Ion-Exchange in Food Industry

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ION-EXCHANGE may be defined as the reversible interchange of ions between a liquid phase and a solid phase without involving any radical change in the solid structure.[1]

The agents of ion-exchange are ion-exchangers. Ion-exchangers are of two types, cation exchangers and anion exchangers. In the class of cation exchangers may be listed processed natural ion-exchangers like greensand and sulphonated coals, synthetic inorganic materials like precipitated aluminosilicates and synthetic organic materials such as modified phenol-formaldehyde resins, sulphonated hydrocarbons and carboxylic acid resins. The class of anion exchanger comprises of aliphatic amine resins and aromatic amine resins. There are many new ion-exchangers manufactured by different companies. Each ion-exchanger has specific properties and hence the choice of proper ion-exchangers is of extreme importance.

Cation exchangers are used for cation exchanges of the two types, base exchange and hydrogen exchange. In the former case, positive ions in solution are replaced by sodium ions of the solid exchanger:

$$Na_2Z + Ca^{++} \rightleftharpoons CaZ + 2Na^+,$$

where, Na_2Z represents the cation exchanger in the sodium cycle. The exhausted exchanger is then regenerated with common salt or brine:

$$CaZ + 2NaCl \rightleftharpoons Na_2Z + CaCl_2.$$

In the hydrogen exchange, cations in solution are replaced by hydrogen ions of the solid exchanger, forming an acid in the effluent. The regeneration of the exhausted exchanger is carried out either with sulphuric acid or hydrochloric acid.

Anion exchangers are employed to bring about either acid removal or true anion exchange:

$R_3N + HCl \rightleftharpoons R_3NHCl$—acid removal,
$2R_3NHCl + SO_4'' \rightleftharpoons (R_3NH)_2SO_4 + 2Cl'$—true anion exchange. The exhausted anion exchanger is regenerated by soda ash, caustic soda or ammonia:

$$2R_3NHCl + Na_2CO_3 \rightleftharpoons 2R_3N + 2NaCl + H_2CO_3.$$

Ion-exchange has been utilised in food industry for (i) removal of ionic impurities from solution, (ii) addition of specific ions to solution, (ii) recovery of valuable substances from solution, (iv) separation of electrolytes in solutions and (v) catalysis. The food industry has found ion-exchange process very helpful, both for water conditioning and for numerous applications outside water treatment.

Water treatment: The largest use of ion-exchange in any industry is in the field of water treatment. Treatment of water is not only necessary for the purpose of feed water for boilers but also for using water of the proper quality as an ingredient of foods. In canning industry, hard water containing calcium and magnesium affects the quality of certain vegetable products such as peas and asparagus. In the manufacture of beverages, demineralising and deashing of water is a prerequisite for getting a definite quality water. In some soft drink industries, ion-exchange is used to produce water of low bi-carbonate alkal-

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inity. For all these purposes, ion-exchangers have proved very convenient, compact and relatively inexpensive tools for conditioning water.

Sugar refining[2]: The largest single field of application of ion-exchange other than water treatment is in the manufacture of sugar. Sugar refining consists of two main operations. In the first one, a maximum amount of dissolved non-sugar solids are removed. The second operation involves the separation of pure sugar from the remaining dissolved impurities. The latter operation is dependent on the former since the presence of non-sugar solids is a major factor affecting the crystallisation of sugar. In this refining operation, ion-exchange has superseded the conventional method of bone char refining in so far as the removal of a greater part of non-sugar solids is concerned. In addition, ion-exchange produces a pleasant tasting edible syrup unlike that obtained in the conventional method, which gives crude molasses. The ion-exchange method also improves the thermal efficiency of the evaporator by removing scale forming substances such as calcium salts.

In beet sugar refining, ion-exchange has been practised on a commercial scale in a number of countries. After liming and carbonation of the beet juice obtained by diffusion of beet slices, it is subjected to demineralisation by ion-exchange. The demineralising unit comprises of (a) one hydrogen exchanger column, (b) one granular carbon column and (c) one anion-exchanger column. In the hydrogen exchanger column, the cations in the influent juice are replaced by hydrogen ions. The granular carbon column removes the colouring matter together with colloidal matter, precipitated as a result of hydrogen exchange. The juice is deacidified in the anion-exchange column and concentrated subsequently in vacuum pans.

The hydrogen exchanger is regenerated by an acid and the anion-exchanger by an alkali. The spent alkali regenerant from the anion-exchanger is used again to regenerate the granular carbon unit. The resulting sugar is found to be superior to that produced by the conventional method, being lower in ash content and developing no odour on storage.

This process, however, is not found to be economical in cane-sugar refining and is still being subjected to investigational work. Ion-exchange process of refining dextrose in place of bone char refining is shown to improve both the acid and the enzyme conversion processes. The process has been commercially adopted at one plant in Texas.

Utilisation of fruit wastes: Waste sugar solutions: The demineralisation of a number of waste sugar solutions has been studied. Among such sugar solutions are the wastes from fruit canneries like the pineapple and citrus fruit canneries which contain about 6-8% sugar. The effluent is purified by ion-exchange and later concentrated to give a syrup which is used in the canning of pineapple slices; citric acid, one of the impurities taken out by ion-exchange, is simultaneously recovered as a by-product from the exchangers.

Pectin manufacture: A unique process for utilising waste grape peel involving ion-exchange has been in factory scale commercial use. This process is the manufacture of pectin from albedo, the rag and peel of the grape fruit that remains after removal of the juice. The peel is washed, depulped, deseeded, washed with hot water to inactivate the enzymes, pressed and dried. The peel is then mixed with wet zeocarb H (sulphonated coal, manufactured by Permutit Co., New York) (39% moisture) in the proportions of 5:1. Water is then added to the mixture and the extraction of pectin is carried out by agitation for one hour at 196°F. Zeocarb H (hydrogen exchanger) converts the residual salts present in the peel to the corresponding acids thus lowering the pH to about 2.7. The pectin thus freed, goes into solution without any breakdown. The mixture is then centrifuged to give a solution containing 0.6% pectin, which is filtered, evaporated and spray dried or drum dried.

