

Adsorption and Ion Exchange: Basic Principles and Their Application in Food Processing

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A comprehensive overview of adsorption and ion exchange technology applied for food and nutraceutical production purposes is given in the present paper. Emanating from these fields of application, the main adsorbent and ion-exchange resin materials, their historical development, industrial production, and the main parameters characterizing these sorbents are covered. Furthermore, adsorption and ion exchange processes are detailed, also providing profound insights into kinetics, thermodynamics, and equilibrium model assumptions. In addition, the most important industrial adsorber and ion exchange processes making use of vessels and columns are summarized. Finally, an extensive overview of selected industrial applications of these technologies is provided, which is divided into general applications, food production applications, and the recovery of valuable bio- and technofunctional compounds from the byproducts of plant food processing, which may be used as natural food additives or for their potential health-beneficial effects in functional or enriched foods and nutraceuticals.

KEYWORDS: Kinetics; equilibrium isotherms; industrial application; polyphenols; byproducts; proteins; tocopherols

1. INTRODUCTION

The aim of the present review is to provide a comprehensive and systematic overview of the application of adsorbent and ion exchange technology in the food industry. This comprises not only the characterization of the main adsorbent and ion exchange materials permitted for food application, their preparation, and a description of the historical development of this technology but also a detailed treatise of the different kinetics, thermodynamics, and equilibrium models, which are commonly used to describe adsorption and ion exchange phenomena in different systems. In addition, the major applications of adsorption and ion exchange technology described in the literature are reported, and this description has been restricted to solid–liquid systems. This section is subdivided into “general applications”, giving an insight into the potential use of this technology, “food production applications”, and “recovery of valuable bio- and technofunctional compounds from the byproducts of food processing”. The clear-cut differentiation between the latter two areas of application was made because of the rising accumulation of byproducts due to an increased production quantity of industrial foods, which is associated with increasing costs for the disposal of such waste streams. On the other hand, plant-processing byproducts are of increasing interest because of their high contents of secondary plant metabolites, which have been intensely discussed in the past decades due to their health-promoting properties. This interest is associated with a growing market of natural food additives and nutraceuticals. Additionally, consumer expectations increasingly force food

producers to abstain from the use of synthetic food additives and to apply natural “healthy” food components, which can be deduced from an increasing importance of the “functional foods” sector. The processes exemplified in the present paper are mainly based on the application of synthetic resins and were taken from scientific publications, patents, and application brochures of resin manufacturers.

2. HISTORICAL DEVELOPMENT OF ADSORPTION AND ION EXCHANGE TECHNOLOGY

Adsorption phenomena were already exploited by the Egyptians and Sumerians, who used charcoal 3750 B.C. for reducing copper, zinc, and tin levels during bronze manufacturing. Following this, the Egyptians and later Hippocrates used charcoal for first medical purposes before the first application for potable water treatment was described by the Phoenicians. Such applications were rather empirical, and a more systematic approach was not developed until 1773, when the first quantitative studies of adsorption phenomena were performed. Nowadays industrial applications of adsorption technology reveal great diversity, and such techniques have become common practice for gas purification, for example, to remove obnoxious smells from the air or in gas masks to protect military personnel from poisonous gas and further to decolorize aqueous or organic liquids, which is further detailed below. Numerous gas–solid and liquid–solid phase adsorption systems using charcoal, clay, carbon of animal origin, zeolite, and, more recently, also activated carbon, synthetic zeolites, and further synthetic resins based on polystyrene, polyacrylic esters, or phenolics have been described, giving rise to very diverse fields of application (1–3).

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The application of ion exchange phenomena can also be traced back to the Old Testament, in the Second Book of Moses (Ex 15, 23 EU), where the preparation of potable water from bitter brackish water is described. This was probably due to the removal of bitter cations through ion exchange by a piece of wood containing rotted cellulose; processed cellulose is known today to be a very efficient ion exchange material. Around a thousand years later, Aristotle (384–322 B.C.) described in his *Problemata* the decrease of the salt concentration of seawater when percolating through sand. The next important observations of ion exchange processes were not made until 1850 when Thompson (4) and Way (5), two English chemists, studied the exchange of ions on cultivated soils. It is assumed that the underlying physical phenomena were not really known at that time. However, in the following years the development of this separation technology has proceeded very rapidly. At first natural mineral ion exchangers were used, such as clay, glauconite, humic acid, and zeolite followed by synthetic inorganic exchanger materials, which came up in 1905. Systematic investigations of ion exchange processes and of the properties of exchange materials have led to the development of synthetic resins with well-designed characteristics (1, 2, 6, 7).

3. BASIC PRINCIPLES OF ADSORPTION AND ION EXCHANGE

Basically, both ion exchange and adsorption may be performed in solid–gas and solid–liquid systems. A strict differentiation between these two types of applications is impossible, because there are exchange and adsorption resins, which are used in both gas–solid and liquid–solid adsorption applications, such as activated carbon or zeolite. Additionally, the most common equilibrium models such as the Langmuir and Freundlich isotherms were derived by studying gas adsorption systems and subsequently applied to solid–liquid systems. In this review, only solid–liquid adsorption and ion exchange systems were regarded, although there are some solid–gas applications in food processing, such as waste air purification, removal of fat, and gas purification, especially of oxygen and nitrogen, prior to their use in food processing (8, 9).

Adsorbent and ion exchange materials are categorized not only on the basis of their matrix composition, polarity, and chemical and physical resistance but also by their particle size distribution, their inner and specific surface areas, density, and porosity as well as their pore radius distribution (10).

3.1. Particle Size Distribution. The resin particle size distribution is important not only because of its influence on the pressure loss upon passing the solvent through the adsorbent and ion exchange columns but also because of its effect on mass transfer rates. Naturally, pressure loss increases with decreasing particle size, at the same time mass exchange rates increase with decreasing particle size because of shorter diffusion paths. For characterizing the particle size distribution the average particle diameter, the most frequently occurring particle diameter, and the particle size range (“mesh”) are usually specified (9).

3.2. Inner or Specific Surface Area. The inner or specific surface area usually is a multiple of the outer surface of an adsorbent and is the site where adsorption occurs. Consequently, this parameter deserves particular attention upon decision-making when choosing a particular resin, and maximal inner surface areas should be aimed at. Due to the fact that the inner surface area is inversely proportional to the pore diameter, the molecular size of the adsorbent constitutes a major limitation of its application, because if the pore diameter is too small, the adsorptive may not diffuse into the adsorbent (9, 11).

3.3. Density. The specification of the density may be further broken down into the density of individual particles and the density of the particle bulk. Individual particle density may be specified as the real density, that is, the quotient of the dry adsorbent amount and the solid volume without considering the pore volume, the apparent density, that is, the quotient of the dry adsorbent amount and the total solid volume including the pore volume, or as the wet density, which means the wet adsorbent amount divided by the total solid volume including the liquid-filled pore volume. In contrast, the particle bulk density is also referred to as the bulk density, that is, the amount of adsorbent needed to fill a vessel divided by the volume including the interparticle volume, the filter bulk density, which is defined as the bulk density measured after a single backwash step, or the vibrated density, which is specified as bulk density measured upon vibration during the filling process (9, 11).

3.4. Porosity or Pore Size Distribution. According to the definition of the density, the porosity may also be further subdivided into particle porosity and bulk material porosity. Thus, the inner porosity of individual particles is defined as the proportion of the pore volume referred to the total volume of the adsorbent particle. In contrast, the bulk porosity or outer porosity is a measure of the interspaces between the adsorbent particles (1, 9, 11).

3.5. Pore Radius Distribution. Pore radius distribution is another important factor affecting adsorption and ion exchange rates. The variability of the pore radius has a major impact on the diffusion of the solutes into the resin material. Pore radii are classified according to International Union of Pure and Applied Chemistry (IUPAC) standards. Accordingly, pores with a diameter of <0.4 nm are referred to as submicropores, whereas the diameter of micropores ranges from 0.1 to 2.0 nm, that of mesopores from 2.0 to 50 nm, and that of macropores above 50 nm. Concerning the large pore radius variability of most sorbents, the different pore classes are assumed to exert particular functions. The macro- and mesopores allow the transport of the solute molecules, whereas inside the micropores adsorption and ion exchange occur (9, 11).

4. ADSORBENT AND ION EXCHANGE MATERIALS

Adsorbent and ion exchange materials, which are allowed for food use, are regulated by the respective national legislation as well as the U.S. Food and Drug Administration (FDA) and the Council of Europe. The most commonly applied and most important materials, which conform to these regulations, are further specified below.

4.1. Activated Carbon. Activated carbon is probably the best-known adsorbent material. It can be manufactured from animal and plant carbonaceous materials, such as bones, coals, petroleum coke, nutshells, peat, wood, and lignite. Its manufacturing process may be partitioned into two phases. The first phase is characterized by carbonization, during which undesirable byproducts are removed from the raw materials at 400–600 °C in an oxygen-depleted atmosphere. In the second phase the material is activated, which may be achieved through gas or by chemical activation. Gas activation is performed at temperatures of 750–1100 °C for the partial gasification of carbon with water vapor, carbon dioxide, and oxygen, respectively. In contrast, chemical activation is achieved using dehydrating chemical agents, such as potassium sulfide, sulfuric acid, zinc chloride, and phosphoric acid at temperatures of 350–600 °C. Under these conditions carbonization, gasification, and activation occur simultaneously (1, 11, 12). Through the selection of the raw material and by controlling the carbonization and activation conditions the tailoring of pore size distribution is possible, and activated carbon for

particular applications may be manufactured. Thus, activated carbon is available with surface areas ranging from 300 to 3000 m²/g and pore volumes from 0.7 to 1.8 cm³/g, in the form of powder (PAC), granules (GAC), pellets, or tissues derived from different raw materials. This great diversity of different types of activated carbon is associated with an immense variability of different applications. It is used to remove unwanted substances from gases, vapors, and liquids in the chemical industry, in medicine, for water and wastewater treatment, in ventilation and air-conditioning technology, and for the adsorptive removal of compounds that may cause contaminations and discoloration or that may negatively affect taste and odor (1, 8).

4.2. Zeolites. Zeolites may be subdivided into 40 natural and more than 150 synthetic crystalline aluminosilicates of alkali or earth alkali elements, such as sodium, potassium, and calcium. Their primary structure is based on the tetrahedra of silicon (SiO₄) and aluminum (AlO₄), which build up secondary polyhedral units of cubes, hexagonal prisms, octahedral, or truncated octahedral systems, respectively, and which are linked via oxygen atoms. Furthermore, the three-dimensional crystalline network of zeolites consists of secondary units, with these secondary structures building up cages, which are connected through channels crossing the three-dimensional structure. The size of the channels is determined by the number of silicon and aluminum atoms, which are linked with each other, and also by the counterion of the negatively charged aluminum, which may partially obstruct the channel and reduce its size. Thus, differences may be observed when Ca²⁺ is substituted by Na⁺. Furthermore, not only does the number of silicon and aluminum atoms have an effect on the channel size but also the Si/Al ratio. With increasing Si proportions, the affinity of water and other polar molecules toward zeolites is lowered, bringing about a more hydrophobic character. Accordingly, numerous different zeolites can be manufactured, with each of them having tailor-made properties and being characterized by its unique surface chemistry and structure, which allows a highly selective application based on ion exchange phenomena and depending on the size and polarity of the adsorptive. The three most frequently used zeolites are types A, X, and Y. Their common basic structure is made up of a truncated octahedron called sodalite cage. Type A is built up of two linked four-member rings of sodalite and a Si/Al ratio of 1. Types X and Y consist of an octahedron with six-member rings of sodalite as base structure, which differ in their Si/Al ratios (type X, 1–1.5; type Y, 1.5–3) (8, 12). Additionally, the substitution of Si or Al through other elements expands the number of zeolite structures, which are then formally not classified as zeolites. The synthesis of zeolites is a two-step process, consisting of gel formation at 25 °C from aqueous NaOH, NaAl(OH)₄, and Na₂SiO₃, probably due to copolymerization of silicate and aluminate, followed by crystallization in a closed hydrothermal system. This process may need a few hours up to several days at temperatures up to 175 °C. Furthermore, the use of organic additives, such as organic amines, mainly quaternary amines, is an interesting tool to influence zeolite formation during crystallization. On the bases of their different structures, zeolites are used for separation and purification and as molecular sieves, for example, for the drying and dehydrating of gases or organic solvents (12, 13).

4.3. Silica Gels. With regard to the increasing use of modified silica gels for column chromatographic purposes and various other applications, this sorbent material shall be considered here as well. In general, there are different routes to obtain this widely used amorphous desiccant with its large water-binding capacity and its easy regeneration. The first synthesis route, which is most commonly used, is characterized by chemical precipitation of alkali silicate, such as sodium silicate, with acids, mostly sulfuric



Figure 1. Hydrolytic formation of silicic acid.

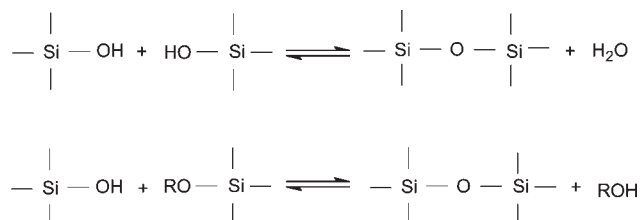


Figure 2. Polymerization of silicic acids.

acid, upon stirring at high temperatures, thus yielding silicic acid precipitates. Upon further neutralization the polycondensation of low molecular silicic acids leads to colloidal SiO₂ particles, which further grow to a certain size. The redundant electrolyte together with van der Waals forces enhances coagulation of these particles to agglomerates, with the agglomerate structures forming aggregates that subsequently precipitate.

