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ION-EXCHANGE PROCESSES IN THE FOOD INDUSTRY

The process of ion exchange is now the most used technology of demineralisation. It has also the ability to remove different components present in foods. A wide range of polymers may be used in ion-exchange resins, depending on the physical and chemical requirements of the system, and different applications are possible. This technology is currently used in the dairy industry (whey demineralisation, lactose hydrolysis), the sugar industry (decolourisation of sugar liquors, separation of glucose and fructose from a liquor, isomerisation of glucose and fructose, demineralisation of sugar), the fruit juice industry (stabilisation apple juice haze, reducing the colour of apple and pear juices, debittering of citrus products), wineries (tartrate stabilisation, immobilised enzymes for wine treatment), etc.

Some of the applications of ion exchange are still being developed or this technology is used only in the laboratory. However, it may be used extensively in the future. It has a number of advantages over the existing techniques, since it can be selective, it cuts down on waste and can transform a batch process into a continuous one, which may also be automated.

INTRODUCTION

In recent years, considerable emphasis has been placed on the demand for biologically produced molecules. Amino acids, peptides, and proteins are often extremely valuable and must be produced with the utmost purity. This demand leads to the technology of bioseparations. Ion exchange is an extremely promising for effecting these separations. It is used in analytical chromatography and small-scale separations, but industrial-scale production like demineralisation or protein recovery is also possible.

Ion exchange is a separation technique in which an aqueous solution containing one or more chemical species of commercial interest are introduced into a column containing an adsorption medium, which adsorbs specific ions selectively. This selectivity is strongly influenced by process conditions. In the adsorption process, specific solute is transferred from the liquid medium to the solid medium. The adsorption mechanism is electrostatic and there are opposite charges on the solute and the ion exchanger. The selectively adsorbed solute is then desorbed to produce the desired separation.

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Up-to-date products such as carbon activated, gelatine, bentonite and others have been used in the food industry for decoullouring, stabilising, etc. In this process, the additive is put into the food to be processed, stirred and then separated by filtration or settling. It is a semicontinuous operation. Usually, for small producers, the additive is separated by settling, which means there is a large amount of solid residue and food losses are great. The settling process normally needs a long time. Another disadvantage is that the process normally requires a large amount of additive, which increases production cost. Using resin exchange makes regeneration possible, so solid residues are reduced. It also means that a continuous process is possible.

EXCHANGE RESINS

Ion-exchange resins are polymerisation products with different types of functional groups. These groups enable them to act as ion exchangers.

Ion-exchange resins can be subdivided into two categories:

- Cation-exchange resins, which have weakly to strongly dissociated acid groups with fixed negative charges, and are therefore able to retain cations.
- Anion-exchange resins, which have functional groups of differing basicity with fixed positive charges.

Ion exchangers are further classified as weak and strong exchangers (depending on how their charges vary with pH). Strong ion exchangers are ionised over a wide range of pH and have a constant capacity within the range, whereas weak exchangers are ionised only over a limited pH range. Weak exchangers may therefore be preferable to strong ones in some situations (for example, when desorptions can be achieved with small changes in pH). It is easier to regenerate weak ion-exchanger groups than strong groups, so they require fewer chemicals.

Ion-exchange resins are solid products supplied in bead form. They are insoluble in water and are stable with respect to a large number of chemical substances. However, since they are acids or bases, they may react and form salts. Their most important property is their ability to remove ions from solutions. In exchange they desorb ions. The functional groups are found inside the beads as well as on their surface. In exchange they desorb equivalent amounts of different ions into the solution. This exchange process can only take place if the ions have the same electric charge. Hence, cation resins exchange cations, and anion resins exchange anions. This process normally occurs quickly by passing a liquid through a unit filled with an ion-exchange resin.

For instance, the process of water softening can be considered as a simple example of the ion-exchange process. An ion-exchange resin loaded with sodium ion is brought into contact with calcium ions dissolved in water. The resin adsorbs the calcium ions and desorbs the sodium ions. We can represent this process by:



The ion-exchange process is completed when the resin has released all its sodium ions. Treating it with a solution of common salt (NaCl) can regenerate it. The reverse process occurs during regeneration:



After regeneration, the ion-exchange resin can once again take up calcium ions. Alternatively, desorption can be achieved by adding H^+ or OH^- ions.

