Wastewater Treatment by Ion-Exchange

B. A. Bolto

L. Pawlowski

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*Division of Chemical and Wood Technology,
CSIRO, Melbourne, Australia*

L. Pawlowski

*Department of Environmental Chemistry and
Technology, Polytechnic of Lublin, Poland*

Preface

The more stringent requirements for the treatment of wastewaters to render them fit for disposal into natural waterways, and the increasing concern over the depletion of supplies of raw materials for industry, have focused attention on methods of both cleaning up effluents and recovering valuable materials from them. The purpose here is to present a concise account of the application of ion exchange to separating the components of wastewaters with particular emphasis on industrial wastewaters. These are more complex than domestic sewage, offer more scope for the isolation of valuable chemicals, and are more readily treated by adsorption techniques.

The problem of disposing of industrial wastes is as old as industry itself; there has also been considerable effort devoted to water reuse. The present emphasis is on the recovery of other wastewater components, the value of which provides the economic incentive. This need must escalate rather than slacken in the years ahead. We have endeavoured to concentrate on treatment methods which are in active use in industry, or have at least progressed to the pilot-plant stage. Our message is that the technology now exists for the separation of wastewater components under almost any set of circumstances.

We would like to pay tribute to two pioneers in the field who have done much to advance the cause of ion exchange with respect to water and chemicals recovery. The late Calvin Calmon and recently retired Don Weiss have been enthusiastic and imaginative proponents of the cause in the two hemispheres; the authors are indebted to them for inspiration guidance and support over many years.

Like most authors, we owe a debt of gratitude to colleagues who have graciously spent time reviewing various chapters, and making constructive criticisms. We wish to thank, in particular R. J. Eldridge, K. H. Eppinger, M. B. Jackson, N. H. Pilkington, A. J. Priestley, S. Stanislawek, E. A. Swinton and T. Winnicki. We also express our gratitude to R. E. Hamilton, G. Młodawska, E. Smulkowska and E. Żołnierczuk for untiring help in preparing the manuscript.

Finally, we would like to acknowledge the tolerant and supportive attitudes of our respective wives and families

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B. A. BOLTO Melbourne
L. PAWLOWSKI Lublin

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Contents

CHAPTER ONE

General introduction

Although some of the leading industrialized nations of the world are taking active measures to control environmental damage caused by chemical pollutants, the problem still exists and is becoming even more complicated as time progresses. For example, over five million chemicals are now known to be in common use, and several thousand new ones are synthesized each year. Inevitably some of these chemicals will penetrate into the environment where a certain number of them will eventually affect all forms of life. Many chemicals will enter waterways because of inadequate treatment and disposal.

At the same time, Man is continuously processing and dispersing natural, non-renewable resources throughout the world. The total quantity of resources may not decrease because of this activity, but they are transformed from a concentrated to a diluted form. Manufactured chemicals follow a similar pathway. In conventional wastewater treatment the emphasis is usually on decreasing the level of non-specific pollutants such as biochemical oxygen demand, suspended solids, grease, surfactants, etc., rather than the selective removal and recovery of particular chemicals. This has the effect of gradually diminishing the resources available for human existence. One could assume that the human race is sufficiently ingenious to devise substitutes for the exhausted materials, and this may well be so in many instances. However, it would be irresponsible to totally base our continued existence on such a belief — there is a natural limit to expansion.

In order to concentrate industrial wastewaters so that particular chemicals can be recovered and reused, there is a great need for the development of suitable separation techniques. Along with other processes, ion exchange is an appropriate technique for such purposes, as it is employed in the separation and concentration of ionic materials from liquids. It is widely used to produce high-purity water for industry, from water which is already of potable quality. Industries as diverse as those producing pharmaceuticals and electronic components are heavily dependent on ion exchange. However, the technique is

Table 1.1 Water and wastewater treatment (papers published during the period 1967–84)

	1967–69	1970–72	1973–75	1976–78	1979–81	1982–84
Ion exchange in general	3390	4647	4819	5057	5168	5106
Water treatment by all methods	4159	6696	12369	12997	9872	8777
Water treatment by ion exchange	469	679	906	914	892	752
Desalination by all methods	707	1011	960	1230	1313	1081
Desalination by ion exchange	89	131	133	158	148	149
Wastewater treatment by all methods	1080	2749	8314	13976	15668	15245
Wastewater treatment by ion exchange	62	129	421	689	638	590

