Polymeric Adsorbent Resins for Industrial Applications

Purolite polymeric adsorbent resins are synthetic spherical beads with defined pore structure, high surface area and selectivity for the purification and extraction of target molecules in aqueous solutions.

Purolite®

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 the needs of our customers, Purolite has built the largest technical sales force in the industry, the widest variety of products and five strategically located Research and Development groups. Our ISO 9001 certified manufacturing facilities in the U.S.A., 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.

Polymeric Adsorbent Resins for Industrial Applications

Although adsorption technologies have been around for decades, adsorption processes are not completely understood by many who can benefit from them. Some of the common practices used to purify molecules can involve toxic solvents as well as expensive distillation and precipitation processes to extract compounds. Activated carbon has been used to remove impurities through adsorption, but the high costs of pyrolysis to regenerate carbon media have made it a complicated, less desirable process. These issues have generated a need for safe, efficient and cost-effective synthetic resins that can extract target molecules more efficiently than solvents precipitations, and activated carbon while providing the additional benefit of recyclability.

Contents

Polymeric adsorbent resins exhibit specific properties and selectivity for purification and extraction of target molecules, and are each very different from one another.

Purolite products are available in a broad range of matrices and porosities, and our portfolio of adsorbent resins presents solutions for many industrial applications — such as the removal of organic compounds from aqueous streams — and are well established in industries such as food and pharmaceutical processing, flavor and fragrance extraction and environmental applications.

Purolite offers the broadest range of synthetic polymers with properties that make them highly effective, selective and unique for individual processes enabling customers to optimize their production yield. This brochure covers the most frequently utilized Purolite adsorbents under the PuroSorb^{TM} (PAD) and Macronet^{TM} (MN) brand names. Purolite can also customize adsorbent resins to meet your production goals.

How Adsorbents Work

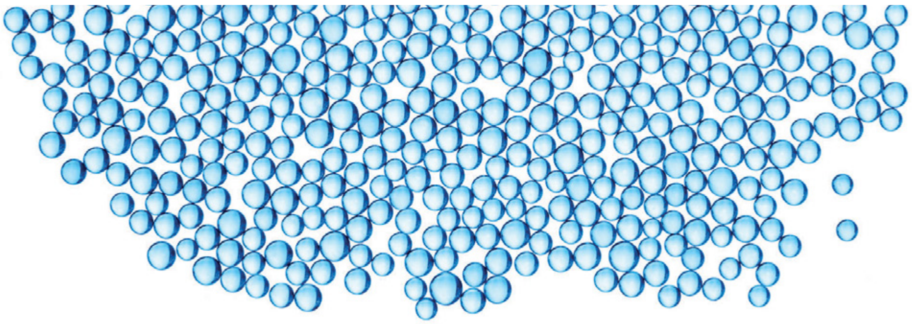
Polymeric adsorbents are spherical synthetic polymers with defined pore structure and high surface area for efficient and selective removal of organic molecules, primarily in aqueous applications.

Adsorbents interact with molecules in different ways depending on the surrounding conditions such as heat, pH, competing molecules, solvents, etc. Forces or interaction factors that influence the adsorption of molecules onto a resin matrix are summarized in Table 1.

TABLE 1 **Interaction Factors Between Resin and Molecule**

Forces Available	Strength (kJ/mol)	Distance (nm) Between Resin and Molecule	Polymeric Resin Structure Needed	Comments
van der Waals	0.4–4.0	0.3–0.6	Any interaction such as electrostatic bonding	Weakest interaction; controls molecule orientation
Hydrogen Bonds	12–30	0.3	Hydroxyl or primary amine groups	Strong interaction with polar and protic molecules
Ionic Interactions	20	0.25	Sulfonate, carboxylate and amine groups	Interaction with ionizable groups of molecules, driven by pH
Hydrophobic Interactions	< 40	Varies	Nonpolar resin surface	Strong interaction with molecules having aromatic groups or alkyl chains

For maximum molecule adsorption, the polymeric resin should have high internal surface area with high porosity as controlled pore size distribution maximizes the surface area. The surface area is inversely proportional to the pore diameter for a given pore volume. Small pores contribute most to the surface area, but the pore diameter must be large enough to enable the molecules to migrate to the adsorbing surface hidden within the pore structure of the resin, Figure 1. The pore structure not only influences the surface area of the resin but also acts as a sieving mechanism to separate/remove larger molecules, Figure 2.



Purolite products are available in a broad range of matrices and porosities, and our portfolio of adsorbent resins presents solutions for many industrial applications.

FIGURE 1

Scanning Electron Microscopy (SEM) Pictures of Different PAD Adsorbents

(a) Picture of an adsorbent bead,
(b) Surface of the bead and
(c) Macro-porosity of the
bead surface.

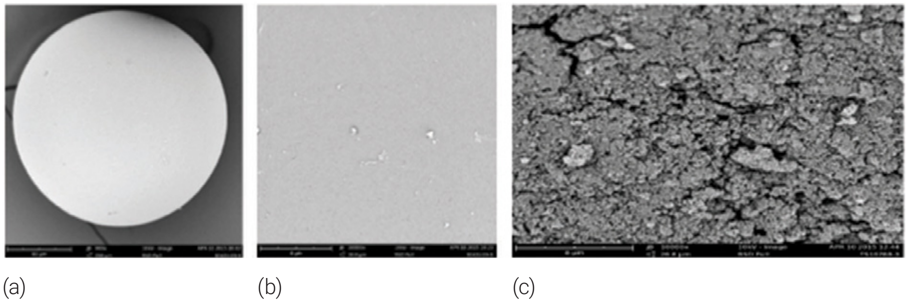
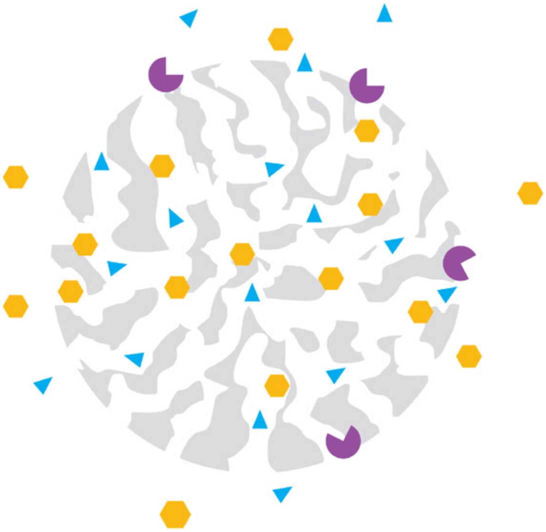


FIGURE 2

Mechanism of Adsorption Through Resin Pores

In this graphic, larger molecules (purple figures) are excluded from entry into the resin due to pore size. Smaller hydrophobic molecules are adsorbed onto the surface (orange figures), while the hydrophilic small molecules (blue figures) freely flow through the structure of the resin.



Adsorption Efficiency

There are different factors that affect adsorption efficiency and the selection of polymeric adsorbents, Table 2.

- **Solvent Characteristics —** An organic solvent may be used in case the target molecules show very low solubility in water. In non-polar organic solvents such as hexane, the interaction is hydrophobic and charges are suppressed with no ionic interaction. In polar and protic solvents such as alcohols and water — organic molecules can be ionized — which causes an attraction with ion exchange groups or hydrophilic groups on the adsorbent.
- **Chemical Interactions —** Organic molecules can interact with the backbone of the adsorbent via hydrophobic interaction (i.e. van der Waals) or hydrophilic interaction (hydrogen bonding, interaction with carbonyl groups, etc.).
- **Molecule Size —** The size of the molecule and its solvation cage (the amount of water molecules surrounding it) should be considered in relation to the porosity of the adsorbent. Molecules that are too large do not penetrate pores and will bypass the resin bed.
- **Capacity —** The greater the surface area of the adsorbent, the greater the capacity. One gram of resin has high surface area, from 400 m^2/gram to 1,200 m^2/gram. The greater the surface area, the more molecules can be adsorbed. However, higher capacity or surface area can make the elution process longer since the resin will become more hydrophobic.

