal

José M. Loureiro LSRE/Department of Chemical Engineering, School of Engineering, University of Oporto, Porto, Portugal

Leandro Martins Institute of Chemistry, Universidade Estadual Paulista – UNESP, Araraquara, SP, Brazil

Ligia M. Moretto Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Venice, Italy

A.A. Moya Departamento de Física, Universidad de Jaén, Jaén, Spain

Tulsi Mukherjee Analytical Chemistry Division, Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai, India

Mohamed Mahmoud Nasef Institute of Hydrogen Economy, Universiti Teknologi Malaysia, Kuala Lumpur, Malaysia

Jin-Soo Park Department of Environmental Engineering, College of Engineering, Sangmyung University, Dongnam-gu, Cheonan, Republic of Korea

Jayshree Ramkumar Analytical Chemistry Division, Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai, India

Victor Anthony Garcia Rivera Institute of Physics and National Institute of Optical and Photonic (INOF) of São Carlos, University of São Paulo, São Carlos, SP, Brazil

Wolfgang Schmidt Max-Planck-Institut für Kohlenfoschung, Mülheim an der Ruhr, Germany

Carlos Manuel Silva CICECO/Department of Chemisty, University of Aveiro, Aveiro, Portugal

V.S. Soldatov Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus, Minsk, Republic of Belarus

Lublin University of Technology, Lublin, Poland

Dhiraj Sud Department of Chemistry, Sant Longowal Institute of Engineering and Technology, (Deemed to be University), Longowal, India

Abdullah S. Sultan Center for Petroleum & Minerals, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

Yoshinobu Tanaka IEM Research, Ushiku-shi, Ibaraki, Japan

Paolo Ugo Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Venice, Italy

Zaini Ujang Institute of Environmental and Water Resources Management, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

S.M. Javaid Zaidi Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

V.M. Zelenkovskii Institute of Physical Organic Chemistry, Belarus National Academy of Sciences, Minsk, Republic of Belarus

Antonis Zorpas Institute of Environmental Technology and Sustainable Development, Department of Research and Development, Laboratory of Environmental Friendly Technology, Paralimni, Cyprus

Abbreviations

α_B^A	Separation factor
12MR	Twelve-membered ring
4MR	Four-membered ring
4-VP	4-Vinylpyridine
6MR	Six-membered ring
8MR	Eight-membered ring
$a_{Az}{}^{b}$, $a_{Bs}{}^{a}$	Activities
APAS	Aminophosphonic acid silica
ASV	Anodic stripping voltammetry
BEA	Zeolite *Beta*
BT	Breakthrough
BV	Bed volumes
CD	Cyclodextrin
CEC	Cation-exchange capacity
CMX	Cation exchange membranes
CPE	Carbon paste electrode
CsEBS	Cesium salts of ethylbenzenesulfoacid
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
Cyt *c*	Cytochrome *c*
D	Diffusion coefficient
D4R	Double four-membered ring
D6R	Double six-membered ring
D_{app}	Apparent diffusion coefficient
DEA	Diethylamine
DEAPA	Diethylaminopropylamine
DETA	Diethylenetriamine

DFs	Decontamination factors
DL	Detection limit
DMAPA	Dimethylaminopropylamine
DMFC	Direct methanol fuel cell
DMG	Dimethylglyoxime
DP-ASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
DS	Degree of sulfonation
D_s	Diffusion coefficient in the solution phase
DVB	Di-vinyl benzene
E(OC)	Open circuit electrochemical potential
$E_{1/2}$	Half-wave potential
E_{appl}	Applied potential
ECL	Electrochemiluminescence
ED	Electrodialysis
EDA	Ethylenediamine
EDR	Electrodialysis reversal
EDTA	Ethylenediaminetetraacetic acid
E_i	Initial potential
EIS	Electrochemical impedance spectroscopy
ENM	Electrospin nano-fiber membrane
Ep_b	Backward peak potential
EPBI(DMG)	Epoxidized polybenzimidazole(Dimethylglyoxime)
Ep_f	Forward peak potential
ETSS	Ethyl styrene sulfonate
EW	Equivalent weight
F	Faraday constant
FAU	*Fau*jasite
Fc	Ferrocene
Fc^+	Ferricinium cation
FCC	Fluid catalytic cracking
FS	Full scale
GCE	Glassy carbon electrode
GIS	*Gis*mondine
GME	*Gme*linite
HASB	Hard soft acid base
HPA	Hydrated tungstophosphoric acid
HPCIC	High performance chelation ion chromatography
IDA	Iminodiacetic acid
IEC	Ion exchange capacity
IEV	Ion-exchange voltammetry
IO	Integrated-optic

Ip_p	Peak current for analytes n the polymer phase
Ip_s	Peak current for analytes in the solution phase
IS	Iontosorb salicyl
ITO	Indium thin oxide
K_a	Equilibrium constant
k_D	Distribution coefficient
k_{ex}	Site to site electron exchange rate constant
$K_X{}^M$	Selectivity coefficient
LB	Langmuir-Blodgett
LBL	Layer-by-layer
LDPE	Low density polyethylene
LS	Lab scale
LTA	*L*inde *T*ype *A*
m- DVB	metha-Divinylbenzene
M_{As}, M_{Bs}	Molarities
m_{Az}, m_{Bz}	Molalities
MEL	Maximum exchange level
MFI	ZS*M*-5 (*fi*ve)
MHL	Metal proton ligand
MINI, MIDI(d), 3-21G*	Basis sets for non-empirical calculations.
MMT	Montmorillonite
MOR	*Mor*denite
MP2/3-21G* and MP2/MIDI(d)	Level of theory of non-empirical calculations with using basis sets 3-21G* and MIDI(d) and with accounting for electronic correlation in the frame of the second order Moeller-Plesset perturbation theory.
MSWV	Multiple square wave voltammetry
MTA	Methylthriamyl ether
MTB	Methylthributhyl ether
MV	Methyl viologen
MWW	*M*CM-22 (t*w*enty-t*w*o)
N	Noise
N-DC	N, N′ di(caroxymethyl)dithiocarbamate
NMP	N-methyl-2-pyrrolidinon
NMR	Nuclear magnetic resonance
PA	Polyamide
PAMAM	Polyamidoamine
PAN	Polyacrylonitrile
PBI	Poly(benzimidazole)
PBI	Polybenzimidazole
PC	Polycarbonate
PDDMACl	Poly(diallyldimethylammonium chloride)
PDDPCl	Poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride)

PEEK	Poly(ether ether ketone)
PEI	Poly(ether imine)
PEK	Poly ether ketone
PEKEKK	Poly(ether ketone ether ketone ketone)
PEM	Proton exchange membrane
PEMFC	Polymer electrolyte membrane fuel cell
PES	Polyether sulphone
PET	Poly(ethyleneterphthalate)
PFSA	Perfluorosulfonic acid
PI	Polyimides
PILC	Pillared clay
PLE's	Polymeric ligand exchangers
PMA	Poly mtharcylate
PMeT	Poly(3-methylthiophene)
PP	Polypropylene
PPO	poly(phenylene oxide)
PP-ST-DVB	Polypropylene with grafted polystyrene with divinylbenzene
PPy	Polypyrrole
PS-DVB copolymer	PSDC
PS-DVB	Polystyrene divinylbenzene
PSS	Poly(4-styrene sulfonate)
PSSH	Poly(styrenesulfonic acid)
PSSNa	Poly(sodium styrenesulfonate)
PSU	Polysulphone udel
$PSU-NH_2$	Aminated polysulfone udel
PTFE	Poly(tetrafluoroethylene)
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
PVP	Polyvinyl pyrollidone
Q	Ion exchange capacity
R	Gas constant
REC	Real exchange level
RHF	Restricted Hartree-Fock method for closed shalls.
RO	Reverse osmosis
ROHF	Restricted open shall Hartree-Fock method.
S	Signal
SCF MO LCAO	Model, in which a molecular orbital (MO) is represented as a linear combination of atomic orbitals (LCAO), are examined in light of ab initio self-consistent field (SCF) computations with bases of various sizes.

s-IPNs	Semi-interpenetrating polymer networks
SMM	Surface modifying macromolecules
SPE	Screen printed electrode
SPEEK	Sulfonated poly(ether ether ketone)
SPI	Sulfonated polyimide
SPME	Solid phase microextraction
SPSU	Ortho-sulfonesulfonated poly (ethersulfone)
ST	Polystyrene
ST-DVB Matrix	Styrene – divinylbenzene matrix
ST-DVB	Styrene–divinylbenzene
SWV	Square wave voltammetry
T	Temperature
t	Time
TCB	Phenol-trichlorobenzene
TEC	Theoretical exchange level
TETA	Triethylenetetraamine
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMFE	Thin mercury film electrode
TPA	Tripropylamine
TPABr	Tetrapropylammonium bromide
UF	Ultra filtration
v	Scan rate
WKB method	Wentzel-Kramers-Brillouin method
XAD	Commercial polystrene divinylbenzene resin
Z_A, Z_B, S_A, S_B	Equivalent fractions
ZrP	Zirconium phosphate
ΔG^0	Free energy change
ΔH	Enthalpy change
ΔS	Entropy change

Nomenclature

a	Minimum approximation distance between ions
A	External particle surface area
A_γ	Debye-Huckel constant
A'_{ij}, A'_{ji}	Margules parameters
$A^{z_A}, B^{z_B}, C^{z_C}$	Counter ions with valences z_A, z_B, z_C
$\bar{A}^{z_A}, \bar{B}^{z_B}$	Counter ions with valences z_A, z_B inside the exchanger
a_i	Activity of species i in solution
$\bar{a}_i$	Activity of species i in exchanger
$A_i^{z_i}$	Generic counter ion i with valence z_i
a_p	External surface area per unit particle volume
B	Second Virial coefficient
$B_{j,i}$	Langmuir constant

C_b	Solute concentration at breakthrough time
$C_\mathrm{ef,i}$	Concentration of sorbate in the effluent
$C_\mathrm{F,i}$	Concentration of species *i* in the feed
C_i	Molar concentration of species *i* in solution
C_i^*	Molar concentration of species *i* at the exchanger/film interface
$C_\mathrm{N,i}$	Normality of species *i*
$C_\mathrm{N,t}$	Total normality of solution
$C_\mathrm{p,i}$	Molar concentration of species *i* inside the pores
$\bar{C}_\mathrm{p,i}$	Average concentration of species *i* inside the pores
C_{sat}	Saturation concentration
C_t	Total molar concentration of ionic species in solution
d	Particle diameter
$D_\mathrm{A}, D_\mathrm{B}$	Self-diffusion coefficients of species *A* and *B*
D_AB	Interdiffusion coefficient
$D_\mathrm{eff,p,i}$	Effective diffusion coefficient of species *i* in macropores
$D_\mathrm{eff,s,i}$	Effective diffusion coefficient of species *i* in micropores
D_f	Diffusion coefficient in the film
D_i	Diffusion coefficient of species *i*
	MS surface diffusivity of the pair *i–j*
	MS surface diffusivity corresponding to the interaction between *i* and the fixed ionic charges
D_L	Axial dispersion coefficient
e	Electron charge
$E_\mathrm{i,j}$	Energy of adsorption of ion *i* on site *j*
$\bar{E}_\mathrm{i}$	Average adsorption of ion *i*
F	Faraday constant
F_i	Fractional attainment of equilibrium of species *i*
g_ij	Energy parameter characteristic of the $i - j$ interaction
I	Ionic strength
J_i	Diffusion flux of species *i*
k	Boltzmann's constant
k_1	Rate constant of the first order sorption
k_2	Rate constant of the second order sorption
K_aB^A	Corrected selectivity coefficient
k_AB	Bohart and Adams rate constant
K_B^A	Thermodynamic (equilibrium) constant
K_C	Selectivity coefficient
K_D	Distribution coefficient
k_f	Convective mass transfer coefficient
K_LDF	Linear driving force coefficient
$K_\mathrm{S}^{\mathrm{M_xM_m}}$	Stability constant
k_Th	Thomas rate constant
k_YN	Yoon-Nelson rate constant
L	Column length

