Granular Activated Carbon From Agricultural By-Products: Carbon Properties and Their Relationship to Sugar Decolorization Potential.

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GRANULAR ACTIVATED CARBON FROM AGRICULTURAL BY­PRODUCTS: CARBON PROPERTIES AND THEIR RELATIONSHIP TO SUGAR DECOLORIZATION POTENTIAL

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Food Science

by

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Representative samples of soft, low density, group 1 (rice straw, rice hulls, sugarcane bagasse) and hard, high density, group 2 agricultural by-products (pecan shells) were converted into granular activated carbons (GACs). Prior to pyrolysis, group 1 by-products were mixed with four binders, sugarcane molasses, sugar beet molasses, corn syrup and coal tar. GACs were produced from group 1 and 2 materials by physical activation (carbon dioxide, steam) or from group 2 materials by chemical activation (phosphoric acid). Carbons were evaluated for their physical (hardness, bulk density), chemical (ash, pH), surface (total surface area, pore size distribution, surface oxides) and adsorption properties (molasses color removal, sugar decolorization). Principal component and cluster analyses were used to compare agricultural by-product-based GACs to two commercial reference carbons. The results show that the type of by-product, binder and activation method determine the properties of activated carbons, with surface properties being the most influential on the decolorizing capacity of GACs. Combination of sugarcane or sugar beet molasses with group 1 materials, for instance, was unsatisfactory because it yielded GACs that were brittle and possessed low surface area, low bulk density, high pH and excessive ash content.
The use of coal tar yielded GACs with good physical, chemical and surface properties, but with very limited surface area and, thus poor adsorption efficiency. Regardless of the binder, sugarcane bagasse showed a better potential than rice straw or rice hulls as precursor of GACs with the desirable properties of a sugar decolorizing carbon. Pecan shells produced GACs that were closest to the reference carbons. Steam and phosphoric acid activation showed promise in producing GACs with characteristics similar to the commercial carbons. Steam activation of pecan shells produced the best carbon among the agricultural by-product-based GACs and produced GAC with high surface area, good pore size distribution and weakly charged surface, which are good characteristics for sugar decolorizers. This study demonstrated that agricultural by-products can be used to produce GACs that are as effective as the commercial carbons in removing sugar colorants, offering a potential low cost alternative to the existing coal-based commercial carbons used in the sugar refining industry.
INTRODUCTION

Every year, about a billion tons of sugarcane are produced worldwide, yielding 100 million tons of raw sugar. Raw cane sugar, however, is not the end product of sugar manufacturing. Raw cane sugar is put through an additional refining processing to yield refined or white sugar. Decolorization is a key step in the refining process. It is commonly achieved through adsorption of sugar colorants by activated carbons (mainly bone char). About 600 million lbs of activated carbon worldwide are used annually for various adsorption processes (Roy, 1995) among which cane sugar refining is the major user of GACs. Currently, there is a large and growing demand for decolorizing carbons worldwide. Such demand presently relies on either a nonrenewable source of supply (coal) or a renewable source (bone), with a limited supply, for producing activated carbons.

Annual harvest and processing of various agricultural crops grown in the United States yield considerable quantities of agricultural by-products. For instance, the United States produced 62 billion lbs of sugarcane, 17 billion lbs of rough rice and 182 million lbs of pecans during the 1997 crop year (Agricultural Statistics, 1997). Productions and processing of these two commodities generated an estimated 21 billion lbs of sugarcane bagasse, 3.8 billion lbs of rice hulls/straw and 91 million lbs of pecan shells. These agricultural by-products have little or no economic value and their disposal is
not only costly but may also cause environmental problems. Conversion of these agricultural by-products into GACs that can be used in food applications such as sugar refining or waste treatments would add value to these agricultural commodities, help reduce the cost of waste disposal and provide a potentially cheap replacement of existing commercial GACs.

While the physical, chemical, surface, and adsorptive properties of coal-based carbons have been investigated, there appears to be little information on such characterization of activated carbons from agricultural by-products. Furthermore, information is scarce on the correlation of carbon properties (especially surface properties) with a particular carbon application, such as sugar decolorization. Therefore, data is needed to understand the effect of activated carbon surface properties on the ability of such carbons to decolorize raw sugar solutions. An assessment of the respective contribution of the porous structure and surface chemistry of by-product-based GACs in decolorizing sugar will provide useful information in developing carbons with good sugar decolorization efficiency.

