Macronet™ Adsorbents

Carbonless Corn Sweetener Refining

Macronet styrenic adsorbents offer economic, aesthetic and process advantages for replacing carbon in the production of bottlers quality syrup.

Purolite®

About Purolite

Purolite is a leading manufacturer of ion exchange, catalyst, adsorbent and specialty resins. With global headquarters in the United States, Purolite is the only company that focuses 100% of its resources on the development and production of resin technology.

Responding to our customers' needs, Purolite has the widest variety of products and the industry's largest technical sales force. Globally, we have five strategically located research and development centers and eight application laboratories. Our ISO 9001 certified manufacturing facilities in the United States of America, United Kingdom, Romania and China combined with more than 40 sales offices in 30 countries ensure complete worldwide coverage.

PREMIER PRODUCTS

The quality and consistency of our products is fundamental to our performance. Throughout all Purolite plants, production is carefully controlled to ensure that our products meet the most stringent criteria, regardless of where they are produced.

RELIABLE SERVICE

We are technical experts and problem solvers. Reliable and well trained, we understand the urgency required to keep businesses operating smoothly. Purolite employs the largest technical sales team in the industry.

INNOVATIVE SOLUTIONS

Our continued investment in research and development means we are always perfecting and discovering innovative uses for ion exchange resins and adsorbents. We strive to make the impossible possible.

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Carbonless Refining of Starch Hydrolyzates With Macronet Adsorbents

Starch hydrolyzate plants around the world are utilizing high surface area synthetic adsorbents to replace granular and powdered activated carbon for removal of color, taste, odor, HMF and other impurities from sweetener solutions. The Purolite Macronet line of chemically regenerated styrenic adsorbents offers economic, aesthetic and ease of process advantages for replacing carbon in the production of bottlers quality syrup.

Organic impurities are attracted and held to adsorbents by surface energies such as Van der Waals forces. Since adsorption is a surface phenomenon, the Macronet adsorbents are manufactured with large surface area in the range of 800–1000 square meters/gram. But molecules are three dimensional and not flat, so it is important for the surface area to conform to the molecular size of the impurities being adsorbed in order for the collective surface energies to be large enough to retain them. Thus, the surface area must be employed in micropores which are small enough to form an "adsorption cavity". As you can see from Figure 1, most of the surface area of Macronet adsorbents are contained in adsorption cavities of less than 20 Angstroms diameter. Macronets also contain a significant population of large transport pores which facilitate rapid diffusion from the bulk fluid into the microporous region where adsorption occurs.

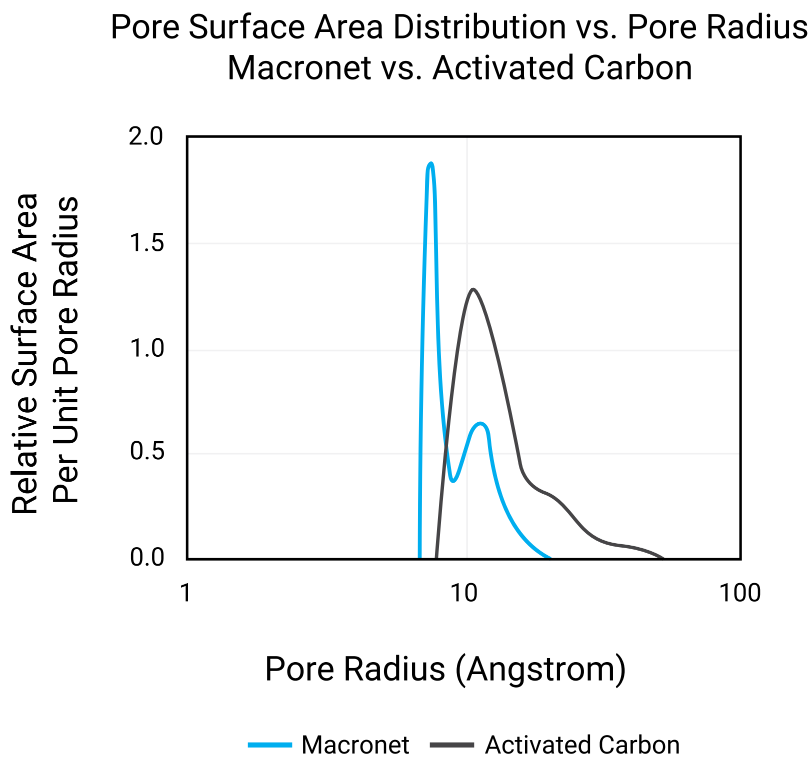
The hydrophobic styrene/divinylbenzene matrix of the Macronet will readily adsorb nonpolar hydrophobic impurities. Since many of the impurities are polar or even ionizable molecules, the presence of hydrophilic ion exchange functional groups on the matrix improves the range of impurities which can be removed by attracting more hydrophilic compounds. The hydrophilic functional groups also improve the ease of regeneration of the adsorbent.