As adsorption is a surface effect, the effective surface area is an important parameter. For industrial processing the maximum surface area with respect to volume should be used to minimise plant size and product dilution.

The ion-exchange resins are normally placed in packed columns. There is a compromise between large and small particles because the pressure drops and mass transfer rates increase. Porous resins are used to increase the surface area and the volume. Nevertheless the effective surface must be accessible to molecules.

The operational life of an ion exchanger is limited by blinding and fouling. These consist in a nonspecific adsorption onto the surface or within the pores, which reduces the capacity and affects the choice of ion exchanger for a particular separation. This phenomenon can prevent it from being used in a particular food process, even though the ion resin adsorbs well.

The elution process depends on the specific separation required. If the adsorbed molecules are not valuable, the regeneration process is not a limiting step, but a strong acid or base is needed to regenerate the resin. On the other hand, if the adsorbed molecules are valuable, the elution process is a limiting step, since denaturalisation or dilution of the product must be avoided.

An emerging problem associated with conventional ion exchange is the handling of waste streams from regeneration cycles. These streams are relatively rich in inorganic ions such as chloride, sulphate, sodium or potassium, depending on the regenerant used. Many regional authorities are becoming more and more concerned about the salinity and ionic strength of wastewater discharges and salt recovery, and water recycling may need to be developed.

Adsorption technology nevertheless has a number of advantages, e.g., effluents are liquid and easy to handle after neutralisation, production is continuous, it is an automatic process, there are a few losses and selectivity is higher.

APPLICATIONS OF ION EXCHANGE

Ion exchange has a number of applications, from removal of minor components and substitution of others to isolation of valuable components. Ion exchangers can also be used as a catalysts.

The main areas of the food industry where the ion-exchange process is currently used are: sugar, dairy products and water purification. It is also used to recover, separate and purify biochemicals and enzymes, and is currently being introduced to the drinks industry for juices and wines.

THE DAIRY INDUSTRY [1, 2]

Whey demineralisation. The aim is to valorise the whey. Salts and soluble acids have to be eliminated. The whey exchanges its salts and acids in water after passing through cationic and anionic resins successively. The cationic resin is in hydrogen form, and the anionic resin is in hydroxylic form. This can produce a reduction in salt content of more than 90%, which is necessary for infant formulae. Lower levels of demineralisation, using a by-pass system, may be sufficient for other applications. Because of the high salt content in whey, the system must be regenerated after treating 10–15 bed volumes of whey. The process continues with rising by treating cation resins with strong acids, and anion resins with bases. The cycle takes about six hours, four hours of which are for regeneration. Two or three parallel systems may therefore be necessary. Countercurrent regeneration reduces the consumption of regeneration chemicals.

Lactose hydrolysis. A lactose solution can be transformed to glucose and fructose if it is treated with a cation resin in hydrogen form.

THE SUGAR INDUSTRY [1–3]

Decolourisation of sugar liquors. Sugar liquors from cane or beet contain colorants such as caramels, melanoidins or polyphenols combined with iron. These components have to be removed in the production of white sugar and materials with large pores are needed to allow colour macromolecules' access to the adsorption sites. It is a simple adsorption process over the resin without chemical active sites.

Separation of glucose and fructose from a liquor. Using cationic resin in calcium form glucose and fructose can be separated by chromatography.

Isomerisation of glucose and fructose. A simple treatment with anionic resins in the hydroxyl form can increase fructose concentration in a liquor of glucose and fructose.

Demineralisation of sugar. Sugar can be demineralised at different stages of its production. In the production of sugar from beet, the beet juice is purified by liming and carbonation and may then be demineralised by ion exchange.

The carbonated juice is then evaporated to a thick one before sugar crystallisation. Alternatively, the thick juice may be demineralised, which has the advantage that the amount handled is much smaller. To produce high-quality sugar the juice should be about 95 per cent pure.

