   

ION EXCHANGE **RESINS**

ADSORBENT **RESINS**

CHROMATOGRAPHIC **RESINS**

IN FOOD INDUSTRY

   

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INTRODUCTION


Standard grade resins

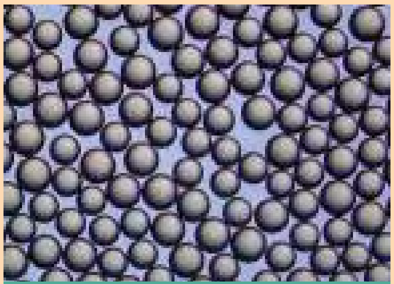
Ion exchange, adsorbent and chromatographic resins are used in industrial applications to modify physico-chemical characteristics of liquids.
The most known applications are softening or demineralization of water for boilers where, by means of resins, encrusting mineral salts are removed.
The resins appear as little beads having a diameter among 0,3 and 1,2 mm with a density higher than water and are used inside stainless steel or hard rubber iron columns equipped with distributors which allow the passage of fluids and avoid the outlet of resins.


Monospheric resins

The resins are real filtering materials that are obtained by polymerization processes at high temperatures which give to the micro spheres a high physico-chemical stability.
The regulations for the application of these products in food industry fix the maximum monomer release allowed (FDA and Res AP 2004 3). The manufacturer is committed to issue the conformity certificate.
Ion exchange resins are mainly used to reduce ashes content (demineralization) and to recover organic acids in food liquids.


Adsorbents resins

Adsorbent resins are suitable for the adsorption of specific organic molecules from food and non-food liquids allowing the selective recovery.
Chromatographic resins are suitable for separation of organic and inorganic molecules.
The plants are built by engineering companies who know processes and resins performances.


Chromatographic resins

Many times new applications are involved, where the process is developed thanks to the accomplishment of laboratory tests and pilot plant trials.
In particular, adsorbent resins, are new products which can replace crystallization and distillation steps. The appropriate knowledge of the resins allows the intervention on liquids in order to solve process problems, giving a value-added to the production and for new products carrying out.

MAIN RESINS
FOR FOOD APPLICATIONS

Main ion exchange resins used in food industry

PRODUCT	TYPE	COPOLYMER	ACTIVE GROUP	IONIC FORM	PARTICLE SIZE	TOT. exchange capacity eq/l	SWELLING
RELITE RP	Strong Cation gel	Styrene-DVB	Sulfonic	Na +	0,425 – 1,2 mm	2	Na+ - H+ < 4%
RELITE RPS	Strong cation porous	Styrene-DVB	Sulfonic	Na +	0,425 – 1,2 mm	1,8	Na+ - H+ < 4%
RELITE RPSM	Strong cation porous	Styrene-DVB	Sulfonic	Na +	0,6 – 0,7 mm	1,8	Na+ - H+ < 4%
RELITE CNS	Week cation	Methacylic	carbxylic	H+	0,425 – 1,2 mm	4	H+ - Na+ < 40%
RELITE RAM1	Weak anion	Styrene-DVB	Amine III	Base libera	0,425 – 1,2 mm	1,6	BL - Cl- < 25%
RELITE RAM1M	Weak anion	Styrene-DVB	Amine III	Base libera	0,6 – 0,7 mm	1,6	BL - Cl- < 25%
RELITE 3A	Strong anion gel	Styrene-DVB	Amine type I	Cl-	0,425 – 1,2 mm	1,3	Cl- - OH- < 22%
RELITE RAP1	Strong anion porous	Styrene-DVB	Amine type I	Cl-	0,425 – 1,2 mm	1,3	Cl- - OH- < 20%
RELITE 2A	Strong anion gel	Styrene-DVB	Amine type II	Cl-	0,425 – 1,2 mm	1,4	Cl- - OH- < 12%
RELITE RAP1	Strong anion porous	Styrene-DVB	Amine type II	Cl-	0,425 – 1,2 mm	1,4	Cl- - OH- < 12%

Main adsorbent resins used in food industry

Characteristics / Resins	SP850	SP825	SP70	SP700	HP20	SP207	HP2MG
Water retention *%*	42 - 52	52 - 62	55 - 65	60 - 70	55 - 65	45 - 55	55 - 65
Particle size *micron*	250 - 600	250 - 600	250 - 700	250 - 700	250 - 600	250 - 600	300 - 700
Specific surface area *m^2/g*	930	930	870	1200	590	590	570
Specific gravity *mg/ml*	1,01	1,01	1,01	1,01	1,01	1,18	1,09
Pore volume *ml/g*	1,2	1,5	1,6	2,2	1,3	1,1	1,3
Average pore radius *Amstrong*	45	62	71	85	260	120	240

Main chromatograpic resins used in food industry

PRODUCT	TYPE	COPOLYMER	ACTIVE GROUP	IONIC FORM	PARTICLE SIZE	WATER RETENTION	UNIFORMITY COEFF.
DIAION UBK530	Strong Cation gel	Styrene-DVB	Sulfonic	Na+	200 - 240 micron	52 - 55 %	1,1
DIAION UBK535	Strong Cation gel	Styrene-DVB	Sulfonic	Ca++	200 - 240 micron	46 - 50 %	1,1
DIAION UBK550	Strong Cation gel	Styrene-DVB	Sulfonic	Na+	200 - 240 micron	52 - 55 %	1,1
DIAION UBK555	Strong Cation gel	Styrene-DVB	Sulfonic	Ca++	200 - 240 micron	46 - 50 %	1,1

RESINS DESCRIPTION

Gel type strongly acidic cation resins

They are micro spheres of 0,3 - 1,2 mm diameter, obtained by means of Styrene and DVB polymerization, with sulphonic active groups, distinguished by a gel physical structure that does not allow the adsorption of organic substances; they are able to reversibly exchange cations (Na+, K+, Ca++ etc.), with ion H+. In food industry they are mostly applied for demineralization of liquids that contain organic stuff which is required to be left in solution. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances.

Porous type strongly acidic cation resins

They are micro spheres of 0,3 - 1,2 mm diameter, obtained by means of Styrene and DVB polymerization, with sulphonic active groups, distinguished by a macro porous physical structure that allows the adsorption and elution of organic substances; they are able to reversibly exchange cations with ion H+. Porous type strongly acidic cation resins have a high mechanosmotic resistance. In food industry they are mostly applied for demineralization of sugar solutions with density higher than water. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances. Porous type strongly acidic cation resins are also available in highly uniform screen grade version.

Weakly acidic cation exchange resins

They are micro spheres of 0,3 mm - 1,2 mm diameter, obtained by means of Acrylate and DVB polymerization with carboxylic active groups, distinguished by a porous physical structure that allows the adsorption and elution of organic substances; they are able to reversibly exchange cations bound to bicarbonates with ion H+. In food industry they are mostly applied for partial demineralization of liquids with density similar to water. They have a high exchange capacity but they cannot completely decationize. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances.

Weakly basic anion exchange resin

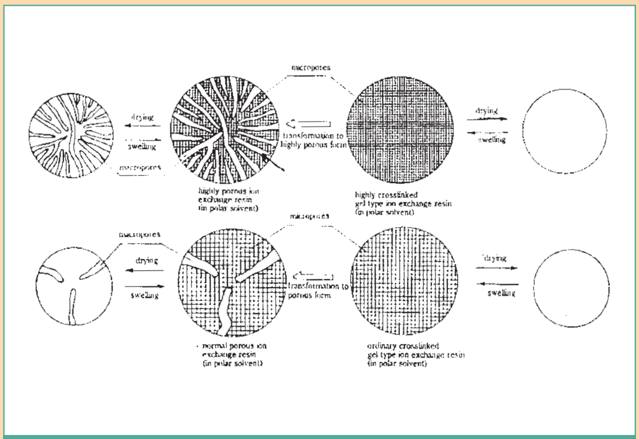
They are micro spheres of 0,3 - 1,2 mm diameter, obtained by means of Styrene and DVB polymerization, with tertiary amine active groups, distinguished by a porous physical structure that allows the adsorption and elution of organic substances; they are able to reversibly exchange anions with ion OH-. They have a high exchange capacity and mechanical resistance. In food industry they are applied for demineralization and decolourization of sugar solutions with density higher than water. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances. Weakly basic anion exchange resins are also available in highly uniform screen grade version.

Gel strongly basic anion exchange resin

They are micro spheres of 0,3 - 1,2 mm diameter, obtained by means of Styrene and DVB polymerization with quaternary amine active groups, distinguished by a gel physical structure that does not allow the adsorption of organic substances; they are able to reversibly exchange anions with ion OH-. In food industry they are mostly applied for demineralization of liquids containing organic stuff which is required to be left in solution. They have a lower exchange capacity compared to weakly basic anion exchange resins. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances.

Porous type strongly basic anion exchange resins

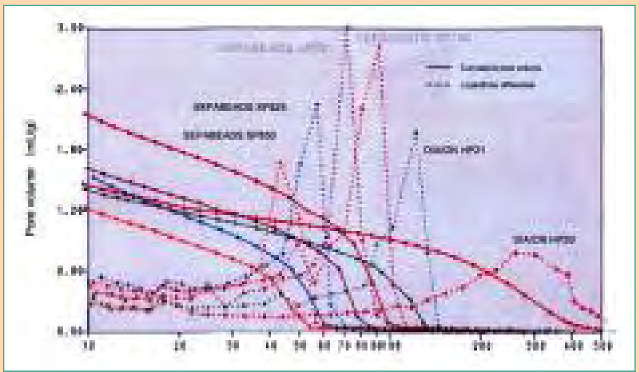
They are micro spheres of 0,3 - 1,2 mm diameter, obtained by means of Styrene and DVB polymerization with quaternary amine active groups, distinguished by a porous physical structure that allows the adsorption and elution of organic substances; they are able to reversibly exchange anions with ion OH-.
In food industry they are applied for demineralization of sugar solutions with density higher than water. They have a lower exchange capacity compared to weakly basic anion exchange resins. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer and its performances.