Recovery of tartaric acid: A pilot plant work has been conducted on the recovery of tartarates from winery wastes. Dilute potassium acid tartarate solution obtained from the extraction of the skins, stems or seeds of grapes is introduced into an ion-exchanger unit. The anion-exchanger removes the free acid leaving potassium tartarate in solution. This is then passed through hydrogen ion-exchanger where the potassium ions are exchanged for hydrogen ions. The resulting tartaric acid is removed by a second anion-exchanger unit. The first anion-exchanger on treatment with 15% H_2SO_4 forms 8-10% tartaric acid. The second one is regenerated with 10% KOH giving 10% potassium tartarate solution. The two effluents are then mixed to neutralise each other.

Dairy products: Since milk is a complex biological fluid containing many ionisable compounds which affect both the physical and chemical characteristics of the milk, ion-exchange can be conveniently used to alter these properties so as to suit the manufacture of a particular product.

Soft curds[3,6]: Cow's milk is valued for the ideal calcium-phosphorus ratio. But because of the high content of calcium, hard curds are formed in the stomach by rennet coagulation and are difficult to digest. By a base exchange treatment, both the problems, the problem of removal of calcium and that of maintenance of calcium-phosphorus ratio can be solved. This is accomplished as follows: Milk at 40-60°F is acidified to 0.25-0.35% by addition of lactic acid. This aids in restoration of original acidity and in removal of calcium and phosphate ions. It is then brought into contact with greensand (a cation exchanger). The spent ion-exchanger is then regenerated by a special technique. A new synthetic ion-exchanger crystallite (sodium alumino silicate, Infilco Inc., Chicago) has been found to be more suitable because it maintains the uniformity and purity of milk.

Evaporated milk[3,7]: In the manufacture of evaporated milk it is often necessary to change the calcium-phosphorus ratio in order to have a product stable to high temperatures during sterilisation. This is accomplished by the use of either sodium phosphate or sodium citrate. In an ion-exchange process only a small portion of the milk is treated with a cation exchanger in the sodium cycle. This operation removes a part of calcium. The treated milk is then blended with whole milk and sterilised. The advantage of this method lies in the fact that addition of chemicals is not required to adjust the calcium-phosphorus ratio.

Dried creams: In the manufacture of dried creams defatted milk is demineralised by ion-exchange method. The treated milk is then blended with high fat cream. The whole mix is then condensed and spray dried. Dried creams so manufactured are stable in hot coffee and disperse very rapidly when added to it.

Ice cream: Normally, a frozen ice cream mix containing more than 11% non-fat solids gives a sandy texture when heat shocked. This is due to lactose crystallisation. If, however, a part of this milk is passed through a base exchanger and then blended with untreated milk, the frozen stuff does not result in sandiness if heat-shocked. The reason for the retarded crystallisation is still unknown. But it is thought that there may be a change in the colloidal phase of the treated solids.

Recovery of lactose from whey[3,7] : Recovery of lactose (milk sugar) from deproteinised whey is accomplished by first treating whey in a hydrogen ion-exchanger and sequentially with an anion-exchanger. The combination treatment results in an almost complete demineralisation of whey which is then condensed and spray dried. Demineralisation enables the recovery of practically all lactose in a high-grade form.

Casein[6] : Preparation of casein, the principal protein of milk, involves first its precipitation by acid followed by dissolution of the precipitate either by alkali treatment or by treatment with a cation exchanger. The casein is again precipitated by citric acid and filtered. It is found that casein obtained by the alkali treatment tends to develop stale odours, whereas that obtained from crystallite retains the natural odour for a long time.

Miscellaneous applications: Applications of ion-exchange have been spread over in many other food manufacturing processes. To improve the quality of apple juice, a method of treatment[3] with ion-exchange has been developed. The bitterness which is due to calcium malate is removed by ion-exchange with a consequent increase in its palatability. Demineralisation with ion-exchange also renders it stable to fermentation[8,3] by removing nutrients such as calcium, magnesium, phosphorus and nitrogen necessary for the growth of micro-organisms. The loss of flavour resulting from this treatment may be avoided by removing the volatile flavour fraction by flash heating before demineralisation and adding it later after ion-exchange treatment. The sodium malate which is removed by ion-exchange can also be recovered.[3]

Ion-exchange has made it possible to remove some of the poisons which might be introduced as a result of insecticidal sprays. Thus, it was shown that arsenic can be removed from apple juice and nearly 97% of lead from apple juice.

Inversion of sucrose[9,10] by catalytic use of air dried zeocarb has been shown to be possible. Catalysis by cation exchange resins in place of acids can greatly simplify subsequent procedures since the catalyst may be readily removed by filtration. It may be mentioned, however, that even the most suitable cation resin IR-120 (Sulphonic acid type, Rohn and Hass Co., Philadelphia) was found to be only 74% as efficient as sulphuric acid.

A variety of applications which ion-exchange process provides, proves how valuable a tool it is in food industry. Due to the promises it holds out, it is being studied and investigated in a large number of food laboratories and pilot plants. In addition to simplifying the otherwise cumbersome conventional processes, it saves a lot of time and requires a comparatively little space for operation. The number of installations for industrial purposes is still small. But it must be stated that this process is gaining ground as a "unit process" in the food industry and we no doubt will witness more applications on industrial scales in near future.

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