THE FRUIT JUICE INDUSTRY [1, 2, 4]

Stabilisation apple juice haze. Resin is an alternative to traditional fining procedures that use gelatine, silica sol and bentonite. The results presented by Lyndon [4] with a plant of 20,000 l/h are quite positive, but synergy means it is better to combine this technique with ultrafiltration. Because of large sizes of macromolecules (such as proteins, polysaccharides etc.) it is possible to remove them by ultrafiltration. These macromolecules are size-excluded from the resins, and the resins remove the smaller components (protein fractions, condensable polyphenols, etc.). Adsorption stabilisation is applied to typical process of apple juice treatment and the stabilisation results are positive.

Reducing the colour of apple and pear juice. The market for light-coloured juices and products with standardised colour continues to increase. Adsorption technology provides the producer with the tool needed to supply this market economically.

In freshly pressed juices, colour is primarily due to the oxidation and polymerisation of enzymatic and nonenzymatic polyphenol. By careful selecting the appropriate resin this browning can be selectively removed to provide extremely light products.

The complexity of colour-generating compounds in a juice increases enormously with storage time, particularly with heating during the pasteurisation or concentration steps. The browning of concentrates is no longer only due to oxidised polyphenolics, but also due to blending of oxidised polymerised phenolics combined with melonoidins (products of Maillard reaction) and products of hydroxymethylfurfural interactions with amino acids and reactants formed by as yet unknown pathways. The chemical structures of the browning compounds remain poorly characterised, largely because they are extremely variable.

Despite their variability, browning components are extensively removed by hydrophobic interaction (van der Waals and London interactions), using adsorbent resins.

Although the final colour of the juice is difficult to predict, a producer can routinely expect to achieve colour reductions continuously. Lyndon's results [4] showed that the decolourisation of pear and apple juices was greater than 70% (expressed as transmittance).

Acidity reduced, deashed and deionised fruit syrups. The juice market continues to expand rapidly. Other less traditional applications are also prospering, especially as the conventional juice used for manufacturing natural fruit sugars and drink bases increases in value and the demand for fruit syrups grows.

There is also increased pressure to utilise wastes to make lower-cost fruit extracts. These lower quality fruit extracts place high demands on ion-exchange technology.

Deionization produces natural fruit-sugar sweeteners. Lyndon's results [4] showed that the reduction in acidity for pear, pineapple, kiwi and citrus-fruit was greater than 95%.

Debittering of citrus products. The problem of delayed bitterness is of serious economic consequence to manufactures of citrus juices and their by-products. The selective removal of limonin (the principal bitter component in most citrus products) and naringin (a major bitter component in varieties of grapefruit) is the largest and most widely accepted use of adsorbent resins in the fruit beverage industry as a whole. This technique is widely used in the USA and in Asian countries, but the legality of the debittering process in European countries is still under debate.

The commercial processing of citrus fruit requires a different procedure because these products are normally marketed cloudy, and cloud stability is important for consumer acceptance. Consequently, the juice has to be prepared before the adsorption process. The usual pre-treatment process consists of extraction, deoiling, screening, pasteurisation, pulp reduction and adsorption debittering.

Screening removes large fragments of pulp. Pasteurisation stabilises pectinase enzymes, converts limonin precursors to limonin for optimum adsorption efficiency and separates the pulp more easily from warm juice. Deoiling is necessary for some types of adsorbent resins with levels as low as 0.005% recommended by some manufacturers of adsorber equipment.

The first stage of the evaporation is often convenient for achieving pasteurisation and some concentration and deoiling. There are two main commercial methods for deoiling with the citrus pulp. The technique chosen affects both the product and the design and operation of the adsorber equipment.

One type of plant uses ultrafiltration to serumise the juice totally before debittering adsorbent resin. The other requires centrifuge to spin the pulp down to approximately 1% so that the still cloudy juice can pass through the adsorbent resin without blocking. For both types of equipment, the pulp fraction is returned to the debittering juice before evaporation or packaging to minimise losses.

WINERIES [5-9]

The application of ion-exchange treatment to wine has been proposed and evaluated for many years. The most common use of ion exchange today is with cation resins in the H^+ form for increasing titratable acidity and removing K^+ from either wine. A combination of cation (H^+) and anion (OH^-) treatments is also used to reduce the pH with essentially constant titratable acidity.

Most cation-exchange resins remove a wide range of nitrogenous compounds from juice as well as potassium ions and secondary metal cations such as calcium and magnesium. Most amino acids and several vitamins occur in cationic form in wine.

