Ion Exchange for Pollution Control

Volume II

Editors

Calvin Calmon

Harris Gold

50.95519
C517
2:2

Ion Exchange for Pollution Control

Volume II

Editors

Calvin Calmon

Environmental Consultant
Princeton, New Jersey
and
Partner, Water Purification Associates
Cambridge, Massachusetts

Harris Gold

Partner, Water Purification Associates
Cambridge, Massachusetts

2

Editor-in-Chief
Water Pollution Control Technology Series

Richard Prober

Adjunct Professor
Department of Chemical Engineering
Case Western Reserve University
Cleveland, Ohio

CRC PRESS, INC.
Boca Raton, Florida 33431

Library of Congress Cataloging in Publication Data

Main entry under title:

Ion exchange for pollution control.

Bibliography: p.
Includes index.
1. Sewage--Purification--Ion exchange process.
I. Calmon, Calvin. II. Gold, Harris. III. Series.
TD757.5.155 628'.3 78-13258
ISBN 0-8493-5153-7 (v. 1)
ISBN 0-8493-5154-5 (v. 2)

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

© 1979 by CRC Press, Inc.

International Standard Book Number 0-8493-5153-7 (Volume I)
International Standard Book Number 0-8493-5154-5 (Volume II)

Library of Congress Card Number 78-13258
Printed in the United States

FOREWORD

These volumes in the Uniscience series on Water Pollution Control Technology are a comprehensive report on applications of ion exchange to treatment of wastewater. They cover existing applications, and by extension of fundamental principles, they show the basis for innovative technology. The authors have been principals in the development of ion-exchange materials and process technology.

Our objective in these volumes and in subsequent volumes of the series is to provide a reference manual for design engineers, planners, and managers in industry and government. This is particularly important in the present critical period for implementation of water pollution control.

Richard Prober
Cleveland, Ohio
July 21, 1978

61276

PREFACE

There are many books on ion exchange dealing with general subject matter and special topics such as the role of ion exchange in analytical, organic, and biochemical applications. While some aspects of ion exchange in pollution control were discussed in these texts, especially with reference to the removal of toxic heavy metals, the purification of metal plating baths, and the recovery of metal ions from metal plating rinse waters, the subject as a whole was never covered. In view of the emphasis in recent years on pollution control, the application of ion exchange in this endeavor has grown so a book on the subject itself is timely.

The aim of these volumes is not to cover all phases of ion-exchange theory, which may be found in in general texts, nor to cover every application in the literature, or to show an engineer ways on how to become an expert in the field so he could "do it all by himself". The main purpose of these books is to show the practical engineer what has been done in various types of applications of ion-exchange processes in pollution control, how to set up laboratory tests, the problems that may be encountered, to identify the individuals and organizations who are experts in the various phases of ion exchange, and most importantly, to emphasize the new developments in polymers with active sites that offer new approaches to wastewater treatment methods.

These books contain over forty chapters written by researchers and engineers from the industrial, academic, and research communities in the United States, United Kingdom, Australia, Canada, and Poland. The books are divided into six major sections:

General Aspects — Twelve chapters dealing with the ion-exchange process, ion exchangers, equipment, systems, and economic factors.

Inorganic Applications — Seven chapters dealing with the removal of heavy metals and ammonia and nitrate recovery from a variety of wastewaters.

Organic Applications — Contains four chapters on base recovery from spent sulfite liquors, decolorizing wood pulp bleaching effluents, and the use of polymeric adsorbents.

Other Applications — Seven chapters involving the treatment of effluents from nuclear and municipal treatment plants, agricultural wastewaters and the use of ion exchange for laboratory and analytical evaluations.

Uses of Polymers with Active Sites — Three chapters covering coagulants, dewatering agents, and dispersants.

New Developments — Ten chapters dealing with novel exchangers and processes developed in the last decade.