The second route is governed by gel–sol conversion, a polymerization reaction obtained by mixing a sodium silicate solution with a mineral acid, such as sulfuric or hydrochloric acids. The reaction products form a dispersion of finely divided particles of hydrated SiO₂, which are also referred to as silica hydrosol or silicic acid (eq 1) and which build up at a particular pH value.

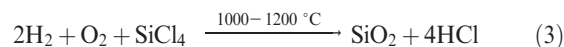


Silicic acid (Si(OH)₄), with its strong tendency to polymerization, forms a white jelly-like precipitate network of siloxanes, which need to be washed, dried, and activated prior to further use. The variable properties of silica gels with respect to pore volume and surface area may be achieved through varying the silica concentration, pH value, and temperature during polymerization or the temperature during activation.

A further process to prepare silica gels is based on the reaction of silicon alkoxides with water in the presence of an alcohol (eq 2), whereas silicic acids can also be formed through hydrolysis (Figure 1). Accordingly, the polymerization of silicic acids may be described as illustrated in Figure 2.



A pyrotechnic process is the third option to obtain silicon gels, where silane tetrachloride is continuously passed over into the gas phase at a temperature of around 1000–1200 °C and reacts within an oxyhydrogen flame with water to form fine particles of silicon oxides (eq 3).



These hydrophilic synthetic silicas are usually modified in subsequent treatment procedures to expand their technological properties. In this way, different silanes carrying various functional groups are obtained, which may be used, for example, as grafting agents, where temperatures of around 70 °C are applied for treating the silica surface. Accordingly, surfaces with improved separation efficiency exhibiting polar or apolar properties may be created by selective modification (12, 14, 15).

Because of their very high adsorption capacity and straightforward regeneration, silica gels are also used for analytical purposes as filter material, column material, and fining agent. Depending

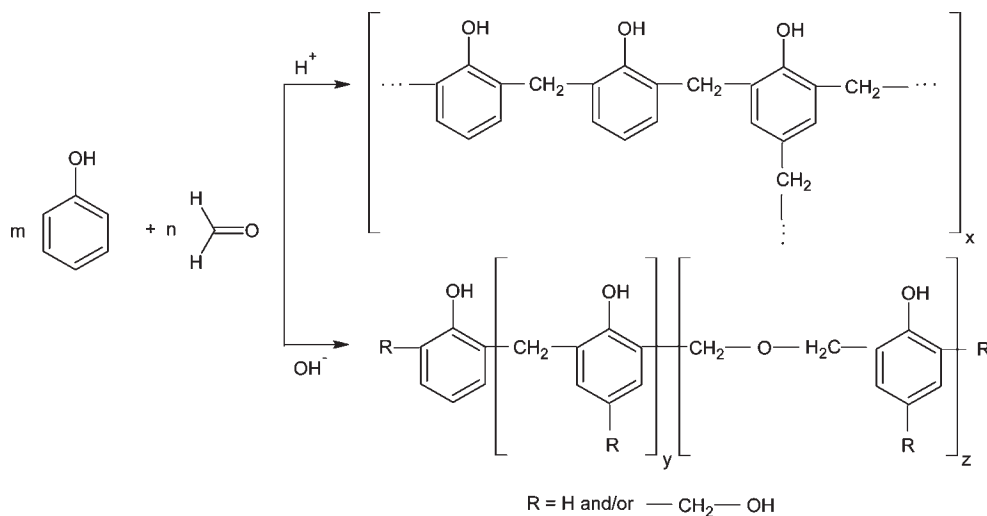


Figure 3. Polycondensation of phenol with formaldehyde via acidic or basic catalysis.

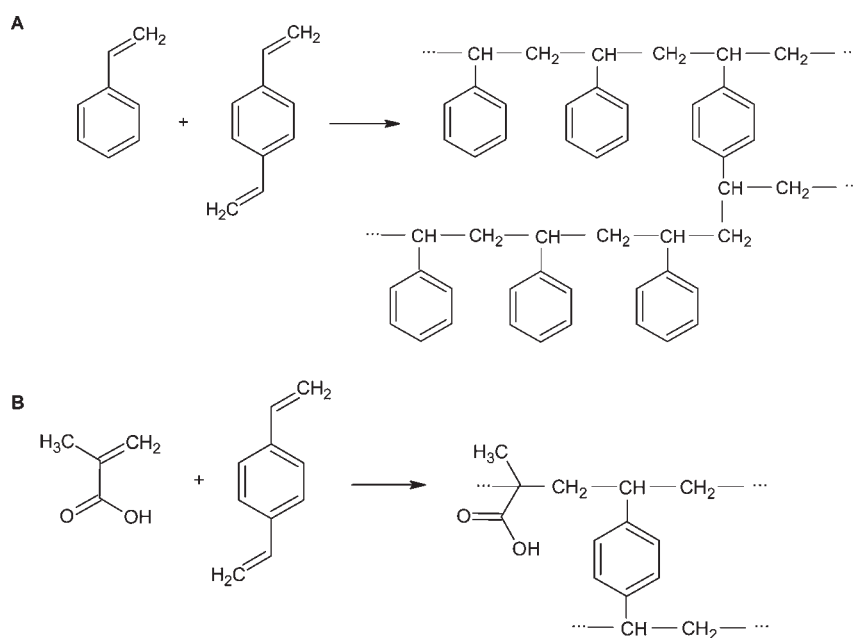


Figure 4. Polymerization of styrene (A) and methacrylic acid (B) with divinylbenzene as cross-linking agent.

on their properties and manufacturing processes, silica is also applicable in food production, such as to adjust the pourability of vegetable, fruit, and sauce powders, to produce flavors in powder form, in the cosmetics industry as carriers of active compounds, as raw material for powders, as dispersing agent, as fining agent, and in the paint industry for adjusting viscosity and thixotropy (12, 14, 15).

4.4. Synthetic Resins. Synthetic resins are polymeric adsorbents with large internal surface areas and a much more consistent structure compared to activated carbon. They are manufactured by polycondensation or polymerization, with the products of the polymerization reaction being more consistent with respect to temperature or chemical influences than the polycondensation products. In this context it is important to note that there are major differences in the literature with regard to the classification of polyreactions and their definitions. In the English literature polymerization may generally be perceived as a transformation of low molecular weight to high molecular weight compounds. On the other hand, the term polymerization is often specifically used to describe chain-growth reactions, thus differentiating such reactions

from step-growth polymerizations, such as polyaddition or polycondensation reactions.

Polycondensation products are obtained through electrophilic aromatic substitution of phenolic compounds with formaldehyde under acidic or basic catalysis (Figure 3) and, as for polyaddition products, are formed in stepwise reactions. The type of phenolic compound and the ratio of the precursor materials used for synthesis define their properties.

Polymerization belongs to the poly reactions, which proceed through chain propagation reactions and may be realized in technical processes such as bulk polymerization, solution polymerization, emulsion polymerization, suspension polymerization, precipitation polymerization, and gas phase polymerization. Upon polymerization, styrene (Figure 4A), acrylic acid, or methacrylic acid (Figure 4B), respectively, may polymerize with divinylbenzene or other divinyl monomers as cross-linking agents, whereas polyacrylamide (Figure 5A), polyvinylpyrrolidone (PVP) (Figure 5B), and polyvinylpolypyrrolidone (PVPP) are also manufactured by radical polymerization but without cross-linking agents. Styrene molecules as well as styrene and divinylbenzene are polymerized

through radical polymerization with benzoyl peroxide as an initiator of the radical chain reaction. Additionally, there are further ways to obtain cross-links between styrene chains after their formation, if the aromatic bodies have been chloromethylated, which is commonly performed in the course of functionalization to produce ion exchange resins. Thus, methylene bridge formation may occur between a chloromethylated styrene chain and a neighbor chain (**Figure 6**); however, such bridges may negatively affect the positive characteristics of an existing pore system (16, 17). A second way of cross-linking is given via the Friedel–Crafts reaction. *p*-Xylylene dichloride (XDC), 1,4-bis(chloromethyl)diphenyl (CMDP), monochlorodimethyl ether (MCDE), dimethylformal, tris(chloromethyl)mesitylene (CMM), and *p,p'*-bis(chloromethyl)-1,4-diphenylbutane (DPB) are cross-linking agents used for this purpose (18); however, these chemicals are not commonly used for manufacturing resins applied in the food sector.

In addition, cationic and anionic copolymerization are two further possible reaction mechanisms for producing polymeric resins, with the initiator being a cation, which reacts via an electrophilic addition, or an anion, which starts the reaction via a nucleophilic addition to a carbon–carbon double bond, respectively (19).

There are also literature reports on the so-called living polymerization, allowing one to specially control the preparation and the uniformity of the polymer architecture of resins, for example, by retaining the termination step. This means that after complete reaction of all monomeric units and further addition of educts, the chains may still continue to grow (19). For this purpose anionic living polymerization (20), reversible addition–fragmentation chain transfer (RAFT), or radical living polymerization, such as free stable radical mediated polymerization (SFRP), is commonly applied.

The polymers formed according to these different mechanisms may be obtained either in gel type form, in macroreticular form or as hypercrosslinked resins, which significantly affects their properties and areas of application.

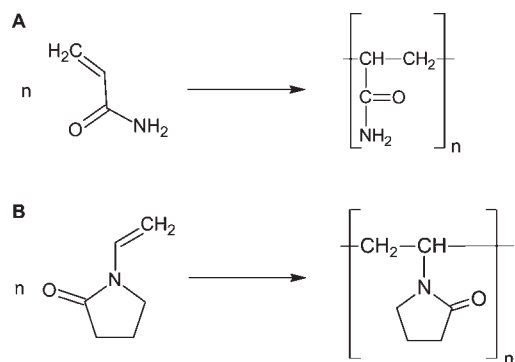


Figure 5. Structural features of polyacrylamide (**A**) and polyvinylpyrrolidone (PVP) (**B**) and of their corresponding monomers.

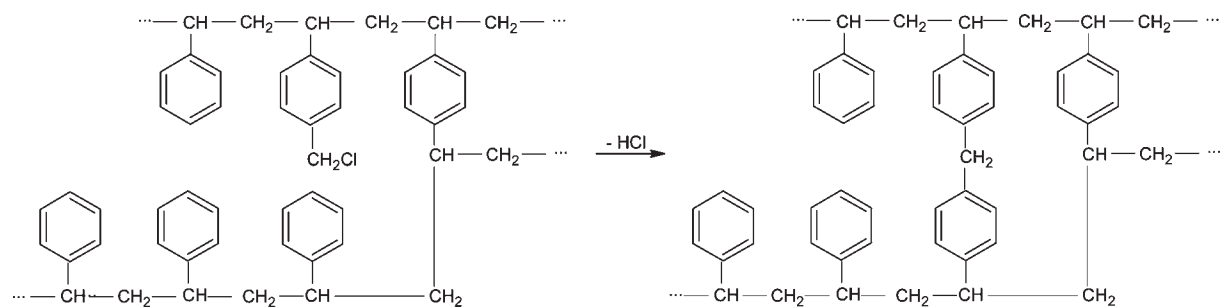


Figure 6. Methylene bridge formation between a chloromethylated polystyrene chain and a neighbor chain.

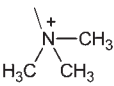
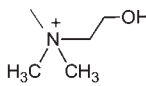
4.4.1. Gel Type Adsorbents and Ion Exchangers. For the production of gel type resins, styrene and relatively low amounts of divinylbenzene (2–12%) are blended with approximately the same amount of water devoid of any organic solvent in a chemical reactor. Subsequently, the mixture is dispersed through stirring to produce small globules with a size of about 1 mm. At this stage the addition of benzoyl peroxide initiates the radical chain reaction and therewith the polymerization, which leads to the formation of small plastic beads of the polystyrene/divinylbenzene molecules. Such resin types are commonly used especially for water treatment (18, 19, 21).

4.4.2. Macroreticular Resins. Macroreticular resins are characterized by high porosity, which can be achieved using an inert material or porogen, which is miscible with the monomeric compounds but which does not influence the chain propagation and is easy to extract or to vaporize, thus forming pores. Inert materials used for this purpose are swelling agents, which are good solvents for the monomers as well as the polymer products or precipitating agents, in which the polymeric products are hardly soluble. The variability of adsorbent resins can be achieved through choosing different types and concentrations of the inert material or porogen and by varying the amount of divinylbenzene and the type and concentrations of other monomers as well as the reaction conditions during polymerization. The large-pored structures produced under such conditions are characterized by a huge inner area and a more homogeneous appearance compared to the gel type. To increase their mechanical stability, higher amounts of cross-linking components are needed as compared to the production of gel-type resins. This coincides with a number of interesting properties, such as a larger free inner volume, lower swelling differences between polar and unpolar solvents, lower volume decrease during resin drying, and higher oxidation stability, and such resins are also suitable for catalytic purposes. Besides the recovery of low molecular weight compounds as described for hyper-cross-linked polystyrenes (4.4.3), macroreticular resins with their large inner volumes provide the opportunity to recover large molecules due to the accessibility of the inner surface areas (6, 11, 18, 19).