The main objectives of this investigation were to convert select agricultural by-products to GACs and to characterize these carbons in terms of those physical (surface area, pore structure) and chemical (surface charge, functional groups) properties directly related to adsorption of raw sugar colorants.
Other physical properties (density, hardness) and chemical properties (pH, mineral content) of the GACs will also be determined. These properties may not directly relate to sugar decolorization effectiveness but they are important to the commercial utilization of these carbons.

The experimental work is presented in two chapters. The first chapter (chapter 2) is entitled “Production of granular activated carbons from agricultural by-products and evaluation of their physical, chemical and adsorption properties.” This chapter describes the conversion of agricultural by-products to GACs using hard, dense feedstock (pecan shells) or soft, low density feedstock (rice straw, rice hulls or sugarcane bagasse, all with binders). Pyrolysis and activation conditions are also described. Principal component and cluster analyses were used as the basis to select the best carbons in terms of adsorption of raw sugar colorants. In Chapter 3, entitled “Surface properties of granular activated carbons and their effects on raw sugar decolorization,” physical and chemical properties of the carbon surface of the best carbons selected in Chapter 2 were correlated with raw sugar decolorization. In Chapter 3, the critical characteristics (surface area, pore structure, surface charge, surface functional groups) were statistically evaluated and used to explain the basis for raw sugar decolorization. Conclusions and recommendations were made to suggest improvement in carbon performance and to outline a manufacturing process for the production of by-product-based GACs specifically designed for sugar decolorization.
CHAPTER 1
REVIEW OF LITERATURE

PRODUCTION OF GRANULAR ACTIVATED CARBONS

Granular activated carbon (GAC) represents one of the most important types of industrial carbons. GACs can be produced from a large number of raw materials of biological origin such as sugarcane bagasse, coconut shells, wood, peat, olive stones, rice hulls, and coal (Gergova et al., 1992; Girgis et al., 1994; Rodriguez-Reinoso and Solano, 1989; Ahmedna et al., 1997b; Pendyal et al., 1998a). Almost any lignocellulose material, in some cases with the association of binders, can be converted to GAC. GACs are normally produced by pyrolysis and activation of the precursor. During carbonization, most of the non-carbon elements, particularly oxygen, nitrogen and sulfur, are removed by the pyrolytic decomposition of the precursor in the presence of an inert gas such as nitrogen. The pyrolyzed product or char consists of more or less disordered elementary graphitic crystallites, with a poorly developed porous structure. Subsequent activation is required to dramatically increase surface area and create a highly developed pore structure for the selective adsorption of molecules of different sizes and polarities. Activation can be a physical process with the use of carbon dioxide or water vapor as activating agents or a chemical process employing activating agents such as phosphoric acid (H₃PO₄) or zinc chloride (ZnCl₂). During the activation process, the spaces between the elementary crystallites become cleared of less organized,
loosely bound carbonaceous material. The resulting channels through the
graphitic regions, the spaces between the elementary crystallites, together
with fissures within and parallel to the graphitic planes, constitute the porous
structure, with large internal surface area (Rodriguez-Reinoso and Solano,
1989). The extensive use of activated carbon is generally attributed to this
large surface area which can attain values up to 2000 m²/g, making it a
powerful adsorbent, capable of adsorbing most organic and many inorganic
compounds. Thus activated carbons are commonly used in water and
wastewater treatment, in the food processing industry such as sugar refining,
and in pharmaceutical purifications (Rivera-Rivera-Utrilla et al., 1991; Ying and

The final porous structure of activated carbon is, however, a function
of the precursor used in its preparation, the activation procedure, and the
extent of activation (Gergova et al., 1992; Mackay and Roberts, 1982; Mattson
and Mark, 1971; Rodriguez-Reinoso and Solano, 1989). Furthermore, the
adsorption capacity of activated carbon is defined not only by its porous
structure but also by its chemical nature. The surfaces at the edges of the
crystalline planes contain a wide variety of functional groups that will influence
the adsorptive properties of the activated carbon, especially for polar or
polarizable molecules. The nature of these functional groups depends to a
large extent on the method of activation as well as on the raw material from
which the carbon is produced (Mattson and Mark, 1971; Rodriguez-Reinoso
and Molina-Sabio, 1992; Rodriguez-Reinoso and Solano, 1989). GACs prepared at temperatures below 400-500°C will develop acidic surface oxides, whereas GACs activated at temperatures between 800-1000°C will develop mainly basic surface oxides (Mattson and Mark, 1971; Weber and Vliet, 1980).