In addition, the volumes contain a bibliography of ion-exchange text books, a listing of ion exchanger and equipment manufacturers, and special tables of data. We have broadened the aspect of the subject to include polymeric polyelectrolytes as we feel it is an extension of ion exchange, and future developements in this field for wastewater treatment will increase with time.

The authors chosen to write the chapters in these volumes are well known for their contributions in the application of polymers with active sites to pollution control. Credit must be given to both the authors and the organizations they represent. The authors, in many instances, wrote their chapters on their own time.

We hope that these volumes will make a contribution to improving the quality of our environment and to saving our resources which grow scarcer every day.

Calvin Calmon
Harris Gold
Cambridge, Massachusetts
July, 1978

此为试读，需要完整PDF请访问：www.ertongbook.com

EDITOR-IN-CHIEF

Richard Prober is a principal engineer with GMP Associates, and Adjunct Professor of Chemical Engineering at Case Western Reserve University, Cleveland, Ohio.

Dr. Prober received his B.S. in chemical engineering in 1957 from the Illinois Institute of Technology. In 1958 he received his M.S. degree and in 1962 his Ph.D. degree in chemical engineering from the University of Wisconsin.

Dr. Prober's accomplishments include curriculum development for wastewater treatment plant operator training; development of low-flow dissolved oxygen models for the Cuyahoga River and Tinkers Creek, including direction of stream surveys to calibrate the models; development of process-design oriented B.S. and graduate level programs in wastewater engineering; and extensive research into process development of activated carbon treatment and treatment for industrial wastes containig cyanides.

His professional associations include the Water Pollution Control Federation, American Institute of Chemical Engineers, and the American Chemical Society. Dr. Prober has also served as Symposium Chairman for national meetings of the U.S. Environmental Protection Agency, American Institute of Chemical Engineers, and Wastewater Equipment Manufacturer's Association.

THE EDITORS

Calvin Calmon, Ph.D., has been in the field of industrial chemical research since he received his Ph.D. degree in physical chemistry from Yale University in 1938. (B.A. from Dartmouth College in 1934.) Except for a period of service from 1944 to 1947 as an officer in the U.S. Army, until his retirement in 1973, he worked continuously with various divisions of the Sybron Corporation. Until 1960 he was with the Permutit Company, where he was Head of Laboratories. He then joined Ionac Chemical Company as Director of Research, later became Vice President of Research and, on retirement, was Senior Vice President and Research Consultant to the Chemical Group of Sybron Corporation. In addition to this various consulting activities he is a limited partner in Water Purification Associates.

Most of his industral work, including about 65 technical publications and 19 patents, has been in water treatment, absorbents, ion exchangers, polymers, membmnes, and pollution control. In 1972 he received the Distinguished Service Award from the Environmental Chemistry Section of the American Chemical Society. In 1976 he received from the U.S. Environmental Protection Agency the Certificate of Appreciation for contributions towards the improvement of the environment.

He has served as Chief Research Scientist on contract projects for the Atomic Energy Commission, the Office of Saline Water, the National Aeronautics and Space Administration, and the U.S. Public Health Service. From 1962 to 1972 he served as Section Editor on Water for Chemical Abstracts, published by the American Chemical Society and is currently a scientific and technical merit reviewer for research demonstration grant applications submitted to the U.S. Environmental Protection Agency. With Dr. R. Kressman of England, he edited *Ion Exchangers in Organic and Biochemistry*. During World War II he was Chief of Biochemistry and Serology Sections of the Command Laboratory of the U.S. Army Forces of the Western Pacific. For his chemical work in developing the desalting kit for converting seawater to potable water, now used by all ocean-flying planes, he received a U.S. Government citation. He has received patents for a calcium sensor, improved condensate demineralizing, desalination, pollution control, and ion-exchange processes. He is a member of many technical societies and a Fellow of the American Association for the Advancement of Science.