4.4.3. Hyper-cross-linked Polystyrenes or Styrosorbs. Hyper-cross-linked resins are extremely rigid networks with a cross-linking degree above 40% showing much greater sorption capacities than that of other known organic and inorganic sorbents. Due to the high inner volume of the network not only the surface of macropores is accessible for the target compounds, which may explain the high capacity of such resins. According to Davankov and Tsyurupa (18) the hyper-cross-linked polymers are able to swell in any liquid and also in gaseous media, whereas harsh treatments such as drying may lead to a decrease of the volume.

Synthetic adsorbent resins are appropriate to and commonly used for the removal and recovery of aromatic components such as polyphenols, naphthalenes, hydrocarbons, pesticides, alcohols, and ketones (11).

Table 1. Ion Exchange Resins Applied in the Food Industry¹

	cation exchanger		anion exchanger			amphoteric exchanger	
	strongly acidic	weakly acidic	strongly basic		weakly basic		
matrix	SDVB ^a	polymerization of acrylic or methacrylic acids with DVB ^b	SDVB ^a	SDVB ^a	products of polycondensation or polymerization (SDVB ^a)	product of the condensation of phenols and amines	SDVB ^a
functional groups	-SO ₃ ⁻	-COO ⁻	 type I	 type II	+ ≡ N + = NH + - NH ₂	weakly acidic phenolic OH group, basic NH ₂ group	implementation of an acidic and basic group -SO ₃ ⁻ , type I quaternary ammonium
production	sulfonation with sulfuric acid, chlorine sulfonic acid, oleum	functional group is part of one of the monomeric matrix components	chloromethylation followed by amination with tertiary amines		chloromethylation after polymerization followed by amination		
counter ion	H ⁺ , Na ⁺ , Ca ²⁺	H ⁺ , Na ⁺	OH ⁻ , Cl ⁻ , SO ₄ ²⁻	OH ⁻	free base, OH ⁻		H ⁺ /OH ⁻ , H ⁺ /free base
properties		high selectivity against Ca ²⁺ and Mg ²⁺	stronger basic compared to type II but difficult to regenerate, high exchange capacity, extremely stable	less temperature-resistant compared to type I, sensitive towards oxidizing agents, high exchange capacity, not as stable as type I	only anions of strong acids (HCl, H ₂ SO ₄) may be exchanged because of the low basicity, anions of weak acids are only poorly exchanged (HCO ₃ ⁻)		
application	water softening, demineralization of sugar solutions, demineralization of liquids containing organic material, removal / recovery of amino acids, chromatographic separation of glucose/fructose, inversion of sugar solutions	removal of cations from basic solutions, separation of basic salts of multivalent cations, partial demineralization	adsorption of organic substances and exchange of ions, demineralization of sugar solutions and removal of acids, demineralization of water, decolorization		demineralization, decolorization of sugar solutions, adsorption of polyphenols, exchange of organic acids	water purification / demineralization	

¹ ^a SDVB, styrene-divinylbenzene; ^b DVB, divinylbenzene (6, 69, 99, 100)

Respective national legislatures as well as the FDA (22, 23) and the Council of Europe (24) regulate the types of resins, monomers, starting components, chemical modifiers, and polymerization aids to be used as well as food production processes, where such resins may be applied.

4.5. Synthetic Ion Exchanger Materials. Ion exchangers are by definition firm and insoluble high molecular weight polyelectrolytes, which may exchange their loosely bound ions against ions of the same charge from the surrounding media. Ion exchange is a reversible and stoichiometric process.

Synthetic ion exchangers are composed of a matrix, a three-dimensional high molecular network, with charged functional groups attached to it by chemical bonds. According to the aforementioned variability of synthetic adsorbent resins, the structural diversity of ion exchangers is even more pronounced, because a number of different functional groups may be attached to the apolar networks. The choice of matrix material depends on the type of ion exchange to be applied. As an example, the resins produced by cross-linking acrylic and methacrylic acids with divinylbenzene, respectively, carry carboxylic groups, which act as weak cation exchangers without further modification of the resins. The charge of the groups attached to the resin matrix determines the kind of ion exchanger. Cation exchangers carry bound anions, and anion exchangers reveal the presence of cationic groups with the respective reversely charged counterions attached by electrostatic interactions. In addition, there are amphoteric ion exchangers, containing both ion types at the same time.

The aforementioned main types of ion exchangers may be differentiated into strong basic, weak basic, or acidic ion exchangers on the basis of their functional groups. **Table 1** provides an overview of the most popular ion exchange types used in the food industry (6, 7).

4.5.1. Functionalization of Synthetic Resins. Cross-linked resins may be functionalized by treatments such as sulfonation,

that is, an electrophilic substitution of the aromatic backbone of the resins occurring upon treatment with concentrated sulfuric acid at elevated temperatures, or by chloromethylation via the Friedel-Crafts/Blanc reaction followed by amination of the intermediate reaction products (**Figure 7**). Additionally, specific ion exchangers may be obtained by the insertion of functional groups with well-desired properties. Among such ion exchangers, chelating, imprinted exchangers, or ligand exchangers, may be found (2, 25).

As mentioned for adsorbent resins, the types of ion exchangers, monomers, starting substances, chemical modifiers, and polymerizations aids, respectively, permitted for the production of resins for food applications are regulated by national legislation, the FDA, and the Council of Europe (22–24).

5. PRINCIPLES OF ADSORPTION AND ION EXCHANGE

5.1. Adsorption. Adsorption may be described as an enrichment of compounds, for example, from fluids on surfaces of solid state bodies. During this accumulation, interactions between the atoms and molecules of the fluid phase (adsorptive) and the solid (adsorbent) occur. The solid surface may be regarded as a site with certain electronic and sterical properties characteristic of the adsorbent matrix structure, which induce energetically heterogeneous energy levels based on the degree of the interaction with the adsorptive. Furthermore, most adsorbents are not only characterized by their exterior surface but are also significantly affected by their inner porous surface, which also contributes to adsorption. However, there are major differences in the interaction forces and the kinetics of adsorption onto the exterior or inner surface (26). Adsorption processes are generally distinguished in three different sorption types depending on the nature of the interactions between the adsorbent matrix and the adsorptive. Physisorption commonly is a reversible and rapid sorption process, which is mainly based on van der Waals forces, dipole

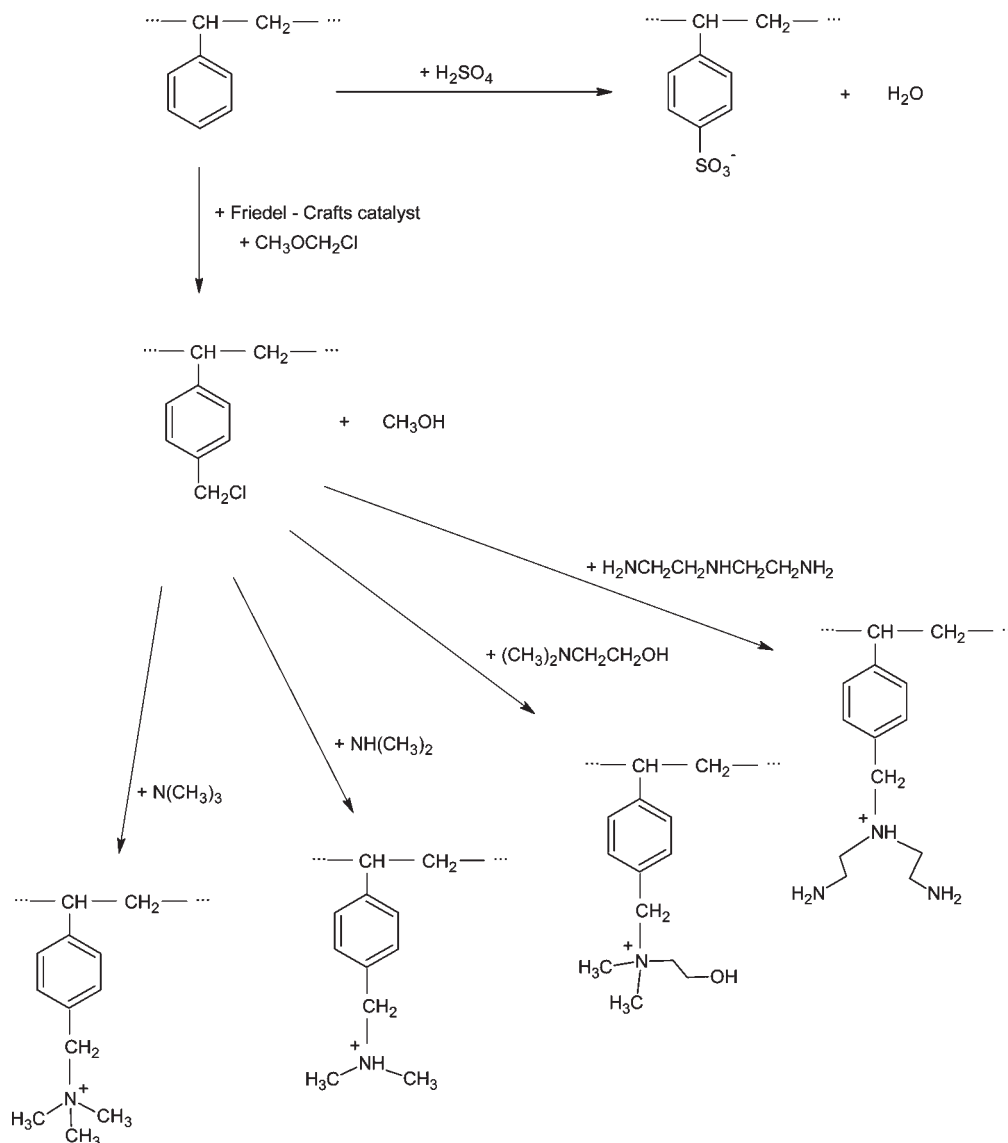


Figure 7. Functionalization of cross-linked resins via sulfonation with concentrated sulfuric acid or by chloromethylation via the Friedel–Crafts/Blanc reaction followed by amination to obtain cation and anion exchange resins.

forces, dipole–dipole forces, and dispersion forces as well as induction forces, which are usually below 50 kJ/mol. In contrast, chemisorption relates to a chemical bonding between the adsorbent and adsorptive. Accordingly, the interaction forces are much higher and are reported to be in the range of 60–450 kJ/mol. Furthermore, in the course of ionosorption an ion transfer occurs (11, 26).

5.1.1. Kinetics and Thermodynamics of Adsorption Processes. Adsorption kinetics describes the time-dependent evolution of the sorption process until equilibrium is reached. The sorption process is divided into mass transport and heat transport, with the first being subdivided into four consecutive steps: (1) transport of the adsorptive from the fluid phase to the subsurface, which is built up around the adsorbent; (2) transport through the subsurface, which is also called film diffusion; (3) simultaneous transport into the pores of the adsorbent through diffusion by the pore fluid, also referred to as pore diffusion and diffusion along the inner surface upon adsorption (surface diffusion); (4) interaction with the active sites of the adsorbent. The first step is not directly related to adsorption. The heat transport is divided into energy transfer inside the sorbent material and energy transfer through the subsurface surrounding the

resin particles, whereas the heat transfer through the liquid phase may be disregarded because of its high heat capacity.

The mathematical description of adsorption kinetics can be realized in two ways, either by considering the global mass and heat transfers separately or by taking into consideration combinations of various processes running in parallel and sequentially. These approaches are called the heterogeneous and homogeneous models, respectively (9, 11), and are further detailed below.

Heterogeneous Model. According to this model both the mass and heat transfer of the film diffusion process are separately predictable (9). In contrast to particle diffusion the mass transfer in the subsurface has a nondominant role, because the pore resistance is the dominating step of mass transfer. The subsurface effect may be further limited through higher flow rates, whereas a sufficient contact time of the adsorptive with the adsorbent needs to be warranted, thus limiting maximal flow rates. In contrast, heat transfer through the subsurface is the dominating step of energy transfer.

The overall mass transfer kinetics is dominated by the mass transport in the pores. The diffusion processes within the particles occurring in the liquid phase are subdivided into free pore diffusion, surface diffusion, and intercrystalline diffusion, all of

which may also occur simultaneously. Due to these different diffusion mechanisms occurring in parallel, the diffusion types cannot clearly be differentiated and, accordingly, the determination of the dominating step is difficult. In liquid phases, both relevant mechanisms, that is, pore diffusion and surface diffusion, are superimposed, because both mechanisms proceed simultaneously in the same pore. In this context, the diffusion differs depending on whether the gradient of particle loading or the concentration gradient is the driving force of the overall process (9).

Homogeneous Model. The homogeneous model is applied when the underlying dominating mechanisms of a system are unknown. In this case, the linear driving forces (LDF) approach describes the overall mass transfer between the adsorbent and the fluid phase. This approach assumes a homogeneous loading of the sorbent surface, which is independent of the particle radius, and the resistance of the mass transfer due to the subsurface (9).

According to Bathen and Breitbach (9), the kinetics of multi-compound systems has been less thoroughly studied because of the difficult assessment of the interactions of different compounds simultaneously diffusing in the pores.