During the manufacture of Macronet adsorbents, they are initially crosslinked similar to standard ion exchange resins and are then crosslinked a second time in a swollen state, making the swollen state the low energy state and producing resins which undergo a minimum amount of swelling when changing ionic forms or electrolyte environment. The high degree of crosslinking also provides a very high bead crush strength, osmotic shock stability and oxidation resistance. Also, most Macronets are stable at temperatures up to 120 °C. Since Macronets are designed to regenerate efficiently, have a low shrink/swell, high thermal stability and high crush strength their anticipated life expectancy is very good, usually around 4–5 years.

Purolite's Macronet adsorbents for starch hydrolyzate refining comply with U.S. FDA Regulations CFR Section 173.25 for food use and have Kosher certification.

FIGURE 1

Macronet Pore Size/ Surface Area



This figure shows the similarity of Macronet with activated carbon in their respective pore surface area characteristics.

TABLE 1 Comparison of Carbon with Macronet

	Granular Carbon	Powdered Carbon	Macronet
Energy	High Temperature Furnace Regeneration	Not Regenerated	Low Temperature Chemical Regeneration
Building Space	Furnace, Carbon Columns Check Filters, Dewatering and Sweetwater Handling Equipment	Candle or Leaf Filters	Ion Exchange Columns
Capital Cost	High	Low	Medium
Operating Cost	Medium	High	Low
Aesthetics	Carbon Dust	Carbon Dust	No Dust
Discharge	Vapor, Solid	Solid	Liquid
Inventory	Carbon Bags	Carbon Bags	None

Sweetener Industry Applications

- Maltodextrin decolorization, taste and odor removal
- Maltose decolorization, HMF removal
- Glucose syrup decolorization, taste and odor removal
- Dextrose decolorization, taste and odor removal
- 42 HFCS decolorization, taste and odor removal
- 55 HFCS decolorization, taste and odor removal
- Organic acid fermentation broth decolorization

Macronet Operating Options

Color Adsorber for Non-Demineralized Syrups

Macronet MN102 or MN152 replaces conventional powdered carbon treatment of glucose syrups.

Expensive and dirty powdered carbon and carbon filters are replaced with a simple chemically regenerated unit operation which produces no solid discharge to handle.

Taste and Odor Polishing

The primary and secondary ion exchange pairs remove the vast majority of impurities, leaving the Macronet MN502 available to remove the difficult taste and odor impurities and polish the color even further.

Color, Taste and Odor Polishing

A layered bed of MN102 or MN152 over MN502 offers improved color and heat color removal in addition to taste and odor polishing.

Color, Taste and Odor Polishing with Enhanced pH and Conductivity

The layered bed of MN102 or MN152 over MN502 is air mixed prior to service to offer mixed bed quality pH and conductivity

Color, Taste and Odor Polishing with Enhanced pH Stability

A layered bed of MN102 or MN152 over a weak acid cation resin is air mixed prior to service to offer better pH stability