M^{m+}	Cation
m_i	Molality of species *i*
m_t	Total molality of ionic species
n	Freundlich constant, number of ionic species in solution
N_0	Avogadro's constant
n_c	Number of counter ions
n_f	Number of functional groups
N_i	Molar flux of species *i*
$N_{p,i}$	Diffusion fluxes of species *i* through the macropores
$N_{s,i}$	Diffusion fluxes of species *i* through the micropores
n_w	Number of water molecules in the zeolite
$n_x + n_y$	Total number of tetrahedral in the unit cell of zeolite
q_i	Molar concentration of ionic species *i* in exchanger
p	Parameter in binomial distribution
p_j	Equivalent fraction of exchanger site of type *j*
$\bar{q}_i$	Average loading of ionic species *i* in exchanger
q_i^*	Resinate concentration in equilibrium with the fluid concentration
Q_i	Equivalent ionic concentration of species *i* in exchanger
Q_i^e	Surface excess of ion *i*
$Q_{j,i}$	Equivalent ionic concentration of species *i* on exchanger site *j*
q_M	Kusik-Meissner parameter
q_{max}	Maximum sorbate concentration in the solid phase
q_s	Molar concentration of ionic fixed groups in exchanger
q_t	Total molar concentration of ionic species in exchanger
Q_t	Ion exchange capacity (in equivalents)
r	Radial position
R	Particle radius
$\Re$	Universal gas constant
t	Time
T	Absolute temperature
$t_{1/2}$	Time required for 50% sorbate breakthrough; stoichiometric time
t_b	Breakthrough time
U_0	Superficial velocity
u_i	Electrochemical mobility of species *i*, velocity of diffusing species *i*
V_{ef}	Volume of effluent
V_L	Volume of fluid phase
V_s	Volume of solid phase
V_{ZLC}	Volume of the ZLC column
W_{exch}	Mass of exchanger
W_{ij}	Weighting factor
x_i	Ionic fraction of species *i* in solution
X_i	Equivalent ionic fraction of species *i* in solution
X^{x-}	Anion
y_i	Ionic fraction of species *i* in exchanger

Y_i	Equivalent ionic fraction of species *i* in exchanger
y_s	Mole fraction of ionic fixed groups in exchanger
z_i	Valence of ionic species *i*

Subscripts

0	Initial condition
e	Equilibrium
f	Free
s	Solid, fixed ionic groups of the exchanger
t	Total
intra	Intraparticle

Greek Letters

α_B^A	Separation factor
$\bar{\alpha}_j^i$	Average separation factor
δ	Film thickness
ε	Dielectric constant
ε_b	Bed porosity
ε_p	Particle porosity
φ	Electric potential
γ_i	Activity coefficient of species *i* in solution
$\bar{\gamma}_i$	Activity coefficient of species *i* in exchanger
Γ_{ij}	Thermodynamic factor
Γ	Reduced activity coefficient of Meissner and Kusik
λ_i	Distribution coefficient of species *i*
$\Lambda_{ij}, \Lambda_{ji}$	Wilson parameters
μ_i	Chemical potential of species *i* in solution
$\bar{\mu}_i$	Surface chemical potential of species *i*
v	Volumetric flow rate, number of site types
v_c	Number of cations per electrolyte
v_i	Pure-component molar volume
v_a	Number of anions per electrolyte
ρ_w	Density of pure solvent
σ_i	Standard deviation of energy distribution
τ_d	Time constant for intraparticle diffusion
$\tau_{d,m}$	Maximum value of τ_d
$\tau_{d,i}$	Minimum value of τ_d

Chapter 1
Introduction to Ion Exchange Processes

Mohamed Mahmoud Nasef and Zaini Ujang

Abstract Ion exchange technology remains the workhorse of various chemical, petrochemical, food, power, and pharmaceutical industries. The success of ion exchange process depends literally on understanding of its basic principles and applying them in a way suiting the nature of the treated feed. This chapter reviews the basic fundamentals and key components of ion exchange process taking into consideration the latest progress taking place in the field. The variation in the ion exchange materials, their nature, forms, and functions are reviewed. The kinetics, sorption equilibrium, operating modes, and engineering configurations for ion exchange processes are also discussed. A brief encounter for the various applications utilizing ion exchange processes is also presented.

1.1 Introduction

Ion exchange is a technology that has been ever receiving growing attention in various industries for several decades. This technology is commonly used to purify solutions by removing the dissolved ions by electrostatic sorption into ion exchange materials of various physical forms. The removed ions are replaced with equivalent amounts of other ions of the same charge in the solutions. The use of ion exchange reaction allows either all ions to be removed from a solution or particular ions to be selectively separated. Therefore, both selective removal of ionic contamination and

---

M.M. Nasef (✉)
Institute of Hydrogen Economy, Universiti Teknologi Malaysia, International City Campus,
Jalan Semarak, 54100 Kuala Lumpur, Malaysia
e-mail: mahmoureithar@cheme.utm.my

Z. Ujang
Institute of Environmental and Water Resources Management, Universiti Teknologi Malaysia,
81310 Skudai, Johor, Malaysia
e-mail: zaini@utm.my

Inamuddin and M. Luqman (eds.), *Ion Exchange Technology I: Theory and Materials*, DOI 10.1007/978-94-007-1700-8_1,

complete deionization can be distinguished. The selection between both depends mainly on the composition of the solution and the extent of decontamination required [1].

The applications of ion exchange are numerous and cover wide ranges of industries and households. These applications mainly cover purification purposes; however, ion exchange is also widely implemented in the separation and extraction of valuable substances such as uranium and plutonium from the nuclear industry waste [2]. Deionization (demineralization) of water and water softening are known to be the most common applications. However, the spectrum of other applications varies from large-scale extraction of metals in hydrometallurgical and metal finishing processes to recovery of precious metals [3, 4]. The applications of ion exchange are also extended to food and beverages, petrochemical and chemical, pharmaceutical, sugar and sweeteners, industrial wastewater, ground and potable water, semiconductor, production power soil remedy, and pulp and paper industry.

In principle, ion exchange is a process involving an exchange of ions between an electrolyte solution (aqueous phase) and similarly charged ions immobilized in an ion exchange material (solid phase), which takes place through a stoichiometric reversible ion exchange reaction. Ion exchange materials represent the heart of ion exchange processes that fall into various categories: polymeric and mineral, cationic and anionic, and resins and membranes depending on their classification. Engineering systems of various configurations meeting the requirements for industrial application are available and vary depending on the morphology of the ion exchange materials. Batch and column systems are the most common configurations to accomplish ion exchange processes using resins, whereas plate and frame modules/cells are favored upon using membrane/sheet forms. Currently, a large number of commercial resins and membranes are available giving high possibility for more than one technically effective solution that allows the utilization of custom-designed ion exchange process. However, having a robust system design requires a thorough knowledge of all available resin types along with a clear understanding of basic fundamentals and economics of ion exchange to ensure highly efficient and cost-effective operations.

This chapter provides an intensive review for the basic fundamentals of ion exchange process covering its essential ion exchange materials, reaction kinetics and sorption equilibrium, operating modes, system configurations, process economy, and industrial applications.

1.2 Historical Perspective

Ion exchange phenomena have been known for many years. The first examples of this phenomena were discovered by Thompson and Way (1850) [5, 6] during their investigations concerning the way in which soluble manures were retained for long periods in the soil, instead of being washed out by rainwater. The importance of this discovery (in ion exchange terms) was not fully understood until later in that decade

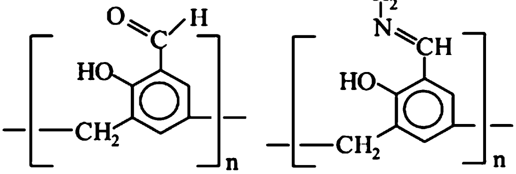


Fig. 1.1 Phenol formaldehyde ion exchange resins

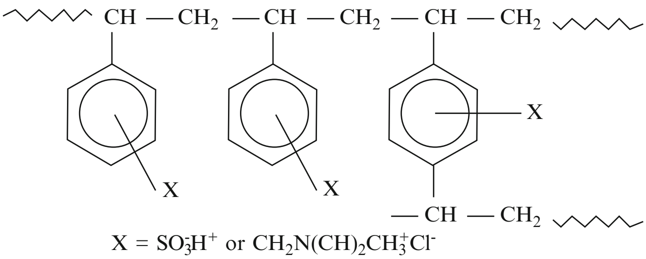


Fig. 1.2 Strong cation- and anion-exchange resins based on polystyrene divinylbenzene copolymer resins

when this reaction was found to be reversible. This phenomenon was caused by certain minerals in the soil as released in the latter half of the nineteenth century. These minerals, called resins, are based on tetrahedron structure of silicon and aluminum compounds called zeolites. In 1905, synthetic zeolites were manufactured and utilized for water treatment in a form of water-softening agent ever since [7]. Synthetic cation-exchange resins were developed during the 1930s using certain types of coal treated with sulfuric acid [8, 9]. This was an important evolution due to the fact that the sulfonated coal would operate in a greater pH range, 1–10. This made the sulfonated coal more versatile for the use in many more industrial applications. However, these resins were found to have serious deficiency caused by their lower exchange capacity compared to the zeolites. A few years later, the phenol formaldehyde polymer resin from the type shown in Fig. 1.1 was synthesized [10]. This polymer was sulfonated forming strong acid ion exchange resin. Using the same base polymer only functionalized with an amine (NH_2) produced the first weak base ion exchange resins. The major development for the power industry came in USA in 1944 when strong acid and strong base resins from the types shown in Fig. 1.2 were produced based on divinylbenzene cross-linked polystyrene, which was treated with sulfuric acid to make a strongly acidic resins or chloromethylated and subsequently aminated to produce strongly basic resins [11–13]. These resins possess much better characteristics than earlier phenol/formaldehyde resins. These new resins are now used almost exclusively in water demineralization plants for high pressure boilers. By the year 1950, weakly acidic ion exchange resins shown in Fig. 1.3 based on polymerization of methacrylic acid and divinylbenzene were developed. Eventually, the macroporous methyl methacrylate and divinylbenzene resins were synthesized with various functionalities (weakly basic, strongly basic,

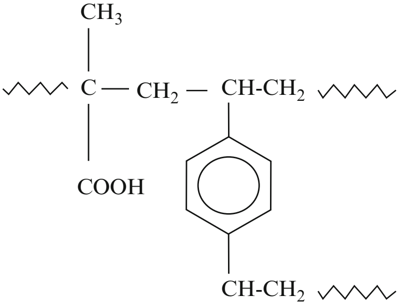


Fig. 1.3 Weak cation-exchange resins based on polymethylmethacrylate divinylbenzene copolymer resins

Table 1.1 The most important milestones in the development of ion exchange resins

Year	Milestones
1850	Agricultural chemists Harry Thompson and John Way discovered ion exchange phenomena
1858	German Chemist Eichom reported that ion exchange is a reversible reaction
1905	Robert Gans introduced first process to soften water using zeolite (sodium aluminosilicate)
1913	American company (Permutit) introduced first commercial zeolites
1935	English chemists Adams and Holmes prepared first synthetic polymer cation and anion exchangers (phenol formaldehyde and polyamine formaldehyde)
1944	D'Alelio developed cation-exchange resins based on polymerization of styrene and divinylbenzene
1946	Anion-exchange resins based on polymerization of styrene and divinylbenzene were developed
1950	Weakly acidic cation-exchange resins based on polymerization of methacrylic acid and divinylbenzene were developed
1965	Weakly basic resins based on polymerization of methyl methacrylate and divinylbenzene were developed
>1965	Bifunctional resins based on polymerization of methyl methacrylate and divinylbenzene were developed

and bipolar), by the year 1965 and above, with each resin having its own niche application in the water treatment industry [3]. Table 1.1 shows the most important milestones in the development of ion exchange resins. Today, hundreds of resins of various types, chemical groups, structures, and morphologies are available in the market with many more materials being researched to introduce more tolerance, cost-effectiveness, and new applications to ion exchange processes.