STRUCTURE AND FUNCTION OF ACTIVATED CARBON

Structure of carbon (crystallite)

Activated carbons and chars are pyrolytic materials similar to graphite. The latter is composed of layered planes formed by carbon atoms ordered in regular hexagons. Each carbon atom within a plane is bonded to three adjacent carbon atoms by σ bonds, with the fourth electron participating in a π bond. The layered planes are parallel to each other and are held together by weak van der Waals forces. Based on X-ray data, there are two types of structures for activated carbons. The first structure consists of elementary crystallites forming parallel layers that are not perfectly oriented and that randomly overlap one another irregularly. The second type of structure is a disordered cross-linked space lattice of the carbon hexagons. Such a structure is stabilized by heteroatoms originating from material rich in oxygen (Reinozo and Solano, 1989). Figure 1.1 shows a schematic of the microstructure of activated carbon.

Surface properties

Both the size and distribution of micropores (< 2 nm), mesopores (2-50 nm) and macropores (>50 nm) as well as the chemistry of oxygen, usually
Figure 1.1: Structure of carbon matrix.
(a) drawing of carbon granule interior and (b) schematic representation of the microstructure of activated carbon (Roy, 1995), (c) structure of elemental carbon in graphite and structure of elemental carbon in activated carbon (Fitzer, 1980).
covalently bonded to the pore surfaces, determine the adsorptive properties of activated carbons. For instance, small pore size will not trap large adsorbate molecules and large pores may not be able to retain small adsorbates. A good porous structure will have the right pore size to trap the targeted species. The electrical charge of the surface groups may also enhance or hinder the adsorption of the target molecules. If, for instance, the adsorbate has the same electrostatic charge as that of the carbon surface, repulsion would occur. Repulsion by like charges would inhibit the process of adsorption. However, the adsorption of such molecules would be enhanced if they and the carbon surface carry opposite charges.

**Pore distribution**

The large internal surface area of activated carbon is due to its porosity. The total porous structure of an activated carbon is formed by a wide range of pore sizes. For practical reasons, pore sizes are classified into three main types according to their width: macropores (> 50 nm), mesopores (2-50 nm), and micropores (< 2 nm). The macropores act as "tunnels" which enable molecules to reach the smaller pores in the interior of the carbon where they are adsorbed or bonded to the carbon surface. Macropores do not significantly contribute to the overall adsorptive process since they have a relatively low surface area but they affect the rate of admission of the molecules to the meso- and micropores. Mesopores, which branch from the macropores, serve as passages by which molecules reach the smaller micropores.
may trap molecules, but their overall contribution is small given their relatively low surface area. The micropores constitute the largest part of the internal surface area of an activated carbon and, consequently, most of the adsorption takes place there. About 90-95% of the total surface area of an activated carbon can correspond to micropores (Rodriguez-Reinoso and Solano, 1989).

The porous structure of activated carbon is a function of the precursor used in its preparation, the activation procedure and the extent of activation. For example, activation with steam expands the micropores with development of greater mesoporosity. On the other hand, regardless of the precursor and activation process, the micropores enlarge with increasing burn-off of the activated carbon. There are three mechanisms that are often invoked to explain the development of porosity during gasification of activation of chars. These are: 1) widening of existing pores, 2) the creation of new pores by selective gasification of certain structural components, and 3) the opening of previously inaccessible pores (Marsh and Rand, 1970; Wojsz and Rozwadowski, 1989). Activation temperature greatly impacts the pore size distribution. Low temperature activation generally yields carbons with high microporosity and less mesopores, while high temperature activation yields carbons with developed mesoporosity. The influence of the activation temperature is such that for the same burnoff, the higher the temperature of gasification the broader the pores developed (Rodriguez-Reinoso and Molina-Sabio, 1992). Thus, pore drilling is the predominant mechanism at low
temperatures whereas pore deepening is favored at high temperatures (Rozwadowski and Wojsz, 1988). The types of activating agents also affect the porous structure of activated carbons. Ehrburger et al. (1992) reported a continuous increase in micropore and mesopore volumes with increasing degree of gasification and that such a pore deepening was more drastic in carbons activated with steam. Steam is generally preferred because water molecules are smaller than carbon dioxide molecules, and consequently the use of steam leads to a faster diffusion into the porous network and easier access to the micropores (Gergova et al., 1992). This inherent and induced change in porosity accounts for the differences in pore structure among carbons generated by different processes and/or different precursors.