Porosity of ion exchange resins

Adsorbent resins

They are micro spheres of 0,3 - 0,8 mm diameter, obtained by means of Styrene or Acrylate and DVB polymerization without active groups, distinguished by a porous physical structure that allows the adsorption and selective elution of organic substances. The pores dimensions and surface area are graded according to the type of adsorbent resins. There are several applications in food industry oriented to removal of undesired organic substances and to recovery of valuable organic substances. These are products in constant development, therefore the new and unknown applications are many. Adsorbent resins reversibly adsorb polar organic molecules as polyhydric phenols, organic acids etc. and according to the eluant it is possible the recovery. Based on the polymeric matrix, type styrenic or acrylic, they show different degree of hydrophobicity.



Pores distribution in adsorbent resins

Strong cation gel type chromatographic resin

They are micro spheres of 0,2 - 0,3 mm diameter, obtained by means of Styrene and DVB polymerization, with sulphonic active groups, distinguished by a gel physical structure that does not allow the adsorption of organic substances. In food industry they are mostly applied for demineralization and separation of sugars. They are products in constant development, therefore the new and unknown applications are many. The percentage of DVB used during production changes the physico-chemical characteristics of the polymer.

DESCRIPTION OF THE COLUMNS CONTAINING RESINS

GENERAL CHARACTERISTICS

Columns containing resins are built in stainless steel AISI316/304 or hard rubber iron. They consist of a cylindrical body shut in by 2 rounded bottoms. A plate equipped with diffusers, welded on the bottom of the column, avoid the outlet of the resin. In the upper part of the column, a distribution system or a further plate allows the inlet of the liquid to be treated that will cross the resin bed. The columns are equipped with portholes and manholes for the inspection of internal parts. According to the applications, the columns are built to work co-currently, counter-currently, or with packed bed. In case of co-current regeneration, the resins fill the column at 50%, in counter-current at 75% , with packed bed at 95%. The columns dimension is established by the product's volume that is required to be treated in the unit of time, by its physico-chemical characteristics and by the operating conditions of the resins.

Columns with co-current regeneration

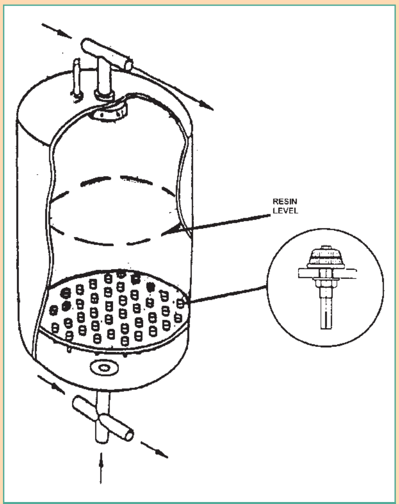
They consist of a cylindrical body in stainless steel or hard rubber iron with rounded bottoms welded at the end. A plate on the bottom, equipped with diffusers, avoids the outlet of the resins. The distributors are made in PVC or PP according to the application and the fissure's width is smaller than the diameter of the smallest beads of resin. The number of distributors depends on the working capacity. On rounded bottoms and cylindrical body are built manholes for maintenance interventions. On the cylindrical body are built 2 or more portholes, in defined position, for the internal vision of the column during working. The resin fills the 50% of the cylindrical body internal volume. In the upper part it is installed a diffuser for the distribution of the product to be treated which goes through the resin from the top to the bottom. The regeneration is made in the same direction of the production cycle.

Columns with counter-current regeneration

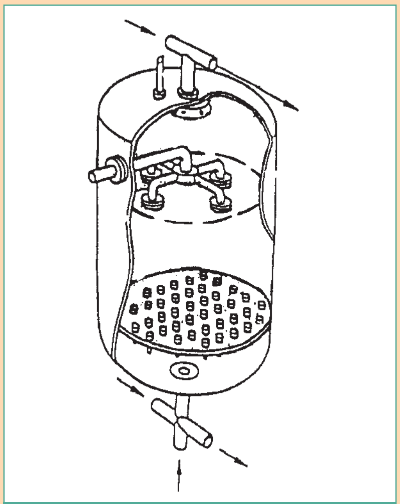
They consist of a cylindrical body in stainless steel or hard rubber iron with rounded bottoms welded at the end. A plate on the bottom, equipped with diffusers, avoids the outlet of the resins. The distributors are made in PVC or PP, according to the application; the fissure's width is smaller than the diameter of the smallest beads of resin. The numbers of distributors depends on the working capacity. Rounded bottoms and cylindrical body are equipped with manholes for maintenance interventions. On the cylindrical body are built 2 or more portholes in defined position for the internal vision of the column during working. The resin fills approximately the 75% of the cylindrical body internal volume. In the upper part of the rounded bottom it is installed a distributor for the inlet of the product to be treated which goes through the resins from the top to the bottom. The regeneration is made in the opposite direction of the running cycle, from the bottom to the top. The regeneration elute comes out from the diffuser which is put over the resin bed level. During this phase, in order to maintain the resin bed compact, counter pressure water is sent from upper collector.

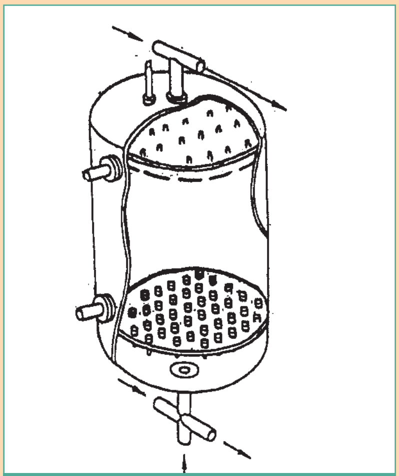
Fixed bed – floating bed columns

They consist of a cylindrical body in stainless steel or hard rubber iron with rounded bottoms welded at the end. Two plates put at the end of the cylinder, equipped with distributors, avoids the outlet of the resins. The distributors are made in PVC or PP according to the application; the fissure's width is smaller than the diameter of the smallest beads of resin. The numbers of distributors depends on the working capacity. On rounded bottoms and cylindrical body are built manholes for maintenance interventions of internal parts of the column. On the cylindrical body, are built 2 or more portholes in defined position for the internal vision of the column during working. The resin fills approximately the 95% of the cylindrical body internal volume. In the columns used in fixed bed system, the product goes through the resin bed from the top to the bottom and regeneration is made on the opposite direction. In floating bed system are used identical columns where the product to be treated goes through the resin bed from the bottom to the top and regeneration is made in the opposite direction.



Co-current


Counter-current


Blocked bed
floating bed

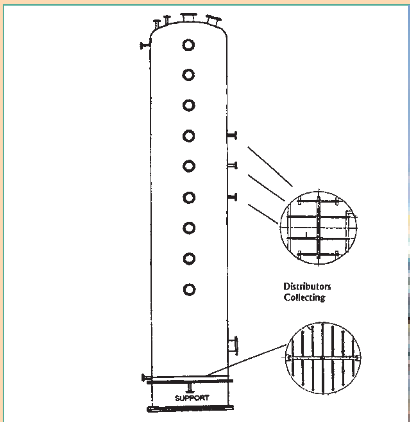

Aisi 316 stainless steel column

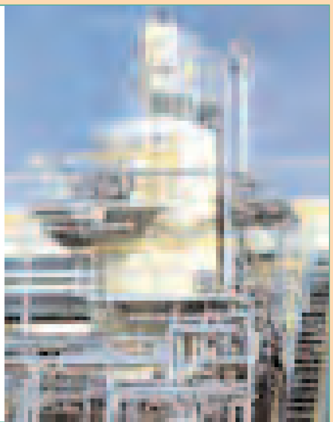

Hard rubber iron double room column


Hard rubber iron single room column

Chromatographic columns

They consist of a cylindrical body in stainless steel with a rounded bottom welded on the top. A stainless steel plate put on the bottom of the cylindrical body is the support for the resins. For the distribution of the fluids are used collectors equipped with distributors with fissures smaller than the resin beads diameter to avoid the outlet. The fluids distribution system is very important and it is essential to avoid the creation of preferential ways in the resin bed. Chromatographic processes in food industry are carried out at high temperatures, therefore the columns are insulated. The most updated chromatographic processes (Improved Simulated Moving Bed) are carried out in four or more rooms built in one or more columns. On the cylindrical part and on the bottom there are manholes and portholes necessary for maintenance interventions of internal parts and for the vision of the resin during working.