Ion exchange membranes are another significant class of materials that have been explored since the discovery of ion exchange phenomena. A significant development in ion exchange membranes was started by studies on ion-permeable membranes, collodion-type membranes which were carried out by Michaelis [14] who recognized the effect of membrane charge on ion permeation through the membrane. The theory of membrane potential was proposed by Meyer et al. [15]

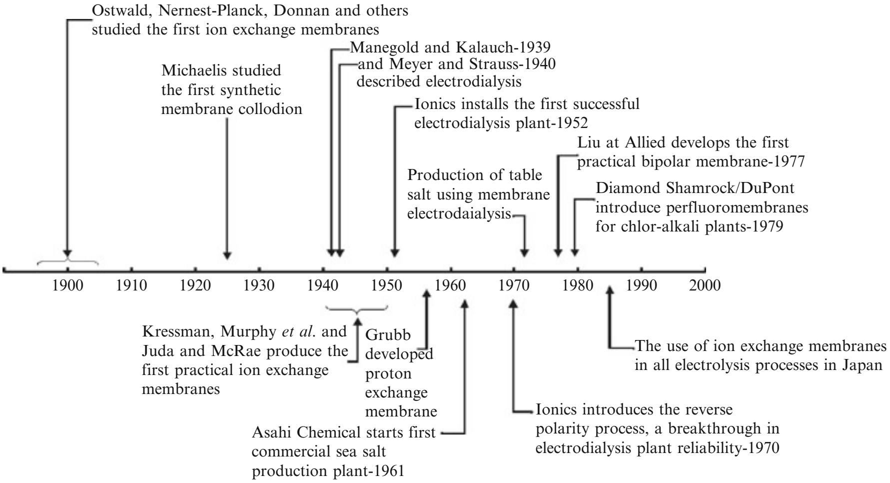


Fig. 1.4 Milestones of the development of ion exchange membranes and related processes

paving the way for the modified collodion membrane to be the first charged artificial membrane. The synthesis of ion exchange membranes was reported in 1950 by Juda and MacRae [16]. The preparation of proton exchange membrane and its use in fuel cells was first reported by Grubb in 1955. Later, in 1961 [17], Asahi Chemicals installed a membrane electrodialysis plant for the production of edible salt in Japan, and as a result, electrolysis in Japan was totally converted from the mercury method to a process using the ion exchange membranes by 1986. In 1977, the membrane chlor-alkali industry was introduced by Asahi Chemicals. This was followed by the introduction of Nafion (perfluorinated sulfonic acid membrane) for chlor-alkali industry by Diamond Shamrock and DuPont in 1979 [18]. The milestones in the development of ion exchange membranes are schematized in Fig. 1.4.

1.3 Ion Exchange Materials

Ion exchangers are a class of functional materials that display ion exchange properties owing to existence of fixed ionic sites bonded to their framework, which is held together by chemical bonds or lattice energy and can be called polyions. Oppositely charged ions move throughout the framework and can be replaced by ions of similar charge. Ion exchange materials are available in different forms and structures varying in their classifications depending on origin, physical form (morphology), immobilized functional group, and their functions, as shown in Fig. 1.5. The mechanism of ion exchange is dictated by various parameters related to the ion exchange materials such as the nature and type of fixed functional groups, the physical forms, and the origin of the ion exchange material [19].

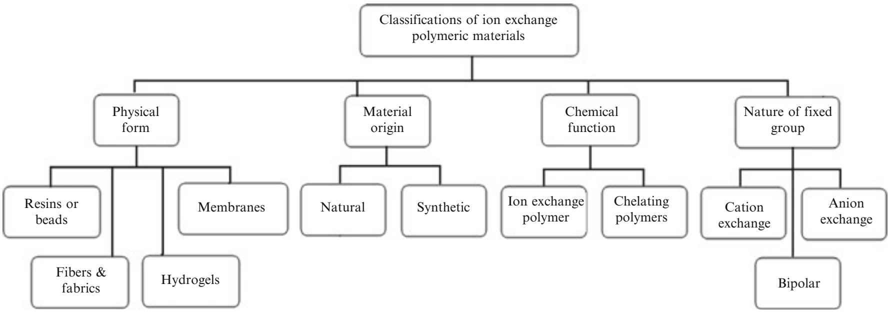


Fig. 1.5 Various classifications of ion exchange materials

1.3.1 Classifications of Ion Exchange Materials

On the basis of origin, there are two general types of ion exchange materials, that is, organic and minerallic; the former majority are synthetic polymers available in cationic and anionic forms whereas the latter exists in cation-exchange form only (e.g., zeolites and betonites). Thus, organic ion exchange materials can be cationic, anionic, and combined cationic/anionic (amphoteric) exchangers considering the nature of fixed ion exchange sites (functional groups).

Since ion exchangers act in a similar way to conventional acids and bases, the main classes of these materials, that is, cation and anion exchangers, can be further classified depending on the type of the functional group into several types: strongly acidic, strongly basic, weakly acidic, and weakly basic materials. Ion exchange materials containing sulfonate ($–SO_3^-$) and phosphorate acid ($–PO_3^-$) groups and those containing tetraammonium ($–NR_3^+$) basic groups are strongly acidic and strongly basic exchangers, respectively. On the other hand, materials containing phenolic (–OH) groups and primary amine ($–NH_2$) and secondary amine (–NRH) groups are weakly acidic and weakly basic exchangers, respectively. Carboxyl groups ($–COO^-$) and tertiary amine ($–NR_2$) groups take a medium position between strong and weak acidic and basic exchangers, respectively.

Practically, most strong acid exchangers contain sulfonate groups, which are active over the entire pH range. Unlikely, most weak acid exchangers have carboxylic groups, which are not active at pH values below 4–6. However, such exchangers often have higher ion exchange capacities than sulfonate exchangers together with other specific advantages [4]. Similarly, strong basic exchangers are active over the entire pH range unlike weak base exchangers which are not active at alkaline pH. A summary of the common functional groups and their negative logarithm of the dissociation constant (pK) are presented in Table 1.2. It can be clearly seen that each of these major resin classes has several physical or chemical variations within the class. Such variations impart different operating properties to the resin. Thus, the terms strong and weak in the ion exchange world do not refer to the strength of binding; it rather reflects the extent of variation of ionization with pH

Table 1.2 Common functional groups of polymeric ion exchange materials and their respective pK values

Anion-exchange materials		Cation-exchange materials	
Fixed ionic groups	pK	Fixed ionic group	pK
$\equiv N^+$	1–2	$-SO_3H$	1–2
$=N$	4–6	$-PO_3H_2$	2–5
$=NH$	6–8	–COOH	4–6
–NH2	8–10	–OH	9–10

of the medium solution. Each of these major resin classes has several physical or chemical variations within the class. Strongly acidic resins are commonly available in Na^+ form or H^+ form with different degrees of cross-linking to meet the requirements in various applications, whereas strongly basic resins are available in Cl^- or OH^- forms.

Physically, organic (polymeric) ion exchange materials are available in various morphologies related to the polymer framework carrying the functional groups. This includes beads, fibers, and membranes. Such variation in the physical forms brings about wide differences in chemical and physical properties of these ion exchangers. The majority of these ionic forms have synthetic polymer structures and mainly exist in a resin form represented by a wide number of commercial resins with polystyrene divinylbenzene backbone. A smaller class of biosorbents obtained from modified natural polymer sources including alginate, chitosan, and cellulose is also under development. Ion exchange resins fall into two main categories: cation- and anion-exchange forms. A combination of cation- and anion-exchange groups can be used to obtain a bipolar form of the resins that can replace mixed bed in ion exchange column. More details on the various types of ion exchange materials can be found in Refs. [4] and [20].

1.3.2 Ion Exchange Resins

Considering the separation mechanism, ion exchangers can be further classified into various categories including ion exchange resins, chelating adsorbents, hydrogels, affinity polymers, and ion exchange membranes. Among all, ion exchange resins, which are covalently cross-linked insoluble polyions supplied as spherical beads (particles), represent the major class of exchanger being commercially produced as stated earlier.

1.3.2.1 Preparation of Ion Exchange Resins

Commercial ion exchange resins that are available in market today are commonly produced by suspension polymerization, polycondensation, or polymer-analogous transformations [19]. Resins based on styrene-divinylbenzene copolymers as a building block involve the preparation of a cross-linked bead copolymer followed

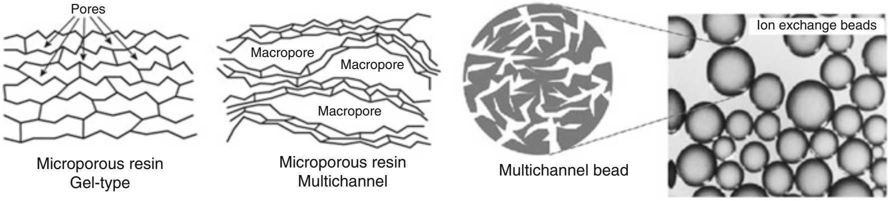


Fig. 1.6 Macroporous ion exchange resin bead with multichannel structure

by chemical treatment with a sulfonating agent in the case of strong acid cation-exchange resins, or chloromethylation and subsequent amination of the copolymer for obtaining anion-exchange resins. The degree of cross-linking achieved in the resin beads depends on the proportions of the styrene monomer and the cross-linking agent (divinylbenzene) used in the polymerization step. Practical ranges of cross-linking are in the range of 4–16%; however, 8% cross-linking level is preferred [4]. It is not straightforwardly known which one of the two resin structures, that is, strongly or weakly, is advantageous without knowing specific operating conditions of the treatment site. This is because the operating properties for acrylic resins differ from those of the corresponding sulfonic acid resin. The preferred resin is the one that has operating properties matching up best with the site's operating parameters, thus maximizing operating efficiency and cost-effectiveness.

1.3.2.2 Physical Characteristics of Ion Exchange Resins

Physically, ion exchange beads have either a dense internal structure with no or minimal discrete pores, that is, gel (microporous) (0.5–20 nm) resins or macroporous (macroreticular) (20–200 nm) resins with multichanneled structure, as schematized in Fig. 1.6. The type of internal structure of the resins beads dictates the selection of an ion exchanger for a particular application. Macroporous resins, with their tridimensional matrix with high effective surface area, obtained by adding porogen (phase extender) during their production followed by its washing out leaving voids in the structure, facilitate the ion exchange process. Also, multichannel structure gives an access to the exchange sites for larger ions allowing the use of almost any solvent, irrespective of whether it is a good for resin solvation together with little or no change in volume upon solvent loss. This confers more rigidity to the resin beads and facilitates their removal from the reaction system. On the other hand, the presence of no discrete pores in the microporous beads leads to a limitation in the solute ions diffusion hindering the interaction with fixed ionic sites and leading to a slowdown in the reaction rates. However, these resins offer certain advantages such as less fragility, less required care in handling, faster in functionalization and applications reactions, and possessing higher loading capacities [20].