Table 1.2 Recovery of water and chemicals from wastewaters (papers published during the period 1967–84)

	1967–69	1970–72	1973–75	1976–78	1979–81	1982–84
Water recovery by all methods	565	896	1599	1728	1618	1546
Water recovery by ion exchange	29	65	140	120	102	101
Recovery of water and chemicals by all methods	5472	6993	9055	12319	14416	16440
Recovery of water and chemicals by ion exchange	156	247	330	432	492	500

not extensively used for treating wastewater, although it can offer significant benefits. Ion exchange is often not employed in wastewater treatment even when it seems ideally suited for a particular problem, such as the removal of metal ions from electroplating effluents. The reasons for this are worth examining.

One explanation is that, since its inception, ion exchange has been regarded more as a method to produce water than as a method to purify water. Ion-exchange equipment commonly resembles manufacturing plant, more so than it does wastewater treatment facilities. Ion-exchange receives little attention in technical education courses, and is also not normally considered a promising research area. As a result, most of the progress in the application of ion-exchange has been made by specialized companies, either resin manufacturers or producers of equipment for water treatment.

The plant to produce high-purity water for industry by ion exchange is usually quite separate from the main manufacturing plant, both physically and in-the mind of the factory management. It is regarded simply as a black box which provides water of the requisite standard, and it normally does this without any difficulty. Problems which arise tend to be referred to the specialist water-treatment companies. Moreover, both the capital and operating costs of the ion-exchange plant are usually only a small proportion of the overall plant costs. From the user's point of view there is therefore little incentive to improve the ion-exchange system, with the result that the industry is rather conservative. Progress has generally resulted from new demands by the water users. The increasing requirement for water of improved quality has forced the development of techniques to meet this demand. In addition, the deteriorating quality of water resources has resulted in both the development of new ion-exchange resins and new techniques. As a result, the ion-exchange industry has evolved to a highly specialized one which now meets the demand for high-purity water, but which shows little sign of extending its horizons to wastewater treatment.

It is interesting to observe the trend in scientific and technical papers mentioned in *Chemical Abstracts* over the period 1967 to 1984 (see Table 1.1). In the triennium 1967 to 1969, 3390 papers were published on all aspects of ion exchange. This increased rapidly in the next triennium and then stabilized from 1976 to 1984 at a level of about 5100 papers per triennium. There was parallel activity for water treatment and desalination by this technique. Papers on its application to wastewater treatment increased much more rapidly from 1967 to 1978 and then stabilized at a triennium level of about 650 papers over 1979 to 1984. Current activity in water treatment by ion exchange is not much greater than that for wastewater treatment. Publications in the latter area are now about 4% of publications on all aspects of wastewater treatment.

There is a noticeable and expanding activity in the application of ion exchange to the recovery and recycling of water and chemicals from wastes (see Table 1.2). The technique is an excellent means for recycling water, and it is relatively straightforward to adapt existing water treatment procedures. The

main expansion in water recycling was in the period 1967 to 1975, at the time when the whole world became seriously concerned about environmental protection, and for the use of ion exchange the peak activity was in 1973 to 1975, when papers on the recycling of water by this method accounted for about 9% of papers covering all aspects of water recycling. The level of papers on water recycling by ion exchange has now stabilized at about 100 per triennium, or about 7% of all papers on recycling. Hence in this area, ion exchange is still intensively used. Papers on the recovery of water and chemicals by ion exchange have also stabilized over the last two triennia, to 500 in 1982 to 1984.

Published papers, however, depict research activity, and the actual application of ion exchange to wastewater treatment has not reached a significant level. It is hoped that this book will show the practical application of the technique to wastewater treatment and to the recovery of wastewater constituents.

From another standpoint, experts working in the wastewater treatment area see ion exchange as too specialized a technique for their needs. A lot of potentially useful processes have been developed by people occupying the middle ground, but because they lack an understanding of the peculiar situation with ion exchange and wastewater applications, they have not been able to translate their findings into industrial practice. The net result is that the technique is not used for wastewater treatment to the extent that it should be. There is an urgent need to highlight the advantages of ion exchange so that they are better appreciated among specialists in the wastewater treatment area.