TABLE 2 Molecule And Resin Characteristics When Choosing a Polymeric Adsorbent

Important Considerations	Molecule Characteristics		Resin Characteristics
Solvent Characteristics: Polar or Non-Polar	Solubility in solvent		Ionic or non-ionic
Possible Chemical Interactions	Molecule structure: Hydrophobic Ionic Carbonyl, etc.	 ↔ ↔ ↔	Surface chemistry: Hydrophobic surface Ionic functionality Hydrogen bonding (primary amine/thiol/ hydroxyl chemistry)
Size of Molecule	Molecular weight		Pore size and distribution
Capacity and Ease of Elution	Concentration and competing molecules		Surface area and particle size

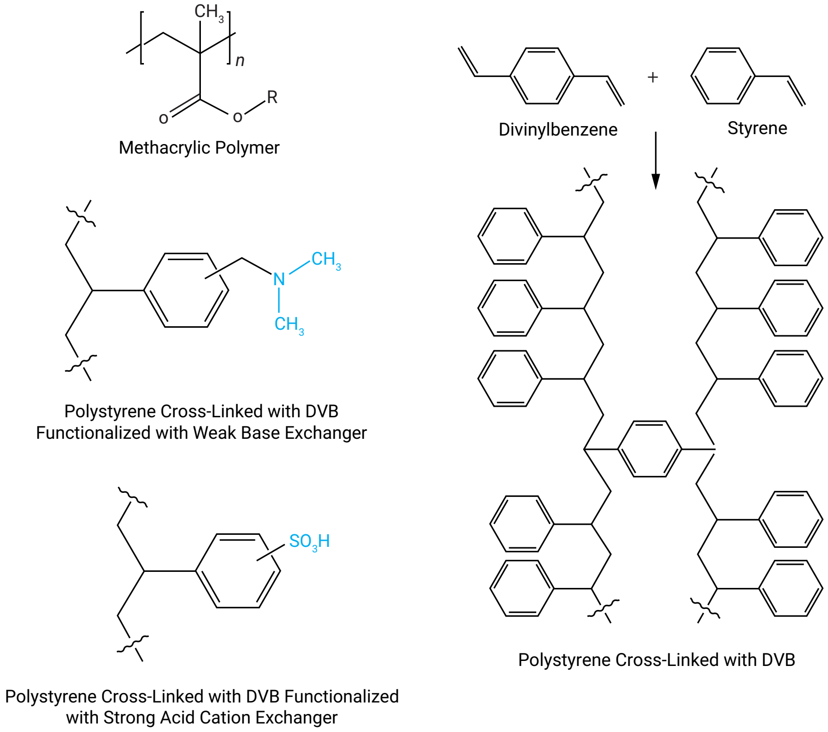
Polymer Matrix

Hydrophobicity of synthetic adsorbents is governed by the chemical structure of the resin and is the most important characteristic when selecting a suitable adsorbent for a target compound, Figure 3. There are different types of non-functionalized (no surface modification or ion-exchange ability) polymer matrices for synthetic adsorbents: aromatic polystyrenic or polydivinylbenzene, and aliphatic methacrylate, Table 3. Polymeric adsorbents can be slightly modified with a tertiary amine weak base anion exchange functionality or strong acid cation exchange functionality that add ion exchange properties to the resins, also shown in Table 3 (i.e. functionalized aromatic).

Polymer Structures

FIGURE 3

Polymer Structures of PuroSorb and Macronet Polymers



Methacrylic Polymer

Divinylbenzene

Styrene

Polystyrene Cross-Linked with DVB Functionalized with Weak Base Exchanger

Polystyrene Cross-Linked with DVB Functionalized with Strong Acid Cation Exchanger

Polystyrene Cross-Linked with DVB

TABLE 3 Features of PuroSorb and Macronet Adsorbents Based on Chemical Structure

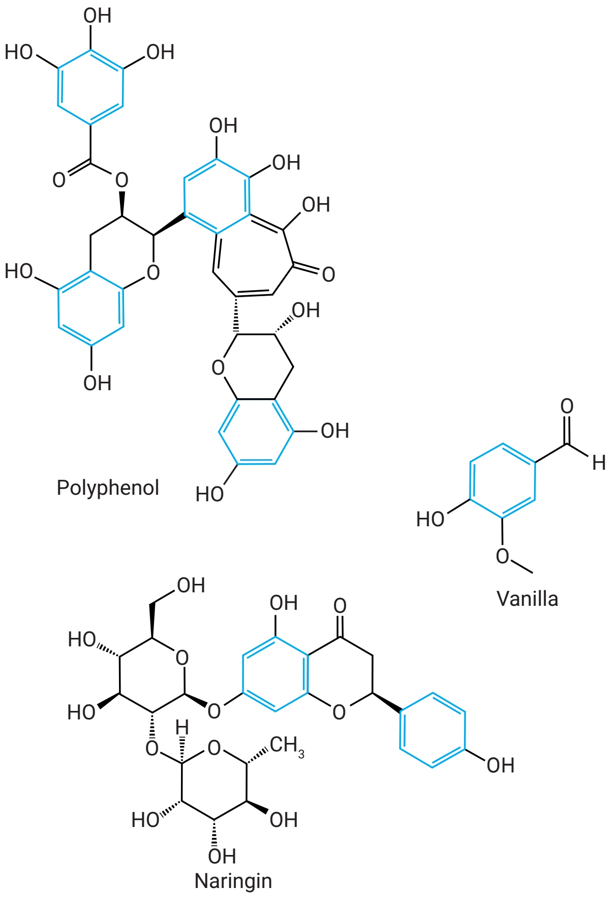
Polymer Matrix	Features	Physical Properties	Corresponding PAD and MN Resins
Aromatic: Polydivinylbenzene	Divinylbenzene base. Widely used in various industries such as food and pharmaceutical applications. Hydrophobic strength and capacity increase with surface area.	Moderate hydrophobicity Specific gravity = 1.01 to 1.03	PuroSorb PAD400 PuroSorb PAD500 PuroSorb PAD600 PuroSorb PAD900 PuroSorb PAD1200
Aliphatic: Methacrylate	Methacrylic adsorbents are based on an ester copolymer, and are more hydrophilic than polydivinylbenzene. They act as hydrophobic adsorbents for very hydrophobic compounds that need to be easily eluted from the resin (i.e. polyphenols and fatty oils).	Low hydrophobicity Specific gravity = 1.09 to 1.11	PuroSorb PAD610 PuroSorb PAD950
Aromatic: Polystyrene Cross-Linked with Divinylbenzene	Premium grade based on cross-linked polystyrenic/polydivinylbenzene matrix. Widely used in various industries such as food and pharmaceutical applications. Hydrophobic strength and capacity increase with surface area.	Moderate hydrophobicity Specific gravity = 1.01 to 1.03	Macronet MN200 Macronet MN202 Macronet MN270
Functionalized Aromatic: Ion Exchange	Highly porous polystyrenic/polydivinylbenzene matrix with a low number of functional groups as sulfonic groups (strong acid cation) or dimethylamine (weak base anion) for easy regeneration with acids or bases.	Low hydrophobicity Specific gravity = 1.05 (weakly basic) to 1.20 (strongly acidic)	Macronet MN100 Macronet MN102 Macronet MN502

Polystyrenic and Polydivinylbenzene Adsorbents

Aromatic adsorbents, such as PuroSorb and Macronet resins, have strong affinity for hydrophobic molecules such as polyphenols, vanilla (natural flavor) and naringin (citrus flavanone) that have high electronic density (i.e. unsaturated ring such as benzene). The resin attracts the aromatic groups of the molecules (shown in blue), Figure 4.

FIGURE 4

Aromatic Polystyrenic and Polydivinylbenzene Adsorbents Attract Hydrophobic Molecules with Aromatic Rings



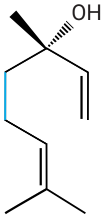
Methacrylic Adsorbents

Aliphatic methacrylic adsorbents exhibit lower hydrophobic behavior and have good affinity for molecules with aliphatic or semi-aliphatic chains and rings (shown in blue), Figure 5. Examples are compounds such as linalool (terpene alcohol fragrance with a pine scent), vitamin D3 (health supplement), PFOA (synthetic carboxylic acid used as a surfactant) or limonin (bitter compound present in citrus juices).