Adsorption processes are commonly exothermic. Normally, adsorption phenomena are characterized by energies ranging up to approximately 100 kcal/mol. Under these conditions, sorption processes may be observed even at temperatures below 100 K, and both adsorption and desorption occur spontaneously. In contrast, desorption may not occur without chemical modification of the target compounds for sorption processes with adsorption energies of ≥ 100 kcal/mol (26).

5.1.1.1. First-Order Kinetic Adsorption Model. First-order sorption phenomena are unimolecular processes based on a reversible equilibrium reaction, which may be characterized as

$$\frac{d(q_e - q_t)}{dt} = -k(q_e - q_t) \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the maximum amount that can be adsorbed per mass of adsorbent and the amount adsorbed after time t , respectively (27). t (s) is the time and k the rate constant (1/s) (1). By integration of the differential form of eq 4 the following equation (eq 5) results:

$$\ln(q_e - q_t) = -kt + C \quad (5)$$

C is an integration constant (mg/g), which is defined as $\ln(q_e)$ at $t = 0$, because $q_t = 0$ at $t = 0$ (28). Furthermore, it is possible to deduce the energy of activation by applying the linearized Arrhenius equation, if the rate constant k is calculated for different temperatures (eq 6).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (6)$$

R is the gas constant, T the absolute temperature (K), and E_a the activation energy of the sorption process, which can be calculated together with the pre-exponential factor A from the slope and intercept of a linear plot of $\ln k$ versus $1/T$ (28, 29). On the basis of this relationship and using the Eyring equation (eq 7) the enthalpy of activation ΔH^* and the entropy of activation ΔS^* may be calculated from the intercept and slope of the linear plot of $\ln(k/T)$ versus $1/T$ (28, 29):

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (7)$$

k_b and h are the Boltzmann and Plank constants, respectively. Following this, the free energy of activation (ΔG^*) may be

determined according to eq 8 (28, 29):

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (8)$$

Furthermore, the half-adsorption time $t_{1/2}$, that is, the time needed to bind half of the equilibrium amounts onto the resin surface, may be determined according to eq 9:

$$t_{1/2} = \frac{\ln 2}{k} \quad (9)$$

5.1.1.2. Pseudo-First-Order Kinetic Model (Lagergren's Rate Equation). According to Rudzinski and Plazinski (30, 31) Lagergren adsorption kinetics (eq 10) is a limiting form of the Langmuir model, if the system is not far from equilibrium conditions:

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (10)$$

k is the rate constant (1/s), and q_e and q_t are the amounts adsorbed per mass of adsorbent (mg/g) at equilibrium and after time t , respectively. By plotting $\ln(q_e - q_t)$ against the time t according to the linearized Lagergren equation (eq 11), the rate constant k and β may be determined from the slope and intercept of the linear graph. Following this, the intercept β can be used to determine the nature of the rate-determining step (31, 32):

$$\ln(q_e - q_t) = \beta - kt \quad (11)$$

Furthermore, according to the first-order kinetics model, the half-adsorption time can be deduced according to eq 12.

$$t_{1/2} = \frac{\ln 2}{k} \quad (12)$$

5.1.1.3. Pseudo-Second-Order Kinetic Model. The pseudo-second-order reaction is a two-site-occupancy adsorption. Thus, according to this model a solute molecule reacts with two adsorption sites, with the reaction rate being defined as

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (13)$$

where k is the rate constant (g/mg·s) and q_e and q_t are the amounts adsorbed per mass of adsorbent (mg/g) at equilibrium and after time t , respectively (1, 27). Most commonly, this model is represented in its linearized form (eq 14), which produces a linear graph if t/q_t is plotted versus time t . The rate constant k and q_e may be determined from the slope and intercept of the graph:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} \times t \quad (14)$$

Summarizing these common kinetic models, the thorough considerations of Rudzinski and Plazinski (27, 30, 31, 33–36) deserve particular attention. The main conclusion of these authors is that adsorption kinetics is better described with different models, which ideally fit to the respective stages of the adsorption process, rather than relying on one kinetic assumption to describe the entire sorption process from the initial stages until equilibrium conditions. These authors based their assumptions on the application of the pseudo-first- and pseudo-second-order kinetic models.

5.1.2. Adsorption Equilibrium. The adjustment and the general parameters of adsorption equilibria depend on the interactions of the adsorptive and adsorbent as well as the properties of the solutions brought into contact with the sorbent material and of the adsorptive. Furthermore, if several compounds coexist in one solution, they will inevitably compete for sorption sites of

the sorbent. Accordingly, equilibrium concentrations of individual compounds in complex mixtures depend on such mutual interactions.

Experimental data obtained under equilibrium conditions may be used for deducing adsorption isotherms by varying experimental conditions, such as pH value, adsorbent amounts, or adsorptive concentrations. Furthermore, it needs to be considered that there are no generally applicable adsorption isotherms, which allow one to describe the experimental results obtained under any condition. Thus, the most familiar isotherms, which are based on theoretical model concepts or which have been deduced empirically, are presented below. These approaches may be classified first into parameter-dependent isotherms and second into isotherms depending on the number of compounds to be considered in the respective adsorption system.

5.1.2.1. Isotherm Equations Describing Single-Compound Systems. Most isotherms dealing with single-compound adsorption are derived from gas phase adsorption systems. However, these models have also been successfully applied to liquid–solid phase adsorption in numerous cases.

5.1.2.1.1. Irreversible Isotherm/Single Parameter Isotherm

5.1.2.1.1.1. Irreversible Isotherms. The irreversible isotherm (eq 15) describes a concentration-independent loading of the adsorbent, which is of relevance in certain limiting cases such as the application of high solute concentrations, when the system is described by the Langmuir isotherm (cf. eq 19) (11):

$$q_e = \text{const} \quad (15)$$

q_e (mg/g) is the amount of adsorbate per gram of sorbent at equilibrium.

5.1.2.1.1.2. Henry Isotherm. This one-parameter equation (eq 16) is based on the assumption that all sorption sites are identical and may be occupied. Furthermore, interactions between the compounds bound onto the resin surface are excluded (9).

$$q_e = k_H C_e \quad (16)$$

q_e (mg/g) is the amount of adsorbate per gram of sorbent at equilibrium, C_e (mg/L) is the equilibrium solute concentration, and k_H is a proportionality factor, also known as the Henry constant, which is equivalent to the slope of an isotherm, when the resin loading approximates zero. This isotherm equation cannot be thermodynamically deduced and, therefore, caution must be exercised when it is applied. However, due to its good linear adjustment for small concentrations, the Henry isotherm is frequently used.

5.1.2.1.2. Two-Parameter Isotherms

5.1.2.1.2.1. Langmuir Isotherm. The Langmuir adsorption model is one of the best known and most frequently applied isotherms. It describes the physisorption of neutral particles, that is, molecules or atoms, by the sorbent surface, which is characterized by energetically homogeneous sorption sites. Furthermore, only a monomolecular coverage of the adsorbent surface is assumed, and the desorption rate from a particular sorption site is thought to be independent of the occupancy of the neighboring sorption sites.

$$q_e = \frac{Q_{mL} a_L C_e}{1 + a_L C_e} = \frac{K_L C_e}{1 + a_L C_e} \quad (17)$$

The Langmuir isotherm is illustrated in eq 17 with Q_{mL} (mg/g) being the monolayer adsorbent capacity under equilibrium conditions, which indicates the maximum concentration retained by

the adsorbent surface when it is completely covered by an adsorbate monolayer. This value may be calculated by dividing the Langmuir constants K_L (L/g) and a_L (L/mg). q_e (mg/g) is defined as the amount of adsorbate per gram of sorbent at equilibrium, whereas C_e (mg/L) is the equilibrium solute concentration.

At low concentrations ($a_L C_e \ll 1$), the Langmuir isotherm can be approximated by the Henry isotherm (11, 37)

$$q_e = Q_{mL} a_L C_e = k_H C_e \quad (18)$$

whereas at high concentrations ($a_L C_e \gg 1$) a constant saturation value (maximal coverage) results, which equates to the irreversible isotherm (11):

$$q_e = Q_{mL} = \text{const} \quad (19)$$

On the basis of the linearized form of the Langmuir isotherm (eq 20), the Langmuir constant K_L and adsorbent capacity Q_{mL} may be obtained from the slope and the intercept of the linear plot of $1/q_e$ values of experimental data against $1/C_e$ (38).

$$\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{1}{Q_{mL}} \quad (20)$$

5.1.2.1.2.2. Freundlich Isotherm. In contrast to the Langmuir equation, the Freundlich isotherm, which is also very frequently applied, assumes monolayer adsorption onto sorbent surfaces, which are characterized by heterogeneous sorption sites (eq 21):

$$q_e = K_F C_e^{b_F} \quad (21)$$

q_e (mg/g) is the amount of adsorbate per gram of sorbent at equilibrium, and C_e (mg/L) is the solute concentration under equilibrium conditions. Furthermore, the Freundlich constant K_F (L/g) describes the adsorption capacity, and the dimensionless parameter b_F is a measure of the adsorption intensity (38). In contrast to the Langmuir isotherm, eq 21 cannot be approximated by the Henry isotherm at low concentrations and does not result in a saturation value at very high solute concentrations (11).

On the basis of the linearized form of the Freundlich equation (eq 22), the adsorption capacity K_F and dimensionless parameter b_F may be obtained from the slope and intercept of the linear plot of $\log q_e$ against $\log C_e$ (38):

$$\log q_e = \log K_F + b_F \log C_e \quad (22)$$

5.1.2.1.2.3. Brunauer–Emmett–Teller Isotherm (BET). The BET isotherm (eq 23) extends Langmuir's idea of a monolayer adsorption system to a multilayer model, where the sorption sites are energetically homogeneous and where interactions between individual molecules of one layer do not exist. In contrast, the BET model assumes such interactions between molecules of different layers. This adsorption isotherm correlates the binding of target compounds in a monolayer with a decrease of binding enthalpy and in addition with a decrease of vaporization enthalpy because of multilayer formation. The sum of the changes of binding and vaporization enthalpy can be measured as adsorption enthalpy. The BET isotherm is specified in eq 23 (39):

$$c = c_m \frac{Kp}{(p_0 + (K - 1)p) \times \left(1 - \frac{p}{p_0}\right)} \quad (23)$$

c (mol/g) is the amount adsorbed under equilibrium conditions, c_m (mol/g) is the amount adsorbed in a monomolecular layer, and

K is a constant. Furthermore, p_0 constitutes the saturation vapor pressure and p the adsorptive partial pressure.

The BET equation can hardly be applied to describe solid–liquid adsorption systems. Nevertheless, it deserves particular attention because it is commonly used to determine the specific inner surface of microporous adsorbents (9, 11).

5.1.2.1.2.4. Tempkin Isotherm. The Tempkin model assumes the existence of indirect adsorbate/adsorbate interactions, which have a significant effect on the adsorption isotherm. These interactions are suggested to cause a linear decrease of the heat of adsorption of all molecules with increasing surface coverage (37).

$$q_e = \frac{RT}{b_T} \times (\ln AC_e) \quad (24)$$

The Tempkin isotherm is given in eq 24, where q_e (mg/g) is the equilibrium solid phase concentration and C_e (mg/L) the equilibrium liquid phase concentration of the target compounds. Furthermore, A is defined as the isotherm constant (L/mg) and b_T (J/mol) as the Tempkin isotherm energy constant. On the basis of the linearized form of the Tempkin equation experimental data are used to obtain the isotherm constants A and B by plotting q_e against $\ln C_e$ (eq 25)

$$q_e = B \ln A + B \ln C_e \quad (25)$$

with B as the isotherm energy constant, which is equivalent to the product of the gas constant R (J/mol·K) and the absolute temperature T (K) divided by the Tempkin isotherm energy constant b_T (J/mol) (eq 26).

$$B = \frac{RT}{b_T} \quad (26)$$

5.1.2.1.3. Three-Parameter Isotherms. Some of the three-parameter equations reported in the literature are further developments of the Langmuir isotherm. The most common of these isotherms are specified below.

5.1.2.1.3.1. Langmuir–Freundlich Isotherm. The Langmuir–Freundlich isotherm, which has been developed by Sips, also takes the energetic heterogeneity of many sorbent surfaces into account by introducing the heterogeneity parameter n_{LF} (eq 27) (11, 40):

$$q_e = \frac{Q_{m_{LF}} a_{LF} C_e^{n_{LF}}}{1 + a_{LF} C_e^{n_{LF}}} \quad (27)$$

$Q_{m_{LF}}$ (mg/g) is the monolayer adsorbent capacity under equilibrium conditions, and a_{LF} (L/mg) is the Langmuir constant. q_e (mg/g) is defined as the amount of adsorbate per gram of sorbent at equilibrium, whereas C_e (mg/L) is the solute concentration under equilibrium conditions.

At low concentrations ($a_{LF} C_e^{n_{LF}} \ll 1$) this equation is approximated by the Freundlich isotherm and not the Henry isotherm, whereas this model predicts saturation at high solute concentrations ($a_{LF} C_e^{n_{LF}} \gg 1$).