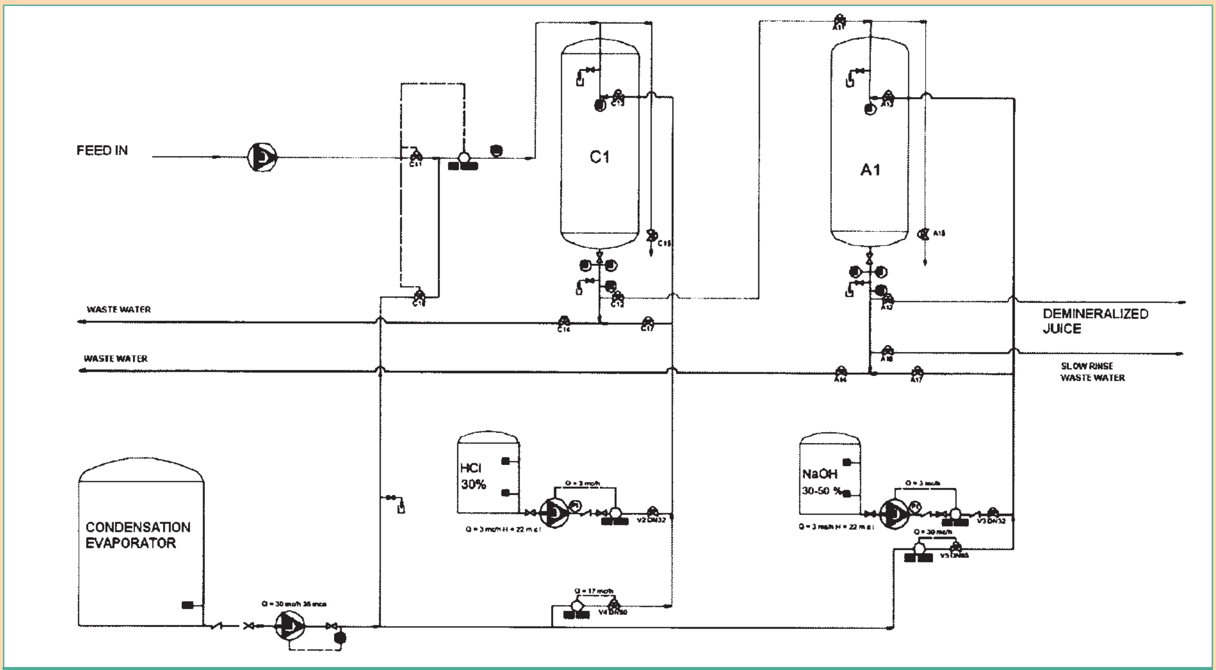

Chromatographic column and I.S.M.B.

DESCRIPTION OF RESINS PROCESSES

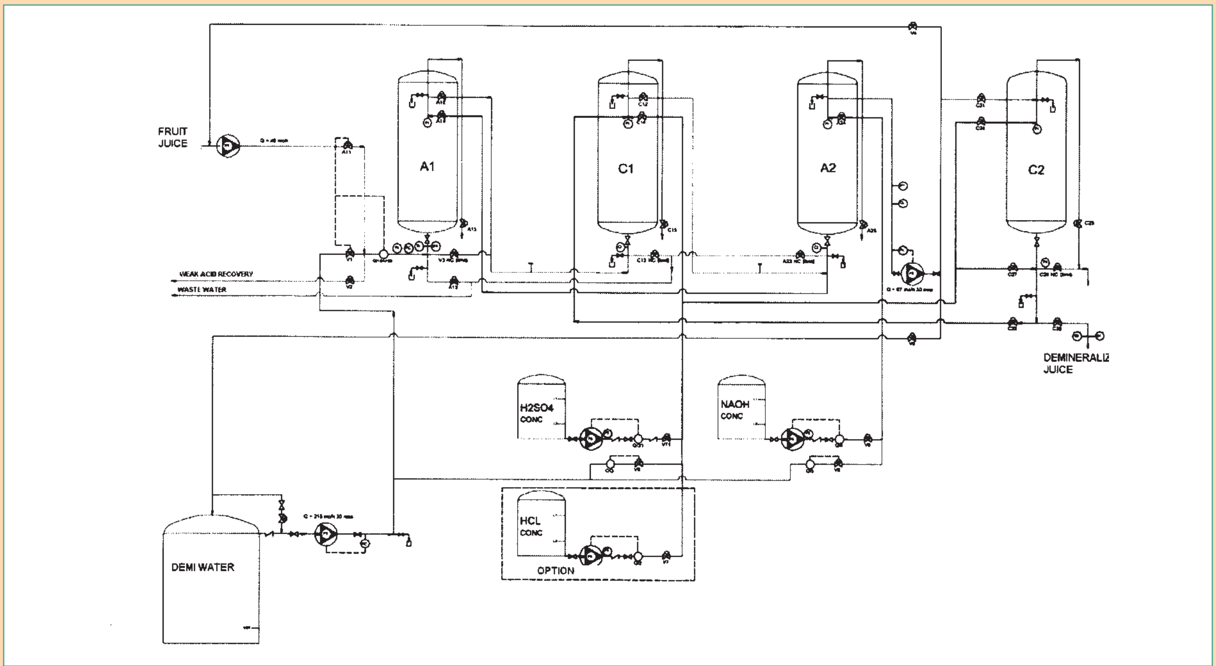
General description of traditional demineralization process

DEMINERALIZATION WITH CATION AND ANION RESINS

Traditional demineralization process by means of ion exchange resins is applied on food liquids when it is necessary to remove mineral salts and organic molecules with positive or negative charges. The liquid goes through the anion and cation columns in series, respecting defined working parameters which allow the ion exchange. The resins reduce to the lowest levels the saline content of the



2 columns plant flow chart for fruit juices demineralization



4 columns plant flow chart for fruit juices demineralization

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liquids, drastically decreasing the conductivity. During working, the resins retain a certain quantity of salts after which they must be regenerated, originating regeneration eluates which need biological treatment before being discharged. Cation resins retain cations releasing H+ ions, consequently the regeneration is made with hydrochloric or sulphuric acid that convert the resin back to the acid form. Anion resins retain anions releasing OH- ions, consequently the regeneration is made with caustic soda which convert the resin back to the basic form.
Sometimes, in order to demineralize a liquid a cation and an anion column are not enough, therefore demineralization processes with more columns in series have been developed.

Biological treatment of regeneration eluates

Regeneration eluates of traditional plants for fruit juices demineralization need an aerobic biological treatment before being discharged. The plant essentially consists of a deposition tank where are piped all the regeneration waters which are pumped at a steady flow to the oxidation tanks.
In these tanks the main water treatments are: oxidation/nitrification and denitrification. The waters are piped from oxidation tanks to a clarifier, where is made the separation between biological active mud and treated water. A final physico-chemical plant, composed by a floater and a system for reagents dosage, eliminates the polluting substances left in solution. The treated water from the floater goes to the final discharge well and floated mud is sent to mud dehydration plant.

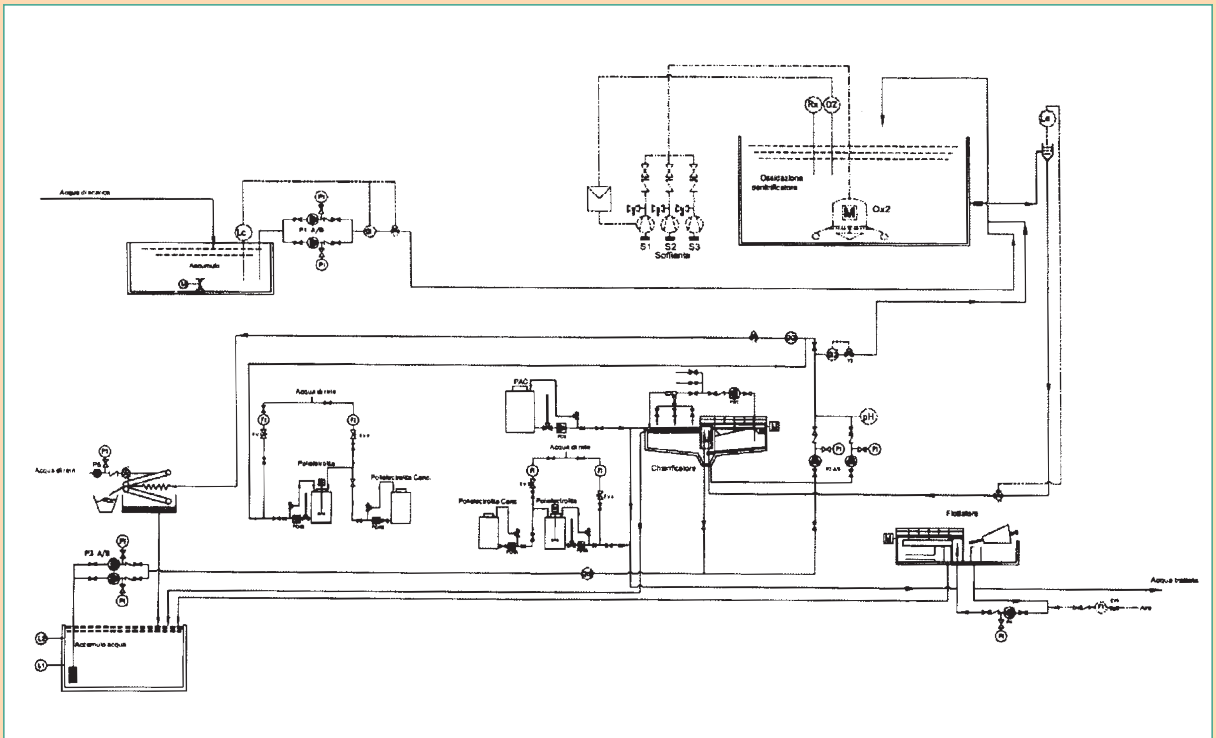


FOTO EUROTECWTT - PADOVA

Aerobic plant flow chart for the treatment of regeneration eluates from fruit juices demineralization plant