Hence the first part of this book is an introduction to ion exchange, which should provide an understanding of its application. It is directed at specialists working on wastewater treatment who are not familiar with the technique. They should get maximum benefit from the second part of the book, which deals with specific examples of the applications of ion exchange to effluent treatment. It should be noted that there is no attempt to discuss the treatment of radioactive wastes.

The earlier part of the book should also be useful to those actively working in the field of ion exchange as it gives an up-to-date picture of the technology, and provides a logical framework for a discussion of the practical aspects of its application in the wastewater area. The second part of the book emphasizes the particular problems frequently associated with wastewater as a resource, such as its high turbidity, its oxidizing properties, and the need to obtain a highly concentrated effluent on regeneration of the ion exchangers. A series of flowsheets is presented as a methodological guide to the diverse applications of the technology in the recovery and reuse of water and chemicals from wastes. We believe this will be of considerable interest to both ion-exchange specialists seeking an extension of the technology beyond the traditional areas, and to wastewater experts, because of its review of practical flowsheets. It is fervently hoped that a much greater acceptance of the technology will result.

Ion-exchange materials

2.1 INTRODUCTION

Ion-exchange resins are insoluble polymers which have active ionogenic groups covalently bonded to the polymer. The fixed groups are either permanently ionized so that they always possess a formal charge, or are capable of ionization or acceptance of protons to form the charged site. The resin interacts with mobile ions from an external solution. Ions of opposite charge to that on the resin, and which are exchanged by the resin, are known as *counter-ions*, while ions of the same charge as that of the exchange sites are known as *co-ions*. The polymeric network of the resin is known as the *matrix*.

Those ion-exchange resins capable of exchanging cations are called *cation exchangers*, and resins capable of exchanging anions are called *anion exchangers*. Certain resins can exchange both cations and anions, and are termed *amphoteric ion exchangers*.

The first systematic studies of ion exchange were carried out on naturally occurring inorganic ion exchangers, but they were soon overshadowed by the much greater interest shown in organic resins, since industrial applications of ion exchange now rely heavily upon the latter materials. The greater stability, higher capacity and ability to control their synthesis to yield products with reproducible properties has meant that organic ion exchangers have largely, but not entirely, displaced their inorganic counterparts in modern technology.

2.2 INORGANIC ION EXCHANGERS

There is still some interest in inorganic ion exchangers, arising mostly from their resistance to degradation in extreme environments such as high temperatures and the presence of ionizing radiation. Also, examples exist of high selectivity towards certain ions, as in the case of clinoptilolite and ammonium ions. The properties of clinoptilolite are summarized in Table 2.1. The capacity and flow rate terminology are discussed further in Chapters 3 and 12.

Table 2.1 Typical properties of clinoptilolite [1].

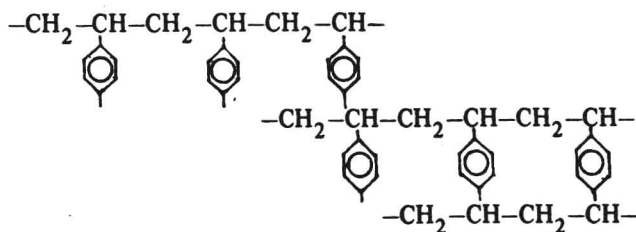|			
Particle size	(mm)	0.3–	2.0
Shipping weight	(kg m^{-3})	880	–960
Moisture content	(wt%)	3 –	7
Impurities	(wt%)	3	– 20
pH range		4 –	8
Backwash rate	(m^3 h^{-1} m^{-2})	20	
Service rate	(m^3 h^{-1} m^{-3})	8 –	16
Regeneration rate	(m^3 h^{-1} m^{-3})	0.8–	1.6
Operating capacity	(eq. NH$_4^+$ per dry g)	1.6–	1.8