Harris Gold, Ph.D., is a Partner with Water Purification Associates, Cambridge Massachusetts. He received a B.M.E. from the Polytechnic Institute of New York in 1958, a M.S.M.E. from Columbia University in 1959, and a Ph.D. from the California Institute of Technology in 1963.

From 1963 through 1974, Dr. Gold was with Avco Systems Division, Wilmington, Massachusetts, where he engaged in and directed theoretical and experimental research in heat and mass transfer in fluid flow systems. He was also responsible for the development of a continuous moving bed ion-exchange system for softening pretreatment. Since 1974, Dr. Gold has been with Water Purification Associates. His primary interests include the development of water management systems for power and fuel producing plants and the application of innovative water treatment technologies for industrial wastewater.

Dr. Gold has published many scientific papers and is the co-author of a recent book on the role of water in synthetic fuel production. He is a member of the American Institute of Chemical Engineers, the American Electroplaters Society, and the American Water Works Association.

TABLE OF CONTENTS

VOLUME I

GENERAL ASPECTS

INORGANIC APPLICATIONS

VOLUME II

ORGANIC APPLICATIONS

OTHER APPLICATIONS

USES OF POLYMERS WITH ACTIVE SITES

NEW DEVELOPMENTS

此为试读，需要完整PDF请访问：www.ertongbook.com

CONTRIBUTORS

I. M. Abrams, Ph.D.
Manager, Technical Development
Diamond Shamrock Corporation
Functional Polymers Division
Redwood City, California

R. M. Ahlgren, B.S.
Technical Director
Aqua Chem, Inc.
Milwaukee, Wisconsin

J. Barcicki, Ph.D.
Associate Professor
Department of Chemical Technology
Institute of Chemistry
University of Maria Curie-Sklodowska
Lublin, Poland

B. A. Bolto, Ph.D.
Assistant Chief
CSIRO Division of Chemical Technology
South Melbourne, Australia

F. L. Burnett, M.S.
Product Development Manager
Functional Polymers Division
Diamond Shamrock Corporation
Redwood City, California

Randhir C. Chopra, B.Ch.E.
Vice President
Process and Commercial Operations
Chemical Separations Corporation
Oak Ridge, Tennessee

G. J. Crits, M.Ch.E., P.E.
Technical Director
Cochrane Environmental Systems
Crane Company
King of Prussia, Pennsylvania

T. R. Dillman
Vice President
Research and Development
Illinois Water Treatment Company
Rockford, Illinois

E. C. Feeney, M.B.A.
Technical Promotions Manager
Rohm and Haas Company
Philadelphia, Pennsylvania

Sallie A. Fisher, Ph.D.
President
Puricons, Inc.
Berwyn, Pennsylvania

J. W. Frankenfeld, Ph.D.
Senior Research Chemist
Exxon Research and Engineering Company
Linden, New Jersey

J. E. Goddard, B.Sc.
Managing Director
Atlas Process Consultants, Limited
Hounslow, Middlesex, England

I. R. Higgins, B.S.
Vice President and Technical Director
Chemical Separations Corporation
Oak Ridge, Tennessee

A. Himsley
President
Himsley Engineering Limited
Toronto, Ontario

G. Klein, M.S.
Research Engineer
Sea Water Conversion Laboratory
University of California
Richmond, California

R. Kunin, Ph.D.
Consultant
Yardley, Pennsylvania

Norman N. Li, Sc.D.
Senior Research Associate
Exxon Research and Engineering Company
Linden, New Jersey

L. B. Luttinger, Ph.D.
Senior Research Scientist
The Permutit Company, Inc.
Princeton, New Jersey

F. X. McGarvey, M.Ch.E.
Manager
Technical Center
Ionac Chemical Company
Birmingham, New Jersey

W. S. Miller, B.S.
Research Associate
The Permutit Company, Inc.
Research and Development Center
Monmouth Junction, New Jersey