Cross-linking of the resins during the preparation step is an essential step toward inheriting toughness and insolubility to the resin. The level of cross-linking plays an important role in affecting the physical and chemical properties of the resins. For example, resins with very low degree of cross-linking tend to adsorb more moisture and change dimensions markedly depending on the type of ionic sites bound to polymer backbone. The main physical properties that get influenced by cross-linking mainly include (1) moisture content and (2) particle size, together with other associated properties such as pore size and morphology, surface area, and partial volume of the resins in a swollen state [4]. The moisture content, which is primarily a hydration of the fixed ionic groups, is a function of the degree of cross-linking and the type of functional group. Low degree of cross-linking in gel resins having sulfonic acid or quaternary ammonium groups allows absorption of large amounts of water resulting in remarkable resin swelling. Water swelling of resins leads to variation in their volume, which varies in turn with degree of hydration that depends on the attached counter (incoming) ion [21]. However, frequent swelling and subsequent contraction during drying may shorten the resins lifetime.

On the other hand, resin particle size causes an impact on their performance. For instance, smaller particles improve the kinetics of the ion exchange reaction but cause an increase in the water pressure drop leading to a decrease of the flow rate [19]. The chemical properties of resins involve ion exchange capacity, type of resin's matrix, and type and concentration of functional groups attached to backbone of the resin.

The stability (chemical, physical, and mechanical) and the behavior of the ion exchange resins depend primarily not only on the structure and the degree of cross-linking of the resin matrix but also on the nature and number of fixed ionic groups. The former determines the porosity of the matrix and accordingly the degree of swelling of the resin and the mobility of the counter ions through it, which in turn controls the rates of ion exchange in the resin. Furthermore, highly cross-linked resins are harder and more resistant to mechanical breakdown but with lesser swelling and counter ion accessibility. However, higher and lower cross-linked resins are also available with less or more water sorption capabilities. Therefore, the most desired combinations of properties in ideal ion exchange resins required of industrial applications are:

1. Fast kinetics, that is, speedy rate of exchange
2. High chemical stability
3. Physical stability in terms of mechanical strength and resistance to wear
4. Reasonable degree of cross-linking
5. Hydrophilic structure of regular particle size and reproducible form
6. Effective and lasting ion exchange capacity
7. Consistent particle size
8. Effective surface area compatible with the hydraulic design requirements for large-scale plant

Finally, it can be stated that the performance of ion exchange resins in terms of kinetics and sorption equilibrium depends on the physical and chemical properties of the resins.

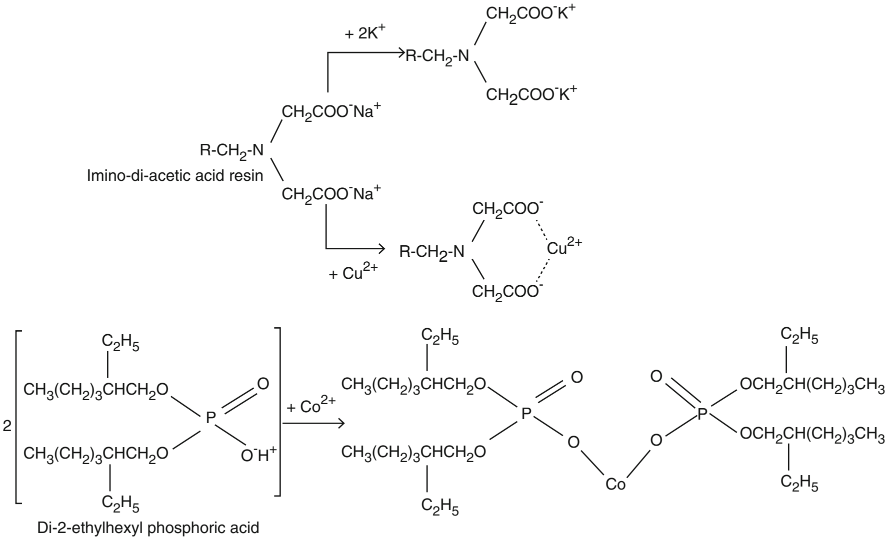


Fig. 1.7 Mechanisms of ion exchange in chelating resins

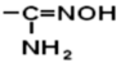
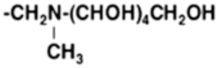
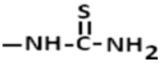
1.3.3 Special Ion Exchange Materials

1.3.3.1 Chelating Resins

Chelating or ligand exchange resins are considered as subgroup of normal ion exchange resins that bind counter ions by coordinate bonds interaction and sometimes by electrostatic interactions, as shown in the mechanisms in Fig. 1.7. Similar to common ion exchange resins, the chelating resins are insoluble in water as they have cross-linked matrix and are characterized by two components: polymer matrix, which provides the stability, and the functional groups, representing the ligands required for metal complexation. The most common coordinating atoms present in the main or side chains are N, O, P, and S in the forms of functional groups such as iminodiacetic acid and aminophosphoric acid, amidoxime, and thiol making the metal complexes, which their stability is a function of pH of the sorption medium. The principal active groups of chelating ion exchangers and their chemical formula are shown in Table 1.3.

Chelating resins have the same bead form and cross-linked polymer matrix as in normal ion exchange resins. They are mainly based on divinylbenzene-cross-linked polystyrene [22]. However, they differ from ordinary resins in their high selectivity toward certain metal ions in the sorption processes. Hence, it is possible to make chelating resins that have selective absorption capacity for certain metal ions by fixing desired ligand groups on the polymer backbone. For example, chelating polymers containing amidoxime groups were found to have high selectivity for uranyl ions and proposed for the recovery of uranium from seawater [23–26].

Table 1.3 Principal active groups of chelating ion exchangers and their chemical formula [76]

Chemical groups	Formula	Selectivity
Iminodiacetate	$-CH_2N(CH_2COOH)_2$	$Hg^{+} > Cu^{2+} > UO_2^{2+} > Pb^{2+} > Fe^{3+} > Al^{3+} > Cr^{3+} > Ni^{2+} > Zn^{2+} > Ag^{+} > Co^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Ba^{2+} > Ca^{2+} > Sr^{3+} > Mg^{2+} > Na^{+}$
Aminophosphonic acid	$-CH_2NHCH_2CH_2PO_3H$	$Th^{4+} > U^{4+} > UO_2^{2+} > Fe^{3+} > Be^{2+} >$ Rare earth $> H^{+} > Ag^{+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Na^{+}$
Thiol	$-SH$	$Ag^{+} > Cu^{+} > > Pb^{2+} > Cd^{2+} >> Zn^{2+} > Ni^{2+} > Fe^{3+} > Ca^{2+}$
Amidoxime	 $-\underset{NH_2}{\underset{\vert}{C}}=NOH$	Cu^{2+}, Ru^{6+}, Au^{3+}, Rh^{3+},V^{4+}, Pd^{2+}, U^{6+}, Pt^{2+}, Fe^{3+}, $Mo^{6+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+}$
N-methylglucamine	 $-CH_2\underset{CH_3}{\underset{\vert}{N}}-(CHOH)_4CH_2OH$	BO_3^{2-}
N-bis-picolylamine	$-CH_2N(CH_2-C_5H_4N)_2$	$Ni^{2+} > Co^{2+}$ at low pH
Triethylammonium	$-N(C_2H_5)_3^{+}OH^{-}$	NO_3^{-}
Thiourea	 $-NH-\overset{S}{\overset{\Vert}{C}}-NH_2$	$Hg^{+} < Cd^{2+}$

Upon use, the selectivity of chelating resins is based on the different stabilities of metal complexes at the appropriate pH values. Chelating polymers are very useful for the purpose of selective adsorption of certain metal ions from their mixtures, removal of metal ions, and recovery of soluble metal ions [27–29]. Adsorption of toxic metal ions using chelating polymers has the advantage of high efficiency, ease of handling, availability of different adsorbents, and cost-effectiveness. Thus, chelating polymers has a great importance in environmental applications including wastewater treatment [30, 31].

Chelating polymers can be divided into two classes: graft adsorbents and graft biosorbents. The former have side chains carrying functional groups attached to a synthetic matrix, whereas the functional groups are attached to biopolymer matrix (e.g., chitosan, alginate, and starch) in the latter [19]. Recently, a great attention has been paid for developing cheaper and effective sorbents based on various natural polymers to overcome the high cost of the synthetic resins. The recent progress in the development of biosorbents from various natural polymers and their applications in heavy metal and color removal from industrial wastewater can be found on other reviews [32, 33].

1.3.3.2 Affinity Ion Exchange Materials

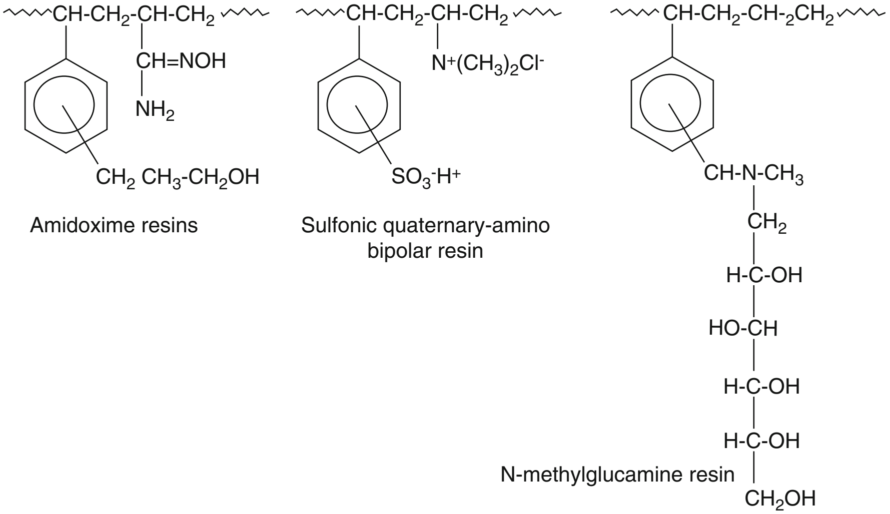
Affinity beads are porous particles having selective affinity ligands including immobilized biological or synthetic molecules attached to their pores. These beads have found a widespread application in separation and purification of biological macromolecules in both analytical and preparative scales in a variety of bioprocesses [34]. Among all, affinity (adsorption) chromatography, which provides an alternative technique to conventional chromatography, has proven its efficiency and time stability [35]. Such adsorption chromatographic techniques are often used for the isolation and purification of fermentation products [36]. They are also used to eliminate toxic effects on growth, reduce feedback repression of production, and ultimately extend fermentation time and product yield [37]. Column operations are commonly adopted for those applications, where affinity resins (beads) are used as chromatographic separation media. The selectivity of beads is largely a function of the three-dimensional geometry of the pores of the beads and occluded functional/ligand groups; therefore, both pore and chemical characteristics of the beads dictate the separation and adsorption capacity of the target compounds [38]. However, conventional packed beds have several major limitations: (1) the pressure drop across a packed bed is generally high and (2) the dependence on intraparticle diffusion transport of biomolecules such as proteins to their binding sites within the pores of such beads. Various chromatographic modes and techniques using beads selective for specific proteins have been introduced to enhance the protein separation and purification processes [39]. More details on the use of affinity resins and their recent progress in protein separation and purification can be found elsewhere [40, 41].

1.3.3.3 Amphoteric Ion Exchange Materials

Amphoteric or bipolar ion exchange materials are ion exchangers that have the ability to exchange cations and anions simultaneously with stoichiometric sorption of the whole dissolved salts. These polyions contain both cationic and anionic groups, or a combinations of groups such as $–SO_3^{-}H^{+}$ and $–N(CH_3)_2$ and –COOH and $–N^{+}(CH_3)_3OH^{-}$ laying back to back on a polymer backbone and also known as *ampholytic* polymers [42]. When ionic groups of opposite signs are incorporated into the same pendant groups, the material is called, depending on the structure of the pendant groups, a zwitterionic polymers or polybetaines. An example for preparation of cross-linked polyzwitterionic carboxybetaines based on the 4-vinylpyridine and divinylbenzene macromolecular supports can be found in Neagu et al. 2010 [43]. Zwitterionic polymers have high selectivity toward specific ionic species depending on the fixed ionic sites and are commonly used in selective separation as their corresponding amphoteric resins. The various trends in synthesis of functional polymer and the corresponding selective ion exchange polymers were early reviewed in Refs. [44] and [45].