TABLE 2 Service and Regeneration Sequence Macronet MN102, MN152 or MN502

Step	Solution	Temp (°C)	Flow (BV/hr)	Volume (BV)	Time (min)	Comments
Service	Syrup	40–60	2–5	30–200	Variable	Downflow
Sweeten Off	Demineralized water or condensate	40–60	2–5	2	Variable	Downflow
Backwash[1]	Demineralized water or condensate	30–60	2.5–3.7 gpm/ft² of vessel area	1.5–2.0	30	Upflow 50% Expansion
NaOH In[2]	1N NaOH	40–60	1	1.5	90	Downflow
Slow Rinse	Demineralized water or condensate	40–60	2	2	60	Downflow
HCl In[3,4]	0.1N HCl	40–60	2	3	90	Upflow
Slow Rinse	Demineralized water or condensate	40–60	2	2	60	Upflow
Fast Rinse[5]	Demineralized water or condensate	40–60	4	4	60	Downflow
Sweeten On	Syrup	40–60	2–5	1	Variable	Downflow

[1]For MN502, the backwash flow rate should be increased to 6.0 gpm/sq ft
[2]For HMF removal the temperature should be increased to 110 °C and the first 1 BV is allowed to soak for 2 hours.
[3]For MN502 regeneration, the HCl concentration should be increased to 0.3 N.
[4]For a 1/3 MN102 or MN152 and 2/3 MN502 layered bed, the HCl concentration should be increased to 0.2 N.
[5]For mixed bed operation, an air mix follows the fast rinse

Laboratory Testing for Sweetener Decolorization/Polishing

Discussion of the Treatment Process

It is anticipated that the feed syrup will have already been treated by a demineralization/decolorization process comprised of a strong acid cation (SAC) resin followed by a weak base anion (WBA) resin step. Any color bodies remaining in the syrup will be adsorbed by the Macronet polymer matrix and these can be removed by chemical treatment in a regeneration step.

The following test protocol is based on Purolite's experience with sweetener syrup decolorization/polishing. It is suitable for demonstrating the feasibility of the process and for testing the effectiveness of the regeneration procedures. The information generated will be a guide to the design of a full scale continuous plant. As this process is well established industrially it is not anticipated that intermediate scale testing will be required.

The customer should have the following information before running the tests:

- A full analysis of the syrup to be treated and its consistency over the anticipated test runs particularly with respect to color and any other impurity to be modified e.g. odor, taste.
- The specification for the color and other components in the treated juice.
- Analytical methods for the color and other properties to be modified.

Delivered Resin

The tests should be carried out using the Purolite Macronet resin supplied by Purolite for the purpose of these tests.

Pretreatment

Prior to running a laboratory test, the Macronet adsorbent sample needs to be conditioned in order to insure full swelling and hydration of the polymer and removal of microscopic air.

Unless otherwise advised, the polymer must be soaked (this is best achieved in a beaker) in a (50:50) solution of water and acetone, or a (50:50) solution of water and ethanol, for 12–24 hours.

Ensure there is no floating adsorbent, an indication of air adhesion to the adsorbent surface. Agitate to assist settling of the adsorbent in the beaker.

Apparatus

The test program will require one column as defined below. As the tests are to be carried out at elevated temperature the column should be water jacketed to maintain the required operating temperature.

The resin should be loaded into the water jacketed glass column fitted with a means of retaining the resin at the base of the column. This may be either:

- A sintered glass disc
- A nylon cloth fitted into a Quickfit or other flanged fitting

The sintered disc method is preferred.

The bottom of the columns should be fitted with a tap for on/off and flow adjustment and for connecting a line for flow entry and exit. The exit line from the column can be raised to the height just above that of the resin bed to prevent the liquid level in the column from falling below the resin bed top. It can also be fitted with a siphon breaker for downflow operation.

The top of each column should be fitted with an attachment for fluid introduction and exit and should have sufficient space between top of the resin bed and the column inlet for at least 75% bed expansion with an additional 25% freeboard.

The column should have a minimum diameter of 1 inch (2.5 cm). Recommended minimum resin volumes for columns of different diameters are as follows:

- 200 ml for a column of 2.5 cm diameter, resulting bed height approximately 40 cm.
- 1200 ml for a column of 5.0 cm diameter, resulting bed height approximately 60 cm.