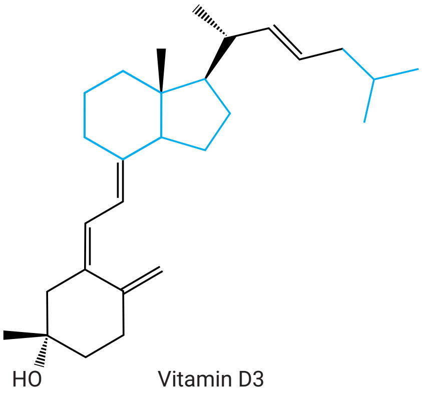
In non-polar conditions, methacrylic adsorbents will develop hydrogen bonding from the interaction of the carbonyl group from the polyester resin matrix with hydrogens associated with amines or hydroxyls on the target molecules. The hydrogen bond will reinforce the adsorption capacity of the methacrylic adsorbent towards this type of molecule.

FIGURE 5

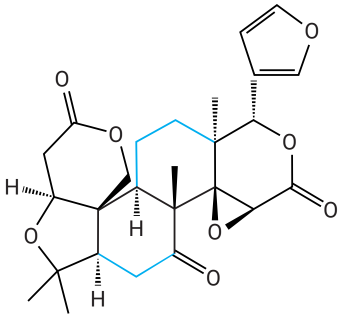
Aliphatic Methacrylic Adsorbents Have Affinity for Aliphatic Structures



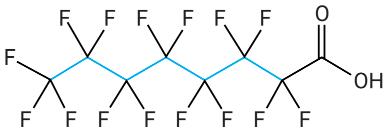
Linalool



Vitamin D3



Limonin



Perfluorooctanoic Acid (PFOA)

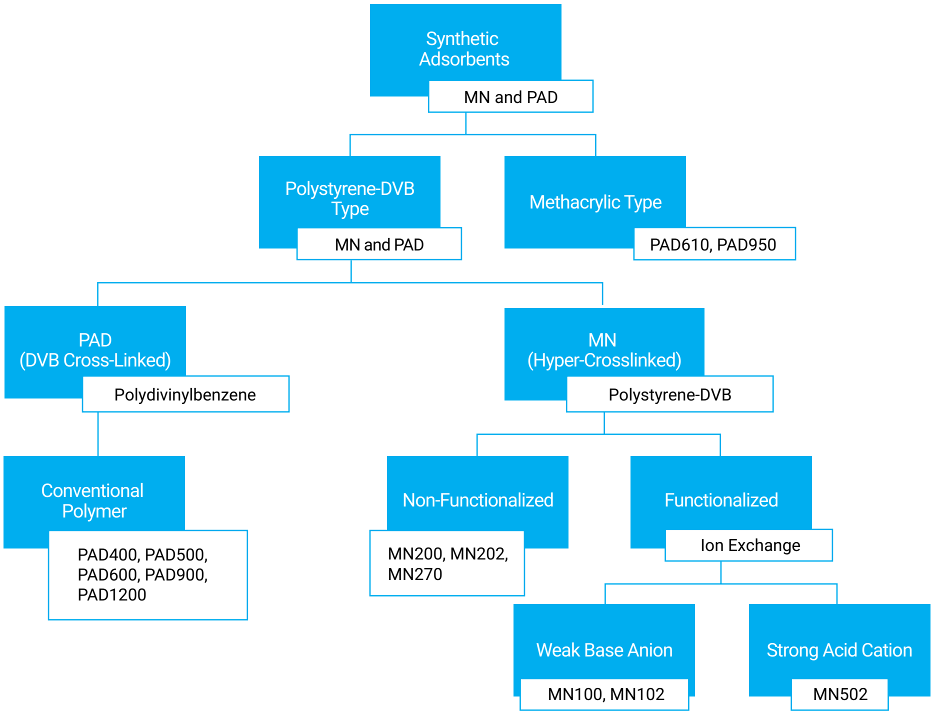
Characteristics of Synthetic Adsorbents

Purolite offers two distinct brands of polymeric adsorbents: PuroSorb and Macronet. These synthetic adsorbents are chemically stable, insoluble, spherical and highly cross-linked polymers. PuroSorb and Macronet adsorbents are stable in acidic or alkaline solutions and in most organic solvents. Additionally, they can be regenerated under mild conditions for prolonged life. PuroSorb and Macronet resins are offered in a variety of base matrices, porosities (or pore volumes), surface areas and pore sizes. They have large measurable surface area and can adsorb various organic and inorganic compounds. These synthetic adsorbents can be classified by their physical characteristics such as chemical structure and physical properties, Figure 6. Three important physical characteristics will be discussed: porosity, which affects capacity; surface chemistry, which affects resin recyclability; and particle size, which affects loading.

PAD and MN Selection Guide

FIGURE 6

Backbone Chemistries of PuroSorb and Macronet Synthetic Adsorbents



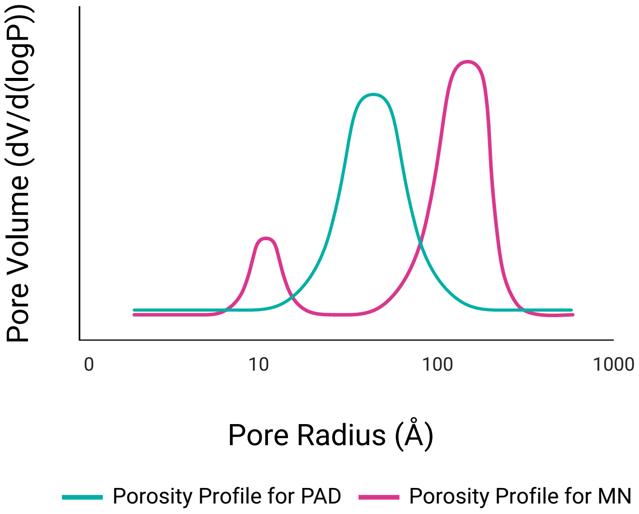
Porosity

PuroSorb resins are produced using classic polymerization, where monomers are mixed in a solvent with a porogen agent to enable high pore volume with consistent pore size distribution. PuroSorb resins show a single porosity profile that can be modified by changing the porogen agent — thus creating a unique pattern of porosity profiles that can find different applications in different industries.

Macronet resins are manufactured through classic polymerization plus an additional step of crosslinking that provide a unique microporosity and extremely high surface area. This unique microporosity is shown in Figure 7 where the dual porosity profile, i.e., the microporosity and macroporosity, was produced by the hyper-crosslinking. The micropores in the range of 10–30 Å are responsible for the adsorption of small molecules as gasses and small chemicals, whereas the macropores are the “transport channels” that ensure the diffusion of small to large molecules inside the resin.

FIGURE 7

Porosity Profile for PAD and MN Resins



The higher proportion of small micropores in the range of 10–30 Å within Macronet adsorbents leads to:

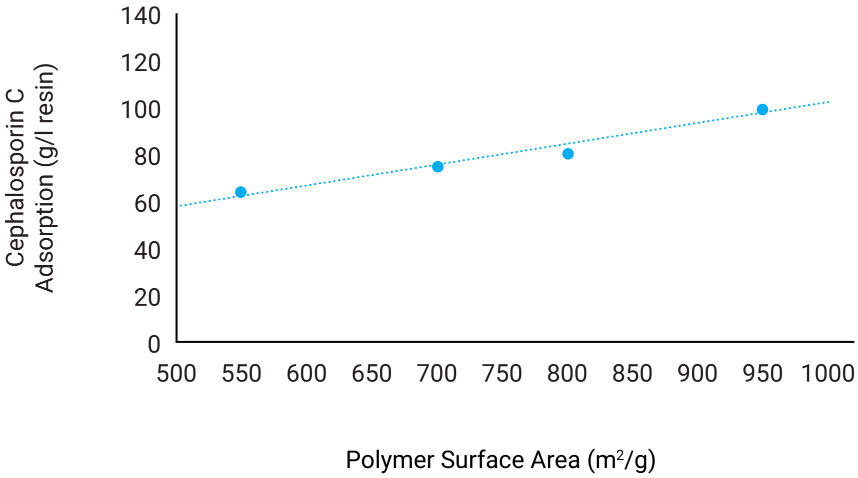
- Very high internal surface area, up to 1,200 m^2/g (similar to the high surface area offered by activated carbon).
- Limited swelling when changing solvents (usually no more than 30%).
- Resin strength that is multiple times higher than any other adsorbent in the industry with bead strength > 750 grams per bead. Macronet resin is easy to handle and produces very little dust during tank loading compared to activated carbon.