1.3.3.4 Snake in Cage Ion Exchange Resins

Snake in cage represents a class bipolar polymeric ion exchangers having network structure in three dimensions with fixed charges and trapped linear polyelectrolytes of



Amidoxime resins

Sulfonic quaternary-amino bipolar resin

N-methylglucamine resin

Fig. 1.8 Some special ion-selective resins

the opposite charge, which have equal values and tend to neutralize each other. These ion exchangers can absorb both anions and cations of equivalent amounts simultaneously. A typical commercial example for this resin is *Retardion* 11-A-8 (Dow Chemicals Co.) [46]. The resin of such type is characterized by having the ionic groups of counter ions not attached to the matrix; thus, the changes in the counter ions and that of the matrix have more freedom to move relative to one another and hence may neutralize one another. As a consequence, it is not necessary for the resin to contain mobile ions to remain electrically neutral provided that the changes of the fixed ionic groups and counter ions are properly balanced [47]. These resins are excellent reversible sorbents of electrolytes. They are used for separation by ion retardation [4, 20]. Examples of special ion-selective resins are shown in Fig. 1.8. N-methylglucamine-containing resins (e.g., Amberlite IRA 743, Dowex XUS 43594, Purolite S 108, and Diaion WA 30) are boron selective [48–50], whereas amidoxime resin is selective for uranyl ions [51–53]. The latest developments and achievements of various ion-selective resins together with ordinary resins in terms of materials and applications have been reviewed by Alexandratos (2009) [54].

1.3.4 Ion Exchange Membranes

Ion exchange membranes is a class of ion exchange materials in a form of highly swollen polymer film carrying fixed charged chemical groups covalently bonded to the polymer backbone that can exchange their mobile ions for ions of similar charge from the surrounding medium [55]. Ion exchange membranes can be divided into (1) cation-exchange membranes, which contain negatively charged groups $\left(-SO_3^-, -COO^-, -PO_3^{2-}, -PO_3H^-\,and - C_6H_4O^-\right)$,

(2) anion-exchange membranes, which contain positively charged groups ($-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$ *and* $-SR_2^+$), and (3) bipolar (amphoteric) membranes containing both negatively and positively charged groups fixed to the polymer matrix in film/sheet forms.

The presence of fixed ionic groups (anionic or/and cationic) in the dense sheet-form structures confers these membranes their essential properties and infringes various interesting phenomena. The former is represented by ion exchange capacity and water uptake (swelling), both of which dictate the electrical resistance. The latter is marked by permselectivity of cations or anions through the membrane, generation of membrane potential and bi-ionic potential, ion conductivity, diffusion of electrolyte and nonelectrolyte through the membrane, water transport involving osmotic water and electroosmotic water, and salt rejection in the presence of hydraulic pressure [56]. Thus far, the separation behavior (cations from anions or vice versa from aqueous solution) of each type of these membranes is determined by the chemical nature of attached charged group, and thus, these membranes possess high permselectivity, that is, high preferential transport number for counter ions [57, 58].

Ion exchange membranes are also broadly classified into strong or weak acid cation-exchange membranes and strong or weak base anion-exchange membranes depending on the strength of the functional groups as explained in the corresponding ion exchange resins. In the amphoteric membranes, one side contains weak or strong anion-exchange layer and the other side possesses weak or strong cation-exchange layer. Ion exchange membranes can be also divided depending on the degree of heterogeneity into (1) homogeneous membranes, (2) interpolymer membranes, (3) microheterogeneous graft- and block-copolymer membranes, (4) chelating membrane, and (5) heterogeneous ion exchange membranes [59, 60]. Ion exchange membrane materials can be further divided into three large classes: (1) high molecular weight membranes based on polymer containing ionic moieties, (2) inorganic membranes, and (3) hybrid membranes composed of organic/inorganic materials [61].

Like their corresponding resins, affinity polymers in the form of membranes are also available. These membranes are capable of overcoming the shortcomings (e.g., fouling) associated with membrane operation based on sieving mechanism such as microfiltration and ultrafiltration. Affinity membranes have selective functional groups immobilized in the porous structure of a film that allow high flow rates to be achieved at low pressures, enabling the processing of large volumes (such as cell culture fluids) within short processing times compared to affinity beads [62]. Ideal film substrates used for affinity membranes should fulfill the following conditions: (1) proper pore structures and mechanical strength for use at high flow rates and low back pressure in rapid processing, (2) availability of reactive groups such as $–OH$, $–NH$, $–SH$, and $–COOH$ for the further coupling of spacer arms or ligands, (3) chemical and physical stability under harsh conditions of high temperature or chemical sterilization, and (4) hydrophilic surfaces to avoid any unspecific interaction between biomolecules and the membrane surface [63]. This has made affinity membrane, which combines a high processing rate with a selective affinity adsorption, proven to be more efficient than the classical column affinity method in chromatography [64].

Ion exchange membranes have been widely used in various industrial applications related to separation processes and ion-selective transport in many electrochemical processes and solid-state devices. The most famous membrane separation systems are utilizing diffusion dialysis, electrodialysis, pervaporation, and reverse osmosis, which operate based on concentration, potential, or pressure gradient as a driving force. Electrochemical devices using ion exchange membranes including fuel cells, batteries, and sensors are also available. To meet the requirements for such applications, ion exchange membranes have to essentially possess (1) low electrical resistance, (2) high ionic permselectivity, (3) moderate degree of swelling, (4) reasonable degree of cross-linking, (5) thermal resistance, (6) chemical stability, and (7) high mechanical strength. The various characteristics of ion exchange membranes and the diversity of their applications have been reviewed in literature on several occasions [60, 65–69].

1.4 Fundamentals of Ion Exchange Reactions

1.4.1 Ion Exchange Equilibrium and Selectivity

Ion exchange process depends on the mechanism by which mobile ions from an external solution are exchanged in the opposite direction for an equivalent number of ions that are electrostatically bound to the functional groups contained within a solid matrix of the ion exchange material.

The preference of one ionic species over another by the ion exchangers can be attributed to several causes [20]:

1. The electrostatic interaction between the charged framework and the counter ions depends on the size and valence of the counter ion.
2. Other effective interactions between ions and their environment.
3. Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

All these effects depend on the nature of the counter ion and thus may lead to preferential uptake of species by the ion exchanger. The ability of the ion exchanger to distinguish between the various counter ion species is called selectivity.

Metal ions initially contained in an aqueous solution are exchanged with ions initially contained in ion exchange materials. This process represents cation-exchange reaction that can be illustrated by the reaction:

$$\overline{R^-H^+} + A^+ \rightarrow \overline{R^-H^+} + H^+ \tag{1.1}$$

where R is ion exchanger and A^+ is a positively charged metal ion. The bars indicate the phase of the ion exchanger. The equilibrium constant (K) is given by the following formula:

$$K = \frac{[RA]}{[RH]} x \frac{[H^+]}{[A^+]} \tag{1.2}$$

The distribution of the two ions between the two solid and liquid phases (ion exchange material and external solution) depends on the reaction constant value. A similar reaction involving anions is called anion exchange:

$$\overline{R^+Y^-} + B^- \rightarrow \overline{R^+B^-} + Y^- \tag{1.3}$$

where B^- and Y^- are anions or negatively charged metal ions. The equilibrium constant (K) is given by the following formula:

$$K = \frac{[RB]}{[RY]} x \frac{[Y^-]}{[A^-]} \tag{1.4}$$

Ion exchange reactions are reversible and follow stoichiometry, as seen in the following reaction:

$$2(R - SO_3H) + NiSO_4 \leftrightarrow (R - SO_3)_2\mathrm{Ni} + \mathrm{H_2SO_4} \tag{1.5}$$

To achieve the removal of both positively and negatively charged ions from solution, a mixture of cation and anion exchanger in a mixed bed system is often used. Alternative, bipolar bed system can replace the cation and anion exchanger in a mixed bed system.

Unlike many other chemical separations, reactions 1 and 3 can be successfully used even if they are shifted to the opposite direction. By taking advantage of the fact that, under certain conditions, ion exchange media has a greater affinity for certain ionic species than for others, a separation of these species can be made. Chemical selectivity of reactions 1 and 3 is desirable but is not a requirement [4]. The selectivity (ion exchange) coefficient for reaction 1 expresses the relative distribution of the ions when a resin in the H^+ form is placed in a solution containing A^+ ions, whereas the selectivity coefficient for reaction 3 expresses the relative distribution of the ions when a resin in Y^- form is placed in a solution containing B^- ions. The selectivity coefficients for reaction (1) ($K_{H^+}^{A^+}$) and (3) ($K_{Y^-}^{B^-}$) are given by:

$$K_{H^+}^{A^+} = \frac{[A^+]_{\mathrm{Re\,sin}}}{[H^+]_{\mathrm{Re\,sin}}} \times \frac{[H^+]_{Solution}}{[A^+]_{Solution}} \quad \text{and} \quad K_{Y^-}^{B^-} = \frac{[B^-]_{\mathrm{Re\,sin}}}{[Y^-]_{\mathrm{Re\,sin}}} \times \frac{[Y^-]_{Solution}}{[B^-]_{Solution}} \tag{1.6}$$

The selectivity coefficients in ion exchange systems can describe the ion exchange equilibrium and provide a means of determining what to expect when various ions are involved. However, they are not constant and vary with the operation conditions such as types and properties of the resins, concentration of the feed solution, pH of the solution, temperature, and the presence of other competing ions in the solution [70].

When two ions have similar charge and ionic radii, the selectivity stemmed from the properties of the ion exchange material (acidity, basicity, and the degree of cross-linking) is not sufficient for performing effective separation. Therefore, an appropriate complexing agent has to be added to the aqueous phase to allow the selectivity to be attained through either the difference in the stability constants, the difference in charges, or the variation in the structures of the complexes formed. As a result, an increased selectivity can be achieved. However, the determination of selectivity coefficients is practically complicated task and is ordinarily not undertaken in the design of ion exchange processes such as wastetreatment systems. In fact most of these parameters can be extracted from manufacturers' data or research literature [1].

The rules of thumb that have to be considered for general design purposes when cationic polymeric ion exchange resins at low concentrations and normal waste processing, the selectivity typically increases with increasing charge on the exchanging cation in the order: $Li^+ < H^+ < Na^+ < K^+ < Cs^+ < Rb^+ < Ag^+ < Be^{+2} < Mg^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Ce^{3+} < La^{3+} < Th^{4+}$. Selectivity also increases with increasing the atomic number (decreasing hydrated ionic radii) of the exchanging cation in the order of $Li^+ < H^+ < Na^+ < K^+ < Cs^+$ (Li^+ is an exception, owing to its high hydration energy).

For anions, a typical series of selectivity is as follows: $F^- \approx OH^- < HCO_3^- < CH_3COO^- < Cl^- < HSO_3^- < Br^- < CrO_4^{2-} < NO_3^- < SCN^- < I^- < ClO_4^- < C_2O_4^{2-} < SO_4^{2-}$.

The ion exchange equilibrium can be also described in terms of the ion exchange isotherm, the thermodynamic equilibrium constant, and the distribution coefficient.