A column of approximately 2.5 cm diameter is preferred for resin comparison purposes as the volumes of resin and solutions are more manageable at this scale.

Column Filling

The column is most easily filled by pouring the measured volume of resin in via a funnel as a slurry in demineralized water. As the column fills with water it can be drained to a level just above resin bed height via the bottom tap. Air bubbles in the resin bed are avoided with this method.

Resin Backwashing

After loading the columns, the resin should be backwashed using an upflow of demineralized water to classify and remove any extraneous material. The flow should be introduced slowly to prevent the resin from rising as a plug in the column. Backwashing is carried out at ambient temperature. The bed should be expanded by approximately 75% and continue for 15 minutes. After stopping the backwash flow, the resin should be allowed to settle and the water drained to just above the top of the resin bed.

Syrup Preparation

For treatment in the ion exchange columns the feed syrup should be that produced by the SAC ⟶ WBA demineralization process at the same temperature as that exiting the WBA unit.

A sufficient quantity of the feed syrup for each run should be available. This may be as a batch of syrup carefully stored at the required temperature.

Before beginning the tests, the syrup should be analyzed for the major components of interest and the treated syrup specification to meet end use requirements should have been identified. Methods of analysis should also have been identified to measure the required components and arrangements made for the analysis.

It is preferable to use a single source of the same sweetener syrup and to operate without interrupting the flow during the length of the syrup feed run.

Service Operation

The feed syrup should be preheated and the resin bed temperature controlled by passing water at the same temperature through the water jacket of the column. The resin beds can be preheated by passing water at the specified temperature through the bed and the bed temperature should be maintained at the same temperature throughout the period of the feed flow.

As noted in item 4 above, the column should be drained to just above the top of resin bed. The feed syrup should be carefully introduced downflow at a rate of 3 to 5 bed volumes (BV) per hour, i.e. for 4 BV/hour and 200 ml of resin the feed flow will be 800 ml/hour. If the resin at the top of the resin bed begins to float it can be retained in position by a plug of polyurethane sponge or glass wool which should be removed at the end of the feed flow cycle. The feed flow rate should be carefully controlled and recorded throughout the syrup flow cycle. A reservoir of feed at the top of the bed should be maintained at all times so that the resin bed never operates dry.

Samples of treated syrup should be taken periodically from the exit of the Macronet column and analyzed for color and any other desired components to obtain a record of the resin performance in the form of a breakthrough profile. A sampling regime, i.e. the frequency of sampling required, may be less frequent at the start of the feed flow period than towards the anticipated end of the cycle.

It is anticipated that 65 to 200 BV of syrup can be treated each cycle.

Flow should be stopped as soon as possible when the color or other component end point is reached. At the end of the cycle the syrup should be drained to just above the resin bed top.

Summarizing the data which should be measured and recorded:

A. Feed syrup analysis for major components of interest.

B. Temperature of the resin bed throughout the feed flow cycle.

C. Flow rate through the column recorded at regular intervals of time after flow is started (at time zero).

D. Treated syrup analysis for major components of interest at the exit of the column at regular recorded intervals of time. These intervals will be widely spaced until breakthrough is anticipated and will then decrease in order to obtain a breakthrough concentration profile for color, etc.

E. Resin color and any gradation of color down the bed noted.

Syrup Displacement (Sweetening Off)

Syrup displacement from the bed is carried out on a full production scale either by air or softened water, preferably at the same temperature as the feed syrup, and the displaced syrup is retained. In the laboratory tests, displacement by 1.5 to 2 BV of softened water downflow at a flow rate of approximately 2 to 4 BV/hour is recommended.

Resin Backwashing

Resin backwashing is carried out by an upflow of demineralized water, preferably at the same temperature as the feed syrup. The flow should be slowly introduced to prevent the resin from rising in the column as a plug. When the resin is fully fluidized the flow should be adjusted to expand the bed by 75% and be continued for 15 minutes. After stopping the backwash flow the bed should be allowed to settle, drained to just above the top of the resin bed.

Resin Regeneration and Rinsing

Refer to the regeneration dosages, concentrations and flow rates listed in the regeneration sequence.