5.1.2.1.3.2. Redlich–Peterson Isotherm. In contrast to the previous model, the Redlich–Peterson equation exhibits an exponent only in the denominator. The isotherm (eq 28) represents an empirical three-parameter equation, which allows the description of adsorption equilibria over a wide concentration range.

$$q_e = \frac{Q_m B_R C_e}{1 + B_R C_e^{\beta_R}} = \frac{A_R C_e}{1 + B_R C_e^{\beta_R}} \quad (28)$$

The equilibrium concentration in the solid phase is described by q_e (mg/g), whereas the equilibrium concentration in the liquid phase

is given through C_e (mg/L). Furthermore, A_R (L/g) and B_R (L/mg) are the Redlich–Peterson isotherm constants, and Q_m (mg/g) is the monolayer adsorbent capacity. β_R is defined as the Redlich–Peterson exponent with values ranging from 0 to 1. The equation may be approximated by the Henry equation if $B_R \cdot C_e \ll 1$. In contrast, saturation cannot be explained with this model ($B_R C_e \gg 1$), but there is an approximation to the Freundlich type (9, 11, 37). This approximation is given in eq 29:

$$q_e = \frac{A_R}{B_R} \times C_e^{1-\beta} \quad (29)$$

where A_R/B_R represents K_F of the Freundlich model and $(1 - \beta)$ is equivalent to $1/b_F$ (41).

The linearized form of this equation can be expressed as follows (eq 30) (42):

$$\ln \left[\frac{A_R C_e}{q_e} - 1 \right] = \ln B_R + \beta_R \ln C_e \quad (30)$$

5.1.2.1.3.3. Tóth Isotherm. The Tóth isotherm equation (eq 31) relies on a combination of the Langmuir and Freundlich isotherms by forming a differential equation through multiplying both differential equations with each other.

$$q_e = \frac{C_e^{A_T}}{\left(\frac{1}{K_T} + C_e^{B_T} \right)^{A_T/B_T}} \quad (31)$$

In solid–liquid phase systems q_e (mg/g) expresses the amount of adsorbate per gram of sorbent at equilibrium and C_e (mg/L) the solute concentration under equilibrium conditions, whereas K_T , A_T , and B_T are temperature-dependent constants. In the following edge cases the three-parameter equation is simplified, yielding the Langmuir isotherm ($A_T = B_T = 1$), Henry isotherm ($A_T = B_T = 1$, and $C_e \ll 1/K_T$) or Freundlich isotherm ($B_T = 1$ and $C_e \ll 1/K_T$), respectively (9, 37).

5.1.2.1.4. Isotherm Equations for Models Considering More than Three Parameters. Isotherm equations considering more than three parameters are rarely used because of the increasing complexity of their determination with an increasing number of parameters. Furthermore, the adjustment of experimental data to such models is limited because of measuring errors. In this context, the Fritz–Schülner isotherm and the vacancy solution theory (VS theory), which has been modified by Fukuchi (43) to adjust this model to liquid systems, need to be mentioned. This work has been reported in the literature, but is of minor importance as compared to the aforementioned theories (8, 9, 11).

5.1.2.2. Adsorption from Mixture Solutions. The aforementioned isotherms are commonly applied to describe the adsorption in single-compound systems. Models for the determination of adsorption equilibrium isotherms using mixture solutions are divided into two groups. In the first, mixture isotherms merely rely on the expansion of common single-isotherm equations, whereas the second comprises thermodynamic determination methods to describe the more complex systems. Both groups have thoroughly been reviewed by Kümmel and Worch (11).

5.2. Ion Exchange. Ion exchange phenomena exhibit numerous similarities with adsorption processes, but there are also some significant differences. The compound species considered in this type of process are ions that are not removed from the solutions but are replaced by ions bound by the solid phase via electrostatic interactions to achieve electroneutrality. Accordingly, there are two ionic fluxes, one into the ion exchange particles and the other in the opposite direction out of the resin particles.

In most cases, adsorption and ion exchange phenomena are not differentiated in practical applications, and most theories and models have been approached by using adsorbent resins. This is due to the fact that the situation is less complex if the resins are devoid of functional groups. In numerous cases, these findings have been translated into ion exchange processes (1).

One aspect, which has attracted little interest so far, is the fact that upon the exchange of ionic organic compounds adsorption also occurs onto the resin matrix due to hydrophobic interactions. This makes the evaluation of ion exchange data much more complex. Accordingly, calculations specific to ion exchange processes based on experimental results obtained from studies with charged organic compounds may only be a rough assessment. This is attributed to the fact that the differentiation between ion exchange and sorption processes is impossible without further analytical investigations, such as the quantification of counterions released during the process.

5.2.1. Kinetics and Thermodynamics of Ion Exchange Processes. The kinetics of ion exchange is much more complicated than that of sorption processes, because there is not only a mass flow directed toward the exchanger material as in the case of adsorbent resins but also a countercurrent of two opposite electrical charges: first, of the target compounds to be bound by the exchange material and, second, of the counterions, which are released during the exchange process and migrate into the surrounding solution. The electroneutrality needs to be preserved throughout the exchange process. This not only depends on these two ion species migrating in opposite direction but also depends on the co-ion transport through the exchange matrix, whereas the latter may be restricted by the Donnan exclusion in many cases.

The rate-determining step may also depend on the film or particle diffusion, which are also affected by the different diffusion rates of the replaced ions and target compounds. Such unequal ion fluxes cause deviation from electroneutrality and induce an electric potential (diffusion potential), which affects the diffusion of both ions types, that is, the potential accelerates slower and decelerates faster ions.

Most models established so far describe the kinetics based on diffusion processes as can be deduced from the decrease of the target compound contents in the solution and not on ion exchange rates. Furthermore, theoretical kinetic models are simplifications of the highly complex ion exchange processes. Accordingly, most models are based on major restrictions, such as the assumption of homogeneous matrices with regard to surface area and pore structure and of constant diffusion coefficients over the whole process and for all ionic compounds. Furthermore, most models consider only one counterion species or assume that significant changes in swelling or in the swelling pressure do not occur, which leads to the assumption that such models may not be applicable to more complex ion exchange systems. Real systems usually comprise several ions, which compete for the functional groups of the resins. This means that they have different affinities for the functional groups and that they interact with each other or with the backbone of the exchange material. Thus, on the basis of these assumptions the kinetics of ion exchange may be specified on the basis of diffusion, applying one of the model assumptions described by Helfferich (7), which are based on Fick's first law taking into consideration the aforementioned restrictions, or utilizing one of the rate laws, that is, the first-, pseudo-first- or pseudo-second-order kinetics (1, 2, 7).

5.2.2. Ion Exchange Equilibrium. Comparable to adsorption processes, equilibrium isotherms of ion exchange phenomena describe the distribution of the target components between the solid and liquid phase at equilibrium. In contrast to adsorption, ion exchange may show more than one isotherm at a particular

temperature. This results from differences in the exchange of ions with different valences due to concentration–valence effects (1). Thus, the expression isotherm–isonormal should rather be used for such equilibrium curves when ion exchange phenomena are characterized. In theory, one isotherm can be obtained for the exchange of ions with the same charge. In the case of different valences, it is necessary to use the same normality for ion exchange experiments.

Using normalized ion exchange isotherms, the interdependence between the ionic composition of the liquid and solid phase in ion exchange systems can be shown. For this purpose, the equivalent ion fraction of one counterion on the ion exchanger surface (\bar{X}) (eq 32) is plotted versus the equivalent ion fraction of the same ion in the solution (X) (eq 33).

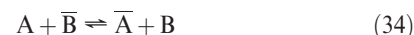
$$\bar{X} = \frac{Z_i[\overline{\text{ion}}_i]}{\sum_{j=i}^n Z_j[\overline{\text{ion}}_j]} = \frac{Z_i[\overline{\text{ion}}_i]}{Q} \quad (32)$$

$$X = \frac{Z_i[\text{ion}_i]}{\sum_{j=i}^n Z_j[\text{ion}_j]} \quad 0 \leq X \leq 1 \quad (33)$$

where Z_i and $[\text{ion}_i]$ or $[\overline{\text{ion}}_i]$ are the charge and molar concentration of the respective ion in the solution (mol/L) or in the solid phase (mol/g), respectively, whereas Q is the ion exchange capacity of the resin. The deviation of this plot from a diagonal isotherm, which indicates no preference for any of the ions, allows selective enrichment of one ion and thus enables selective extract purification. An S-shaped isotherm indicates a two-step process, with one process dominating at lower and the other at higher loading degrees (2, 7).

With regard to the appropriateness of individual isotherms for particular ion exchange systems, there are no general rules or established isotherms, and commonly the isotherm that best fits the analytical data is used (cf. 1.4.1.2).

5.2.2.1. Selectivity Characteristics. Ion exchange processes can generally be expressed as follows:



where A and B illustrate the ions present in the solution brought into contact with the resin and \bar{A} and \bar{B} are the counterions bound by the functional groups of the exchanger. Accordingly, ion B is exchanged against A.

The separation parameters described below give a first overview of the most common characteristics, which have been described in the literature but which can only partially be used for the comparison of different exchanger systems. In general, the comparison of equivalent proportions of one ion between the two phases is the simplest method to obtain information on the selectivity of ion exchange processes.

5.2.2.1.1. Separation Factor. On the basis of eq 35 it is possible to determine the separation factor α of the ion exchange process at equilibrium.

$$\alpha_{A-B} = \frac{\bar{m}_A m_B}{\bar{m}_B m_A} = \frac{\bar{X}_A X_B}{\bar{X}_B X_A} = \frac{\bar{C}_A C_B}{\bar{C}_B C_A} = \frac{\lambda_A}{\lambda_B} \quad (35)$$

In this expression m_i and \bar{m}_i are the molalities and C_i and \bar{C}_i the molarities of the respective ions, whereas X and \bar{X} represent the proportions of the ion in the solid phase and liquid phase at equilibrium, respectively. Separation factor values above 1 indicate a preference of ion A, whereas ion B is preferably bound at α values of < 1 . The numerical value of the separation factor α

and its independence from the concentration scale is a great advantage with regard to the application as parameter for comparison (2, 7).

5.2.2.1.2. *Distribution Coefficient.* The molal or molar distribution coefficient λ_i and λ_i' , of the ion i , respectively, is another parameter helpful for describing the equilibrium distribution of ions between the liquid phase and the solid phase of the ion exchanger (1, 2, 7). These parameters are defined as follows (eqs 36 and 37):

$$\lambda_i = \frac{\bar{m}_i}{m_i} \quad (36)$$

$$\lambda_i' = \frac{\bar{C}_i}{C_i} \quad (37)$$

5.2.2.1.3. *Selectivity Coefficient.* The selectivity coefficient can also be used instead of the separation factor to describe ion exchange equilibria. This may apply if the ion exchange reaction (eq 34) obeys the mass action law and is described by its term, because the ion exchange process can be regarded as a physical redistribution of ions without chemical reaction.

$$k_{A-B}' = \frac{\bar{m}_A^{Z_B} m_B^{Z_A}}{\bar{m}_B^{Z_A} m_A^{Z_B}} \quad (38)$$

$$k_{A-B}'' = \frac{\bar{C}_A^{Z_B} C_B^{Z_A}}{\bar{C}_B^{Z_A} C_A^{Z_B}} \quad (39)$$

Equation 38 describes the selectivity coefficient k_{A-B}' using the molality of the ions, whereas k_{A-B}'' (eq 39) is calculated using molarities. Z_A and Z_B are the electrochemical valences of the species A and B.

If the selectivity coefficient is used for comparing different systems, it should be kept in mind that this parameter strongly depends on the operation conditions. Consequently, selectivity coefficients obtained through applying different experimental conditions may not be compared (2, 7).

However, it has also been noted that eq 39 may only be calculated using the equilibrium concentrations $\bar{C}_i^{Z_i}$ and $C_i^{Z_i}$ if complex formation in the solution does not occur and if interactions between the counterions are not observed (2).

The selectivity coefficient may also be calculated using equivalent ionic fractions and is then equated with the rational selectivity coefficient

$$K_{A-B} = \frac{\bar{X}_A^{Z_B} X_B^{Z_A}}{\bar{X}_B^{Z_A} X_A^{Z_B}} \quad (40)$$

where only in the case of identical valences of the counterions ($Z_A = Z_B$) is the selectivity coefficient predicted by the molality (eq 38) or the molarity (eq 39), respectively, identical to the selectivity coefficient determined according to eq 40.

As mentioned by Helfferich (7), unfortunately the notation of the aforementioned equations in the literature strongly differs, which also aggravates direct comparison. As an example, Zagorodni (2) differentiates between the selectivity coefficient and equilibrium coefficient, whereas the latter is consistent with the expression given as eq 40.

6. TECHNIQUES OF ADSORPTION AND ION EXCHANGE

As described further below, the applications of adsorbent and ion exchange technology and the industrial equipment, which is used for different requirements, are highly variable. Consequently, it is only possible to provide a brief overview of the currently used adsorbent and ion exchange processes.