1.4.2 Ion Exchange Thermodynamics

The distribution coefficient (K_d) is a measure of the effectiveness of the ion exchange resins to remove particular ionic species (metal ion) from a liquid solution. It is defined as the ratio of metal ion concentration in the solid to metal concentration in the liquid. The K_d is generally determined with batch contacts between the exchanger and solution and is calculated according to the following formula:

$$K_d = \frac{(C_i - C_f)}{C_i} \cdot \frac{V_s}{m_e} \qquad (1.7)$$

where C_i is the initial concentration (before contact), C_f is the final concentration of metal in solution, m_s is the mass of exchanger used, and V_s is the volume of solution. The K_d is specific to the temperature and concentration of other ions in the solution. Systematic information of the K_d forms fundamental base from ion exchange process to be planned. High values of the distribution coefficient are always desirable. Changes in the physical parameters and the concentration of functional groups affect the K_d and can affect the driving force for the ion exchange process.

The K_d value is used in the following equation to determine the Gibbs free energy of adsorption ($\varDelta G^o$):

$$\Delta G^o = -RT \,.\, \ln \,.\, K_d \tag{1.8}$$

where ΔG^{o} is standard free energy change (J), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K).

1.4.3 Ion Exchange Kinetics

Kinetics of the ion exchange reaction represents the speed with which reaction takes place. Upon designing an ion exchange process system, the rate of exchange, which is subjected to mass-transfer resistances in both liquid and solid phases, is highly significant in the design and operation of the ion exchange process. The exchange rate has impact on the size of the ion exchange columns required and/or its flow rate. The kinetics of the ion exchange reaction is affected by the type and nature of the exchanger, solution concentration, and temperature at which the exchanger is operated.

When an ion exchange bead is brought into contact with a solution, a static liquid film of a thickness varying in the range of 10–100 nm depending on the rate of flow of liquid passes the particle, is formed around it. The ion exchange process taking place between the resin particle and the solution involves six distinct steps; any combination thereof can be the rate controlling step. They are [4, 20]:

1. Diffusion of counter ions through the bulk solution surrounding the bead
2. Diffusion of counter ions through the hydrated film of solution that is in close contact with the bead matrix
3. Diffusion of counter ions within the bead matrix
4. The actual ion exchange reaction
5. Diffusion of the exchanged species out of the ion exchange bead
6. Diffusion of the exchanged species from the bead surface particle into the bulk solution

It is noteworthy mentioning that the concentration differences that might occur in the bulk solution are constantly leveled out by agitation, which disturbs the necessary transfer by convection. Nonetheless, agitation neither affects the interior of the beads nor the thin liquid film, which adheres to the bead surfaces. The ion transfer takes place within the beads and through the thin film only by diffusion, and as a result, the actual ion exchange reaction occurs very quickly and is not generally considered to be rate limiting. Thus, the rate-determining step is either the interdiffusion of counter ions within the ion exchanger itself (particle diffusion) or interdiffusion of counter ions in the adherent film (film diffusion). In practice, either step can be the rate-determining step. However, the slower of these two steps controls the overall reaction rate. In intermediate cases, the rate may be affected by both steps [4]. Moreover, the particle size of the resin being used is also a determining factor. Uniform particle-sized resins exhibit enhanced kinetic performance compared to conventional polydispersed resins due to the absence of kinetically slow larger beads. Recent studies showed that ion exchange resins in fibrous forms have improved the kinetics allowing greater adsorption of toxic and precious metals [71, 72].

It is important to mention that in systems with ion exchange through organic solvents, the transfer of the counter ions in the resin is usually lower than in aqueous systems because swelling is less pronounced and electrostatic interactions with the fixed charges are stronger. Particle diffusion, thus, is relatively slow and, hence, usually controls the rate-controlling mechanism [2]. Finally, the actual rates of ion exchange can vary over a wide range, requiring a few seconds to several months to reach equilibrium.

1.4.4 Exchange Capacity

Capacity of the ion exchange materials is a significant chemical characteristic that is defined as the number of counter ion equivalents that can be adsorbed in a specified amount of ion exchange material. The ion exchange capacity and related data are primarily used for (1) describing the total available exchange capacity of ion exchange materials and (2) the use in the numerical predesign calculations of ion exchange processes. This value is expressed in milliequivalents per gram (meq/g) or milliequivalents per milliliter (meq/mL) based on the dry and wet weights of the material in a given form (H^+ or Cl^-), respectively. The capacity of the resins can be described in various ways depending on the conditions. For example, maximum ion exchange capacity (meq/g dry H^+ or Cl^- form) is represented by the total static exchange capacity when it is determined under static conditions, whereas the dynamic or volume-exchange capacity (eq/L packed bed in H^+ or Cl^- form and fully water-swollen) is determined by passing a solution through a bed of the exchanger. The extent of the use of the total exchange capacity depends on the level of ionization of the functional groups of the exchanger together with the chemical and physical conditions of the process. The total dynamic capacity can be also expressed as breakthrough capacity, which characterizes the column operation and depends on (1) column design and operating parameters, (2) the concentration of the ions being removed, and (3) the effects of interference from other competing ions.

Under dynamic conditions, in which the ion exchange resin is used in a packed bed or a column, the distribution coefficient K_d can be used to calculate the theoretical maximum capacity of the ion exchange bed in terms of weight. If the bed includes m (kg) of ion exchange resin, the total capacity of the bed V_{tot} can be calculated as:

$$V_{tot} = K_d \times m \tag{1.9}$$

In water purification, the volume of each type of the resins can be determined as a function of the operating time chosen between two regenerations using the calculated operating capacities:

$$V = (Q\ .\ t\ .\ S)/C \tag{1.10}$$

where

V = resin volume, m^3
Q = flow rate, m^3/h
t = operating time, h
S = salinity to be adsorbed by the resin, eq/m^3 of water or meq/L
C = operating capacity of the resin, eq/m^3 of resin

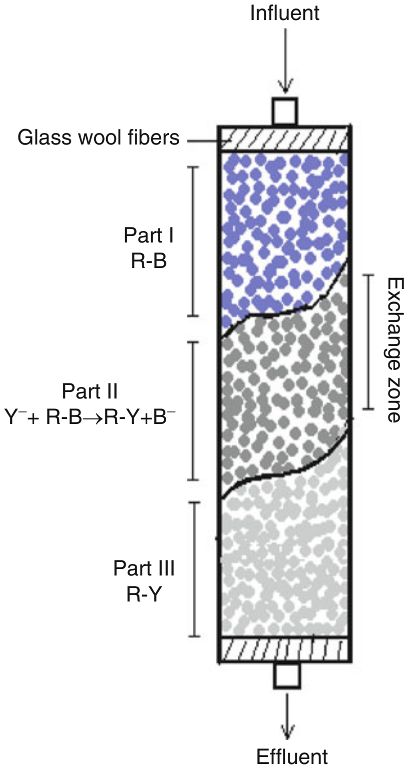
In column operation, the total capacity or breakthrough capacity generally refers to the volume of the solution that can be treated before a sharp increase in the effluent concentration of the ionic species being removed is observed. At this point, the ion exchange medium is considered to be exhausted and must be replaced or regenerated. This trend can be clearly seen in the column schematic representation shown in Fig. 1.9. Part I refers to the resin, which has finished exchange reaction; part II refers to the exchange zone in the resin, which is working until it moves downward with the continuous flow of Y^- ions (ion to be removed); and part III represents the zone in which the resin is exhausted and Y^- ions completely break through the resins [73].

Thus, the performance of ion exchanger is measured by comparing the solution concentration or conductivity of both influent and effluent, which can be monitored in terms of ion-exchanger effectiveness known as *decontamination factor (DF)*, which is defined as a ratio of the concentration (or activity) of the fluid at the inlet compared to the concentration (or activity) at the effluent (Eq. 1.11), which expresses the effectiveness of an ion exchange process.

$$DF = \frac{\text{Influent concentration or conductivity}}{\text{Effluent concentration or conductivity}} \tag{1.11}$$

In practice, the operator of the ion exchange system has to have a requirement for DF. For example, if the decontamination factor requirement is 100, the ion exchange bed has to be replaced when 1% breakthrough occurs. Therefore, the breakthrough capacity is practically the most interesting parameter in the design of a column type ion exchange system and is generally given as the number of bed volumes (the ratio of the volume of the liquid processed before the breakthrough point to the volume of the settled bed of the exchanger).

Fig. 1.9 Schematic diagram of ion exchange column



A typical breakthrough curve is shown in Fig. 1.10. The points C_o and C_x are the concentrations of Y^- in the influent and effluent, respectively. The breakthrough begins at point *c*, and the extent of breakthrough increases until point *e* (end point) beyond which no further ion exchange takes place (i.e., a complete exhaustion point of the column). The breakthrough capacity is proportional to the area *abcd* and so is the overall capacity to the area *aecd*. The shape of the breakthrough curve and the breakthrough capacity (i.e., the total liquid volume treated up to a particular percentage breakthrough) depend on the operating parameters.

Some important parameters that affect the breakthrough capacity include [1, 4, 20, 73]:

1. The nature of the functional group on the exchanger
2. The ion exchange medium grain size
3. The degree of cross-linking of the resins
4. The concentration and type of ions in the solution to be treated
5. The flow rate of the feed solution
6. The rate of percolation
7. Depth of the resin bed
8. Type, concentration, and quantity of regenerant

In practical operations, it is desirable to have the breakthrough curve as steep as possible to increase the extent of column utilization (i.e., bringing the ratio of the

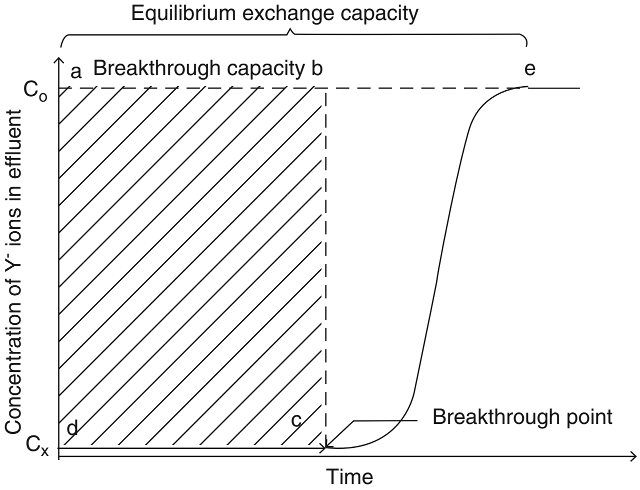


Fig. 1.10 Schematic representation of breakthrough curve

breakthrough capacity to the total capacity closer to unity). It is worth noting that upon requirement of high DF, the degree of column utilization can vary considerably for different ion exchange resins.

1.5 Ion Exchange Process Equipment and Operation

The feasibility and success of ion exchange processes depend on the nature of the ion exchange material and its process operating conditions. For instance, the morphology and type of the ion exchanger dictate the selection of the process configuration and its operating mode. As mentioned earlier, the basic morphologies of ion exchange materials include resins or beads, membranes, fibers, and hydrogels. To bring such polymer forms into applications, they have to be hosted in a proper engineering system that provides a set of adjustable operating parameters to control their performance. Accordingly, the ion exchange systems take various configurations depending primarily on the physical form of ion exchange material, as indicated in Fig. 1.11 which depicts a schematic representation of various morphologies of ion exchangers and their respective operating systems. In addition, the volume of the solution to be treated and the concentration of the ionic species to be separated also play a role in selection of system configuration but to lesser extent.