The suitability of an activated carbon for a particular application depends on the macropore:mesopore:micropore ratio. While an essentially microporous carbon is suitable for the adsorption of gases and vapors, a well developed meso- and macropore structure is, in addition, required for the adsorption of solutes from aqueous solutions. Therefore, depending on the projected use of the activated carbon, one can select a suitable precursor and modify the activation conditions in order to produce a carbon with a favorable surface structure for the task at hand.

Carbon surface groups

The adsorption capacity of activated carbons is determined by their porous structure and surface area, but is also strongly influenced by the
presence of functional groups at the carbon surface. Activated carbons are known to contain a variety of heteroatoms such as oxygen, hydrogen, chlorine, and sulfur. Heteroatoms are either derived from the starting material, and become a part of the chemical structure as a result of imperfect carbonization, or chemically bonded to the carbon during activation or during subsequent additional treatments, such as oxidation. These heteroatoms are bound to the edges of the carbon layers and form surface groups that greatly affect the adsorption behavior of the activated carbon, with carbon-oxygen surface structures being by far the most important in influencing surface characteristics (Bansal et al., 1988; Boehm, 1994).

The surface chemistry of activated carbons is mainly determined by the nature and extent of carbon-oxygen compounds. As a result, carbons exhibit acidic or basic properties depending on the temperature at which it was oxidized. In general, depending on the extent of the oxidizing reaction, two forms of activated carbons can be produced, H-type and L-type. The H-type of activated carbon assumes a positive charge upon introduction into water, can neutralize strong acids, and is hydrophobic. The L-type activated carbon assumes a negative charge in water, can neutralize strong bases, and is hydrophilic. L-type carbons are obtained by heating the precursor in air at temperatures of 200-400°C, whereas the H-type carbons are prepared at higher temperatures of 1200°C under vacuum or in a carbon dioxide atmosphere, then exposed to air at room temperature. Oxidation of the
carbon surface by chemical oxidants (i.e. nitric acid, sodium hypochlorite) or "aging" in air at room temperature can convert H-type carbons to the L-type (Corapcioglu and Huang, 1987).

As a result of surface oxidation, many functional groups are formed. The most common are carboxyl, carbonyl, carbonyl (quinone type), phenolic hydroxyl, anhydride, ether-type, lactone and lactal. Due to the presence of such functional groups, carbons can show basic or acidic pH values in aqueous dispersions. According to Boehm (1994), a good correlation between pH and oxygen content of active carbons has been found. Carbons with high oxygen content were found to yield acidic dispersion, due to the presence of acidic surface groups, and have cation exchange properties. In contrast, carbons with low oxygen content exhibit basic surface properties and anion exchange behavior due to the presence of basic surface oxides and to the π electron system prevalent in the basal planes of the carbon.

Acidic carbons have the ability to bind protons from aqueous solutions of acids. They are generally obtained when carbons are outgassed at a high temperature in vacuum or inert gas, then exposed to oxygen at 200-700°C. Basic carbons are prepared by contacting outgassed carbons, which have been cooled to room temperature in the absence of oxygen, with oxygen below 200°C or above 700°C forming surface oxides with basic properties (Bansal, et al., 1988). Figure 1.2 shows the chemical structures of the major oxides that can be found on the surface of activated carbons.
Figure 1.2: Examples of oxides commonly found on the surface of activated carbon (Boehm, 1994).
DETERMINATION OF SURFACE PROPERTIES OF ACTIVATED CARBON

Several methods are available to evaluate the physical and chemical properties of GACs. Important physical properties relate to the carbon's porous structure and important chemical properties refer to the carbon's surface chemistry. The adsorption of gas, usually nitrogen or helium, at different partial pressures, along with the uptake of metallic mercury at various pressures (mercury porosimetry) are probably the best available methods for the characterization of the porous structure of activated carbon. Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and acid-base titration are commonly used to study the surface chemistry of carbonaceous materials (Bansal et al., 1988; Rodriguez-Reinoso and Solano, 1989; Zawadski, 1989).