Table 4 shows that pore volume of PuroSorb adsorbents is higher than that for Macronet. The small pores of Macronet resins contribute little to the pore volume but greatly increase the internal surface area. This feature gives Macronet similar properties to activated carbon but with no costs due to pyrolysis in furnaces as they can be regenerated with solvents or steam stripping. Purosorb, in comparison, due to the higher pore volume, has better capacity for larger molecules as they are able to diffuse through its highly porous structure.

As mentioned, increasing the surface area can improve the capacity of the resin for the target molecule. Figure 8 demonstrates the linear relationship between surface area and capacity for a molecule that is small enough to diffuse through the pore structure. Surface areas are extrapolated from the amount of nitrogen (very small molecule) adsorbed onto the surface of the resin at very low temperatures (called B.E.T. for the method of nitrogen adsorption/desorption).

FIGURE 8

Adsorption Isotherm of a Solution of Cephalosporin C (1% w/v Solution) vs. Surface Area



PuroSorb and Macronet Adsorbents

TABLE 4 Typical Characteristics of PuroSorb and Macronet Adsorbents

Resin	Polymer Matrix	Pore Diameter (Å)[a]	Pore Volume (mL/g)[a]	Surface Area (m^2/g)[a]	Moisture Retention (%)	Remarks and Applications
PAD400	Polydivinylbenzene *(Aromatic adsorbent with medium to high hydrophobicity)*	360	1.0	700	47–55	- Decolorization - Polyphenol extraction - Large antibiotics (e.g., macrolides & peptides)
PAD500		110	1.5	800	63–69	- Anthocyanin recovery - Patulin removal - Antibiotic extraction
PAD600		90	1.3	850	56–64	- Beta lactam & other small antibiotics - Isolation and catechin extraction
PAD900		220	1.9	850	67–73	- Polyphenol extraction - Juice debittering - Flavor extraction - Pesticide removal - Curcumin purification
PAD1200		240	1.7	700	57–65	- Peptide purification (e.g., insulin, flavor extraction, hormone and statin drugs isolation) - Stevia purification
PAD610	Polymethacrylic/ divinylbenzene macroporous adsorbent *(Moderately polar hydrophilic adsorbent)*	300	1.2	490	60–66	- Protein and enzyme extraction - Peptide purification - Hormone removal - Vitamin recovery
PAD950	Polymethacrylic macroporous adsorbent *(Moderately polar hydrophilic adsorbent)*	120	0.6	450	65–71	- Juice debittering - Anthocyanin extraction - Removal of terpenes & carotenoids - Curcumin purification

Table continued on next page

Table continued from previous page

Resin	Polymer Matrix	Pore Diameter (Å)[a]	Pore Volume (mL/g)[a]	Surface Area (m^2/g)[a]	Moisture Retention (%)	Remarks and Applications
MN200	Polystyrene cross-linked with DVB *(Rigid adsorbent with various pore structures: micro, meso and macro)*	700/15*	0.4	1,100	57–61	- Adsorption of pyridine & phenols - Removal of benzene & pesticide - VOC extraction
MN202		220/15*	0.3	950	50–60	
MN270		80/15*	0.5	1,200	35–50	- Extraction of VOC & organic halides - Size exclusion
MN100	Polystyrene cross-linked with DVB functionalized with weak base exchanger *(Rigid adsorbent with various pore structures: micro, meso and macro)*	650/15*	0.4	1,200	57–61	Functionalized with 0.1 to 0.2 meq per ml of weak base functionality for easy regeneration with caustic. - Decolorization & debittering of juices, beer and sweeteners - Patulin removal
MN102		350/15*	0.4	800	50–60	
MN502	Polystyrene cross-linked with DVB functionalized with strong acid cation exchanger *(Rigid adsorbent with various pore structures: micro, meso and macro)*	650/15*	0.3	660	55–60	Sulfonated to 0.8 meq per ml giving them the dual functionality of a strong acid cation in the H^+ form. - Taste & odor removal - Pesticide removal

* Transport Pores/Micropores

[a] Pore Diameter, Pore Volume and Surface Area measured by N_2 adsorption

Elution

PuroSorb resins are only available unfunctionalized. Macronet resins are offered as non-functionalized and as functionalized (both weak free base or strong acid). Although some Macronet resins are technically functionalized, they have limited ion exchange capability (only 0.1–0.3 meq/mL) and function primarily as adsorbents. The functional groups make the resin more hydrophilic and easier to regenerate with dilute acid and/or caustic. They also aid in the removal of molecules based on the dual interaction of ion exchange and hydrophobicity.

Straight inorganic chemical (acid and caustic) regeneration procedures are more applicable to functionalized adsorbents such as Macronet MN100, MN102 and MN502. Steam stripping or solvent elution with recovery can be more efficient with non-functionalized Macronet and PuroSorb resins (methanol and other alcohols are a better fit in this case). Non-functionalized resins have great thermal stability so temperatures above 150°C (302°F) can be used to strip or sterilize the resins, but oxidation can occur at very high temperatures (200°C/392°F) and care should be taken to reduce the oxygen level to minimize the damage of the resin matrix.

Although increasing the surface area seems like it would universally beneficial for adsorbents, it can lead to higher hydrophobicity. As hydrophobicity increases, the resin will also require more eluant and regenerant to clean the larger surface area. This, in turn, can significantly impact processing time and costs. This could be balanced by choosing the most efficient eluant or regenerant to the process. See Table 5 for some examples of eluents used.

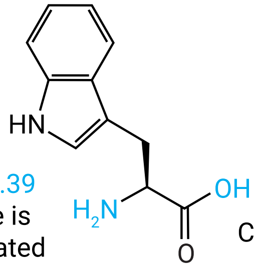
TABLE 5 Typical Elution Methods for Removing Organic Molecules from PuroSorb Adsorbents

Process	Eluent
Chlorinated Solvents, Chloroform	Low pressure steam
BTX (Benzene, Toluene, Xylene)	Alcohol or acetone
Citrus Juice Processing	4% NaOH/KOH + 0.5% H_3PO_4/H_2SO_4 + 0.2% H_2O_2
Anthocyanins from Grape Must	Alcohol or acetone
Polyphenols	Alcohol or acetone
Patulin from Apple Juice	Alcohol or acetone
Natural Colors and Flavors	Alcohol or acetone

Depending on the molecule, alcohol or acetone are usually preferred as eluents since they increase the solubility of the molecule into the regenerant/eluent and are safer to use than other organic solvents. However, if the molecule has an amine or a carboxylic acid group, like tryptophan, Figure 9, an acid can protonate the amine at pH < 9.39 (it will become a positively charged molecule) and a base can dehydrogenate the carboxylic acid at pH > 2.37 (it will become a negatively charged molecule) making the hydrophilic molecule more soluble and elutable in water.

FIGURE 9

Example of Protonation State of an Amino Acid (Tryptophan), Depending on Mobile Phase pH



pH < 9.39
Amine is Protonated

Tryptophan

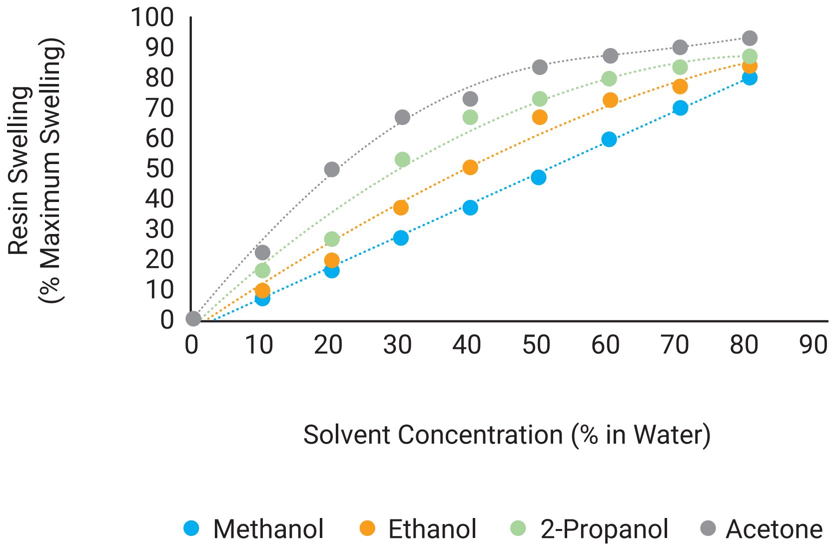
pH > 2.37
Carboxylic Group in Ionic Form

Some key parameters need to be considered in the elution/rinse step:

- The resin needs to be rinsed prior to elution to ensure that no remixing occurs between the feed and the eluent.
- Eluent strength or concentration will result in controlled elution. For example, a 25% methanol solution will elute molecules that are less hydrophobic than molecules requiring 50% methanol to elute. This can allow step-wise elution where a target molecule can be removed at high purity efficiently at a controlled eluent concentration.
- Eluent volume should be 2–3 resin bed volumes (BVs) to control the overall process cost. If more eluent is needed, a different or stronger eluent should be used.
- A longer chain alcohol is a stronger eluent than a shorter chain alcohol as seen in the below eluent strength comparison. Figure 10 illustrates the hydrating (swelling) effect that acetone can have over 2-propanol, ethanol and methanol. More swelling means that the resin is becoming less hydrophobic (taking in more water) and therefore releases its adsorbed molecules. Since methacrylic based resin is not very hydrophobic, swelling is limited when using alcohol or acetone (< 2% swelling).