The regenerant flow rates should be carefully controlled to achieve even flow through the bed. A reservoir of regenerant should be maintained above the resin bed top.

Number of Cycles

The above procedure should be repeated using the same Macronet bed for a sufficient number of cycles to achieve equilibrium and to observe the extent of any fouling of the resins. If fouling is observed, or if cycle times are observed to decrease from cycle to cycle, then Purolite will advise what action should be taken. This will normally involve modifying the regeneration procedure.

Application of Test Data

The results from the above tests will demonstrate the Macronet polishing process and will provide a guide for the design of the next scale of operation for syrup decolorization polishing.

All test results should be forwarded to Purolite for technical comment and advice.

Macronet MN102 Polymeric Adsorbent

(Replaces carbon in sweetener decolorization, taste and odor removal)

Technical Data

Product Description

Macronets are highly and rigidly crosslinked adsorbents characterized by very high internal surface area approximating that of activated carbon. Purolite Macronet MN102 is a macroporous styrene-divinylbenzene adsorbent containing weak base anion functionality. A general advantage of this type of product is the ease of regeneration.

MN102 is chemically regenerated in place in simple ion exchange equipment rather than transferred externally for thermal regeneration like carbon. The low shrink/swell minimizes pressure drop in the columns and maintains the physical integrity of the adsorbent over hundreds of cycles.

The large amount of surface area and pore volume, coupled with the proper pore diameter makes Purolite MN102 an effective replacement for carbon for the efficient removal of color, taste and odor bodies and other impurities found in sweetener solutions.

Typical Physical and Chemical Characteristics

Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical beads
Functional Group	Tertiary amine
Shipping Weight (Approx.)	610–640 g/L (38.1–40.0 lb/ft^3)
Particle Size Range	300–1200 µm
Moisture Retention	50–60% (FB form)
Reversible Swelling, FB → Cl^- (Max.)	5%
Specific Gravity	1.07
Typical Surface Area by Nitrogen Adsorption	800 m^2/g
Temperature Limit	60 °C (140.0 °F) (FB form)
Typical Pore Diameter by Nitrogen Adsorption (Micropores)	15 Å

Macronet MN152 Polymeric Adsorbent

(Replaces carbon in sweetener decolorization, taste and odor removal)

Technical Data

Product Description

Macronets are highly and rigidly crosslinked adsorbents characterized by very high internal surface area approximating that of activated carbon. Purolite Macronet MN152 is a macroporous styrene-divinylbenzene adsorbent containing weak base anion functionality. A general advantage of this type of product is the ease of regeneration.

The MN152 is chemically regenerated in place in simple ion exchange equipment rather than transferred externally for thermal regeneration like carbon. The low shrink/swell minimizes pressure drop in the columns and maintains the physical integrity of the adsorbent over hundreds of cycles.

The large amount of surface area and pore volume, coupled with the proper pore diameter makes Purolite MN152 an effective replacement for carbon for the efficient removal of color, taste and odor bodies and other impurities found in sweetener solutions.

Typical Physical and Chemical Characteristics

Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical beads
Functional Group	Tertiary amine
Shipping Weight (Approx.)	685–720 g/L (42.8–45.0 lb/ft^3)
Particle Size Range	300–1200 µm
Moisture Retention	44–50% (Cl^- form)
Reversible Swelling, FB → Cl^- (Max.)	5% max
Specific Gravity	1.09
Surface Area (Min.)	750 m^2/g
Temperature Limit	60 °C (140.0 °F) (FB form)
d50, Micropores	14 Å