6.1. **Bed Processes with Fixed Bed Reactors.** The bed process is the most commonly used and simplest technology for fluid adsorption and ion exchange processes. In this type of process, resin loading is performed until the concentration of the solution leaving the bed exceeds a certain threshold level. This stage of the process indicates exhaustion of the resin capacity and is referred to as breakthrough. In bed sorption processes breakthrough loading is commonly performed instead of equilibrium loading, which is characterized by much higher compound leakage. Subsequently, the resin needs to be regenerated or substituted. For a better utilization of the resin in bed processes, adsorber and ion exchange columns are commonly connected in series using either several columns in different loading states or one adsorber with several adsorption layers. Alternatively, adsorbent or ion exchange columns in different loading states may be connected in parallel to obtain a mixed concentration of the column eluates. Bed processes may be further differentiated on the basis of the method of regeneration. In cocurrent regeneration procedures both the loading and regeneration of the resin are performed in the same flow direction. In contrast, countercurrent regeneration means that the solutions used for regeneration are applied to the column in the opposite direction as compared to sample application. This procedure yields higher concentrations upon desorption, because the resin particles at the end of the sorbent column are not brought into contact with highly concentrated eluates. Consequently, countercurrent processes require less desorbent and afford higher eluate concentrations. Besides some disadvantages, bed processes have crucial advantages with regard to marginal instrument and metrological equipment requirements (1, 2, 9, 11).

6.2. **Batch Processes in Agitated Reactors.** Batch processes may be operated in continuous and discontinuous modes. Agitating a fixed amount of adsorbent in a defined fluid volume is the simplest application of such a discontinuous batch process. After reaching equilibrium conditions, the adsorbent needs to be removed from the fluid, for example, by filtration or sedimentation, after which the adsorbent can be reused or disposed of. However, in industrial applications equilibrium is normally not reached, because the recovery of the target compounds per time is optimized. In contrast, continuous processes are based on multistage purification or separation steps, with an economic evaluation being required to deduce optimum conditions for each application. The sorbent amount needed can be lowered through optimized utilization. For this purpose, the adsorbent and the fluid, which is to be purified or contains the target compounds to be recovered, may be brought in contact in countercurrent processes. Furthermore, an increase in the number of process stages also contributes to the need for lower resin amounts. Additionally, the wide variation of residence time of the adsorbent in the reactor gives rise to uneven loading of the resin particles. Due to the lower exploitation of adsorbent capacity in batch processes as compared to bed process technology as well as higher acquisition and operating costs, bed processes are commonly preferred. Nevertheless, the comparatively expensive batch adsorption process using agitated reactors is mainly applied for producing high-quality biotechnological and pharmaceutical products, such as antibiotics or proteins. Furthermore, batch processes are also commonly applied in the beverage industry and for potable water preparation using powdered activated carbon (1, 2, 8, 9, 11).

6.3. **Moving Bed Processes Performed in Reactors with Moving Solid Phase.** This technology consists of continuous sorption processes applicable to sorbent materials, which are not delivered in powder form. Here the sorbent material crosses the system from top to bottom without being kept in suspension and is removed from the system from time to time. The solution containing the adsorptive is applied in countercurrent direction,

thus introduced at the bottom end and removed at the top end of the reactor. Another moving bed process variant is characterized by the periodic application of a solvent flow through the adsorber from bottom to top that leads to a pulsative rise of the adsorbent (expanded bed, semifluidized bed, or suspended bed). The flow rate of the adsorbent is controlled via the continuous quantification of the target compounds in the feed stream and by the maximum tolerable level of these components in the fluid stream after adsorption or ion exchange. Even though circumventing major disadvantages of bed processes, moving bed technology also has some significant disadvantages, such as high investment costs and the complexity of resin dosage and suspension and the control of the fluid and solid phase transport. Fluidized bed adsorbers have a further advantage common to all moving bed processes, because these technologies may be applied even if the solutions to be purified contain solid particles. However, such processes are currently still limited to research applications (1, 2, 8, 9).

7. APPLICATIONS OF ADSORPTION AND ION EXCHANGE TECHNOLOGY

7.1. General Applications. Together with the development of more sophisticated synthetic ion exchange and adsorbent resins, the number of potential applications on industrial scale rose as well. In recent decades, profound knowledge has been accumulated concerning the structure and properties of ion exchange and adsorbent resins. Concomitantly, the bonding types and interactions between the adsorptive and adsorbent as well as between the counterion and the ion exchanger were studied, resulting in more detailed information, which is useful for process optimization and further investigations (1–3, 8, 32, 44–49).

7.1.1. Adsorbent Resins. Water purification is one of the most important applications of adsorbent technology in solid–liquid systems, providing water in high quality, which is required for industrial purposes, for example, for the production of paper, synthetic fibers, electrical power, or electronic components as well as for pharmaceutical and food production and for laboratory purposes (1, 2, 50). Furthermore, there are many biotechnological processes making use of sorbent recovery to enrich and purify components used in foods, beverages, cosmetics, and pharmaceuticals. As an example, Hua et al. (51) reported enhanced vanillin production from ferulic acid through a biotransformation strategy by selectively adsorbing vanillin throughout the process. Consequently, increased vanillin yields may be reached by avoiding toxic effects on the *Streptomyces* sp. strain V-1 used in this study for converting ferulic acid. In addition, inhibition of the microorganisms due to product accumulation can be prevented by sorptive recovery of the target compound.

In another process, adsorbent resins were applied to purify rosmarinic acid from *Lavandula vera* DC. biomass, which was cultivated in bioreactors (52). Rosmarinic acid is used for pharmaceutical purposes due to its antibacterial, antiviral, anti-inflammatory, antioxidant properties, and concomitant low toxicity.

From a pharmacological and cosmetics point of view, oregonin is another interesting compound, and its recovery from alder species such as *Alnus glutinosa* L. and *Alnus incana* L. has been described (53). For this purpose, oregonin was extracted from the bark with hot water, subsequently concentrated by binding onto an adsorbent resin based on acrylic esters, and finally eluted with alcoholic solutions.

7.1.2. Ion Exchange Resins. In accordance with adsorbent resins, water softening and purification are by far the economically most important applications of ion exchange, thus providing water in high quality required for industrial purposes, for example, for pharmaceutical, food, and textile production as well as power generation (2, 44, 50, 54).

Moreover, biotechnological processes make use of not only adsorbent technology but also ion exchange techniques. In this context, in the production and application of microbial transglutaminase, extracellular transglutaminase was separated from the fermentation broth in a downstream process *inter alia* by a strongly acidic ion exchanger (55). The production of microbial transglutaminase instead of its isolation from animal and plant tissues allowed for the first time mass production of this technologically important enzyme from relatively cheap substrates. Consequently, such novel production strategies enable the application of enzymes, such as transglutaminase, on a large scale in food processing and the cosmetics and pharmaceutical industries as well as for medical treatments. The very diverse applications of this particular enzyme comprise the modification of the functional properties of food proteins, such as whey and soy proteins, gluten, myosin, and actomyosin by catalyzing the cross-linking of proteins (56). These modifications may bring about textured products and yield food proteins of higher nutritive values by cross-linking proteins, which complement each other with regard to their limiting amino acids. Such cross-linking reactions also significantly affect the technofunctional properties; they may improve the elasticity and water-holding capacity and modify the solubility and further functional properties of the proteins, and they help to avoid the heat treatment necessary for gelation. Furthermore, transglutaminase-catalyzed reactions contribute to the protection of lysine against a number of chemical reactions involving food proteins or can be used to encapsulate lipids and lipid-soluble materials or to produce heat- and water-resistant films.

The purification of lactic acid produced through fermentation processes is a further application of ion exchange on an industrial scale. Inhibitory effects due to product accumulation usually characterize the microbial production of lactic acid using different natural feedstocks. Because this inhibition is already induced by relatively low amounts of lactic acid in the fermentation broths, Ataei and Vasheghani-Farahani (57) proposed an *in situ* separation of lactic acid from the fermentation media using a strongly basic ion exchanger. On the other hand, the purification of lactic acid following fermentative production has also been reported using weak anionic (58) and strong anionic ion exchange materials (59), respectively. Furthermore, combinations of cation and anion exchange resins, which are applicable either to recover lactic acid (60, 61) or to remove all other compounds from the fermentation broth except lactic acid (62) have been described as well. Lactic acid is widely applied in the food industry, in medicine, chemical, and pharmaceutical fields, and as educt for the production of biodegradable and biocompatible polymers in the packaging industry and in medicine (63, 64). In this case, ion exchange technology proves to be a suitable and relatively simple and inexpensive alternative to other tedious purification methods used so far (57, 62, 64).

Further applications of ion exchangers comprise the purification of blood, vitamins (65), and enzymes as well as of pharmacologically active compounds (2, 44, 54), such as antibiotics (66–68). Sometimes ion exchange resins themselves are used as active pharmaceutical ingredients or as excipients (69).

7.2. Food Production. In food production, ion exchange and adsorption technology is applied for numerous purposes, not only during food production itself but also for wastewater treatment. With respect to holistic and sustainable agricultural production, the residues of food production are of increasing interest to processing companies, because these byproducts are normally still rich in a number of valuable compounds. Accordingly, they can be used to obtain, for example, proteins or pectins and to recover non-nutritive plant secondary metabolites, such as

polyphenols, which are used as supplements of functional or enriched foods. The most important applications for these purposes are summarized below.

7.2.1. Adsorbent Resins in Food Production. As mentioned before, adsorbent technology is not only implemented into existing food production lines but also commonly applied to treat the huge amounts of wastewater originating from such processes. In this context, adsorbent technology may form a substantial part of the respective concept of water treatment for removing organic compounds (1, 70). For example, olive oil mill effluents are decolorized prior to their anaerobic digestion (71).

Fruit juice technology is one of the most important application areas of adsorbent resins in the food industry. As an example, Vivekanand et al. (72) have described a process for the quality improvement of UF-clarified pear juice by successively using an adsorbent resin and a weak ion exchanger at different operating temperatures. The adsorbent resin brings about the removal of most colored organic compounds from the preconcentrated pear juice, whereas the ion exchanger significantly lowers color intensity and titratable acidity, thus leading to desirable clear, light-colored, and weakly flavored juices. Such products have been designed to retain their nutritional values and extended their shelf life. They are used as a substitute for sugar syrup in canned fruits or as a source of natural sugar when mixed with other juices, because they are devoid of precursor compounds, which may cause haze formation and discoloration upon storage (72).

Adsorbent resins may not only be used for the aforementioned juice and syrup production for the fruit canning industry but also for the stabilization and decoloration of fruit juices as well as for reducing the bitterness of citrus juices. In this context, adsorbent technology appears to be an appropriate alternative to common fining methods using bentonite, gelatin, and silica sol, respectively. The combination of adsorbent technology with an upstream ultrafiltration step reveals synergistic effects by removing compounds above a particular molecular size and additionally by exploiting hydrophobic interactions of juice components with the adsorbent resin. In general, adsorption processes provide the opportunity to standardize juices and even to produce light-colored almost water-clear juices (73–75). On the other hand, fruit juices such as apple juice have been applied as model solutions in laboratory-scale experiments for studying the selective recovery and fractionation of phenolic compounds using adsorbent resins. These efforts aim at the systematic optimization of purification and separation processes by adaptation of process parameters to obtain polyphenol preparations with well-defined functional properties, which may be applied in functional or enriched foods (76). Furthermore, the recovery of phenolic compounds with adsorbent resins using apple polyphenol model solutions has also been performed at pilot scale. The leakage rates during column loading as well as the elution of individual compounds with hydroalcoholic and NaOH solutions were demonstrated to be structure-dependent, which allows selective enrichment of certain polyphenol classes (77).

Off-tastes and off-flavors are another issue associated with juice production. Such problems may arise immediately after processing or during storage. The bitterness of grapefruits and navel oranges caused by naringin and limonin and by hesperidin and limonin, respectively, are examples of such off-tastes occurring prestorage (78–83). Furthermore, consumers may reject highly acidic juices (79, 80). According to literature reports, such off-tastes and off-flavors can be removed by treating the juices with adsorbents as a final step of juice production. With regard to the reduction of juice acidity, it has been demonstrated that in comparison to adsorbent resins organic acids may be more effectively removed by using weak anion exchangers (79, 80).

However, off-tastes and off-flavors developed during storage are unaffected by such a treatment. These off-tastes and off-flavors are formed from precursors, which themselves do not negatively affect the sensory properties of the fresh juice, if they are degraded or react with other juice components. Precursor components, which contribute to off-flavor formation, may result from the heating process in the course of thermal preservation of the juices, from degradation processes such as the Strecker reaction or from other nonenzymatic browning reactions. Ferulic acid is an example of such a precursor compound, because it may lead to the formation of *p*-vinylguaiacol, which contributes to an “old fruit” or “rotten” flavor (84, 85). Processes to cope with off-tastes and off-flavors arising during storage by removing such precursor components from juices using adsorbent resins have been described with the changes being immediately noticeable. Such a process enhances the sensory quality of the juices without affecting their nutritional values and at the same time extending shelf life over a long period even if stored at ambient temperature, provided that microbiological stability is given (84, 85).

The selective removal of unwanted compounds from olive oil miscella is a completely different application of adsorbent resins (86). In this process, *n*-hexane extracts from crushed olives, containing pigments, such as carotenoids, chlorophylls, and pheophytins, and also free fatty acids, phospholipids, and various oxidation products, need to be refined by using adsorbent materials in single-step or multistep processes after oil extraction. After sorptive removal of these compounds, the oil can be used for edible purposes. A systematic comparison revealed the efficiency of activated carbon and activated earth to be much higher compared to synthetic resins with regard to the removal of the aforementioned components. Furthermore, the selectivity of the recovery of these different compound classes significantly depended on the type of adsorbent material and the adsorbent/oil ratio. In addition, due to the different selectivities of the sorbents the sequential application of different materials might be useful (86).