FOTO EUROTECWTT - PADOVA

Biological oxidation tanks

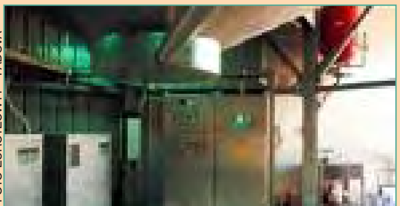


FOTO EUROTECWTT - PADOVA

Purification plant engine room

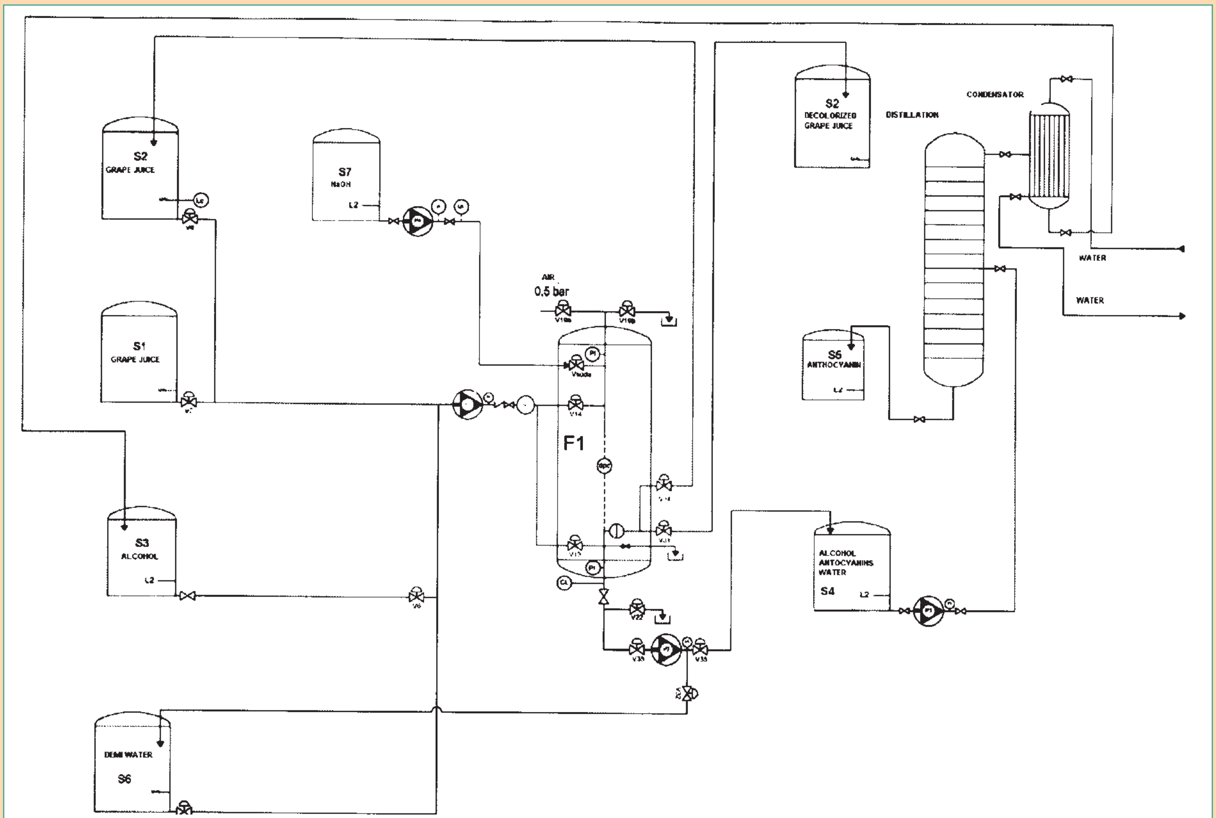
FOTO EUROTECWTT - PADOVA

Press filter and blower

General description of adsorbtion process

REMOVAL OF UNDESIRED ORGANIC SUBSTANCES
Adsorbent resins allow the selective removal of undesired organic substances from food liquids and from waste waters. There are different kind of adsorbent resins distinguished by a specific hydrophobic capacity, by a particular size and volume of the pores. Being polymers without functional group, they do not make any ion exchange with mineral salts but adsorb organic molecules exploiting Van der Waals' forces. The suitable adsorbent resins is selected according to the molecule to be removed. They are new product in constant development which allow the product's quality improvement and the recovery of liquids with disagreeable taste or smell. The suitable operating system is selected according to the liquid to be treated. The adsorption phase is made at a specific low flow rate. The regeneration is made with NaOH at 2-4% in the measure of 50-80 g of NaOH at 100%/l resin.
During this phase it is obtained a regeneration eluate with NaOH and organic substances that need a biological treatment before being discharged.

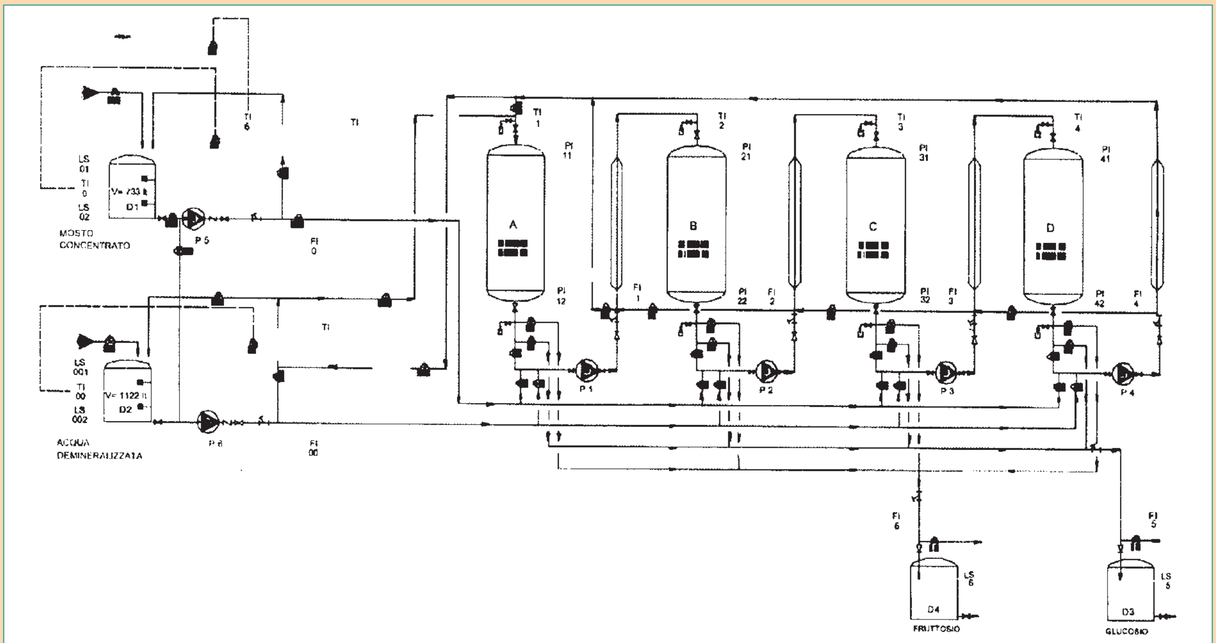
RECOVERY OF VALUABLE ORGANIC SUBSTANCES
Adsorbent resins selectively adsorb organic molecules in a reversible way. There are various kind of adsorbent resins distinguished by a specific hydrophobic capacity, by a particular size and volume of the pores. The suitable adsorbent resins is selected according to the molecule to be removed. The adsorption phase is made at specific low flow rates. The recovery of adsorbed organic substances is made with alcohol or with organic solvents and according to the concentration of the eluant it is possible to make a further selective recovery. They are products in constant development which allow the realization of new natural extracts on industrial scale, to reach high purities and to replace crystallization phases. The suitable operating system is selected according to the liquid to be treated.
Regeneration eluate constituting the product contains alcohol or solvent recoverable by distillation.
In this process there are no eluates to be treated.



Organic substance recovery plant flow chart

General description of chromatographic process

Chromatographic process in column, by means of chromatographic grade resins, is mostly applied for sugars separation and for sugary juices demineralization.
In this process are not applied reagents for regeneration and the resins work as a separation vehicle of atoms and molecules. Each molecule in solution has a specific affinity with the resin and thanks to this property the separation takes place.
For example, beet molasses is rich in sugar and mineral salts which are recovered by means of ionic exclusion chromatographic process. In this case it is applied a chromatographic resin that is more similar to sugars compared to mineral salts and polyphenols. The process is developed at high temperatures; the concentrated molasses is put inside the column at fixed specific flow rates and then demineralised water is injected to move the product from the resin bed. From the bottom of the column will be recovered in sequence a first fraction of mineral salts and polyphenols and in a second fraction purified sugars.
This process is applied also where there are 2 or more molecules in solution to be separated using suitable resins.
Up-to-date chromatographic systems with four or eight columns allow to obtain high purity grade and low dilutions of the recovered fractions. The most fine and uniform resins have shown the best performances.



4 columns chromatographic plant flow chart

FOTO EUROTECWITT - PADOVA

GENERAL DESCRIPTION OF OPERATING SYSTEMS FOR TRADITIONAL DEMINERALIZATION PLANTS AND ORGANIC SUBSTANCE ADSORPTION

Co-current system

Co-current system is suggested when it is necessary to treat liquids with suspended solid material since it is easier the washing of the resins. During the cycle the liquid goes through the columns from the top to the bottom, transferring to the resins all the mineral salts and organic molecules with positive or negative charge (organic acids, amino acids etc.). The resins have a fixed exchange capacity and the volumes of cation and anion are calculated according to the specific exhaustion flow rate and are balanced according to the analysis of the liquid to be treated. The higher is the density and mineral salts content, the lower will be the specific exhaustion flow rate.
When the resins are exhausted, it is necessary to apply a regeneration phase which, in this system, is performed in 4 phases: counter wash, injection of regenerant, moving of regenerant and wash.
During counter wash, the solids left on resin bed are removed and the beads are classified again. It is made at a flow rate sufficient to expand the bed at least of 50%. This operation goes on for 10-15 minutes, after which the resins will be drained. In cation resins is injected hydrochloric or sulphuric acid at 3-5% in the measure of 80-120 g at 100% for litre of resin and in anion resins is injected caustic soda at 4-5% in the measure of 60-80 g at 100% for litre of resin in the same direction of working cycle that is from the top to the bottom. Therefore the regenerant is moved with demineralized water from the top to the bottom at the same regeneration flow rate. The wash is always made with demineralised water in the same direction but at higher flow rates compared to the previous phases.
During these phases are produced acid and basic regeneration eluates containing salts removed from the product, the excess of the product and the excess of regenerants. During treatment of food fluids are obtained eluates with high organic content that normally need a biological treatment before being discharged. In this process, it's used a higher quantity of regenerant compared to counter current and fixed bed or floating bed systems, since the lower part of the resin bed is the last to be involved. Normally these operations are carried out automatically, by means of a PLC that calculates opening and closing of pneumatic valves. When the resins are regenerated and drained, the production starts. The resins are immersed in demineralised water and during inlet and outlet of the product in the plant there are dilutions which, due to the empty spaces, in this system are very high.