The inorganic materials initially used were natural crystalline aluminosilicates which had cation-exchange properties. The zeolites are the best known of these, and included the minerals: analcite [Na(Si$_2$AlO$_6$)$_2$·H$_2$O], chabazite [CaNa(Si$_2$AlO$_6$)$_2$·6H$_2$O], harmotome [KBa(Si$_5$Al$_2$O$_{14}$)·5H$_2$O], heulandite [Ca(Si$_3$AlO$_8$)·5H$_2$O], natrolite [Na$_2$(Si$_3$Al$_2$O$_{10}$)·2H$_2$O], montmorillonite Al$_2$[Si$_4$O$_{10}$(OH)$_2$]·nH$_2$O , and clinoptilolite [(Na$_2$O)$_7$CaO(H$_2$O)$_{1.5}$(MgO)$_{0.5}$·Al$_2$O$_3$·85–105 SiO$_2$·60–70H$_2$O].

The first commercial cation exchangers were prepared by fusing mixtures of feldspar, kaolin and similar components with sodium and potassium oxides. Recently, materials with superior properties have been prepared by combining Group IV oxides with the more acidic Group V and VI oxides. Very few synthetic inorganic ion exchangers have been made. Others include hydrous oxide gels of zirconium, titanium and tin, which have anion-exchange properties.

In the applications of ion exchange to be discussed in this book inorganic adsorbents play only a marginal role. Further details of these materials may be found in the book on this topic written by Amphlett [2].

2.3 ORGANIC ION EXCHANGERS

The majority of organic resins have a matrix of an irregular, three-dimensional network of macromolecular hydrocarbon chains. In most cases this consists of a copolymer of styrene and divinylbenzene (DVB), with the latter providing the crosslinking:

⊖ Fixed negatively charged exchange site,
  ie, SO_3^-
◉ Mobile positively charged exchangeable
  cation, ie, Na^+
∾ Polystyrene chain
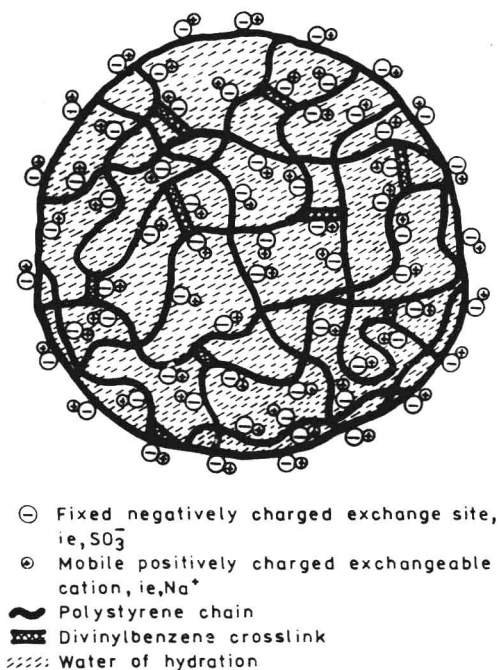▨ Divinylbenzene crosslink
⌇⌇ Water of hydration

Fig. 2.1 Schematic picture of a gel-type strong acid cation exchanger [3].

The properties of the resins are determined above all else by the ion-exchange groups present on the matrix. In general, these may be divided into three groups: cation exchangers (strong acid or weak acid groups); anion exchangers (strong base or weak base groups); specific ion exchangers (selective chelating groups). However, the chemical activity of the exchange sites can be modified by the nature of the matrix.

2.3.1 Physical structure

(a) Gel resins

The organic ion exchangers first developed were the so-called gel resins. They have an essentially homogeneous distribution of water throughout the resin matrix, as depicted in Fig. 2.1. The resin swells under some exchange conditions and the imbibed water causes an increase in the distance between the polymeric chains.

The ability to swell depends on the degree of crosslinking, which for polystyrene resins can vary between 2 and 20% DVB. High degrees of crosslinking make the resin less susceptible to swelling, but more brittle in nature. It is

not possible to achieve an even distribution of crosslinks throughout the resin matrix. The crosslinking is less uniform when the resin bead is larger, and this inhomogeneity causes some problems in practical use of the resin. With some regions within a resin bead having a different swelling ability to other regions, internal pressures result and the bead fractures. The existence of a region of denser crosslinking can also hinder the release of large organic molecules from the bead during regeneration of the exhausted resin.