7.2.2. Ion Exchangers in Food Production. As mentioned for adsorbent resins, ion exchangers also play a dominant role in wastewater treatment as well as in water softening, desalination, and purification to provide water in sufficient purity for the respective applications (1, 2, 50, 87).

The decolorization of sugar beet and sugar cane extracts during sugar production is another very important application of ion exchange technology. The spoiling pigments result from Maillard reactions and alkaline degradation of hexoses (88, 89), but may also be of phenolic nature (90). To produce colorless sucrose crystals sugar syrups may be decolorized by highly cross-linked, macroporous styrenic copolymers functionalized with weakly basic as well as weakly acidic functional groups, respectively (90), or by styrene divinylbenzene copolymer based adsorbent resins (88). Furthermore, a macroporous copolymeric resin, made up of a monovinyl aromatic monomer, which was post-cross-linked in the swollen state and additionally functionalized with hydrophilic groups, has also been reported to be applicable for the decolorization of aqueous sugar solutions. This also allows the subsequent recovery of the colorants and of their precursors (91). It is well-known that the nature of colorants is quite different in sugar beet and sugar cane extracts, which also has an impact on the requirements of the resin materials used for decolorization (89). Furthermore, the evolution of colorants in sugar beet juices during decolorization using a strong anionic styrene resin has been studied in detail, revealing that operating conditions and the type of solvent have significant impacts on the binding and elution of the colorants and also showing that different affinities

of the colorants depend on the differences in their molecular weights (89).

The decaffeination of liquid extracts such as of coffee, tea, and cocoa is another very interesting application of ion exchangers. Using a gel copolymer composed of monovinyl aromatic monomer units, cross-linked after polymerization in swollen state and functionalized with hydrophilic groups, has been shown to be efficient in binding caffeine without removing substantial amounts of chlorogenic acid from coffee extracts. The subsequent elution of bound caffeine may be performed with organic solvents. Compared to other decaffeination processes, this procedure affords a very aromatic, dark colored, and very flavorful product (92). By applying ion exchange and adsorption technology the disadvantages of other processes, such as the extraction of caffeine with organic solvents, supercritical extraction requiring cost-intensive equipment and high pressures, or the Swiss extraction using carbon beds that act abrasively, thus causing costly maintenance, may be avoided (92).

Ion exchange technology has a wide area of application in the beverage industry, where it is used to resolve a number of problems. In this context, haze formation in beer, wine, and fruit juices upon storage is a major problem. To prevent haze formation in these beverages, the precursors, that is, proteins and polyphenols, need to be lowered in their contents, whereas the removal of phenolic compounds also causes undesirable color losses. A procedure used so far, which also brings about partial color loss, implies the application of bentonite in combination with diatomaceous earth filters to remove the bentonite after its use. This process is characterized by the disadvantage of causing negative taste in wines and being responsible for decreased product recovery rates (73, 93). Due to these drawbacks the application of an anion exchange resin in sulfonated form has been suggested to selectively remove haze-forming proteins in beer and wine without markedly affecting color (93). Another ion exchange- and reverse osmosis-based process to remove divalent ions from tea beverages has been reported to obtain a product containing tea polyphenols from black and/or green tea leaves, which is stable in color and devoid of any turbidity (94).

Furthermore, ion exchange technology is commonly used for the reduction of organic acid contents of fruit juices, mostly of citrus juices (79, 80). In addition, the production of fruit syrups from apples, pears, plums, damsons, cherries, figs, dates, grapes, pineapples, bananas, and carobs using anion and cation exchange resins for the demineralization, deionization, and decolorization has been described (95).

There are also studies describing the improvement of white and rosé wine decoloration by applying continuous ion exchange processes instead of the common discontinuous decoloration with activated carbon, which is a time-consuming process due to the settling and filtration process, respectively, which is associated with considerable losses regarding production quantity and a considerable amount of solid wastes (96).

Additionally, the application of ion exchangers has been suggested to produce low-acid fruit juice/vegetable–milk beverages (97). For this purpose, the juices were decationized using a strong cation exchange resin, causing a pH decrease to 2.5–3.0. Subsequently, a strong anion exchanger was applied to increase the pH value to 8.0–11.5 and deanionize the vegetable or fruit juices. As a further step, the juices were once more treated with a strong cation exchange resin, resulting in a pH value of 3.5–4.5. The milk component of the beverage was obtained by contacting the milk with a strong cation exchange resin, thus, decreasing the pH value to 1.5–3.2. Following this, the milk was treated with a strong anion exchanger to remove anions and increase the pH value to 3.5–4.5. The resulting mineral content of the obtained

milk preparation was below 0.25 g/L. Finally, the juice and milk components were blended, homogenized, and subsequently pasteurized or sterilized, respectively, and/or carbonated. The beverages obtained did not show any precipitation or curdling, although the pH of the beverages was below the isoelectric point of casein.

Processes for the selective removal of sugars from beverages, such as citrus juice, cranberry juice, apple juice, or pineapple juice, alcoholic beverages, and dairy products are a completely different application of ion exchange technology (98). The resin used for that particular purpose is composed of a cation exchanger, which builds up a complex with the sugars via its counterions Ca^{2+} , Na^+ , and K^+ . This process helps to reduce energy costs significantly during juice concentration, to bring down costs of storage and transport, and to produce low-calorie juices and alcoholic beverages sweetened with synthetic additives without affecting the natural contents of minerals, vitamins, and other beneficial compounds as well as flavor, aroma, and color. Accordingly, ion exchangers also allow reducing the lactose contents in milk and other dairy products.

Furthermore, ion exchange technology and combinations with adsorbent resins may be applied in a wide range of other fields as can be deduced from the product descriptions of resin manufacturers (99, 100). As an example, the desalination of inulin from chicory and Jerusalem artichoke and the desalination and preparation of syrups from corn, wheat, potatoes, and cassava have been described. Ion exchange is also applicable for the selective purification of sugar alcohols, obtained from mono- and disaccharides by nickel catalysis. For this purpose, the catalysts are recovered and the solution decolorized and desalted. Finally, resins are available for the softening of gelatin and the desalting of pectins.

7.3. Recovery of Bio- and Technofunctional Compounds from Byproducts of Food Processing. Food production is commonly associated with large amounts of byproducts, which are still very rich in valuable compounds. This provides the opportunity to recover such components as added value and to contribute to sustainable agricultural production (101, 102). Ion exchangers and adsorbent resins may be applied to enrich and purify such products from food-processing byproducts, and some of these applications are further described below. However, not all of these processes are applied on an industrial scale so far.

7.3.1. Protein and Peptide Recovery. Among other methods ion exchangers are used for the purification and isolation of proteins and amino acids, for example, of whey proteins originating in huge amounts as byproducts of cheese production. Whey proteins are mainly composed of α -lactalbumin and β -lactoglobulin as well as lower amounts of immunoglobulin, bovine serum albumin, glycomacropeptides, lactoferrin, and lactoperoxidase. These different proteins may be separated by exploiting the selective binding onto or desorption from exchanger resins under optimized operating conditions (103). Thus, a number of methods for whey protein isolation using cation exchangers have been patented, preventing protein denaturation during purification (104). These purified proteins of high nutritional value can be applied as a mixture in food products, for example, as thickening or stabilizing agents in clear beverages and as infant or enteral formula or pharmaceutical formulations, respectively. The purification of individual whey proteins has been studied in detail. As an example, the dependency of the purification of glycomacropeptide, a decomposition product formed because of enzymatic cleavage of κ -casein during cheese production, from conductivity, pH value, and elution buffer salinity when using an anion exchanger was assessed (105). Great importance has been attached in this study to the use of food-grade resins, food-grade eluent buffers,

and operating conditions relevant to industrial procedures, showing that highest recovery may be reached at decreasing conductivity and increasing pH value of the mozzarella whey feed stream used in this study. Glycomacropeptides have attracted much interest because they are devoid of aromatic amino acids, such as phenylalanine, tryptophan, and tyrosine, thus making them an interesting protein source for people suffering from phenylketonuria.

Furthermore, the purification of whey permeate using bentonite and ion exchangers yields syrups containing hydrolyzed lactose, which may be used as potential sweetener or as energy source in nutrient solutions applied for fermentation purposes (106). Gonzales et al. (107) described the production of a modified whey powder characterized by low mineral contents, low hygroscopicity, and beneficial organoleptic properties using ion exchange resins. This product may be applied in dry form, for example, in biscuits, confectionery, or powdered soft drinks.

Additionally, adsorbent technology is useful for desalting and debittering whey, soy, defatted sesame, and fish skin protein hydrolysates (108–111). For this purpose, protein hydrolysates are adsorbed onto a macroporous resin. Subsequently, the resin is washed with deionized water to remove salts, and the adsorbed peptides may be desorbed fractionwise by using different alcohol concentrations (110, 111). Accordingly, bitter peptides can be selectively removed from the hydrolysates. With regard to fish skin hydrolysates it was noted that the washing step causes a significant reduction of fish flavor and of the bitter taste of the final product (110). These hydrolysates may find application in pharmaceutical products, in functional foods, and in infant formula, as well as in clinical nutrition (111).

The recovery of grass carp fish scale peptides using nonpolar macroporous resins is another quite different approach demonstrating the broad applicability of this technique (112). Protein hydrolysates are of particular interest to both the food and pharmaceutical industries due to their biofunctional properties. In the case of grass carp peptides the inhibition of the angiotensin-I converting enzyme (ACE), resulting in a decrease of blood pressure, is the bioactive principle rendering their recovery worthwhile. On the other hand, increasing costs for the disposal of the filleting residues in the growing grass carp fish production, and the fact that they are underutilized so far, spark interest in their exploitation to recover novel value-added products. In summary, such grass carp peptide preparations were obtained by dissolving freeze-dried powders of the scale hydrolysates in water and applying them to adsorbent resins, followed by the desalting with distilled water and the fractionwise elution of the peptides with aqueous ethanol solutions of increasing alcohol proportions.

In addition, resin adsorption and ion exchange were demonstrated to be valuable tools for the recovery of protein isolates of high nutritional and sensory quality from the byproducts of sunflower oil processing. These proteins have not been utilized for human consumption so far because of major drawbacks due to coextracted phenolic compounds, which may covalently bind to the proteins bringing about discoloration and impaired technofunctional characteristics of the protein isolates. For this purpose, adsorbent and ion exchange resins, which show minimal interactions with the proteins, are instrumental to selectively bind the phenolic compounds from crude protein extracts, thus yielding proteins devoid of polyphenols with improved functional and sensory properties (113).

7.3.2. Tocopherol Recovery from Food Processing Byproducts. The separation and purification of tocopherols and tocotrienols from natural sources, especially the byproducts of plant oil refining, synthetic and semisynthetic tocopherol products,

demonstrate another application area of ion exchange and adsorbent technology (114). Tocopherols and tocotrienols, commonly referred to as vitamin E, are the most important natural fat-soluble antioxidants, which are able to donate their phenolic hydrogen to free radicals, thus acting as radical scavengers. Tocopherols and tocotrienols can be recovered using strongly basic anion exchangers or nonionic adsorbent resins. The selectivity of the recovery process when using nonionic adsorbent resins is mainly determined by the elution step. For this purpose, tocopherol mixtures are dissolved in a long-chain alkane and applied to the adsorbent column. During the fractionated desorption of the tocopherols, the polarity of the eluent is constantly increased. The desorption starts with a long-chain alkane to elute α -tocopherol, followed by a mixture of long-chain alkane solvents containing ketones to elute γ -tocopherol and finally by a monohydric alcohol or mixtures thereof to recover all other tocopherols. In contrast, when strongly basic anion exchangers are used, the sample containing the tocopherol mixture is dissolved in a polar solvent mixture, containing, for example, methanol and acetone. In this case, fractionation may be obtained due to the weaker interaction of nonpolar tocopherols with the ion exchanger as compared to more polar ones (114). Khare (115) used organic solvents such as methanol for the elution of γ -tocopherol, whereas α -tocopherol was also eluted with this solvent. In contrast, δ -tocopherol was eluted by using an acidified organic solvent. According to another process the isolation of tocopherol isomers from crude palm oil, palm oil products, or palm oil byproducts as well as vegetable oils or vitamin E-comprising preparations can be achieved. For this purpose, free fatty acids and triacylglycerols were esterified or transesterified and, subsequently, the esters were removed by distillation before the obtained vitamin E concentrate was selectively bound onto an adsorbent resin. The fractionated elution of the tocopherols was realized using a supercritical fluid, such as CO₂, in combination with a modifier or other solvent such as propane, propene, or ethylene (116). Using this technology, tocopherols can also directly be isolated from plant oils. Thus, such a recovery process is not restricted to the byproducts of plant oil production.

7.3.3. Polyphenol Recovery from Food Processing Byproducts. Byproducts originating from plant food processing are usually particularly rich in plant secondary metabolites, especially polyphenols. Due to the technofunctional properties of phenolic compounds, such as their antioxidant and antimicrobial potential or their protective and stabilizing effects on food color and aroma as well as their biofunctional characteristics, including anticarcinogenic, antithrombotic, anti-inflammatory, antimicrobial, and antioxidant properties, they are highly interesting for the food, pharmaceutical, and cosmetics industries. The characteristics and fields of application of extracts obtained from food-processing byproducts may significantly differ depending on the type of fruit or vegetable residue used for polyphenol recovery.