Determination of porosity

For activated carbon, the degree of microporosity is the best determinant of adsorption capacity. Microporosity, along with total porosity, is normally determined by the physical adsorption of gases such as nitrogen and carbon dioxide. Other methods have also been developed, based on the adsorption of hydrocarbons or the adsorption of small solute molecules, such as iodine. These methods allow one to determine adsorption isotherms of gases or solutes and use theoretical models such as the Dubinin-Radushkevich (DRK) and Langmuir equations to evaluate the pore structure of the carbon (Rodriguez-Reinoso et al., 1989; Rodriguez-Reinoso and...
Mercury porosimetry can also be used to determine pore size and pore size distribution and is considered to be more accurate than gas or solute adsorption methods. Mercury porosimetry suffers from the possible danger of mercury contamination of the area surrounding the instrument and the cost of instrumentation.

**Determination of surface area**

Activated carbon surface area measurements can be determined from the same gas or solute adsorption data as used to measure porosity. The two most common models used to determine surface area from adsorption isotherms are the Brunauer, Emmet and Teller (BET) and Langmuir models. The BET model is probably the most popular and is based on complete monolayer coverage of a carbon's surface under saturating conditions of the adsorbate, normally nitrogen gas. The BET equation is:

\[
\frac{P}{n(P_0 - P)} = \frac{1}{n_m C} + \frac{(C-1)(n_m C) \cdot P}{P_0}.
\]

Where: \( n \) is the amount of gas adsorbed per gram of solid at the equilibrium pressure \( P \), \( n_m \) is the amount of gas adsorbed per gram of solid to complete a monolayer, \( P_0 \) is the saturation vapor pressure of the adsorbate (gas) at temperature \( T \) in degrees Kelvin, and \( C \) is a constant given by

\[
C = \exp\left[\frac{(q_i - q_L)}{RT}\right],
\]

in which \( q_i \) and \( q_L \) are the heats of adsorption for monolayer and multilayers, respectively, the latter being equivalent to the latent heat of condensation of
the adsorbate. A plot of $P/n(P_0-P)$ vs. $P/P_0$ should yield a straight line with a
slope of $(C-1)/(n_mC)$ and an intercept of $1/(n_mC)$ from which the values of $C$
and $n_m$ can be calculated. After $n_m$ has been calculated, the next step is to
determine the BET surface area ($S_{BET}$) from the monolayer capacity ($n_m$).
This requires a knowledge of the average molecular cross-sectional area ($a_m$)
occupied by the adsorbate molecule (for $N_2$, the value is 0.162 nm$^2$ at 77°K)
in the complete monolayer. $S_{BET}$ is calculated from the following equation:

$$S_{BET} = (n_ma_mL)/m,$$

Where: $L$ is the Avogadro constant and $m$ is the mass of adsorbent in grams.

Identification of carbon surface groups

Carbon-oxygen surface structures are the most important structures in
influencing the surface properties of activated carbons. Several techniques
have been deployed to identify and quantify these structures or functional
groups. Among the techniques, neutralization by different bases and
potentiometric titration are the most common chemical methods, whereas
infrared spectroscopy, particularly Fourier transform infrared (FT-IR)
spectroscopy and X-ray photoelectron spectroscopy (XPS), also known as
ESCA (electron spectroscopy for chemical analysis), are the best available
physical methods. Bansal et al. (1988) has suggested that carbons prepared
by various pyrolytic processes were like condensed aromatic hydrocarbons,
and possess the properties of Lewis bases (electron donors) that preferentially
exchange hydrogen ions for hydroxyl ions from aqueous solution. As a result,
the surrounding liquid will have an excess of hydroxyl ions responsible of the basic character of such carbons.