FIGURE 2

MN102 and MN152 Backwash Expansion

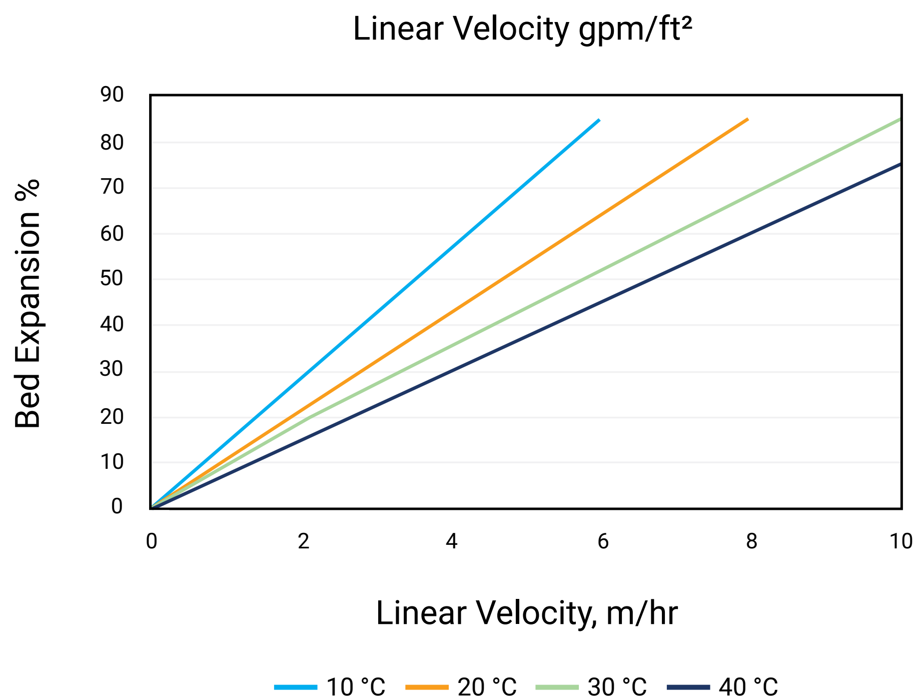
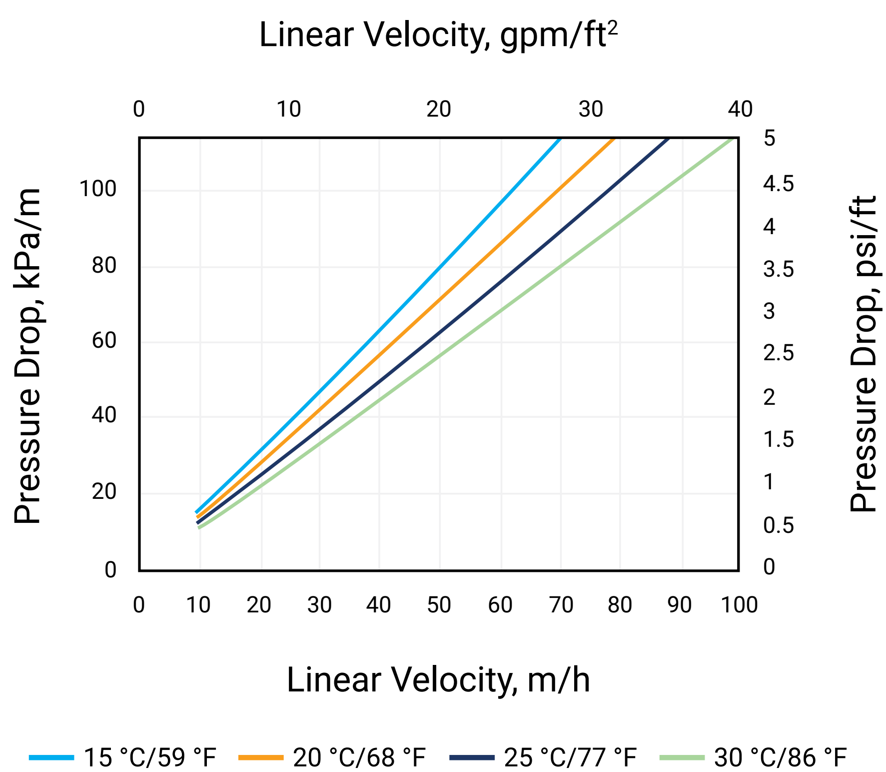


FIGURE 3

Macronet Pressure Drop



Macronet MN502 Polymeric Adsorbent

(Replaces carbon in sweetener decolorization, taste and odor removal)

Technical Data

Product Description

Macronets are highly and rigidly crosslinked adsorbents characterized by very high internal surface area approximating that of activated carbon. Purolite Macronet MN502 is a macroporous styrene-divinylbenzene adsorbent containing strong acid cation functionality. A general advantage of this type of product is the ease of regeneration.