1.5.1 Cycle of Ion Exchange Process

When ion exchangers are in a resin form, the separation is conventionally accomplished by either batch or column method. Most commonly, the ion

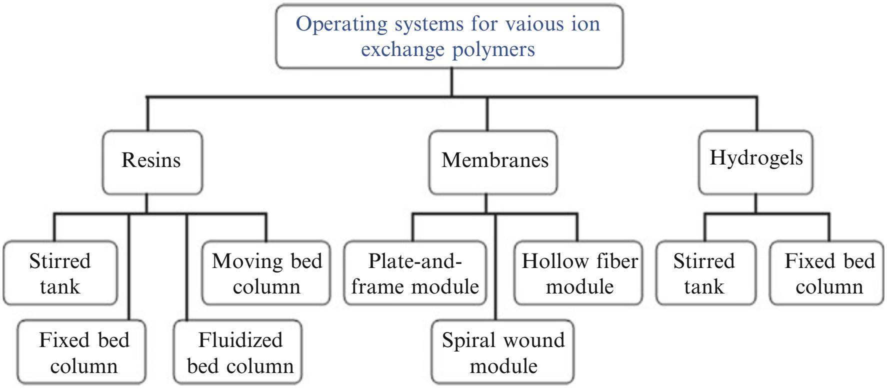


Fig. 1.11 Various operating configurations for different morphologies of ion exchange materials

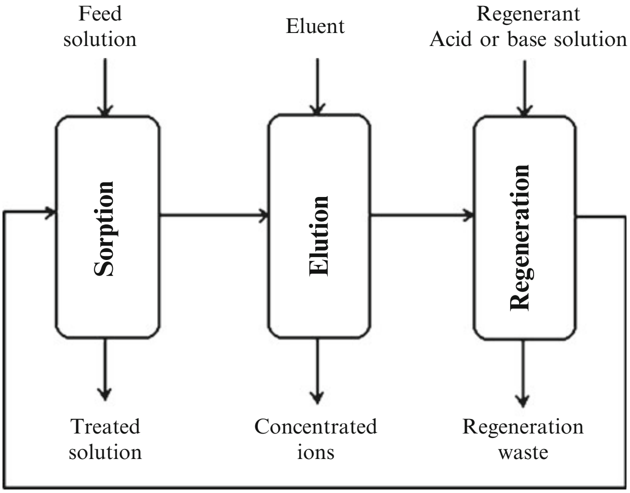


Fig. 1.12 Schematic representation of ion exchange operation cycle

exchange is performed in cyclic operations. Each cycle is divided into three main stages: (1) sorption, (2) elution, and (3) regeneration, as shown in the ion operation cycle schematized in Fig. 1.12. Details of ion operation cycle are as follows:

1. Sorption: The solution containing the targeted ions is passed slowly through to reaction vessel. The ions bind into the resins. Ions initially contained in the exchanger are released.
2. Elution (stripping): The target ions are subsequently stripped from the loaded resin with a small volume of an eluent. The eluent replaces and hence also releases the target ions from the resin into the solution phase.
3. Regeneration: The principle of displacement of selectively binding ions by less selective binding ion is the basis for each regeneration procedure. Depending on

the type of the ion exchanger and the stripping agent, most of the ion exchanger can be regenerated by acids (excess of H^+ ions), salt-brines (excess of sodium or chloride ions), or alkali (excess of OH^- ions). During regeneration, the adsorbed ions are removed and replaced by suitable ions. For example, if the sorption step uses a cation exchanger loaded with H^+ ions but the elution leaves Na^+ ions in the exchanger phase, the material has to be protonated. A strong acid could be applied in order to convert (regenerate) the exchanger in the initial state. It is important to mention that designing an optimized cyclic ion exchange process requires efficient utilization of bed through selection of resins having high selectivity toward the target ions.

1.5.2 Operating Configurations of Ion Exchange Processes with Resins

Upon utilization of ion exchange process, solution (influent) is pumped through a vessel loaded with the ion exchange resin and represents one of four basic operating configurations (1) continuous stirred (batch) tank, (2) fixed bed column, (3) fluidized bed column, and (4) a moving bed (closed loop) system.

In a batch method, the resin and solution are mixed in a batch tank, the exchange reaction is allowed to come to equilibrium, and then the resin is separated from the solution. The degree to which the exchange takes place is limited by the preference the resin exhibits for the target ions in solution. Consequently, the use of the resin's exchange capacity is limited unless the selectivity for the ions in solution is far greater than for the exchangeable ion attached to the resin. Because batch regeneration of the resin is chemically inefficient, batch processing by ion exchange has limited potential for industrial applications and often used in laboratories for fundamental sorption equilibrium and kinetic studies [74].

The fixed bed column operation is the most usable ion exchange configuration in industrial applications. It has a basic component of which the bead column is considered to be analogous of several batch reactors in series [1, 4]. The purpose of the column operation is to work around the limitation of selectivity of the resin. To favor high selectivity, more stages can be used (multicolumn system). Three types of column operation modes are available: (1) down flow, (2) up flow, and (3) counterflow. Most column beds operate with down flow operation, as shown in Fig. 1.13 that depicts a schematic representation of fixed bed ion exchange column system with operation and regeneration modes. This is where feed and beads pass down through the resin bed. On the contrary, up flow operation is used when the feed and resin are raised through a bed. The final flow is counterflow, and it consists of the feed flowing down from the top and the regenerate flows up from the bottom. Most industrial applications of ion exchange use fixed bed column systems, the basic component of which is the resin column.

Ion exchange column is typically applied in a pressure vessel, as shown in Fig. 1.14. It is equipped with appropriate internal plumbing that has two purposes:

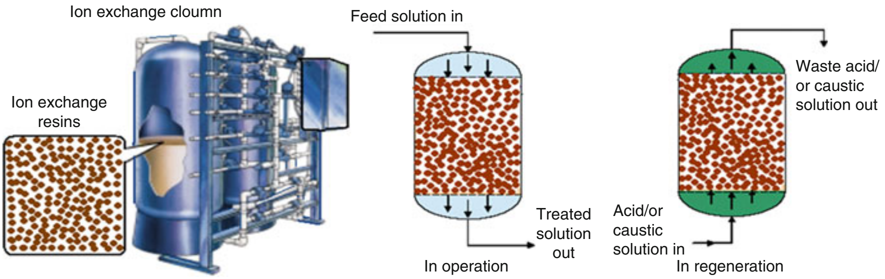
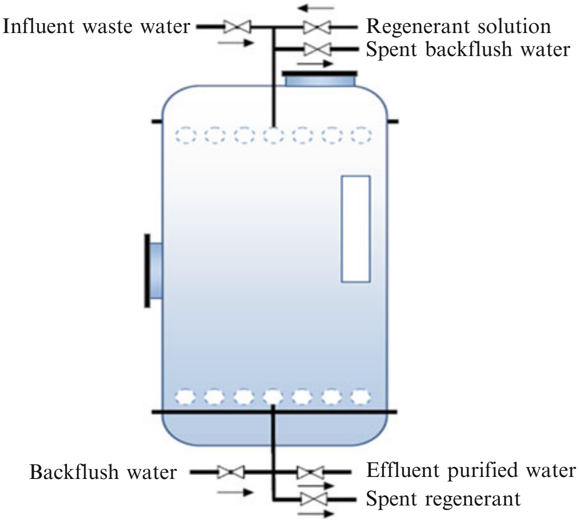


Fig. 1.13 Schematic representation of fixed bed ion exchange column system showing operation and regeneration modes

Fig. 1.14 Typical structure of ion exchange column [Reproduced from Ref. [1] with kind permission of © Wiley-VCH Verlag GmbH & Co (2005)]



(1) it prevents the ion exchange resin from being washed out of the vessel and (2) it provides an appropriate distribution of liquid flow through the ion exchange resin bed. The internal system is a corrosion-resistant screen mounted above a porous backing plate. The pressure vessel is also equipped with slit nozzles (strainers), piping, and fittings to maintain low pressure drop. During the operation, the pressure vessel is filled to only half of its volume with the empty space above the ion exchange resin bed (called freeboard) to allow free volume for swelling and shrinking during operations of exhaustion and regeneration.

In summary, the column design must consider the following [1]:

1. Contain and support the ion exchange resin.
2. Uniformly distribute the service and regeneration flow through the resin bed.
3. Provide space to allow the resins to swell, shrink, and be fluidized during backwash.
4. Include the piping, valves, and instruments needed to regulate flow of feed, regenerant, and backwash solutions.

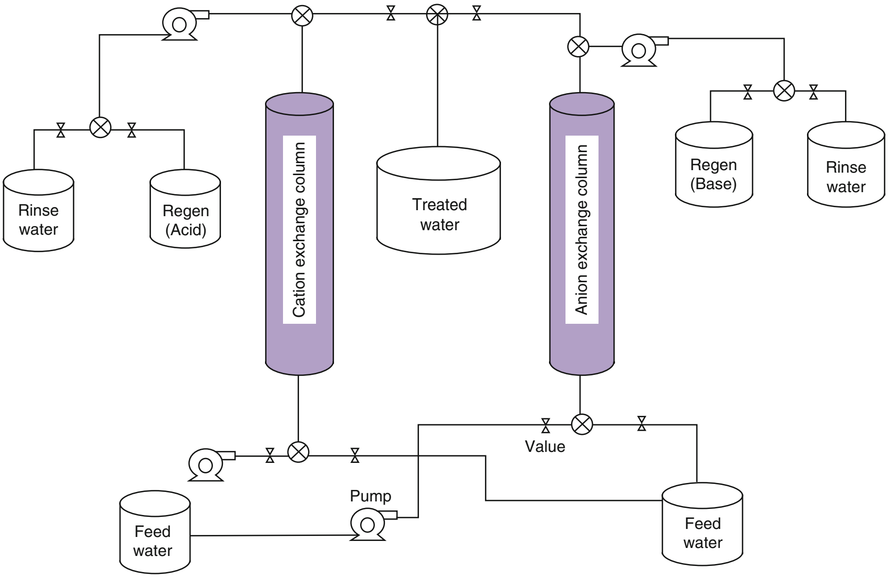


Fig. 1.15 Schematic diagram of a laboratory scale ion exchange column system

The operating or breakthrough capacity of an ion exchange column system depends on its design and operating parameters, the concentration of the ions being removed, and the effects of interference from other ions. In a column system, capacity generally refers to the volume of the solution that can be treated before a sharp increase in the effluent concentration of the species being removed is observed. At this point, the ion exchange medium is considered to be spent and must be replaced or regenerated. The operating or breakthrough capacity is the most significant parameter in the design of a column-type ion exchange system and is generally given as the number of bed volumes (the ratio of the volume of liquid processed before the breakthrough point to the volume of the settled bed of the exchanger). Some important parameters that affect the breakthrough capacity include (1) the nature of the functional group on the exchanger, (2) the degree of cross-linking of the resins, (3) the concentration of the solution to be treated, (4) the valence and the size of ions to be exchanged, and (5) the operating temperature. Figures 1.15 and 1.16 show a schematic diagram and picture, respectively, of a laboratory-scale fixed bed column ion exchange system. In practical operations, it is desirable to have the breakthrough curve as steep as possible. A steeper breakthrough curve will increase the extent of column utilization, that is, to bring the ratio of the breakthrough capacity to the total capacity closer to unity as early mentioned. If the required decontamination factor is high, the degree of column utilization can vary considerably for different ion exchange media.

The fluidized bed column operation is used when the raw feed contains suspended solids. The column is partially filled with the ion exchange beds. The feed solution flows down up through the bed with a speed sufficient to push up the

Fig. 1.16 Picture of a laboratory scale ion exchange column system schematized in Fig. 1.15

beads up into the column causing them to float and swirl around. The floating of the ion exchange beads reduces the hydrodynamic resistance of the column. The presence of free-pass ways between beads allows the solid suspended particles to be transferred through the column giving fluidized bed column the advantage of processing solid-containing solution without any pretreatment. Therefore, fluidized beds are commonly used for biochemical filtration such as fermentation broth where treated solutions are highly contained with suspended solids.