**Neutralization with bases**

This method is one of the earliest and simplest methods developed to identify and quantify carbon acidic surface groups using bases with varying neutralization potential. The alkali used should be sufficiently strong (0.1-0.2 N) and the contact time should be long enough (24-72 hr) to obtain reproducible neutralization endpoints. These endpoints are established from titration curves and help determine the amount of specific functional groups present. Functional group identification is based on *relative* acidity of the group and the base used for the titration of the specific group. Four bases (sodium bicarbonate, sodium carbonate, sodium hydroxide, sodium ethoxide) of different neutralizing potential are used to titrate acidic groups of various strength. The strongly acidic groups neutralized by sodium bicarbonate (NaHCO₃) were postulated as carboxylate groups, whereas those neutralized by sodium carbonate (Na₂CO₃) but not by NaHCO₃ were believed to be lactones. The weakly acidic groups neutralized by sodium hydroxide (NaOH) but not by NaHCO₃ were postulated as phenols. The most weakly acidic groups on the carbon reacted with sodium ethoxide (C₂H₅ONa) but not with NaOH and these were thought to be carbonyls (Bansal et al., 1988).
**Electrochemical titration**

Electrochemical titrations are more advantageous than titration with different bases because they require very little sample and can measure very low acidity values due to the sensitivity and accuracy by which an electrical current can be measured. The procedure consists of preparing a suspension of carbon in carbon dioxide-free distilled water. Standard base is added in small quantities to the suspension and small changes in pH are recorded using a precision pH-meter. Bases such as NaOH, barium hydroxide [Ba(OH)\(_2\)], NaHCO\(_3\), or Na\(_2\)CO\(_3\) can be used. The resulting titration curve (pH vs. mEq/100g of base) provides an estimation of the pK\(_a\)'s by which the different functional groups can be identified. Acidic groups with pK\(_a\)'s below 7 are postulated as carboxylate moieties, while weaker acids such as phenols have pK\(_a\)'s between 9 and 10. The carbon titration curve can provide a check for the existence of lactones after the carbons have been esterified with n-butanol followed by acid hydrolysis (Bansal et al., 1988).

**Fourier transform infrared spectroscopy**

Infrared (IR) spectroscopy refers to measurements of the absorption of different frequencies of infrared radiation by foods or other solids, liquids or gases (Wehling, 1998). Infrared radiation is electromagnetic energy with wavelength longer than visible but shorter than microwave. IR radiation is often measured in wavenumber (reciprocal of the frequency of radiation). When molecules absorb IR energy, they move to a higher excited state with
each functional group within the molecule absorbing IR energy in distinct wavelength bands rather than as a continuum. Absorption of IR energy by a given functional group occurs at a specific wavenumber and causes vibrational modes such as stretching or bending of the covalent bonds between atoms.

Fourier transform IR is a popular technique in which the radiation is not dispersed and all wavelengths arrive at the detector simultaneously. A mathematical treatment called a Fourier transform is then used to convert the result into a typical IR spectrum (Wehling, 1998). Fourier transform infrared spectroscopy (FT-IR) is a valuable tool in the study of surface chemistry of highly adsorbing materials such as carbon. The success of FT-IR is due the fact that it is one of the few methods that allow direct examination of the adsorbed molecules on solid surfaces. This technique offers considerable advantage over conventional dispersive infrared methods for the characterization of highly porous solids such as carbon. The use of an interferometer rather than dispersive grating or prism allows more energy to reach the detector, thereby improving the spectrum (Ferraro and Basile, 1982; Zawadski, 1989). As such, FT-IR can be used to detect surface functional groups at relatively low concentrations. Based on the wavenumber of the absorption bands, a shift in band frequency, and the strength of absorption, studied by the removal of characteristic bands at various temperatures, the absorbing functional group can usually be identified. The quantity of the absorbed species can be determined from the intensity of the
absorption bands. Different functional groups adsorb IR radiation at characteristic wavenumbers (cm\(^{-1}\)). For example, carboxyl groups absorb at 1720 cm\(^{-1}\), while lactones absorb in the 1750-1790 cm\(^{-1}\) range, and quinones absorb at 1580 cm\(^{-1}\). Water absorbs at 3430 cm\(^{-1}\), while the wavenumber region of 1400-1450 cm\(^{-1}\) is characteristic of C-O stretching, 1585 cm\(^{-1}\) is assigned to the C-C stretching mode, and 1480-1340 cm\(^{-1}\) is characteristic of O-H bending vibrations (Bansal et al., 1988; Sellitti et al., 1990).