7.3.3.1. Fruit Phenolics. The byproducts of citrus juice production, that is, peels as well as core, cell, and membrane residues, are commonly used as cattle feed, but may also be exploited for pectin recovery. Furthermore, citrus byproducts might serve as sources of cold-pressed oils, D-limonene, natural flavors, aroma, ethanol, molasses, pulp wash, and flavonoids (102, 117). Citrus fruits and products derived therefrom are known to be particularly rich in flavanones and flavanone glycosides.

Accordingly, Di Mauro et al. (118) developed and optimized a process for the recovery of hesperidin from orange peels through concentration on a styrene–divinylbenzene copolymerisate. For this purpose, extraction was carried out with an aqueous calcium hydroxide solution, causing the precipitation of colloidal pectins as calcium pectate, which otherwise may interfere with the subsequent

separation and concentration of hesperidin by adsorbent resins. The neutralized crude extract was loaded onto the adsorbent resin and subsequently eluted with a 0.5 N sodium hydroxide solution containing 10% ethanol, prior to crystallizing hesperidin upon acidification of the solution. Hesperidin was obtained in high purity and concentrated form with the pectins being removed.

Furthermore, adsorbent resins may also be used for the recovery of anthocyanins from the pulp wash of pigmented oranges, for example, from water-extractable orange solids obtained through several washing and refinishing steps by sorptive binding and subsequent desorption with ethanol. Besides great amounts of anthocyanins, eluates obtained under these conditions contain hesperidin and hydroxycinnamic acid derivatives, which may further stabilize anthocyanins through intermolecular copigmentation (119). This valorization process has been further expanded by deacidification of the adsorbent column eluates, which are devoid of polyphenols, using ion exchange resins followed by ultrafiltration and reverse osmosis steps to remove enzymes, microorganisms, and 80% of the water, respectively. According to this process, a brilliant and almost colorless natural sweetener can be obtained (120). Not only are solid plant residues a source of polyphenols such as hesperidin but also wastewater originating from citrus processing. Such wastewaters arise from the essential oil recovery process and still contain considerable amounts of hesperidin. In this case hesperidin may be separated through solubilization by adding calcium hydroxide to reach a pH value of 12 followed by filtration and neutralization of the solution (pH 6) prior to adsorptive binding of hesperidin onto an adsorbent resin. Desorption can be realized using a 10% aqueous ethanol solution containing 0.46 M sodium hydroxide as eluent and subsequent precipitation at pH 5, yielding high purities of the flavanone (121). Furthermore, the treatment of citrus peel juice and molasses by macroporous adsorbent resins has been thoroughly studied, aiming at the removal of bitter limonoids and phenolic compounds, whereas other polyphenols not significantly affecting sensory properties, organic and inorganic acids, may be removed by activated carbon or anion exchange resins, respectively (122). Styrene-divinylbenzene copolymerisates are also applicable for the recovery of cold-pressed grapefruit oil constituents, such as α -limonene, α -terpineol, nootkatone, linalool, octanal, and decanal, from wastewater of citrus fruit processing. The bound essential oil was recovered from the resin using 95% ethanol (123).

Apple juice production is also associated with great amounts of wet pomace, increasingly posing environmental problems and causing high disposal costs for the juice-producing companies. So far, these byproducts are mostly used as forage, as game feed, and for biogas or fertilizer production. Apple pomace is also often incinerated or used for land filling, even though the press residues are particularly rich in pectins and plant secondary metabolites, mainly polyphenols. Having this in mind, the utilization of the apple pomace for pectin recovery is profitable (124) and thus performed on an industrial scale. On the other hand, polyphenol recovery from apple pomace has only become increasingly attractive in recent years due to increased knowledge of biofunctional properties of polyphenols.

For this purpose, and to improve the visual appearance of apple pectin, a process for the simultaneous recovery of phenolic compounds and pectins from apple pomace has been developed, which is applicable on an industrial scale (125, 126). This process requires extraction of the dried apple pomace with diluted mineral acid, thereby recovering both pectins and phenolic compounds. Subsequently, the polyphenols are bound using a hydrophobic styrene divinylbenzene copolymerisate by applying the apple pomace crude extract onto the adsorber column. After washing the column with deionized water to remove pectins quantitatively,

the phenolic compounds are desorbed with methanol, which allows gentle concentration by evaporating the alcohol. The almost colorless pectins were recovered through precipitation with alcohols from the eluates, which were collected during column loading with the crude apple pomace extract.

Besides apple pomace, the byproducts of pomegranate processing have also been identified as rich sources of phenolic compounds. To exploit the potential, a recovery process for rapid large-scale purification of ellagitannins from pomegranate husks has been described (127). For this purpose, pomegranate husks, the byproducts of juice preparation, were extracted, and the aqueous polyphenol extract was purified using an evacuated column filled with Amberlite XAD-16. This procedure yielded pomegranate tannins, punicalagin, ellagic acid, punicalin, and ellagic acid-glycosides, that is, a pentoside, hexoside, and rhamnoside, in substantial yields. This low-cost recovery method is also applicable on an industrial scale to exploit a currently underutilized food-processing byproduct for the recovery of food and cosmetic additives acting as biopreservatives or phytochemicals based on the potential health benefits of these components.

The discovery of sources for the recovery of colored plant secondary metabolites, such as anthocyanins, betalains, and carotenoids, has attracted even more interest, which is due to the so-called Southampton study revealing a correlation between the consumption of beverages colored with synthetic additives and the occurrence of attention-deficit hyperactivity disorder in 3- and 8/9-year-old children (128). Consequently, foods colored with synthetic pigments need to be labeled with a warning according to the newest European Food Safety Authority (EFSA) regulations. This study significantly enhanced consumer rejection of artificial colorants and resulted in an increased demand for natural food colorants and coloring foodstuffs.

One of the potential sources for the recovery of natural colorants and coloring foodstuffs is red grape pomace. Together with white grape pomace, it represents a valuable source of phenolic compounds, which are present in high amounts in grape skins and seeds and which are only poorly extracted upon vinification. Even though grape pomace is a valuable source of ethanol, organic acids, and grape seed oil, it is still largely used for compost production and as soil conditioner (102, 129). Besides that, the extraction of phenolic compounds from grape pomace becomes increasingly important, and numerous studies have been performed concerning this matter (130). The reports include the optimization of pigment extraction (131), the isolation of individual hydroxycinnamoyltartaric acids by high-speed countercurrent chromatography (HSCCC) from grape pomace (132), and the recovery of polyphenols from the byproducts of grape seed oil production (133). Among these studies, processes for the recovery of anthocyanins using adsorbent resins have been described (134). For this purpose, grape pomace extracts were produced by sulfite-free aqueous enzyme-assisted extraction of the grape skins, followed by solid-liquid separation using a decanter centrifuge. To optimize operating conditions systematically, the aqueous extracts were loaded onto a laboratory-scale column filled with Amberlite XAD 16 HP and washed with water; fractionated elution was performed with acidified ethanol, methanol, and 2-propanol, respectively, at 25 and 50 °C, revealing that the pigments bound by the resin may be recovered almost quantitatively under optimal conditions. To demonstrate the applicability of this process, the optimized process was scaled up to pilot scale. Furthermore, a patent has been filed describing a novel process for the extraction, purification, and concentration of polyphenols from whole grapes, seeds, and grape pomace. This process consists of hot water extraction mostly comprising the acidification of the extracts followed by neutralization to precipitate

polymers, such as proteins, polysaccharides, and other macromolecules. Subsequently, the clear extracts are concentrated and purified using trimethylolpropane trimethacrylate adsorbent resins, such as Amberlite XAD-7HP, eluting the target compounds with aqueous ethanol, methanol, or acetone (135). Numerous processes have also been reported combining sulfite-assisted extraction of anthocyanins from food-processing byproducts with their selective purification using adsorbent resins. However, due to potential pseudoallergenic reactions after consumption caused by trace amounts of sulfite inevitably associated with such anthocyanin preparations, the use of sulfite is increasingly avoided.

Furthermore, anthocyanins of purple-fleshed potatoes are also highly interesting with regard to their potential application as natural colorants or coloring foodstuff (38), and early studies demonstrated the potential to recover these pigments by different adsorbent resins. Anthocyanins can also be recovered from other sources, such as mulberries, and the optimization of process parameters for their industrial recovery using macroporous resins is reported in the literature (136).

7.3.3.2. Vegetable Polyphenols. Vegetables may also serve as a rich source of valuable plant phenolics, which can be recovered by adsorbent resins. As an example, various macroporous resins have been applied for optimizing the isolation of luteolin, one of the main phenolic compounds of pigeon pea (*Cajanus cajan* (L.) Millsp.) (137). Pigeon pea is cultivated not only to produce animal feed and as valuable source of proteins and vitamin B in Africa and India but also for medical purposes, such as the stabilization of menstruation or to treat dysentery. The leaves find application in Chinese folk medicine as an anthelmintic drug, to ease pain or arrest blood, which is due to their antibiotic and anti-inflammatory properties, abirritation effects, and their potential to lower capillary permeability. Luteolin has been associated, for example, with antiallergenic, antioxidant, antiproliferative and anti-inflammatory properties as well as cytotoxicity toward certain cancer cells, thus rendering its recovery, for example, from pigeon pea highly interesting.

A further application of adsorbent technology was reported by Aehle et al. (138), who developed a natural antioxidant preparation enriched in phenolic compounds from aqueous spinach extracts because of the increasing commercial value of spinach wastes. The results revealed higher antioxidant recovery rates with synthetic adsorbent resins as compared to charcoal, and in this regard, macroporous polystyrene cross-linked polymers appeared to be better suited than macroreticular aliphatic acrylic cross-linked polymers for the selective enrichment of spinach antioxidants.

Also, the cell wall matrix of fruit and vegetable byproducts may also still be exploited to recover phenolic antioxidants. Ferulic acid can be obtained upon alkaline hydrolysis of polysaccharides, such as arabinogalactans and xyloglucans, which are covalently bound to the hydroxycinnamate. The subsequent purification of the alkaline hydrolysate to yield the phenolic acid is possible by using a combination of activated charcoal and a strongly basic anion exchanger (139). Feedstocks such as sugar cane bagasse, sugar beet pulp, and wheat or grain bran could be used for that particular purpose.

Soy is well-known to contain 12 isoflavones supposedly playing a role in the prevention of certain cancers, such as breast cancer, by inhibiting different stages of cancer development through the reduction of certain risk factors. Furthermore, various isoflavones may be beneficial for women because of their phytoestrogen activity, whereas other compounds are interesting as additives of enriched or functional foods and beverages. To recover these phytoestrogens, a process for the temperature-dependent selective enrichment of soy isoflavone fractions from

soy protein extracts, soy molasses, or soy whey feed stream has been developed (140). For this purpose, the respective temperature was selected on the basis of the solubility of the isoflavones in the soy feed stream. Subsequently, the heated solution was ultrafiltered or subjected to reverse osmosis to further concentrate the solutes. Finally, the permeate was used for further selective enrichment of the isoflavones using an adsorbent resin, with the column being washed with water prior to the elution of isoflavones with aqueous alcohols and the drying of the eluates. Thus, the resulting dried product is obtained in a comparatively straightforward and rapid process. This procedure allows one to obtain storable products and to enrich certain isoflavone fractions or individual isoflavones selectively, thus yielding preparations with neutral color and flavor. Accordingly, this approach helps to produce pharmacologically active preparations from soy whey, which are so far affected by unpleasant color and taste.

Soybeans are not only interesting because of their isoflavones, but also because of their carbohydrates, such as D-pinitol (D-3-O-methyl-*chiro*-inositol) and the cyclitol D-*chiro*-inositol, showing efficacy in lowering blood glucose levels. Consequently, there is an increasing industrial demand for the recovery preferably of pure pinitol by applying simple methods for the use as insulin substitutes and food supplements. Thus, a simple two-step extraction procedure has been suggested comprising the maceration of soybean leaves with ethanol solutions and chloroform followed by an ion exchange step applying the aqueous supernatants after centrifugation to two columns filled with a strong cation and strong anion exchanger resin, respectively, which are connected in series. The cyclitols may be finally eluted using water devoid of CO₂. After freeze-drying, a white, crystalline product was obtained, which can be rehydrated with deionized water. However, prior to its production on industrial scale, the safety of the product with respect to human consumption still needs to be demonstrated (141).

8. CONCLUSIONS

In summary, the broad range of applications of ion exchange and adsorbent resins in food production and for the cost-efficient valorization of food processing byproducts demonstrates the high potential of these technologies for the food, pharmaceutical, and cosmetics industries. Ion exchange and adsorbent technology have been significantly improved in recent years and decades, not only with regard to process optimization during the sorption and desorption step but also with regard to the development of highly sophisticated resin materials allowing novel applications. In contrast to many other extraction methods, adsorption and ion exchange technology offers higher selectivity and improved cost efficiency and can be realized with relatively simple technical equipment. However, the prediction of sorption and ion exchange behavior, when multicomponent solute systems are considered, is highly complex and should not be underestimated upon optimization of such processes. Nevertheless, with a steady increase in knowledge of the underlying theory, processes will increasingly be tailored, thus yielding products with well-desired compositions and functional properties, which will certainly expand the application of these technologies to further areas in the future.

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