ABSTRACT
Cane sugar decolorization can be accomplished by employing either carbonaceous adsorbents, such as bone char or granular activated carbon, or ion exchange resins. Macroreticular polyacrylic and polystyrene strong base anion resins are typically used in this application. Ion exchange resins offer a less costly and more easily operated system for decolorizing sugar syrups as compared to carbonaceous adsorbents. A comparison of these two decolorization materials is presented.

Key words: Ion exchange resin, carbonaceous adsorbents, bone char, granular activated carbon, cane sugar, color body, regeneration, service cycle, waste disposal, separation.

INTRODUCTION
Raw cane sugar has varying amounts of color associated with it. These color bodies are undesirable to food and beverage processors, as they can potentially contribute color, taste and odor to their products. Hence, sugar decolorization procedures have been developed to separate the color bodies from the sugar syrup. These processes involve several steps which can be generalized as outlined below.

1. Affination—Also referred to as washing, this process removes the molasses film which covers the sugar crystals.

2. Defecation/Clarification—The affinated sugar is dissolved in water to form a liquid sugar syrup. This syrup is defecated or clarified by one of several methods.
   a. Phosphoric acid and lime.
      i. Polymeric flocculants and flotation aids.
   b. Carbon dioxide and lime.
3. Fixed media color removal – Various materials are employed in this process where the color bodies are adsorbed or exchanged out of the the sugar syrup in a continuous, flow-through fashion.
   
a. Carbonaceous adsorbents.
   i. Bone char.
   ii. Granular activated carbon.
   iii. Powdered carbon.
   
b. Ion exchange resin.
   
4. Boil down – Water is evaporated from the sugar to increase its concentration prior to crystallization.
   
5. Crystallization – Water is evaporated from the sugar in a vacuum pan to form crystalline sugar.

The raw sugar crystals are washed to remove the molasses film which covers them and separation of the molasses from sucrose is accomplished by centrifugation. The washed sugar is dissolved in water to form a liquid sugar syrup for further processing.

The sugar syrup is clarified (or defecated) by phosphate-lime treatment or carbonate-lime treatment. In the phosphate-lime case, polymeric flocculants can be added, with or without polymeric flotation aids, to enhance the clarification process. These clarification processes are very effective in coagulating and precipitating fine particles, colloids and other impurities found in the sugar syrup. The result of treating the sugar syrup by any of these methods, followed by filtration with an inert filter aid, such as diatomaceous earth, can be the removal of virtually all insoluble contaminants from the syrup. Typically, a 50% reduction in the color level can be achieved through clarification.

The very clear syrup produced by clarification is now ready for further color reduction by contacting the sugar solution with a fixed bed of materials which selectively remove color from the syrup by ion exchange and/or adsorption. Other contaminants still present in the sugar syrup are easily removed in the final, crystallization step. The selection of the material for decolorization can have significant economic and environmental ramifications. The service cycle and regeneration operations of reusable carbonaceous adsorbents, bone char and granular activated carbon, are compared to ion exchange resins.
MATERIALS AND METHODS

Carbonaceous adsorbents

Bone char and activated carbon are naturally occurring materials used to decolorize sugar syrups. Animal bones and coal are ground to a desired size and activated by heat and steam. Bone char can remove color and ash from sugar syrups, while granular activated carbon can only remove color. Bone char is approx. 10% carbon and 90% calcium phosphate and activated carbon is more than 60% carbon. Powdered carbon is finely ground activated carbon which is used once and subsequently disposed of. The carbonaceous adsorbent used in this study was granular activated carbon from a sugar factory in Brazil.

Ion exchange materials

Ion exchange resins are crosslinked polymers in the form of small beads, usually based on acrylic or styrenic matrices, functionalized to contain immobilized negatively charged groups for exchanging cations, or positively charged groups for exchanging anions. In reality, these ion exchange materials can be considered to have two potential roles: 1) as exchangers of desirable ions for undesirable ions; 2) as adsorbents with hydrophobic adsorption sites embedded within a polar environment. Depending on the application requirements, either or both mechanisms may be occurring. In the sugar decolorization application, macroreticular polyacrylic and polystyrene strong base anion resins, which have quaternary amine functionality, are employed. Amberlite IRA-958 (polyacrylic) and Amberlite IRA-900 (polystyrene) were the ion exchange materials used in this study (Figure 1).

![Figure 1. Structures of acrylic and styrenic strong base anion exchange resins.](image-url)
Laboratory apparatus and reagents

Four feet by one-half inch inside diameter jacketed glass columns were used to contain the carbonaceous adsorbent and ion exchange resin. Twenty-four inch resin bed depths were used in all experiments (Figure 2). Analytical grade reagents were used for preparing all solutions in this study. Deionized water was used to prepare solutions and for rinsing decolorizing materials.