The MN502 is chemically regenerated in place in simple ion exchange equipment rather than transferred externally for thermal regeneration like carbon. The low shrink/swell minimizes pressure drop in the columns and maintains the physical integrity of the adsorbent over hundreds of cycles.

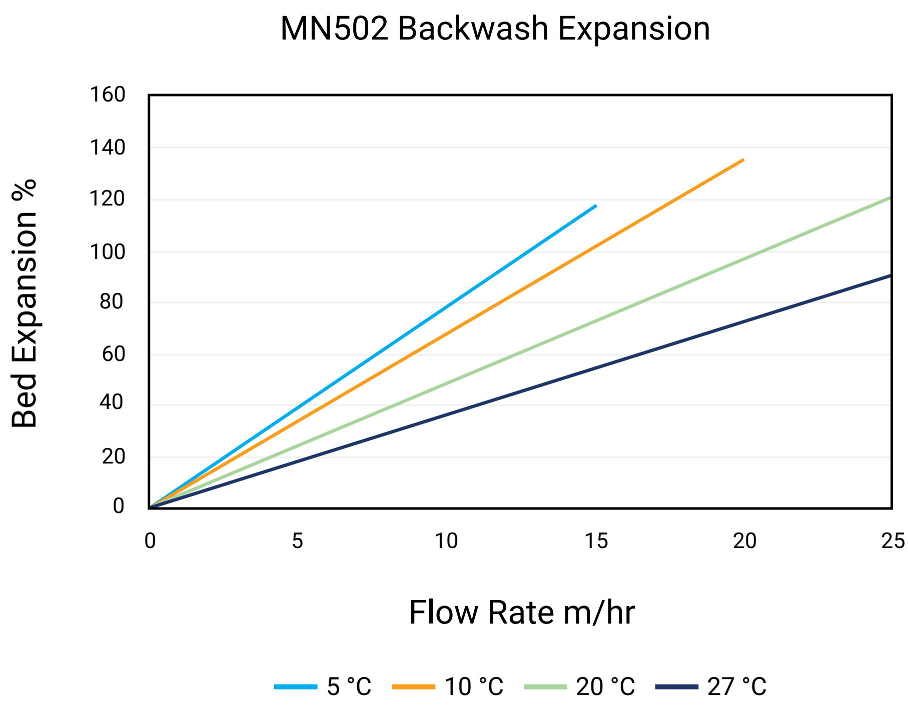
The large amount of surface area and pore volume, coupled with the proper pore diameter makes Purolite MN502 an effective replacement for carbon for the efficient removal of taste and odor bodies and other impurities found in sweetener solutions.

Typical Physical and Chemical Characteristics

Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical beads
Functional Group	Sulfonic Acid
Shipping Weight (Approx.)	770–810 g/L (48.1–50.6 lb/ft^3)
Particle Size Range	300–1200 µm
Moisture Retention	55–60% (H^+ form)
Reversible Swelling, $Na^+ \rightarrow H^+$ (Max.)	5%
Specific Gravity	1.19
Typical Surface Area by Nitrogen Adsorption	660 m^2/g
Temperature Limit	120 °C (248.0 °F) (H^+ form)
Typical Pore Diameter by Nitrogen Adsorption (Meso/Macro Transport Pores)	650 Å
Typical Pore Diameter by Nitrogen Adsorption (Micropores)	15 Å

FIGURE 4

MN502 Backwash Expansion



Notes

Notes

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Purolite, the leading manufacturer of quality ion exchange, catalyst, adsorbent and specialty high-performance resins, is the only company that focuses 100% of its resources on the development and production of resin technology.

We're ready to solve your process challenges. For further information on Purolite products and services, visit www.purolite.com or contact your nearest Technical Sales Office.

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