In general, when ions diffuse through a resin bead their progress is retarded by the matrix polymer. This limitation is less when there are fewer crosslinks and the bead is more swollen. However, resins having a low degree of crosslinking are not physically strong and are more sensitive to an oxidizing environment. More highly crosslinked resins are more stable in every respect, but then the tighter network in the matrix provides a greater resistance to diffusion, and hence lower rates of ion exchange.

(b) Macroporous resins

As a way around the dilemma resins having a *macroporous* structure were developed. By appropriate synthetic methods based on having a solvent present during the polymerization so that the growing polymer chains are precipitated in the form of microspheres, macropores are formed between the precipitated regions, as illustrated in Fig. 2.2. The resin bead is now heterogeneous and consists of two phases: homogeneous regions containing matrix and water, and water-filled voids between these regions.
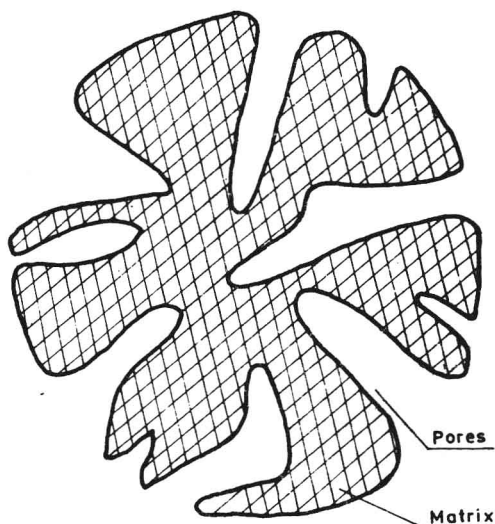

Fig. 2.2 Schematic picture of a macroporous ion-exchange bead.

Ions entering the resin can now do so via the large pores, and the amount of matrix they must diffuse through is much less than in a gel-type resin. A more highly crosslinked matrix is employed (and is part of the synthetic requirements) which means that the bead is mechanically stronger and is less susceptible to penetration by large organic molecules which cause fouling problems.

As the resin bead now contains a second discrete phase in the form of voids, the amount of matrix and hence the number of exchange sites is lower on a volume basis. Also, the quantity of chemicals required for regeneration of the resin is increased.

(c) Isoporous resins

It is claimed that some of the disadvantages of macroporous resins can be overcome by the synthesis of *isoporous* resins, in which the matrix has a substantially uniform network, free of highly crosslinked regions. The differences between the various physical formats of resins are shown in Fig. 2.3.
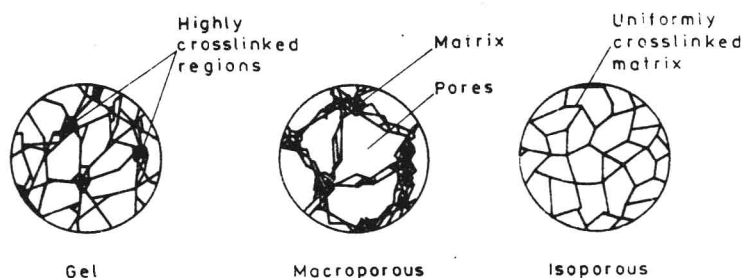

Fig. 2.3 Schematic picture of different types of ion exchangers [4].

(d) Micro resins

In practically all the applications of the resin types mentioned so far the diameter of the bead is 0.3 to 1.2 mm. As will be further discussed in Chapter 3, improved rates of exchange can be obtained by using smaller particles which make a larger surface area available. Powdered ion exchangers are employed in what has been termed precoat filters, which combine in one unit the operations of filtration and demineralization. They are successfully employed in the removal of trace amounts of impurities in condensate water in the power industry. However, because they are very fine particles (even though they are present in a coagulated form) they cause a high pressure loss in operation, and must be employed as a 1 cm layer on specially designed candle filters (see Chapter 12). Being a powdered mixture of cation- and anion-exchange resins, it is not practical to regenerate them, so they are employed on a throwaway basis. Because of the high pressure loss which would result they cannot be employed in a column system [5].