A. B. Mindler, B. Ch. E., P. E.
Research Group Leader
The Permutit Company, Inc.
Research and Development Center
Monmouth Junction, New Jersey

L. Pawłowski, Ph.D.
Assstant Professor
Department of Chemical Technology
Institute of Chemistry
University of Maria Curie-Sklodowska
Lublin, Poland

F. X. Pollio, M.S.
International Sales Manager
Ionac Chemical Company
Birmingham, New Jersey

M. C. Rowe, C.Chem., M.R.I.C.
Marketing Specialist
Portals Water Treatment Ltd.
Isleworth, Middlesex, England

E. Salem, M.Ch.E., M.B.A.
Vice President
Technical Department
Ecodyne Corporation
Graver Water Division
Union, New Jersey

W. Schwoyer, B.S.
Research Group Leader
The Permutit Company, Inc.
Research and Development Center
Monmouth Junction, New Jersey

H. H. Sephton, D.Sc.
Research Chemist and Principal
Investigator
Sea Water Conversion Laboratory
University of California
Richmond, California

J. D. Sherman, Sc.D.
Senior Development Consultant
Molecular Sieve Department
Union Carbide Corporation
Tarrytown, New York

G. P. Simon
Manager
Special Applications
Ionac Chemical Company
Birmingham, New Jersey

P. C. Singer, Ph.D.
Professor
Department of Environmental
Sciences and Engineering
University of North Carolina
Chapel Hill, North Carolina

G. K. Stephens, Ph.D.
Section Head
Process Development
I.C.I. Australia Limited
Ascot Vale, Victoria, Australia

H. F. Walton, D.Phil.
Professor
Department of Chemistry
University of Colorado
Boulder, Colorado

J. F. Wilkes, M.Ch.E.
Consulting Chemical Engineer
LaGrange, Illinois

R. E. Wing, Ph.D.
Research Chemist
Northern Regional Research Center
U.S. Department of Agriculture
Peoria, Illinois

Organic Applications

Chapter 1

SORPTION OF ORGANIC SUBSTANCES

F. X. Pollio

TABLE OF CONTENTS

I. INTRODUCTION

The use of ion-exchange resins is certainly not limited to conventional water softening and demineralization applications with which most of us are well familiar. Ion-exchange resins are also most useful for reversibly exchanging or sorbing organic matter from liquids. This chapter, accordingly, is devoted to the uptake of organic substances from water and nonaqueous solutions. The removal of inorganic solutes from such organic-bearing systems as glycerine, gelatin, sugar, and similar types of solutions will not be discussed.

Through the use of ion-exchange resins, a liquid may be purified from an organic impurity, and the organic substance may be concentrated so that it can be recovered for a useful purpose or discarded, if need be, into the environment. Ion-exchange resins can also be employed for separating and isolating organic substances whose recovery otherwise, using conventional techniques, might represent a problem. The use of ion-exchange resins for these applications has not been limited to aqueous systems particularly since the introduction of macroporous type ion-exchange resins toward the end of the 1950s.

Prior to the availability of the macroporous ion-exchange resins, which exhibit definite porous properties in media other than water, the utility of gel or conventional type exchangers was usually limited to aqueous or polar liquid systems because the gel or conventional type resins exhibited unfavorable kinetics of sorption for organic species from liquids nonpolar in character. In addition, the resins were found to suffer from physical instability with prolonged cyclic use, particularly where the ion-exchange resins were regenerated with an aqueous or polar regenerant solution.