Analytical methods

Sugar color measured using ICUMSA spectrophotometric method at 420 nm.

\[
\text{Color, mau} = \frac{1000 \times \text{Absorbance} @ 420 \text{ nm (pH 7)}}{\text{Cell length (cm)} \times \text{Syrup conc. (g/mL)}}
\]

![Diagram of two bed decolorization system.](image)

RESULTS AND DISCUSSION

Decolorization service cycle

One of the major advantages of using ion exchange resins in sugar decolorization is the required contact time. Carbonaceous adsorbents are very effective in removing
color from sugar, however, they require 2-4 h of contact time with the sugar syrup. Ion exchange resins require only 15-30 min contact time. Another way of looking at this is flow rate. Carbon is operated at 0.25-0.50 bed volumes per h, while resins are operated at 2-4 bed volumes per h.

Sugar decolorization with carbonaceous adsorbents is primarily due to hydrophobic bonding. Aromatic color bodies are removed from the syrup by interacting with the aromatic character of carbon by pi electron sharing. The carbon is very effective in removing the color and very strong bonds are formed between the carbon and color bodies. This reaction requires time for proper molecular orientation.

TABLE 1. Service cycle comparison for ion exchange resin and carbonaceous adsorbents used in sugar decolorization.

<table>
<thead>
<tr>
<th></th>
<th>Ion Exchange Resin</th>
<th>Carbonaceous Adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>2 - 4 BV/h</td>
<td>0.25 - 0.50 BV/h</td>
</tr>
<tr>
<td>Contact time</td>
<td>15 - 30 min</td>
<td>2 - 4 h</td>
</tr>
<tr>
<td>Degree of decolorization</td>
<td>50 - 90%¹</td>
<td>50 - 90%¹</td>
</tr>
</tbody>
</table>

¹Degree of decolorization is a function of color load and run length. These values are based on a 600 mau sugar syrup and 100 bed volume service cycle.

A resin decolorization process typically consists of two columns of quaternary ammonium anion exchange resin operated in the chloride form. The first column in acrylic-based material, while the second column is styrene-based resin. The former removes the aromatic, large molecular weight compounds which tend to foul the latter. The styrene-based resin forms strong hydrophobic bonds with the aromatic portion of the color bodies through van der Waals interaction. The acrylic-based resin is a more hydrophilic matrix and, therefore, does not form irreversible bonds with the color bodies. The second bed is styrene-based resin, which has superior adsorption ability compared to the acrylic-based resin and removes the more difficult to remove species from the syrup (Figure 3).

The mechanism of adsorption in the acrylic anion resin is a combination of simple ion exchange and weak hydrophobic adsorption by the polymer backbone. This accounts for the partial color removal but good regenerability of the first bed. The mechanism in the second, styrenic anion bed is only temporarily ion exchange with the weak acid groups of the color body just long enough for the pi electron fields of the styrene to orient and interact with the conjugated electrons of the color bodies. This explains the high affinity this type of resin has for sugar color bodies and its incomplete regenerability. The protective function of the acrylic anion bed for the
Acrylic and Styrenic Resin in Series

Styrenic Resin Alone

FIGURE 3. Comparison of % decolorization between one column of styrenic resin and two columns of acrylic and styrenic resin in series.

styrenic anion bed permits this system configuration to work effectively a significantly longer period of time as compared to using only a single bed of styrene anion resin.

The resulting color removal efficiency depends on several operational parameters, most importantly, the concentration of color in the syrup and the amount of syrup treated between regenerations. Other important factors influencing color removal include operating temperature, flow rate, and resin bed depth.

For the purpose of comparison, it is convenient to group sugar color load into three general categories:

- **Low color** < 300 mau
- **Medium color** 300 to 1,000 mau
- **High color** > 1,000 mau (Figure 4).

The carbonaceous adsorbents and ion exchange resins show the same general rates of decolorization when operated at their optimum flow rates as discussed previously. The endpoint for a given run is a function of the final color specification and influent
color level. Therefore, for low color sugar syrups, decolorization rates range between 80 and 90% over 100 bed volumes. The product syrup is quite constant over the duration of the entire run. For medium color sugar syrups, the range is between 70 and 90% over 100 bed volumes and there is more variability in product sugar. Finally, for high color sugar syrups, the range is between 65 and 90% decolorization over 50 bed volumes with significant variability in product sugar. Of course, degree of decolorization will vary depending on the nature of the sugar color bodies.