FIGURE 10

Typical Swelling Behavior for Non-Functionalized Styrenic Resins in Different Organic Solvents



Strength of Eluents

> ***Steam < Caustic Wash < Methanol < Ethanol < Isopropanol or 2-Propanol (IPA) < Alcohol/Caustic Mix = Acetone***

The adsorbent resin will perform best on the first and second cycle and will reach equilibrium after 3–5 cycles. Multiple loadings and elutions may be needed as some adsorbents are more difficult to elute due to surface area and pore size distribution. Additionally, adsorbents with high surface area may exhibit a shorter life span due to fouling with hydrophobic impurities.

Particle Size

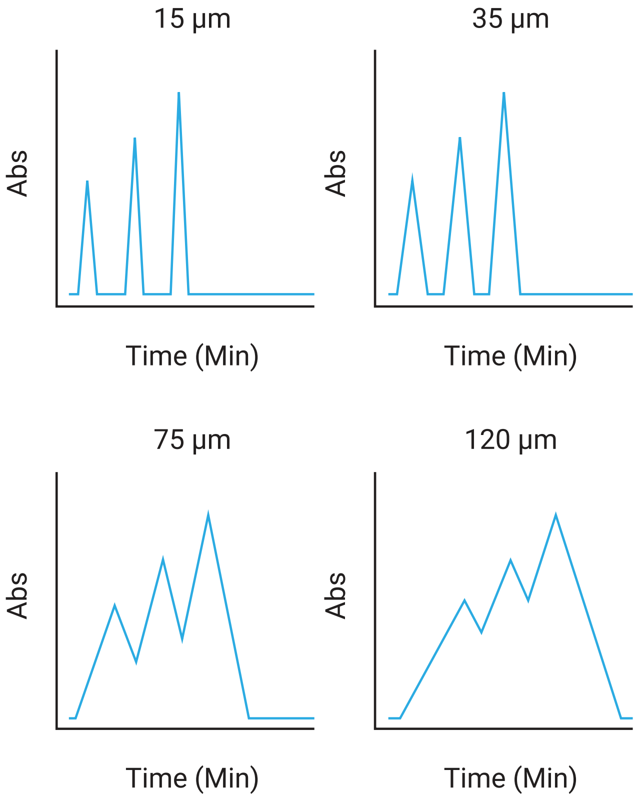
The typical particle size range for PuroSorb and Macronet adsorbents is 300–1,200 µm with a uniformity coefficient of less than 1.6, which is optimal for most industrial-scale processes. Smaller particle size adsorbents are used for fine separation/purification applications (flavors, neutraceuticals, etc.) and are marketed as reversed-phase chromatographic resins under the brand name of Chromalite® PCG or Chromalite AD (see Table 6 and Chromalite brochure for additional information). Using small-bead adsorbents enables better molecule separation and increased separation efficiency. As demonstrated in the peak resolution chromatograms in Figure 11, a decreasing particle size increases the efficiency of the separation. However, while better results are expected from smaller resin, it will significantly increase the cost of the resin and the overall system. There are instances when smaller bead resins are the only option for a successful separation. This includes the separation of a high concentration of target molecules (> 5% w/v concentration) from a similar high concentration of impurities. High concentration can deplete the resin capacity quickly; therefore, smaller resin allows the fractionation of target molecules.

TABLE 6 Characteristics of Chromalite Adsorbent Resins

Chromalite	Matrix	Functional Group	Porosity, Å	Surface Area, m^2/g	Particle Size Available
PCG600	Polydivinylbenzene	None	75–50	> 600	F (20–50 micron) M (50–100 micron) C (100–200 micron)
PCG900	Polydivinylbenzene	None	150–300	> 600	
PCG1200	Polydivinylbenzene	None	300–500	> 600	

FIGURE 11

Particle Size Effect on the Separation of Three Hydrophobic Molecules



Typical Applications for Adsorbent Resins

Citrus Juice Debittering

Bitterness in citrus juices is mainly caused by the presence of limonoids (tri-terpenes) and flavanone glycosides (flavonoids), such as limonin in orange juice and naringin in grapefruit juice (for chemical structures see Figure 5 and Figure 6). These molecules are undesirable and must be removed and disposed of in the juice production process. As the human bitterness threshold for limonin is 6 ppm in orange juice at pH 3.8, several techniques have been used to reduce the content of limonoids in citrus juice. These include:

- Adsorption using resins or activated carbon
- Addition of bitterness suppressing agents (e.g., sugars, cyclodextrins)
- Post-harvest treatment of fruits with ethylene prior to processing
- Biodegradation by enzymes or cells

Some removal methods have drawbacks since flavor and other components subsequently get modified, decreasing the quality of final citrus juice.

Adsorption has gained wide acceptance for large-scale separation due to the low-energy nature of adsorptive processes when compared to other processes — such as distillation and solvent extraction — as these require a substantial amount of energy.

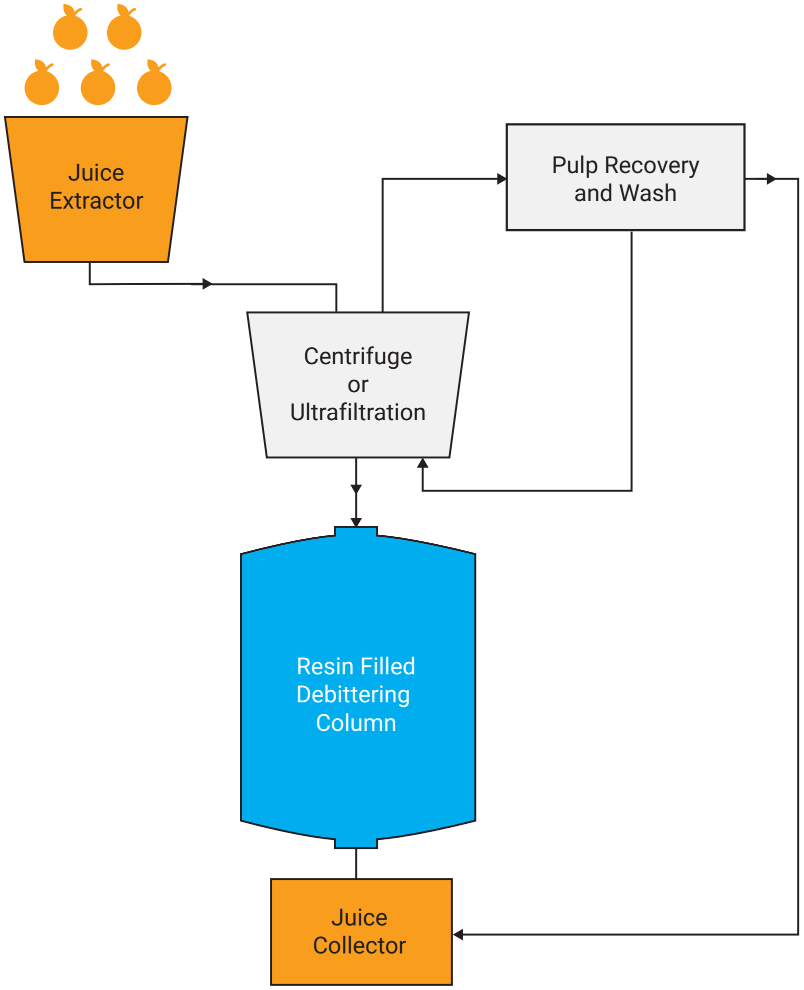
When a debittering process is operated with a polymethacrylic resin such as PuroSorb PAD950 or a polydivinylbenzenic resin such as PAD900, 90–95% of soluble limonin is removed from the portion of juice passing through the resin (Table 7). Typical limonin content of the feed juice may be 5–25 ppm (corrected to 11.5º Brix through concentration). For optimum limonin reduction, the juice must be heated before debittering to ensure maximum limonin development from the non-bitter limonoate. The juice is usually subjected to ultrafiltration in an industrial plant with hollow fibers in order to reduce the content of pectin and colloids as well as remove any residual pulp, Figure 12. This helps to prevent problems arising from a physical plugging of the upper part of the adsorbent resin bed. Debittering resin is typically regenerated with caustic (NaOH) rinsed with water treated by reverse osmosis (RO water) followed by a citric or phosphoric acid rinse to remove residual caustic.