II. SORPTION FROM AQUEOUS MEDIA

A. Organics in Water Supplies

Most water supplies have at least some amount of organic matter present. The quantity may vary from a few to several hundred parts per million, depending on the geographic location and the type of water source. While well waters may have only trace amounts of organic matter, surface waters may contain up to several hundred parts per million. The nature of the organic matter may be quite varied, depending on whether the organics are natural or synthetic in origin. Natural organics arise from the decay of vegetation from soil contacted by the water source. The products from the decaying process are rather complex but are usually acidic in character and polymeric in nature. Classification of the polymeric organic structures has been made in generic terms due to the complexity of the structures. The organic substances originating from decaying vegetational sources have been generically termed as humic and fulvic acids, based primarily on solubility considerations. Tannins, tannic acids, proteins, fatty acids, and polyols are among some of the less complex structures which have been specifically identified.

Synthetic organics may originate from a variety of sources, such as from the waste effluents of industrial operations and/or the discharge of domestic sewage. Many of the organic materials impart color to the waters and are eliminated only with great difficulty using conventional techniques.

Organic matter found in water supplies is usually acidic in nature and accordingly can be adsorbed by anion exchange resins. For most surface type waters, where organic matter is usually found, pretreatment of the waters can significantly reduce the organic content. Through the use of coagulation and clarification, organics present as turbidity (colloids) can be readily eliminated. Some of the soluble organics may also be reduced when organic polyelectrolytes (flocculants) are used in conjunction with an inorganic type coagulant. Chlorination of the waters does bring about some destruction of organics, but the prime purpose of chlorination is to render the biologically active organics innocuous.

Organic scavenger resins, such as Ionac® A-642, have, for example, been found useful for eliminating organic substances from a water supply prior to conventional demineralization. Organic scavenger resins commonly employed for this purpose are strong anion macroporous resins especially designed for this type of operation. Scavenger resins characteristically possess a highly porous structure and are capable of reversibly sorbing the organic species. That is to say, the organic matter, once adsorbed by the resin, can be quantitatively eluted from the resin under proper regeneration conditions.

It is customary to operate scavenger resins in the salt (chloride) cycle and to regenerate the resins with a warm brine solution. In many cases, for both economical and ecological reasons, the waste regenerants from the resin demineralization system can be effectively used to regenerate the scavenger resins, with or without a final short regeneration with fresh brine solutions.

TABLE 1

Organic Capacity — Ionac® A-642 Scavenger Resin

Organic Content (ppm as $KMnO_4$)	Service flowrate (bed volumes per hour)	Capacity (pounds of Organics, $KMnO_4/ft^3$)
1—10	16—20	0.6—0.8
10—25	16—20	0.8—1.0
25—50	12—16	1.0—1.2
50—100	6—10	1.2—1.5

Where a new demineralization system is being considered, a suitable macroporous anion resin can be employed instead of a conventional gel-type anion resin, eliminating altogether the need to use a scavenger unit prior to the demineralization train. This practice is recommended only in cases where the organic content of the clarified water supply to be treated is relatively low in soluble organics. Foregoing the use of a scavenger resin in favor of a macroporous strong base resin in the demineralization train should generally be considered only when the organic matter in the water supply is less than 30 ppm as $KMnO_4$ (i.e., this is the permanganate necessary to oxidize organic matter).

It is difficult to predict what organic loading capacities can be achieved using a scavenger resin because of the undefined nature of the organics present in the water supply. Nevertheless, approximate loadings that may be expected as a function of the organic content of the water supply are given in Table 1.

Regeneration of the scavenger resin is best achieved using a 10% NaCl solution at a 15 lb/ft^3 NaCl regeneration level applied at a two bed volume per hour flowrate. It is recommended that the salt regenerant be used at 120°F, particularly if the organic content exceeds 50 ppm as $KMnO_4$. For more aggressive waters and where inorganic colloidal compounds may also have been removed by the scavenger resin along with the organic matter, it is recommended that up to 2 lb NaOH per cubic foot of resin be incorporated into the salt regenerant solution.

The removal of organic tannins from residential water supplies cannot be accomplished by standard water filters and water softeners which employ a strong cation-exchange resin. When tannins are present in the water supply, they impart to the water a yellow or brownish tinge. A strong macroporous anion resin, such as Ionac A-642, can be added to the water softener unit to remove the tannins while the water is being softened. The same brine solution used to regenerate the softener resin will simultaneously regenerate the Ionac A-642 scavenger resin.