Counter-current system

Counter-current system is more elaborate compared to co-current system, but it allows the reduction of regenerants consumption. The empty space in the column is reduced and the resins washing is more difficult. This system is not suggested if the liquid to be treated contains suspended solids. During working, the liquid goes through the columns from the top to the bottom, transferring to the resins all the mineral salts and organic molecules with positive and negative charges (organic acids, amino acids etc.). The resins have a fixed exchange capacity and the cation and anion resin's volumes are calculated according to a specific exhausting flow rate and are balanced based on the liquid to be treated. The higher is the density and the mineral salts content, the lower will be the specific exhaustion flow rate. When the resins are exhausted, it is necessary to apply a regeneration cycle that is performed in 4 phases: counter wash, injection of regenerant, moving of regenerant and wash. During counter wash, the solids left on resin bed are removed and the beads are classified again. It is made at a flow rate sufficient to expand the bed at least of 25%. This operation goes on for 10-15 minutes, after which the resins will be drained. Therefore, in cation resins is injected hydrochloric or sulphuric acid at 3-5% in the measure of 60-80 g of HCl or H2S04 at 100% for litre of resin and in anion resins is injected caustic soda at 4-5% in the measure of 50-60 g of NaOH at 100% for litre of resin in the opposite direction of working, from the bottom to the top. Then, the regenerant is moved with demineralised water in the same direction of regeneration. The wash is made with demineralised water from the top to the bottom at higher flow rates compared to the previous phases. During these phases are produced acid and basic regeneration eluates containing salts removed from the product and the excess of regenerants. During treatment of food fluids are obtained eluates with high organic contents that need a biological treatment. In this system it's used a lower quantity of regenerants compared to the previous one since the lower part of the resin bed is the first to be involved during regeneration. Normally these operations are carried out automatically, by means of a PLC that calculates opening and closing of the valves. When the resins are regenerated and drained, the production starts. The resins are immersed in demineralised water and during inlet and outlet of the product in the plant there are dilutions which, due to the empty spaces, in this system are high.

Fixed bed – floating bed system

Fixed bed and floating bed systems are designed for a regeneration in the opposite side of working and the columns are completely filled with resin. They could be considered as counter-current systems with reduced empty spaces and regeneration times. The resins suffer a higher mechanical stress and washing is often made in columns outside the process plant.

This system is suggested when the liquid to be treated is clear, without turbidity or suspended matters. The liquid goes through the columns from the top to the bottom, transferring to the resins the mineral salts and organic molecules with positive or negative charges (organic acids, amino acids etc.). The resins have a fixed exchange capacity and cation and anion resin's volumes are calculated according to a specific exhausting flow rate and are balanced based on the liquid to be treated. The higher is the density and the mineral salts content, the lower will be the specific exhaustion flow rate. When the resins are exhausted, it is necessary to apply a regeneration cycle that is developed in 2 phases: injection of regenerant and wash. In cation resins is injected hydrochloric or sulphuric acid at 3-5% in the measure of 60-80 g of HCl or H2S04 at 100% for litre of resin and in anion resins is injected caustic soda at 4-5% in the measure of 60-80 g of NaOH at 100% for litre of resin in the opposite direction of working (floating bed: from the top to the bottom).

The wash is made with demineralised water in the same direction of regeneration at higher flow rates compared to the previous phase. During this phase are produced acid and basic regeneration eluates containing salts removed from the product and the excess of regenerants. During treatment of food fluids are obtained eluates with high organic contents that need a biological treatment. In this system is used a lower quantity of regenerants compared to co-current system since the lower parts of the resin bed are the first to be involved during regeneration. Normally these operations are carried out automatically, by means of a PLC that calculates opening and closing of the valves. When the resins are regenerated and drained, the production starts. In the column, in addition to the resin, it is loaded a floating inert polymer that avoid the clogging of the diffusers due to fragments of resin. In floating bed system, the flows of various phases opposite compared to fixed bed system.

In the first one, the working flow goes through the resins from the bottom to the top and it is necessary that the resin stays compact. It is applied where the production is made at high specific exhaustion flow rate or where the liquid to be treated has a high density. The resins are immersed in demineralised water and during inlet and outlet of the product in the plant there are dilutions which, in this system are reduced to a minimum.

Floating bed columns are built also with a double room to contain two different type of resins.

INDUSTRIAL APPLICATIONS: GRAPES SUGAR PRODUCTION (M.C.R.)

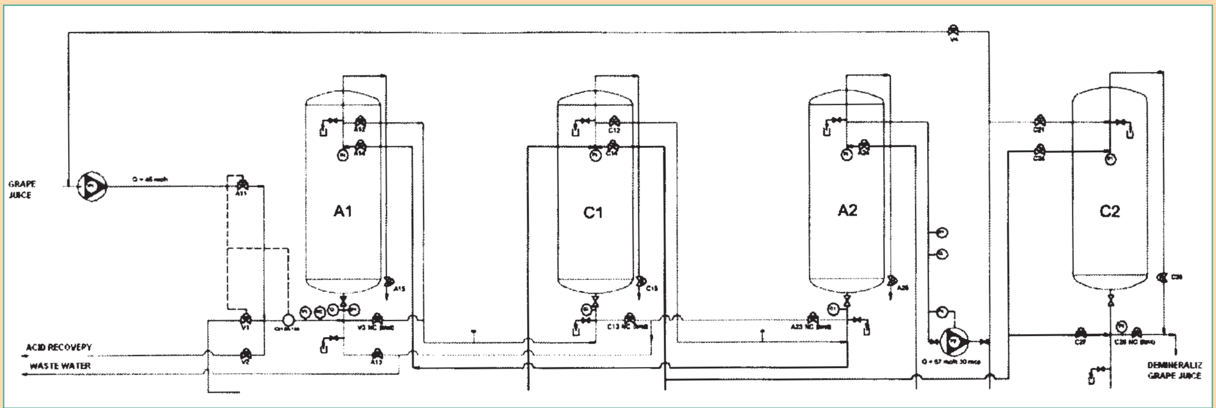
Description of the process

Grape sugar, commonly called must, is submitted to a demineralization process by means of ion exchange resins for the production of grape sugar, composed of about 50% fructose and about 50% glucose. Red or white must contains about 200 g/l of sugars, organic acids, polyphenols, amino acids and mineral salts. During demineralization the mineral cations and amino acids are exchanged by cation resin, the mineral anions and organic acids by anion resin. This last, reversibly adsorbs polyphenols and the outcoming product is a transparent water solution containing about 200 g/l of sugars. The concentration of these sugars is commonly expressed in "Brix" (1° Brix = 10 g/l). The conductivity of starting must is around 2500 µS/cm given by the presence of mineral salts etc., demineralised and decolorized must has a conductivity below 10 µS/cm. It is mostly used to raise alcoholic content of wines but also as diet sweetener. Grape sugar is commercialized at 70° Brix to reduce transportation cost impact and is commonly called MCR, concentrated rectified must.

Typical analysis of white grape sugar

pH	**3,3**
Conductivity	**2260 µS/cm**
Dry substance	**20,2 ° Brix**
Total acidity	**30,02 g/l**
Sulphur dioxide	**1400 mg/l**
Sulphates	**0,47 g/l**
Chlorides	**0,21 g/l**

Phosphates	**0,65 g/l**
Cation loading	**34 meq/l**
Total nitrogen	**0,38 g/l**
Phenol index	**15,6 (280 nm)**
Total Polyphenols	**1085 gallic ac.**
Sugars	**195 g/l**



Floating bed plant

Characteristics of demineralised and decoloured must

pH	**3,5**
Conductivity	**< 10 µS/cm**
Dry substance	**19,5 ° Brix**
Fructose	**105 g/l**
Glucose	**90 g/l**

Regenerants consumption

1,90 Kg HCl 33%/hl must
1,80 Kg NaOH 50%/hl must

Resin type and volumes ratio

ANIONIC1 : RELITE RAM1
CATIONIC1 : RELITE RPS
ANIONIC2 : RELITE RAM1/RELITE RAP1
CATIONIC2 : RELITE RPS

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Volumes of regeneration eluates for production of 300 m² 20° Brix rectified must

130 m³	/ regeneration eluates of anion resins
170 m³	/ regeneration eluates of cation resins
300 m³	/ total eluates

Characteristics of regeneration eluates after recovery of tartrates and neutralization – discharge

COD	6600 mg/l
Total nitrogen	249 mg/l
Phosphates	243 mg/l
Chlorides	3700 mg/l
Sulphites (SO2)	1400 mg/l
pH	6 - 8

FOTO EUROTECWIT - PADOVA

500 m³/day grapes juice demineralization plant

Organic acids recovery (tartaric/malic acid)

During demineralization of grapes must, weak anion resin exchanges organic acids and adsorbs polyphenols. In grapes, are mostly present tartaric acid and malic acid which are exchanged by the anion resin. Before proceeding with regeneration, it is made the extraction of organic acids using sulphuric acid and water. Strong acids have the property to move the weaker acids from the resins since they are more similar. About 10% less of sulphuric acid is used compared to organic acids exchanged by the resin so as to make the movement of solution losing a minimum quantity of organic acids. It is proceeded with the injection in the column of sulphuric acid at 10 - 15% followed by demineralised water. From the bottom of the column it is collected a solution containing 30 – 35 g/l of tartaric acid and malic acid with a portion of polyphenols released by weak anion resin. In order to purify the acids, the solution is passed on adsorbent resin. The organic acids are concentrated and used as they are in wine-making industry, otherwise they are separated by means of precipitation of calcium tartrate and commercialized in food industry.