TABLE 7 Operational Conditions for Orange Juice Debittering Using PuroSorb Resin

Feed to be Processed	• Orange juice, freshly extracted and treated • Not more than 0.01% oil by volume • Less than 1% pulp by centrifugation or ultrafiltration	
Service Flow Rate	3–5 BV/h	–
Bed Depth	1.2–1.5 m	–
Regeneration		
1 — Backwash	15–30 minutes	–
2 — Sweetening Off	4 BV/h	RO water with previous gas displacement (N_2) for minimum dilution
3 — NaOH or KOH Injection	2–4% w/w	2 BV @ 2 BV/h, 40–60°C
4 — Displacement with Water	2 BV/h	1–2 BV, 60–90°C RO water
5 — Water Rinse	3–5 BV	15 min RO water with optional 0.2% H_2O_2
Acid Rinse		
1 — Citric Acid (Optional)	0.3–0.5% w/w	2BV @ 2 BV/h
2 — H_2SO_4 or H_3PO_4	0.2–1% w/w	2 BV mainly used to neutralize caustic @ 2 BV/h
3 — Final Rinse	4 BV/h	–

FIGURE 12

Basic Flow Scheme for Juice Debittering



Polyphenol Removal

Polyphenols are target molecules that are extracted and concentrated for their antioxidant properties. Found primarily in blueberries, cranberries and pomegranates, these molecules are also found in grape seeds and skins, pine bark, olive pulp, etc. and are widely used for nutraceutical purposes. Adsorption with elution is an effective way to isolate these compounds without the need for additional processing.

Two adsorbent resins, PuroSorb PAD900 and PAD950, are particularly effective for adsorption of polyphenolic compounds, such as anthocyanins and flavonoids, but they differ in the nature of their polymeric structure. Since polydivinylbenzenic resins are more hydrophobic than polymethacrylic resins, a longer elution process can be expected. This is why the regeneration procedure is slightly different between both resins, Table 8.

TABLE 8 Operational Conditions for PAD900 and PAD950 for Anthocyanin and Flavonoid Extraction

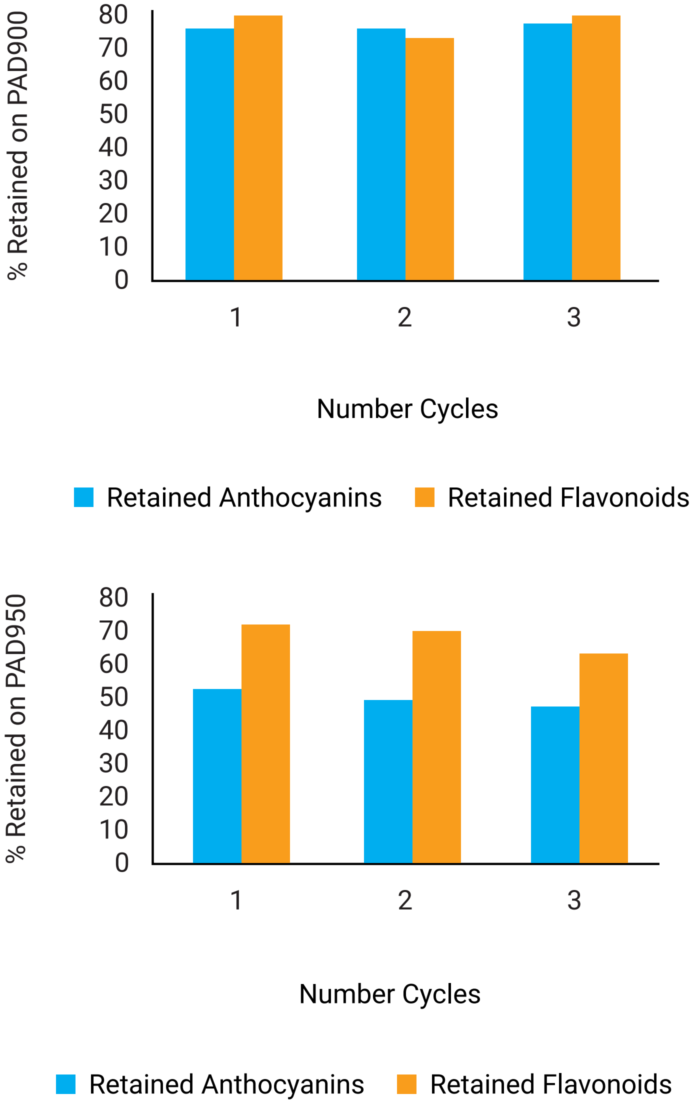
Preparation	Conditioned (using 50% ethanol solution)	
Feed	Filtered juice at 3–5 BV/h	
Resin	PAD900 (Polydivinylbenzene)	PAD950 (Methacrylate)
Quantity of Treated Juice	19 BV	21 BV
Flow Rate	5 BV/h	5 BV/h
Rinse	3.5 BV	3.5 BV
Regeneration	50% ethanol solution	
Regenerant Quantity	2.25 BV	1.55 BV
Displacement Water Quantity	1.6 BV	0.55 BV

Both PuroSorb PAD900 and PAD950 show excellent performance for flavonoid and anthocyanin removal in the berry juice industry. The results show the different behavior of the methacrylic PAD950 versus the polydivinylbenzene PAD900, highlighting the higher affinity of acrylic resin for flavonoids than the anthocyanins, Figure 13. In general, PAD900 has better capacity for adsorption than PAD950. It is important to note, however, that higher capacity is directly related to the higher hydrophobicity of the polydivinylbenzene resin over the polymethacrylic resin. More regenerant will be needed for the polystyrenic resins and an economical decision is needed to determine whether higher capacity or higher elutability is the driving factor.

Found primarily in blueberries, cranberries and pomegranates, polyphenols are also found in grape seeds/ skins, pine bark and olive pulp.

FIGURE 13

Extraction of Polyphenols Using PAD900 (Polydivinylbenzene Based) and PAD950 (Methacrylate Based)



Patulin Removal

Patulin is a mycotoxin, produced by fungi (Penicillium expansum) growing on the fruit (mainly on fruit that has already fallen from the tree), Figure 14. Patulin is common on apples and pears, but can also be present on grapes. It is flavorless, yet must be removed from juices as it can be toxic to human health.

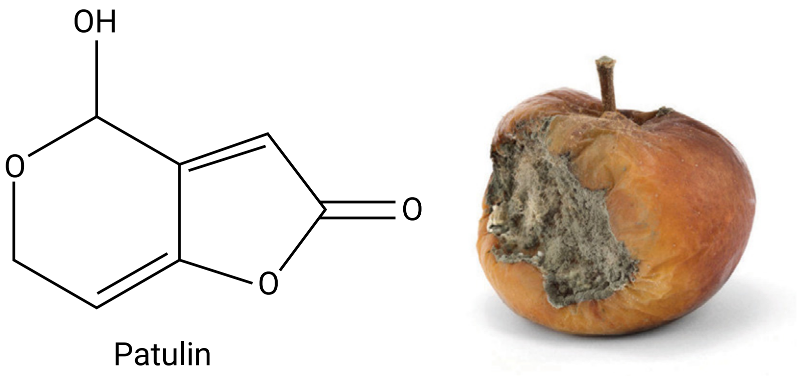
The World Health Organization and European authorities have fixed the following maximum content levels for patulin:[2]

- Apple juice and cider: 50 µg/kg (50 ppb)
- Solid apple products (dried fruit, apple sauce): 25 µg/kg (25 ppb)
- Products for infants: 10 µg/Kg (10 ppb)

When the concentration is higher than the above values, patulin can be removed by treating the juice through a bed of polymeric adsorbent like PuroSorb PAD900 following the procedure listed in Table 9. The process for removing patulin is similar to the juice debittering process since they both involve impurity removal. Additionally, together with patulin, the adsorbent will also remove other hydrophobic organics such as color.