The moving beds are the most economical beds of ion exchange systems. The principle of this operation relies on bringing the beads and the solution to flow through the system. The beads are contacted countercurrently with the exhausting and regenerated streams. The advantage of this operation is featured by continuous product of uniform quality at less space, capital, and labor. However, the

Table 1.4 Comparison between the advantages and disadvantages of various ion exchange systems

System configuration	Advantages	Disadvantages
Batch system	Simple to construct and operate Good for small-scale applications A wide variety if ion exchange media can be used Easy to be customized for specific treatment problems Operate with resins of various shapes	Manual operation may be cumbersome to operate with large volumes of waste The separation of liquid and ion exchange media is required Can only be operated at atmospheric pressures and ambient temperatures Once through use only
Conventional column system	Good throughput Simple to operate A wide variety of media are available Can be operated at elevated temperatures and pressures High decontamination factors are possible	Large equipment can be costly The regeneration of media may require extra equipment There are difficulties in transporting inorganic ion exchangers through pipelines Cannot treat solid-containing solutions and thus prefiltration is necessary Limited part of the bed particle is involved in ion exchange in the same time
Moving bed system	The process is continuous Very high decontamination factors Less operation space Requires less number of supplementary equipments Low pressure drop Can treat solid-containing solution without bed plugging	Instability of the process Longitudinal mixing problem Difficulty in providing circular motion Extensive mechanical deterioration of resin beads
Membrane system	Can be used either as a waste treatment or fluid concentration technique Prefiltration is not necessary Does not need granular materials High decontamination factors are possible	Equipment can be costly to construct and operate on a large scale

complexity of the design poses a problem during operation. Comparison between the advantages and disadvantages of various ion exchange systems is presented in Table 1.4.

With the wide number of resin types available in the marketplace, it is probable that there is more than one technically effective solution that will meet all the system's design specifications. This is where experience and knowledge are required to help selecting a system design suitable for the separation expected by the customer under the conditions existing at the desired site. This experience includes a thorough knowledge of all available resin types along with their various advantages and disadvantages so they can be applied in ion exchange systems that are both technically sound and cost-effective. Sound equipment design, effective use of available resins, and readily available services that meet all the expectations of the industrial customer will lead to a win/win long-term customer relationship that benefits both the supplier and the customer.

1.5.3 Operating Configurations of Ion Exchange Membrane Processes

Putting ion exchange membrane into practical application requires the membrane to be housed in a vessel called module. Membrane module provides support and protection against operating pressures (if any) and daily wear and tear of a production environment and allows applying control strategy over the system performance. More detail on the requirements for efficient module designs to house various membrane types can be found elsewhere [75]. The most common configurations of membrane modules are (1) plate and frame, (2) spiral wound, (3) tubular, and (4) hollow fiber. Among all, plate-and-frame module is the most common module used in ion exchange membrane processes.

Plate-and-frame module consists of layers of membranes separated by corrugated structural sheets. Corrugations run at right angles in alternating layers with feed material flowing in and retentate flowing out in one direction, while a carrier fluid flows in and permeate out in the other direction. Advantages of this system include ability to accommodate low levels of suspended solids and viscous fluids and the ability to change out membranes if needed (though it is not difficult). Disadvantages of this module include relatively low packing density, high initial cost, and difficulty of cleaning. The common uses for this module configuration are in electrodialysis and electrochemical membranes; other membrane types may be differently configured [65, 68]. Based on their applications, ion exchange membrane processes can be classified into five categories:

1. Mass separation processes such as electrodialysis, diffusional dialysis, and Donnan dialysis
2. Chemical synthesis processes such as chlorine-alkaline electrodialysis and production of H_2 and O_2 by water electrolysis
3. Catalysis processes such as inversion of sugar and production of biodiesel
4. Energy conversion and storage processes such as fuel cell and batteries
5. Sensing and stimuli-response such as sensors and actuators

Potential applications of novel ion exchange membrane-based processes, their state of development, and possible advantages and experienced problems were summarized in Table 1.5. More details on various ion exchange membrane processes and their fundamental operation and essential process parameters can be found in Refs. [65] and [67].

Table 1.5 Potential applications of novel ion exchange membrane-based process, their state of development, and possible advantages and experienced problems [65, 67]

Applications	State of process development	Potential advantages	Problems related to application
Electrodialysis with bipolar membranes: Production of mineral acids and bases from corresponding salts	Pilot plant operation	Lower energy consumption	Contamination of products and low current utilization due to poor membrane permselectivity
Recovering/producing of organic acids from fermentation processes	Commercial and pilot plant operation	Simple integrated process, lower costs	Unsatisfactory membrane stability and fouling application experience
Removal of SO_2 from flue gas	Extensive pilot plant test	Decreased salt production, reduced salt disposal costs	High investment costs, long-term membrane stability
Recovering and recycling of H_2SO_4 and NaOH from wastewaters, such as the rayon production effluent	Laboratory and pilot plant tests, some commercial plants	Purity of the recovered products is not critical, savings in chemicals and sludge disposal costs	No long-term experience, membrane stability under operating conditions, membrane fouling, high investment costs
Recycling of HF and HNO_3 from steel pickling solutions	Commercial plants	Cost savings due to recovered acids and decreased salt disposal	Relatively complex process, high investment costs
In food industry	Laboratory and pilot plant tests	Fewer by-products, less chemicals, and salt production and disposal	Application experience, process costs, investment costs
Energy storage: Battery separator	Commercial plant	Economical advantages, enhanced efficiency, and button battery production	Uses only radiation-induced grafting method and process cost
Energy conversion: Polymer electrolyte membrane fuel cell Direct method fuel cell	Extensive laboratory and pilot tests	High efficiency and power density	High cost of membranes and performance at 80°C

Production of sodium methoxide from methanol	Laboratory tests	More economic than conventional production process	No long-term experience
Elector-deionization and ultra-pure water production	Commercial plants	Continuous process without by-products, high efficiency	Higher investment costs, waste disposal, care pretreatment
Electrodialysis and membrane electrolysis	Commercial plants	Continuous process, high efficiency	High investment costs, membrane stability and selectivity
Electrodialysis and reactor: Denitrification of drinking water, fermentation process	Pilot plant tests, some commercial plants	Continuous process, high efficiency	Membrane stability and selectivity, relatively complex process
Electrodialysis and filtration: Waste recovery	Commercial plants	Continuous process, more compacted process	Relatively complex process, connection with care for each process

1.6 Selection of Ion Exchange Materials and Systems

Selection of ion exchange materials and system is a crucial step toward achieving the economic and technical goals of treatment. To summarize the process of selection of ion exchange materials, system configuration, and operating mode, three major factors have to be carefully taken into account: (1) Waste characteristics where the concentration of total suspended solids in the waste should be less than 4 mg/L and the total dissolved salts content is less than 1–2 g/L. (2) Ion exchange material and system where the selection of appropriate materials (resin, hydrogel, or fibers) depends on the needs of the system. The ion exchange media must be compatible with the chemical nature of the waste (such as the pH and type of ionic species present) and the operating parameters, notably temperature and pressure. However, if there are large concentrations of chemically similar ions in the waste, the process of selection becomes more difficult. (3) Cost consideration where the total cost of operating a process is the sum of the capital costs, the initial cost of the ion exchange media, the operating costs, and the costs associated with the treatment and disposal of the exhausted ion exchange resins. The total costs can be reduced by a frequent regeneration of the exhausted ion exchange resin instead of using it once through process.

A good ion exchange system designer not only will design the system to meet all design specifications but also will utilize resins that will allow the system to operate at peak efficiency and maximum cost-effectiveness. The presence of a wide number of commercial resins available in the marketplace gives high possibility for finding more than one technically effective solution to meet all the system's design specifications.

1.7 Advantages of Ion Exchange Processes

The widespread applications of ion exchange processes in various industrial aspects are supported by a combination of various advantages including the following:

- Proven ability to remove variety of impurities from various volumes with the availability of a wide number of resins.
- Tolerance for fluctuating feed flow rates.
- Low energy consumption.
- Accumulated experience that provides technically effective solutions that meet all system's design specifications.
- Large varieties of specific resins are available from suppliers. Each resin is effective in removing specific contaminants.
- Fast reaction and simple process operation.
- Can be operated at a high flow rate.
- The discharged effluents can achieve regulator acceptance.

- Cost-effectiveness which can be further improved by technical innovation including introducing cheap and highly tolerant ion exchange materials.
- The regenerant chemicals are cheap, and if well maintained, resin beds can last for many years before replacement is needed.

1.8 Limitations of Ion Exchange Process

Despite the extendable and diverse uses of the ion exchange process applications, there are a number of limitations which must be taken into consideration very carefully during the design stages. They include:

– High levels of suspended solids (greater than 10 ppm) and oil together with grease in wastewater may cause clogging of nonselective resins.
– Waste brine from regeneration step requires treatment and disposal, though waste volume can be reduced.
– Spent nonselective resins require frequent replacement and careful disposal.
– Competitive uptake by other ions may limit the effectiveness of nonselective exchange resins.
– Effectiveness of treatment is strongly influenced by water chemistry of the site (e.g., the presence of competing ions and pH of the water source).
– Oxidants present in the ground water may damage the ion exchange resin.
– Usually not feasible with high levels of total dissolved solids (TDS).
– Pretreatment required for most surface water treatments.
– Wastewater is generated during the regeneration step, and it requires additional treatment and disposal.

1.9 Economy of Ion Exchange Processes

Ion exchange has long been proven to be capable technology for removing many dissolved contaminants from various streams despite concerns over capital cost. Capital and operational costs for ion exchange systems vary depending on a number of factors, such as the effluent discharge requirements, the volume of water to be treated, contaminant concentration, the presence of other contaminants, type of utilized resin and regenerant utilization, brine disposal, and site-specific hydrological and geochemical conditions. Among all, the key cost factors include (1) pretreatment requirements, (2) discharge requirements and resin utilization, (3) regenerant used, and (4) efficiency.

The economy of the ion exchange process in an application can be optimized by [4]:

1. Selection of the right process based on the feed composition and the requirement of effluent to be discharged

2. Selection of the type of ion exchange materials based on raw solution characteristics and optimum combinations of the operating parameters
3. Selection of sorption and elution conditions taking into consideration that
    - (a) Sharper sorption front allows more efficiency in bed utilization
    - (b) Higher pumping rates allow higher productivity per unit time
    - (c) Higher concentration in the effluent causes more regeneration time
4. Optimization of regeneration including the type of regeneration agent and the degree of regeneration and the reuse of incompletely exhausted regenerating solution
5. Utilization of waste solution

The economy of the ion exchange processes can be further improved by process innovation. Particularly, introducing new ion exchange materials with low cost and high tolerance to feed concentrations are key issues in boosting cost reduction and expanding the usage of the technology to new frontiers. Also, introducing computer software and automation help very much to enhance the ion exchange process efficiency.

1.10 Applications of Ion Exchange Processes

The applications for ion exchange processes are numerous and cover wide range of industries and house appliances. The purpose of separation dictates the selection of the type of the ion exchange materials, their physical form, and system configuration for practical application and thus forms the basis of a large number of ion exchange processes, which can be functionally divided into three main categories [1]:

1. Substitution: A valuable ion (e.g., copper and silver) can be recovered from solution and replaced by worthless one. Toxic ion such as cyanide can be similarly removed from solution and replaced by nontoxic one.
2. Separation: A solution containing a number of different ions passes through a column containing beads of an ion exchange resin. The ions are separated and emerge following the order of their increasing affinity for the resin.
3. Removal: By using combination of cation-exchange resin (in the H^+ form) and an anion-exchange resin (in the OH^- form) or bipolar resins, all ions are removed and replaced by water (H^+OH^-). The solution is thus demineralized.

Despite the diversity of ion exchange processes, their chief application of today is still the treatment of water with the principle offering of unlimited possibilities in other fields. Commercial ion exchange installations are serving in water and water treatment, food, and chemical industries include processes such as purification of sugar solutions, separation and purification of drugs and fine chemicals, purification of waste effluents, and the recovery of valuable wastes, for example, in the metallurgical industries, the extraction and quantitative separation of elements