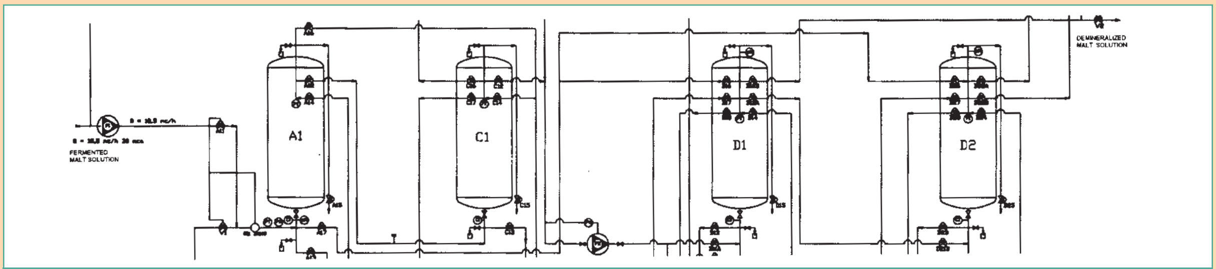
INDUSTRIAL APPLICATIONS: PURIFICATION OF MALT ALCOHOLIC SOLUTION

Description of the process

The alcoholic solutions obtained from malt fermentation are submitted to demineralization and decolourization process with ion exchange and adsorbent resins to produce a clear alcoholic solution without mineral salts, amino acids, polyphenols, organic acids, aldehydes and ketones. The alcoholic solution of malt contains from 140 to 190 ml/l of alcohol. This process is an efficacious alternative to distillation; mineral cations and amino acids are exchanged by cation resin, mineral anions and organic acids by anion resin. Adsorbent resin, after demineralization, reversibly adsorbs polyphenols and the outcoming product is clear and odourless.
A column with disposable activated carbons as final is placed safety filter.
The conductivity of starting solution is around 2000 µS /cm due to the presence of mineral salts etc.; demineralised and decolourised product has a conductivity less than 20 µS/cm and is applied for low alcoholic content beverages.

Typical analysis of fermented malt

pH	**3,22**	Density	**0,96 mg/ml**
Sulphites and Chlorides	**8,8 meq/ml**	Total Polyphenols	**430 gallic ac.**
Conductivity	**2036 µS/cm**	Total acidity	**37,6 meq/l**
Potassium	**520 mg/l**	Ethyl Alcohol	**195 g/l**



Co-current plant

Characteristics of demineralised and decoloured malt

pH	**3,5**
Conductivity	**< 20 µS/cm**
Density	**0,97**
Ethyl alcohol	**190 g/l**

Regenerants consumption

1,1 Kg HCl 33% / hl malt
1,00 Kg NaOH 50% / hl must

Resin type and volumes ratio

ANIONIC 1 : RELITE RAM1
CATIONIC 1 : RELITE RPS
ADSORBENT : SEPABEADS SP700
ACTIVATED CARBON : RELITE P50

Volumes of regeneration eluates for production of 100 m³ demi/deco malt

50 m² regeneration eluates of anion / adsorbent resins
30 m² regeneration eluates of cation resins
80 m² total eluates

Characteristics of regeneration eluates after neutralization – discharge

COD	**5200 mg/l**
Total nitrogen	**206 mg/l**
Phosphates	**206 mg/l**
Chlorides	**3700 mg/l**
pH	**6 - 7**

INDUSTRIAL APPLICATIONS: DEMINERALIZED POWDER WHEY PRODUCTION

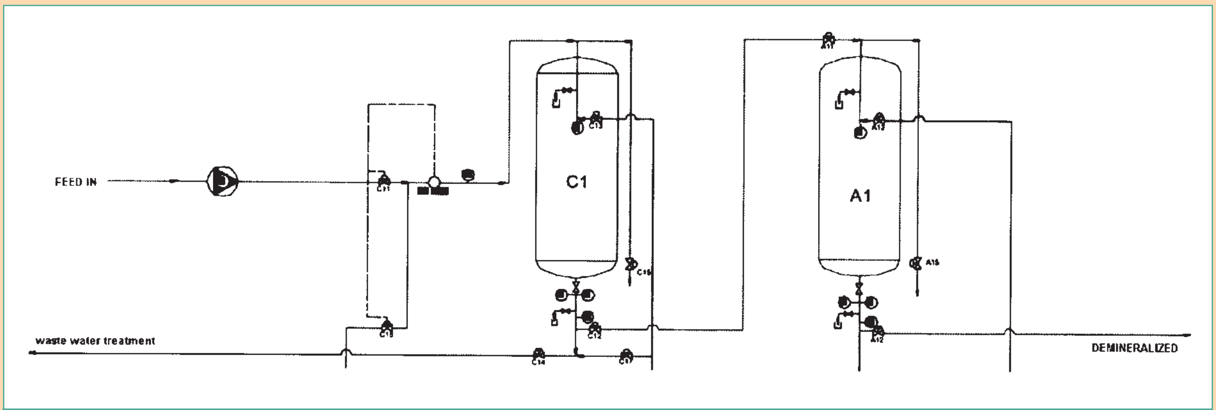
Description of the process

Whey coming from cheese production is submitted to a demineralization process by means of ion exchange resins for the production of demineralised powder whey enriched (with proteins). Whey contains approximately 50 g/l lactose, proteins, beta-carotene, amino acids, organic acids and mineral salts. During demineralization, mineral cations and amino acids are exchanged by a cation resin, the anions and organic acids by a special anion resin with a minimum loss of protein. The latter reversibly adsorb beta-carotene. The outcoming product is a water solution containing about 50 g/l of lactose with proteins. In order to reach good performances is crucial the choice of suitable resins. The conductivity of starting whey is around 2500 μS/cm given particularly from the presence of mineral salts. Demineralised whey has a conductivity less than 20 μS/cm and is concentrated at 60 °Brix to be powdered. It is applied for the production of milk for babies and as ingredient in food industry.

Typical analysis of whey

Na	760 mg/l
K	1510 mg/l
Mg	75 mg/l
Ca	415 mg/l
Cl	1850 mg/l
HPO4	1230 mg/l
SO4	155 mg/l

Lactose	49,5 g/l
Proteins	80 g/Kg dry substance
NPN	20 g/Kg dry substance
Ashes	60 g/Kg dry substance
Solids	60 g/l
Fats	0,2 g/Kg dry substance
Density	1,06 Kg/l as it is



Counter-current plant – 2 lines

Characteristics of demineralised whey

Lactose	49 g/l as it is
Proteins	74 g/Kg dry substance
NPN	18 g/Kg dry substance
Ashes	0,2 g/Kg dry substance
Solids	57 g/l as it is
Fats	0,01 g/Kg dry substance
Densityà	1,05 Kg/l as it is

Regenerants consumptions

1,15 Kg HCl 33% / hl demi whey
0,63 Kg NaOH 50% / hl demi whey

Resin type and volumes ratio

CATIONIC 1 : RELITE C250FB
ANIONIC1 : DIAION WA55

Volumes of regeneration eluates for production of 220 m³ demi whey

190 m³ regeneration eluates of anion resins
140 m³ regeneration eluates of cation resins
330 m³ total eluates

Characteristics of regeneration eluates after neutralization

COD	**2500 - 2800 mg/l**
Total Phosphorus	**15 - 20 mg/l**
Soluble Phosphates	**< 30 mg P205/l**
BOD5	**800 - 1000 mg 02/l**
Ammoniacal Nitrogen	**15 - 20 mg NH4/l**
Conductivity	**> 10.000 μS/cm**
pH	**6 - 7**

Whey demineralization plant

INDUSTRIAL APPLICATIONS: LACTOSE PRODUCTION

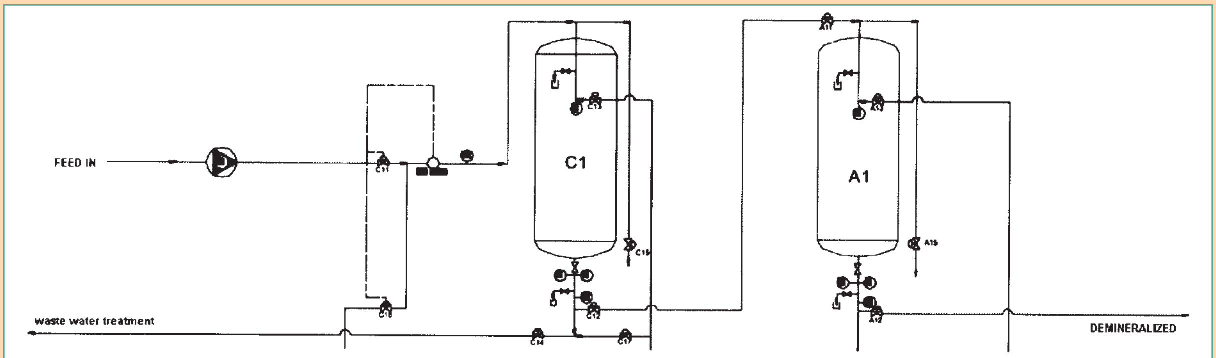
Description of the process

Whey is filtered through Ultra Filtration membranes which allow the separation of proteins from other components. Concentrated proteins are commercialized for the production of ricotta (soft white unsalted cheese) or as WPI (whey protein concentrated).
The permeate contains about 50 g/l of lactose, proteins, beta-carotene, amino acids, organic acids and mineral salts. During demineralization, mineral cations and amino acids are exchanged by a cation resin; mineral anions and organic acids by an anion resin. The latter reversibly adsorbs beta-carotene. The outcoming product is a water solution containing about 50 g/l of lactose. The conductivity of starting permeate is around 2500 μS/cm given particularly from the presence of mineral salts. Demineralised permeate has a conductivity less than 20 μS/cm and is constituted by lactose in solution that is concentrated and crystallized. Due to the very low salt content the production of mother waters is reduced to the minimum. In some cases it is preferred decolorize the permeate with an adsorbent resin and make crystallization but with a high production of mother waters. Lactose finds several applications as ingredient in food and pharmaceutical industry.