FIGURE 14

Penicillium Expansum Growing on an Apple



Weak anion exchangers in the free base form can also work for removing patulin. This is due to the hydroxylation of lactone within the patulin to create a weak acid that can be removed easily. A weak anion exchanger such as Macronet MN100 or MN102 can be used to extract the newly created carboxylic acid.

These resins are hydrophobic due to the high surface area of their styrenic backbone and minimum tertiary amine present (less than 0.3 meq/mL). They combine the functionality of an anion exchanger and an adsorbent to achieve good patulin removal, and are easily regenerated with NaOH — no alcohols or solvents are needed.

TABLE 9 Operational Conditions for Patulin Removal from Apple Juice Using PuroSorb Resins

Feed to be Processed	10–12 Brix°	Juice concentration
Service Flow Rate	6–8 BV/h	–
Bed Depth	1.2–1.5 m	–
Regeneration Steps	15–30 minutes	–
Backwash	6–8 BV/h	–
Sweetening Off	2–4 BV/h	RO water with previous gas displacement (N_2) for minimum dilution
NaOH or KOH Rinse (or Alcohol Rinse)	2–4 BV	2 BV at 2 BV/h, 40–60°C (50% ethanol or 25% ethanol/25% IPA with 50% water)
Displacement with Water	6–8 BV/h	1–2 BV at 60–90°C RO water
Water Rinse	3–5 BV	15 min RO water with optional 0.2% H_2O_2
Acid Rinse (Only if Caustic is Used)		–
H_2SO_4 or H_3PO_4	0.2–1% w/w	2 BV mainly used to neutralize caustic
Final Rinse	4 BV/h	–

Corn Sweetener Refining

Starch hydrolysate plants (wheat, corn, etc.) around the world utilize high surface area synthetic adsorbents to replace granular and powdered activated carbon to remove color, taste, odor, hydroxymethylfurfural (HMF) and other impurities from sweetener solutions, Table 10. The Macronet line of chemically regenerable styrenic adsorbents offers economic, purity and process advantages for replacing carbon in the production of quality syrup.

Liquid and solid sweeteners are produced around the world from several starch sources including corn, wheat, tapioca, potatoes and cellulose hydrolyzate. High fructose corn syrup is the largest single sweetener syrup produced.

TABLE 10 Macronet Operating Options in Corn Sweetener Refining

Color Adsorbent for Non-Demineralized Syrups	Macronet MN100 or MN102 replace conventional carbon powdered treatment of glucose syrups. Expensive and dirty powdered carbon and carbon filters are replaced with a simple chemically regenerated unit that produces no solid discharge to handle.
Taste and Odor Polishing	The primary and secondary ion exchange pairs remove the majority of impurities, leaving Macronet MN100 or MN102 to remove taste and odor impurities and further polish the color.
Color, Taste and Odor Polishing	A layered bed of Macronet MN100 or MN102 with MN502 offers improved color removal in addition to taste and odor polishing.
Color, Taste and Odor Polishing with Enhanced pH Stability	A layered bed of Macronet MN100 or MN102 over a weak acid cation resin is air mixed prior to service to offer better pH stability.
Color, Taste and Odor Polishing with Enhanced pH and Conductivity Stability	A layered bed of Macronet MN100 or MN102 with MN502 is air mixed prior to service to offer mixed bed quality pH and conductivity.

The process of using Macronet MN100 or MN102 and Macronet MN502 is summarized in Table 11.

TABLE 11 Service and Regeneration Sequence of Macronet Resins

Step	Solution	Temp (°C)	Flow (BV/h)	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/ft^2 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 BV/h
[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 0.3N
[4] For a 1/3 MN100 or MN102 and 2/3 MN502 layered bed, the HCl concentration should be increased to 0.2N
[5] For mixed bed operation, an air mix follows the fast rinse

In the sweeten off process, syrup is displaced by introduction of condensate or demineralized water through the adsorbent bed. This step continues until the effluent syrup concentration has decreased to 0.1–0.5% of dry solids. In the backwash sequence that follows, process water is passed in an upflow direction to fluidize the resin and allow particulates to pass up through the bed and out of the vessel. In the final step for sweeten on, syrup is introduced to the bed displacing the rinse water. Sweeten on is terminated when the effluent dry solids concentration reaches in excess of 90% of the feed syrup solids concentration.[3]

Adsorption of Gases and Organic Vapors

Denomination of volatile organic compounds (VOCs) refers to organic compounds where vapor pressure is at least 0.01 kPa at 20°C. VOCs are also characterized by their low water solubility. VOCs are associated with emissions from motor vehicle exhaust, evaporated fuel, industrial activities, petroleum refining, etc. and contribute to a wide range of atmospheric pollutants as well as the degradation of the ozone layer.

Hexane is part of the n-alkanes class of VOCs and is widely used as a solvent for inks or paints, a cleaning agent for metal and plastic components, an extraction agent for vegetable oils from oil seeds and more. Due to its broad range of uses, the amount of hexane emitted into the atmosphere can be significant, making it necessary to control VOC emissions. Adsorption is a very effective way to do this. Activated carbon adsorption is widely used for controlling VOCs at low concentrations with potential to recover valuable vapors. However, activated carbon adsorption can experience problems such as combustion and pore blocking.

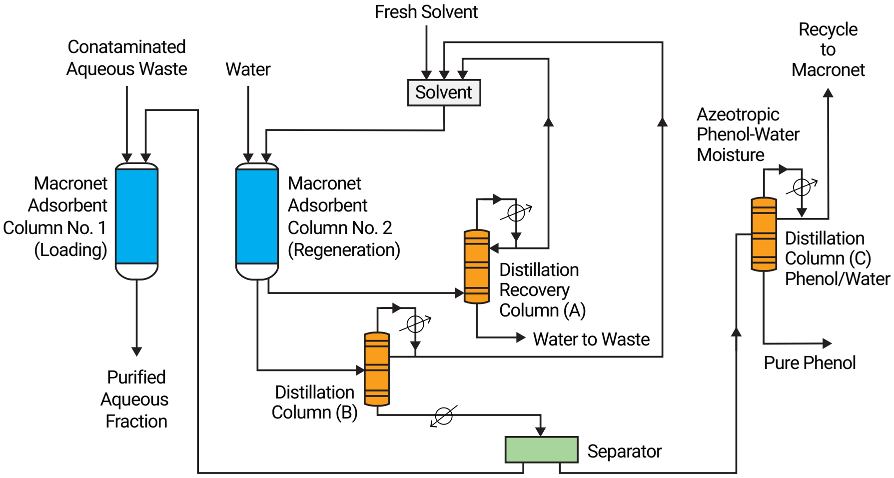
In a study done by Halela et. al., non-functionalized styrenic resins such as Macronet MN202 and MN270 displayed similar capacity to granular activated carbon for removing n-hexane vapors from gaseous flux at different concentrations and at different adsorption temperatures. In the study, the initial n-hexane concentration in the air stream ranged from 2,100–4,500 ppm and the adsorption temperatures were 30°C, 40°C and 50°C. Results showed that MN202 had higher adsorption capacities of n-hexane in all studied conditions. The experimental results were plotted to show that the maximum adsorption capacity for n-hexane were similar between MN202 and activated carbon.[4]

Adsorption of Organic Pollutants from Aqueous Solutions

Macronet MN200 and MN202 are extremely efficient at successfully removing and recovering organic pollutants from water and wastewater. These pollutants include common pesticides and herbicides used in the agricultural industry as well as complex organics such as aromatic and polyaromatic compounds (phenol, naphthalene, fluorene, anthracene, acenaphthene, pyrene and fluoranthene). A study that used resins to remove pesticides from water showed that 100–1,000 liters of the Macronet resin is enough for high linear flow rates such as 0.1–2 m/day.[5] The resin was reported to have a concentration ratio of 120,000 liters of feed to 1 liter of resin in treating a wastewater containing 0.1 ppm of pesticides like atrazine, benazolin, bentazone and imazapyr.[6] Other pesticides such as Simazine, Chlorotoluron, Isoproturon and Diuron have also been removed using Macronet resins and using methanol or acetone for regeneration.[6] Figure 15 presents a process schematic for the removal of phenol from waste water using Macronet MN100 or MN202.