B. Phenol Removal

Wastewaters containing phenols present a serious disposal problem from an ecological standpoint. Though quaternary ammonium type anion-exchange resins have a good capacity for phenols, weak base anion-exchange resins of the polyamine or tertiary amine type are preferred since they can be regenerated with either dilute alkali or solvents such as low boiling alcohols.[1]

The sorption of phenol by weak base anion resins, based upon a styrene-divinylbenzene matrix, appears to proceed through two distinct mechanisms, depending upon the type and the ionic form of the ion exchange resin involved. For quaternary ammonium exchange resins in the salt form, the mechanism clearly does not involve ion-exchange, since no anions are displaced from the resin during the adsorption of phenol.

TABLE 2

Phenol Capacity — Ionac® AFP-329

Influent phenol	Capacity (lb/ft^3, phenol)
100 ppm	0.22
500 ppm	0.62
1000 ppm	1.28
4000 ppm	3.60

This is supported by the fact that phenol may be eluted from the anion-exchange resin readily with an alcohol. This conclusion was also proposed by Anderson and Hansen[2] who, after determining the sorption isotherm for phenol on Dowex® 1-Cl, found the phenol isotherm curve to have the usual characteristics associated with sorption observed on common porous sorbents. Phenol sorption increased rapidly at low concentrations and approached a limiting value as the concentration of solute approached the water miscibility limit.

In the case of strong base anion-exchange resins in the hydroxide form, the phenols are removed primarily by an exchange for hydroxide ions. Under normal circumstances, regeneration of a quaternary amine exchanger to the hydroxide form is such that the resin functional sites will exist partially in the hydroxide form and partially in the salt form. The relative ratio of the two existing forms after regeneration depends, of course, on the caustic regeneration level. Under such conditions, two concurrently different sorption processes will be occurring, one involving adsorption of phenol at the salt functional sites, the other an interaction at the functional sites involving phenol and the hydroxide ion to form the phenolate ion.

Sorption of phenol on the weak, free base form polyamine anion-exchange resins appears to proceed mainly through an adsorption process, at least in the case of polyamine anion-exchange resins which do not contain quaternary ammonium functional groups. Waste aqueous streams and process streams containing phenol levels between 100 and 4000 ppm phenol can readily be processed yielding treated solutions containing less than 1 ppm phenol.

The working capacity of the resin for phenol is greatly dependent upon the initial concentration of phenol in the influent to be treated. In general, the capacity increases rapidly with an increase in the phenol content of the water to be treated. Typical capacities that can be realized using, for example, the weak base anion-exchange resin Ionac AFP-329 are listed in Table 2.

It should be noted that the phenol capacity of the Ionac AFP-329 resin is not adversely affected if the wastewater contains a neutral salt background, since weak base resins will not split salts to any appreciable extent. On the other hand, the presence of free mineral acidity in the influent may result in a reduced phenol loading. Likewise, the presence of alkali in the wastewater will also have the effect of reducing the phenol capacity.

The phenol sorption operation is carried out at flow rates between two to eight bed volumes per hour. A lower flow rate is beneficial for treating phenolic influents containing higher levels of phenol. In the case of a phenol influent containing 4000 ppm phenol (pH = 4.0), a flow rate of two to four bed volumes per hour results in a capacity of 3.6 pounds of phenol per cubic feet of resin to a 1% breakthrough while giving an average leakage of less than 1 ppm phenol.

Regeneration of the weak base ion-exchange resin is achieved using either a solvent such as methanol or isopropanol or a dilute NaOH solution. The use of alcoholic solvents allows for the recovery of phenol (as phenol) since the alcohol can be stripped

此为试读，需要完整PDF请访问：www.ertongbook.com