Typical analysis of permeate

Na	2105 mg/l
K	4180 mg/l
Mg	207 mg/l
Ca	1150 mg/l
Cl	5125 mg/l
HPO4	3400 mg/l
SO4	430 mg/l

Lactose	137 g/l
Proteins	2 g/Kg dry substance
NPN	1 g/Kg dry substance
Ashes	182 g/Kg dry substance
Fats	0,06 g/Kg dry substance
Density	1,18 Kg/l



Counter-current plant

Characteristics of demineralised permeate (lactose)

Lactose	115 g/l as it is
Proteins	1 g/kg dry substance
NPN	0,5 g/kg dry substance
Ashes	0,7 g/kg dry substance
Fats	0,05 g/kg dry substance
Density	1,14 kg/l as it is

Regenerants consumptions

3,4 Kg HCl 33% / hl demi whey
1,94 Kg NaOH 50% / hl demi whey

Resin type and volumes ratio

CATIONIC 1 : RELITE C250FB
ANIONIC 1 : RELITE RAM1

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Volumes of regeneration eluates for production of 300 m^3 demineralized permeate

670 m^3 regeneration eluates of anion resins
930 m^3 regeneration eluates of cation resins
1600 m^3 total eluates

Characteristics of regeneration eluates after neutralization

COD	**1800 - 2300 mg/l**
BOD5	**800 - 1000 mg 02/l**
Total Phosphorus	**5 - 10 mg/l**
Ammoniacal Nitrogen	**10 - 15 mg NH4/l**
Soluble Phosphates	**< 20 mg P205/l**
Conductivity	**> 10.000 µS/cm**
pH	**6 - 7**

INDUSTRIAL APPLICATIONS: LIQUID DATE SUGAR PRODUCTION

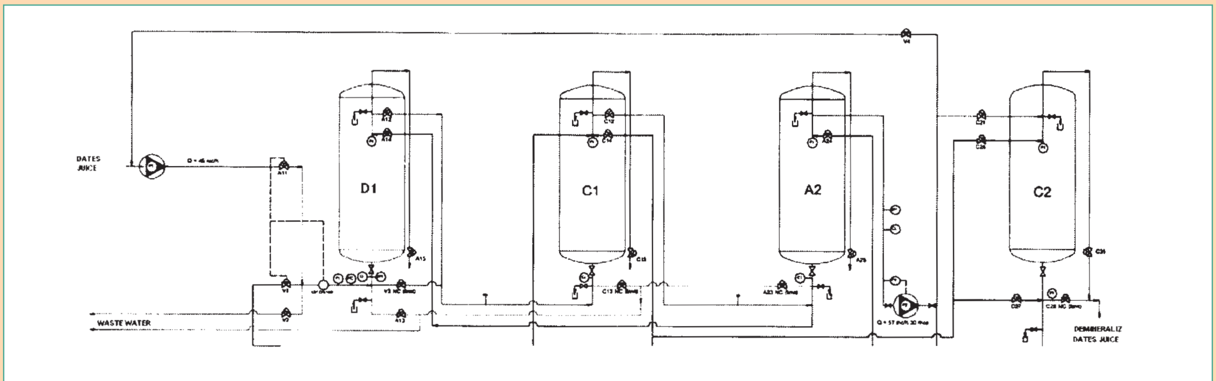
Description of the process

Date juice is submitted to a demineralization and decolourization process by means of ion exchange and adsorbent resins for the production of liquid sugar composed by approximately 50% of fructose, about 45% glucose, about 5% saccharose and water. Date juice contains about 200 g/l of sugars, organic acids, polyphenols, amino acids and mineral salts. Due to the quantity and the quality of polyphenols contained in the juice, demineralization it is necessary to decolourize the juice with an adsorbent resin regenerable with NaOH. Then, cation resin exchanges amino acids and cations whereas organic acids and mineral anions are exchanged by anion resin.
The outcoming product is a water solution containing about 200 g/l of sugars; the concentration is normally expressed in °Brix (1° Brix = 10 g/l). The colour of juice is expressed in ICUMSA; in the starting product is around 3000 and conductivity around 3500 µS/cm given particularly from the presence of mineral salts. The concentrated date sugar is commercialized at 60 -70 Brix (600 – 700 g/l sugars), has a conductivity less than 50 µS/cm and 100 – 150 ICUMSA. It is mostly applied as diet sweetener for preparation of beverages and canned fruit.

Typical analysis of date juice

pH	**3,3**
Conductivity	**3206 µS/cm**
Dry substance	**18,3 °Brix**
Total acidity	**12,5 meq/l**
Sulphates	**0,38 g/l**
Chlorides	**0,17 g/l**

Phosphates	**0,32 g/l**
Cation loading	**74 meq/l**
Total Nitrogen	**0,26 g/l**
Phenol index	**28,2 (280nm)**
Total Polyphenols	**2196 gallic ac.**
Sugars	**176 g/l**



Floating bed plant

Characteristics of demineralised and decolourized juice

pH	**3,5**
Conductivity	**< 20 µS/cm**
Dry substance	**17,6 °Brix**
Fructose	**89 g/l**
Glucose	**82 g/l**
Saccharose	**5 g/l**

Resin type and volumes ratio

ADSORBENT1 : RELITE SP411
CATIONIC1 : RELITE RPS
ANIONIC1 : RELITE RAM1
CATIONIC2 : RELITE RPS

Regenerants consumptions

1,32 Kg HCl 33% / hl date juice
0,86 Kg NaOH 50% / hl date juice

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Volumes of regeneration eluates for production of 250 m2 demineralised date sugar

130 m^3 regeneration eluates of anion resins	
100 m^3 regeneration eluates of cation resins	
230m^3 total eluates	

Characteristics of regeneration eluates after neutralization

pH	**6 - 8**
COD	**7200 mg/l**
Total Nitrogen	**232 mg/l**
Phosphates	**220 mg/l**
Chlorides	**3600 mg/l**

FOTO EUROTECWTT - PADOVA

Date juice demineralization plant

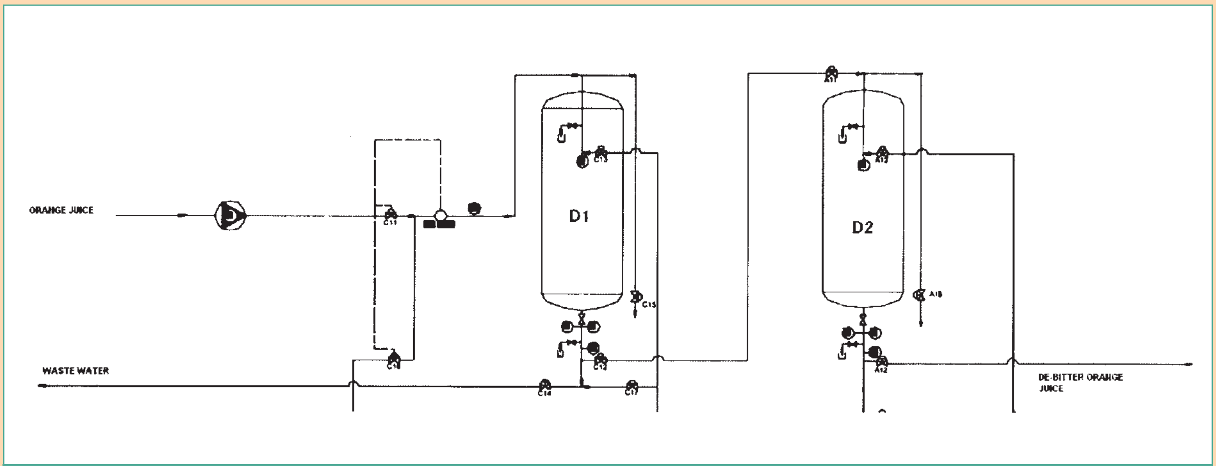
INDUSTRIAL APPLICATIONS
ORANGE JUICE DEBITTERING

Description of the process

Orange juice is submitted to debittering process by means of adsorbent resin. The molecules in charge of bitter taste, Limonine, Naringine etc. are selectively removed from orange juice with the purpose of obtaining a sweet product without added sugars. In orange juice there are many types of polyphenols and organic molecules; by means of a specific adsorbent resin it is possible to selectively intervene so as not to spoil the organoleptic characteristics of the juice. In these processes, the juices goes through the resin bed at a specific very low flow rate. The concentration of dry substance in the juice is around 80 g/l of which 90% sugars. The pulp content must not be higher than 1% otherwise, in the columns, the increase of differential pressure avoids the juice passage. Normally, above the filters are installed some quartzite safety prefilters are installed above the filters.