Tartrate stabilisation. Ion exchange can be used in the tartrate-stabilisation process. It involves passing the wine through a resin-containing column. During passage,

ions in the wine exchange with those in the column. The types of ions exchanged can be adjusted by the type of resin used and the ions present for exchange on the resin.

For deacidification, the column is packed with an anion-exchange resin. Tartrate ions are commonly exchanged with hydroxyl ions (OH^-), thus removing tartrate from wine. The hydroxyl ions released from the resin associate with hydrogen ions to form water. Alternatively, malate may be removed by exchange with a tartrate-charged resin. The excess tartaric acid may be subsequently removed by neutralisation and precipitation.

The major factor which limits the use of ion exchange today, other than legal restrictions and cost, is its tendency to remove flavouring and colour, so reducing the quality of the wine.

Immobilised enzymes for wine treatment. There are several reasons for using immobilised enzymes in wine making. In some cases, their activity or stability can be improved. The enzyme may be expensive, so its recovery and reuse are of economic interest. The immobilised enzyme could be used packed and its activity improved by exposing the wine to a higher temperature for short periods of time during treatment. Such reactors would speed up the reaction rate considerably because of the high concentrations of enzyme. Some applications are:

Proteases: hydrolysis of wine proteins and peptides to improve colloidal and heat stability of white wines and replace the use of bentonite.

Pectinases: hydrolysis of pectines to improve colloidal stability and perhaps filterability rather than the recovery of free-run juice, which is the most common use.

Glucanases: hydrolysis of β -glucans to improve the filterability of late-harvest and botrytized wines.

Other applications in the oenological field are the recovery of anthocyanes from winery waste, wine softening, decolourization of vinegar, removal of iso-valeric acid from vinegar, etc.

OTHER INDUSTRIES [1, 2]

Recovery of acetic acid from effluent. Acetic acid can be recovered from polluted condensate (1 g/l). Acetic acid is fixed to anionic resin with hydroxylic form (120 g/l of resin). After regeneration we can obtain a solution of around 10%. The acid is then purified and concentrated. The condensate can be used again.

De-acidification of oil. In the rectification process of oils, free-fatty acids must be removed from the glycerides. The oil de-acidified after the treatment will be dried.

CONCLUSIONS

The resin can be used in a variety of ways, depending on whether the resin acts as an ion exchanger, as an adsorber or as a catalyst. Some of the applications of ion ex-

change are still being developed or it is used only in the laboratory. However, it may be used extensively in the future, especially in the food industry and in biotechnological processes. It has a number of advantages over existing techniques, since it can be selective, it cuts down on waste and can transform a batch process into a continuous one, which may also be automated.

REFERENCES

- [1] GRANDISON A.S., *Application of ion-exchange in food processing*, Food Technology International Europe, 1994, 53–57.
- [2] TONDEUR D., LANCRENON X., *L'échange d'ions dans l'industrie alimentaire*, Cahiers du Génie Industriel Alimentaire, ENSIA, ed. Sepaic, 1977.
- [3] LE HENAFF Y., PRINTEMPS P., *Les résines échangeuses d'ions dans l'industrie sucrière*, Liquides magazine, 1988, No. 8, 61–64.
- [4] LYNDON R., *Commercialisation of Adsorbtechnology in Fruit Juice Industry*, Fruit Processing, 4/96, 1996, 130–134.
- [5] BOULTON R.B., SINGLETON V.L., BISSON L.F., KUNKEE R.E., *Principles and practice of winemaking*, Chapman and Hall, 1996.
- [6] JACKSON R.S., *Wine Science. Principles and Applications*, Academic Press, 1994.
- [7] MOURGUES J., *Utilisation des résines échangeuses d'ions*, Revue des Oenologues, 1993, No. 69S, 51–54.
- [8] CUVELIER, J.M., *Les échangeuses d'ions IMAC HP*, Revue des Oenologues, 1993, No. 69S, 55–56.
- [9] ITO K.I., UENAKI O.K., MATSUDA N.H., MIZUKAMI Y.M., TANIJIRI O.S., *Process for the removal of iso-valeric acid from vinegar*, US patent No. 4994292, 1991.