**FIGURE 4.** Rates of decolorization for carbonaceous adsorbents and ion exchange resins with low, medium and high influent sugar colors.

Regeneration of carbonaceous adsorbents and ion exchange resins

As previously stated, carbon forms very strong bonds with the color bodies which makes their removal quite difficult. The color bodies are not affected by chemical regenerants, so the carbon must be reactivated thermally. This is done at the char house in kilns at approx. 550°C. Approx. 5% of the carbonaceous adsorbent is lost to thermal oxidation during each reactivation. This translates into a total loss of all
starting material after 20 cycles. The carbon is rinsed with five bed volumes of water prior to reuse. A very labor intensive aspect of this regeneration sequence is transferring the carbon from the cisterns to the char house for rejuvenation and subsequently transferring the material back to the cisterns for the next service cycle. Another expensive part of thermal regeneration is the energy costs associated with burning the carbon (Table 2).

**TABLE 2. Methods of regenerant reclamation.**

- Reverse Thoroughfare Through Styrenic Resin and Acrylic Resin
- Chemical Oxidation of Organic Matter in Regenerant
  - Sodium Hypochlorite
  - Ozonation
- Regenerant Filtration
  - Hollow Fiber Ultrafiltration
  - Granular Activated Carbon

**CONCLUSIONS**

Ion exchange resins and carbonaceous adsorbents are very effective in decolorizing cane sugar syrups. As compared to carbonaceous adsorbents, ion exchange resins have operational advantages including: 1) higher flow rates and less contact time, 2) lower cost of regeneration, 3) lower manpower requirements, 4) no char house or kiln operation required, 5) less plant discharges.

Ion exchange resins are regenerated with inexpensive sodium chloride and the regenerant and rinse water can be reclaimed for reuse. The regeneration procedure can be done automatically by preset control equipment, only requiring someone to oversee the operation. All char operations are different, but several individuals are required to transfer, char and replace the carbon. Also, an ion exchange regeneration system is very small as compared to the amount of space required for a char house (Table 3).

Disposable powdered activated carbon can successfully reduce the color load to ion exchange systems without the costs associated with handling and regenerating granular activated carbon. Also, used in combination with ion exchange resins, the amount of granular activated carbon can be reduced, thereby lowering costs.
### TABLE 3. Comparing methods of regeneration for ion exchange resins and carbonaceous adsorbents in sugar decolorization.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ion Exchange Resin</th>
<th>Carbonaceous Adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerant</td>
<td>Aqueous NaCl</td>
<td>Heat</td>
</tr>
<tr>
<td>Reusable Regenerant</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Rinse Volume</td>
<td>3 Bed Volumes</td>
<td>5 Bed Volumes</td>
</tr>
<tr>
<td>Material Loss Per Cycle</td>
<td>&lt; 0.1%</td>
<td>5%</td>
</tr>
<tr>
<td>Space Requirement</td>
<td>Minimal</td>
<td>Char House</td>
</tr>
<tr>
<td>Transfer Operations</td>
<td>None</td>
<td>To and From Char House</td>
</tr>
<tr>
<td>Manpower Requirement</td>
<td>1</td>
<td>5 or more</td>
</tr>
</tbody>
</table>

**REFERENCES**

L'EMPLOIE DES RESINES ACRYLIQUES ET STYRENIQUES, EN FORME BASIQUES, A LA PLACE DES ADSORBANTS CHARBONNEUX, POUR LA DECOLORISATION DU SUCRE DE CANNES

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RESUME
La decolorisation du sucre de cannes peut être entreprise en se servant de produits charbonneux, tel que le charbon actif ou des résines échangeuses d'ions. Des résines macroreticulaires polyacriliques et polystyreniques en formes basiques sont employées. Ces résines offrent un procédé moins coûteux et plus facile, pour la decolorisation des liqueurs sucrées, en comparaison aux produits charbonneux. Ces deux méthodes sont comparées.

REEMPLAZO DE CARBONES ADSORBENTES POR RESINAS ACRILICAS Y ESTIRENICAS DE FUERTE BASE ANIONICA EN LA DECOLORIZACION DE SIROPES DE CAÑA DE AZÚCAR

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RESUMEN
La decolorización de siropes de caña de azúcar se puede efectuar empleando como adsorbentes carbón animal, carbón activado granular o resinas de intercambio iónico. Resinas poliacrilicas y de poliestireno de fuerte base aniónica son típicamente usadas en esta aplicación. Las resinas intercambiadoras de iones son menos costosas y el sistema de operación es mas simple. Un estudio comparativo de estos dos agentes decolorantes es presentado.