Analisi tipica del succo d'arancia

pH	5 - 6	Naringine	40 - 50 mg/l
Density	1,08 g/l	Pulps	max 1%
Lemonine	15 - 25 mg/l	Sugars	75 g/l



Co-current plant – 2 columns in parallel

Characteristics of debittered juice

pH	5 - 6
Density	1,08 g/l
Lemonine	< 0,5 mg/l
Naringine	< 1 mg/l
Sugars	75 g/l

Regenerants consumptions

1,66 Kg NaOH 50% / hl date juice
0,15 Kg H2SO4 20% / hl date juice

Resin type

ADSORBENT : RELITE SP490

Volumes of regeneration eluates for production of 80 m^2 debittered orange juice

34 m^3 regeneration basic eluates

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Characteristics of regeneration eluates

pH	12 - 14
COD	6000 - 6500 mg/l
Total nitrogen	290 - 300 mg/l
Phosphates	40 mg/l
Sodium	5200 mg/l

Oranges juice debittering plant

INDUSTRIAL APPLICATIONS: SEPARATION OF FRUCTOSE/GRAPES GLUCOSE

Description of the process

Concentrated grapes sugar at 65° Brix contains 250 g/l glucose and 360 g/l fructose. With chromatographic technology it is possible to separate the two sugars using a cation chromatographic resin in calcium form. The process is performed at 65°C to reduce viscosity of sugar liquid. A fixed quantity of solution at a specific flow rate is sent to the plant and some demineralised water elutes the resin's sugars. The resin is more similar to fructose and from the bottom of the column will be collected in sequence the first fraction full of glucose and the second one full of fructose maintaining unchanged the chemico-physical characteristics of sugar molecules.
In 4 columns systems the production is made continuously. If the 2 fractions are collected separately separated sugars at required purity degree are obtained. The higher is the purity, the higher will be the water quantity to be applied. With modern multiple columns chromatographic systems the dilution effect is mostly reduced.

Fructose/Glucose separation plant

Average flow rate of sugars	**3,6 m^3/ h**
Average flow rate of water	**3,9 m^3/h**

Plant scheme

4 chromatographic columns

Operating system

Simulated Moving Bed

Resin type and resin volume for each column

Chromatographic / 10.000 lt DIAION UBK 555

FOTO EUROTECWTT - PADOVA

Chromatographic plant

Typical analysis grapes sugar

pH	**3,5**
Conductivity	**< 20 µS/cm**
Dry substance	**65 ° Brix**
Glucose	**29 g/l**
Fructose	**36 g/l**

Production

Fructose 98,5 % 42 ° Brix 2,5 m^3 / h
Glucose 97,5 % 26 ° Brix 5 m^3 / h
Fructose 99,8 % 20 Ton / day
Glucose 99,8 % 20 Ton / day

INDUSTRIAL APPLICATIONS: NATURAL COLOURINGS RECOVERY – ENOCYANINE

Description of the process

Adsorbent resins are able to adsorb the anthocyanins present in red grapes juice and to release them in alcoholic solutions. Grape juices previously filtered slowly go through the adsorbent resin releasing the colouring organic substances mainly composed of anthocyanins, catechins and proanthocyanins. From the bottom of the column it is collected a transparent grape juice that normally is applied for the production of grape sugar. When the resin is loaded of natural colouring (anthocyanins) it is washed with demineralised water to remove sugars and then regenerated with an alcoholic solution higher than 50°. The deep red eluate is collected and, by means of a distillation tower, alcohol it is separated from natural colouring in water solution. The concentrated colouring solution is powdered and commercialized as natural colouring. With the same technology it is possible to extract tannins from white grapes juices.

Typical analysis of red grapes juice

pH	3,3	Total anthocyanins	2,44 g/l
Conductivity	2360 µS/cm	Free anthocyanins	2,79 g/l
Dry substance	21,6 Brix	Catechins and proanthocyanins	1,47 g/l

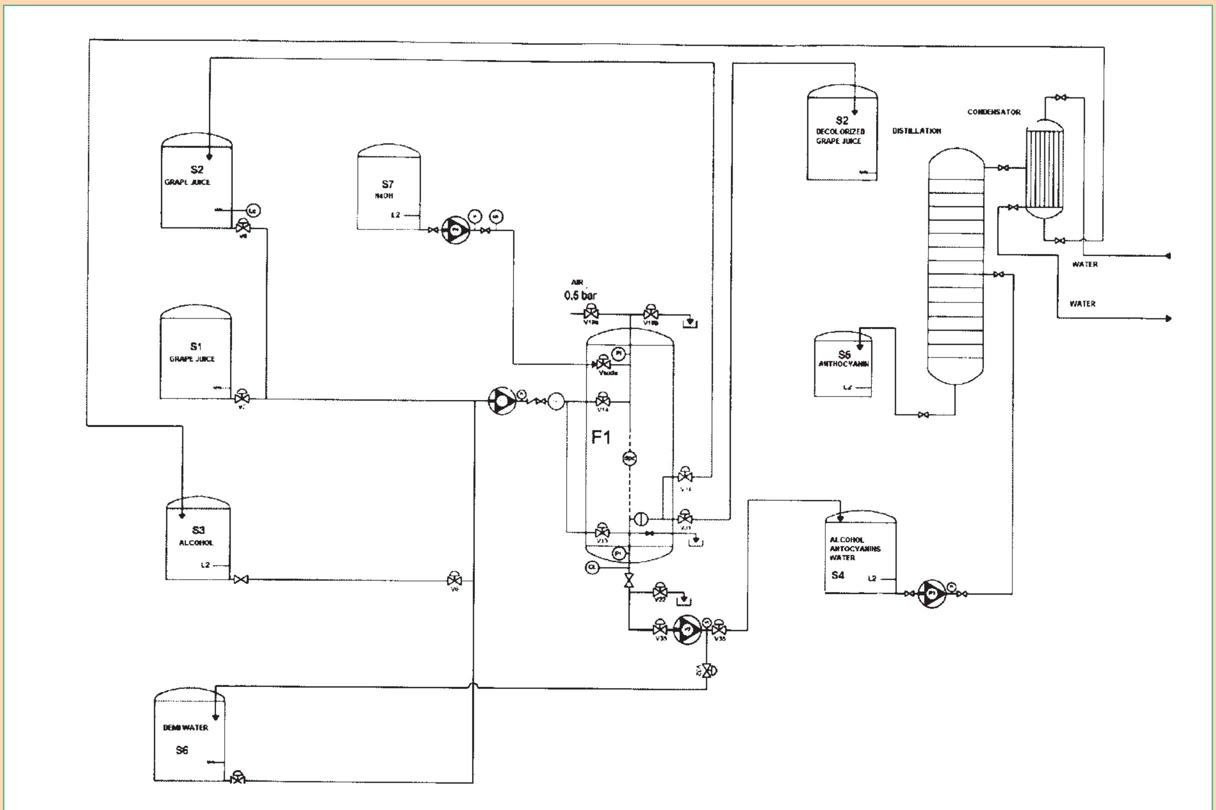

FOTO EUROTECWTT - PADOVA

Enocianina recovery plant flow chart

Characteristics of the extract - enocyanine

pH	3,5
Total anthocyanins	21,2 g/l
Free anthocyanins	16,1 g/l
Catechins and proanthocyanins	10,6 g/l

Resin type and volumes

ADSORBENT : RELITE SP411

Alcohol for enocyanine extrac. x 5000 l resin

5500 lt 60° ethyl alcohol

Washing water x 5000 l resin

10 m³ demineralised water

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FOOD APPLICATIONS OF RESINS

- Apple juice demineralization
- Polyphenols recovery from apple peels extract
- Patulin removal from apple juice

- Pineapple juice demineralization
- Pineapple juice deodorization and decolourization
- Demineralization and decolourization of date juice
- Demineralization and purification of alcoholic malt solution

- Grape juice demineralization
- Grape juice decolourization
- Anthocyanins recovery from grapes juices
- Tannins recovery from grapes juices
- Anthocyanins recovery from washing water of grapes peels
- Proanthocyanidins purification from grapes seeds
- Tartaric acid decationization
- Heavy metals removal from grapes juices

- Debittering of orange/lemon peels extract
- Citrus juices debittering
- Citrus juices deacidification
- Anthocyanins recovery from red oranges

- Pomegranate juice decolourization
- Ellagic acid recovery from pomegranate juice
- Anthocyanins recovery from wooden fruits/ onion/cabbages
- Deodorization of anthocyanins extract from red anions/cabbages
- Betacyanine/betaxantine recovery from red beet
- Pinitol recovery from carob juice

- Epigallocatechins separation from green tea
- Glycyrrhizic acid purification
- Betain recovery from molasses

- Milk whey demineralization
- Milk whey decolourization
- Lactose decalcification
- Lactose demineralization
- Lactose hydrolysis
- Proteins separation of milk whey

- Demineralization-decolourization of citric acid
- Demineralization-decolourization of lactic acid
- Extraction/Purification amino acids (Glutamic, Lysine, Tryptophan)

- Decalcification of saccharose from beet
- Alkalinization of saccharose from beet
- Demineralization of saccharose from beet
- Demineralization of hydrogenated syrups (Sorbitol, Mannitol, Maltitol, Xylitol)
- Quentin Process
- Saccharose hydrolysis
- Sugar cane decolourization
- Saccharose extraction from beet molasses - chromatography
- Saccharose extraction from cane molasses - chromatography
- Glucose/fructose separation - chromatography
- Dextrose purification - chromatography
- Maltose purification - chromatography
- Sorbitol purification - chromatography
- Mannose purification - chromatography

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Resindion