FIGURE 15

Process for Phenol Removal During Waste Water Treatment



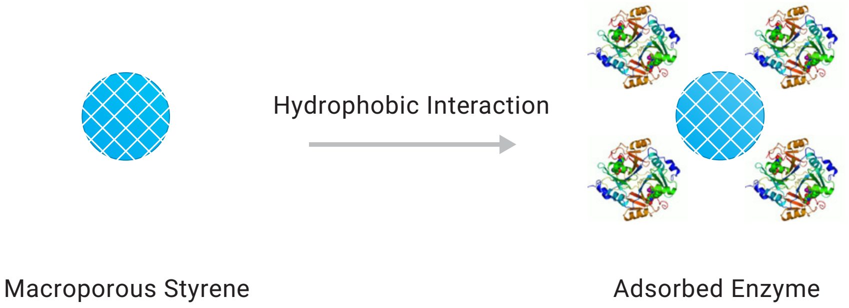
Enzyme Immobilization

Due to their hydrophobic properties, some enzymes like lipases can be efficiently immobilized by simple adsorption onto PuroSorb or Macronet resins. Immobilization of enzymes is based on the physical adsorption of an enzyme onto the surface of water-insoluble carriers. The method is very gentle and will not affect the active sites where biocatalysis occurs as long as the hydrophobic interaction is controlled to prevent conformation change or denaturing of the enzyme. This method is particularly suitable for biocatalysis applications in organic solvents or hydrophobic media such as oils.

A major advantage of adsorption as a method of immobilizing enzymes is that it is simple and does not require special reagents. As mentioned above, PuroSorb and Macronet resins have a high degree of hydrophobicity and are optimal for the immobilization of lipases by hydrophobic interaction, Figure 16. However, PuroSorb and Macronet resins have a very large particle size range, therefore, corresponding Lifetech™ ECR resins (see brochure on Enzyme Carriers) are sometimes a better choice, since they have a narrow particle size range optimized for the large sizes of the enzymes.

FIGURE 16

Immobilization of Enzymes on Macroporous Carriers



Size Exclusion Chromatography for Inorganic Salts

Inorganic salts are hydrophilic and will pass through the resin bed. Due to their size, the smaller the molecule, the longer the path they will take through the resin structure. Therefore, smaller salts will take longer to pass through the resin bed. In a study by Davankov et al., the hypercrosslinked polystyrene matrix of Macronet resin — due to its micropore structure — was found to provide efficient separation of inorganic electrolytes ($CaCl_2$, HCl, NaCl, NaOH, H_2SO_4, etc.) under conditions of size exclusion chromatography (SEC). The process, based on the difference in size of hydrated competing ions, permits separations of many pairs of salts, acids and bases. The productivity of separation increases with the rise in the concentration of the feed solution.[7]

Adsorption Applications in Pharmaceutical Production

Adsorbents are widely used and accepted for the extraction of valuable pharmaceutical ingredients such as antibiotics, peptides and proteins. By controlling the pore structure of the resin matrix, one can maximize the removal of the smaller molecules while excluding the larger ones, similar to size exclusion chromatography. For example, Macronet resins are size-selective, hemocompatible, porous polymeric adsorbents with a pore structure capable of excluding molecules larger than 50 KDa. The pore system of Macronet resins, however, allows good adsorption and desorption of molecules smaller than 35 KDa. Most of the surface area of the resin is located in pores smaller than 300 Å in diameter with an effective pore diameter range of 100–300 Å. The porous polymeric adsorbents are very selective for extracting midsize proteins, such as cytokines (5–20 KDa) and ß2-microglobulin (12 KDa) from blood and other physiologic fluids, while keeping the components required for good health such as cells, platelets, albumin, hemoglobin, fibrinogen and other serum proteins intact.[8]

Adsorbents are widely used for the extraction of pharmaceutical ingredients such as antibiotics, peptides and proteins.

Storage Conditions

Since most adsorbent resins are non-functionalized, there is a high risk for mold growth if they are not stored properly. The PuroSorb and Macronet resins can typically last for a year after production before the onset of any such growth. This condition does not affect ion exchange resins since the functional groups act like a salt layer on the resin surface that hinders mold growth.

Therefore, a 10% salt solution (such as NaCl) or higher can be used to preserve the new or used adsorbent resin during long storage.

In case salt cannot be used, a dilute NaOH solution is also acceptable (0.01 to 0.02 N) as no mold can survive at pH >12.

The best storage is in 20% alcohol such as ethanol or 2-propanol since such solvents can also help in keeping the resin clean during storage.

Freezing temperatures should be avoided as it will put unnecessary stress on the resin matrix resulting in breakage and an increase of resin particulates.

Regulatory

Purosorb and Macronet resins are compliant with Resap, Halal and Kosher standards. Some Purosorb and Macronet are also compliant with FDA regulations, Table 12.

TABLE 12 Regulatory Compliance for Purolite Macronet and PuroSorb Resins at a Glance

	Compliant With							
Product	***FDA 21CFR173.25**	****FDA 21CFR173.65**	*****FDA 21CFR177.2710**	**†Resap (2004) 3**	**††Halal**	**‡Kosher**	**‡‡GMO Free**	**§TSE/BSE Free**
PAD400	–	Yes	–	Yes	Yes	Yes	Yes	Yes
PAD500	–	Yes	–	Yes	Yes	Yes	Yes	Yes
PAD600	–	Yes	–	Yes	Yes	Yes	Yes	Yes
PAD610	–	–	–	Yes	Yes	Yes	Yes	Yes
PAD900	–	Yes	–	Yes	Yes	Yes	Yes	Yes
PAD950	–	–	–	Yes	Yes	Yes	Yes	Yes
PAD1200	–	Yes	–	Yes	Yes	Yes	Yes	Yes
MN100	Yes	–	–	Yes	Yes	Yes	Yes	Yes
MN102	Yes	–	–	Yes	Yes	Yes	Yes	Yes
MN200	–	–	Yes	Yes	Yes	Yes	Yes	Yes
MN202	–	–	Yes	Yes	Yes	Yes	Yes	Yes
MN270	–	–	Yes	Yes	Yes	Yes	Yes	Yes
MN502	Yes	–	–	Yes	Yes	Yes	Yes	Yes

[*] 21CFR173.25: Secondary direct food additives permitted in food for human consumption/ion exchangers.

[**] 21CFR173.65: Secondary direct food additives permitted in food for human consumption/divinylbenzene copolymers.

[***] 21CFR177.2710: Substances for use only as components or articles intended for repeated use/styrene-divinylbenzene resins, cross-linked.

[†] ResAP(2004) 3: Ion exchange and adsorbents resins used in food processing.

[††] Halal: Products certified, manufactured plant and raw materials audited by certifying agency. Raw materials free of porcine, alcohol, blood, etc.

[‡] Kosher: Products certified, manufactured plant and raw materials certified and audited for orthodox compliance. Raw materials free of porcine, alcohol, blood, etc.

[‡‡] GMO Free: Product does not contain any GMOs or any GM derived material and no modified genetic material is present.

[§] TSE/BSE: The product has been manufactured without the use or inclusion of any animal products, which carry a TSE/BSE risk.

Conclusion

When choosing an adsorbent resin, hydrophobicity, capacity and elution are the most important considerations. Other characteristics such as porosity, resin matrix and particle size are other important factors that will determine the best Purolite resin for your application. Purolite offers the largest portfolio of adsorbents in the industry. With the broadest scope of pore diameters, resin sizes and base matrices, Purolite can help you optimize your project, making it economically feasible. For any questions regarding any product mentioned in this brochure, or to discuss your process, contact a Purolite technical sales expert.

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Notes

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