When compared to the observed absorption bands characteristic of oxygen surface compounds on various carbons, the FT-IR spectra of carbon should provide useful information regarding the identification and magnitude of its surface groups.

**X-ray photoelectron spectroscopy**

This technique measures the kinetic energy of electrons emitted from atoms under the influence of irradiation with X-rays. Such energy is related to the binding energy of the electron, which in turn is dependent upon the chemical environment of the atom from which the electron has been emitted (Bansal et al., 1988). X-ray photoelectron spectroscopy (XPS or ESCA) is an ideal technique for the study of the carbon surface and of the molecules adsorbed on its surface. However, due to the limited penetration depth from which photoelectrons emerge (10-15 nm), XPS has been mainly used to study the surface chemistry of carbon fibers. Despite this limitation, many researchers believe that XPS will also apply to activated carbon surfaces as
well, especially to powdered activated carbons of small mesh size. Like FT-IR, XPS analysis yields spectra with characteristic peaks that can be assigned to specific atoms in a particular chemical environment. For example, assignments have been made for the C-H bond at 285 eV binding energy, C-O at 288.5 eV, C-OH at 286 eV and C=O at 287 eV binding energy. (Bansal et al., 1988).

APPLICATION OF ACTIVATED CARBON IN SUGAR REFINING

Activated carbons have been extensively used in drinking water purification, removal of organics and heavy metals from industrial wastewater, food processing to remove taste, odor and/or color, and in pharmaceutical purifications (Table 1.1). This investigation will be, however, limited to the use of carbons to decolorize raw sugar during the process of refining.

Processing of cane sugar is generally carried out in two stages, which are the crystallization of the clarified/concentrated juice into raw sugar, and the refining of the raw sugar to produce white sugar. Raw sugar decolorization is the major step in the refining process. The removal of coloring matter from raw sugar in a refinery is achieved by one or more of the following processes: affination, clarification, decolorization (by adsorption), and crystallization followed by centrifugation. Of these, decolorization by adsorption is the final purification step in the manufacture of white sugar (Valter, 1970; Chou, 1985). The typical process of sugar decolorization consists of passing clarified raw sugar liquor through vertical columns packed with activated carbon.
### Table 1.1: Selected applications of activated carbons

<table>
<thead>
<tr>
<th>SITUATION</th>
<th>PROBLEM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Industrial Application</strong></td>
<td></td>
</tr>
<tr>
<td>Acid purification</td>
<td>Color or end-product removal from by-product acid stream</td>
</tr>
<tr>
<td>Product purification</td>
<td>Decolorization or removal of contaminants</td>
</tr>
<tr>
<td><strong>Environmental Remediation</strong></td>
<td></td>
</tr>
<tr>
<td>Municipal wastewater treatment</td>
<td>Odor control</td>
</tr>
<tr>
<td>Incinerator flue gas</td>
<td>Mercury and dioxin emissions control</td>
</tr>
<tr>
<td>Fumigation venting</td>
<td>Phosphine emissions control</td>
</tr>
<tr>
<td>Chemical plant wastewater</td>
<td>Toxicity reduction, removal of odor, removal of organic and inorganic contaminants</td>
</tr>
<tr>
<td><strong>Food Processing</strong></td>
<td></td>
</tr>
<tr>
<td>Dextrose and high fructose com</td>
<td>Decolorization of end-product</td>
</tr>
<tr>
<td>syrup purification</td>
<td>Decolorization and removal of ash</td>
</tr>
<tr>
<td>Cane sugar refining</td>
<td></td>
</tr>
<tr>
<td>Process water treatment</td>
<td>Removal of taste, odor and organics</td>
</tr>
<tr>
<td>Decaffeination of coffee</td>
<td>Removal of caffeine in extract liquids</td>
</tr>
<tr>
<td>Glycerin purification</td>
<td>Removal of color and odor</td>
</tr>
<tr>
<td>Citric acid purification</td>
<td>Removal of odor</td>
</tr>
</tbody>
</table>

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The temperature and pH of the liquor are carefully controlled to prevent color formation. In addition, factors such as sugar concentration, liquor/carbon ratio, and time of contact are monitored to ensure optimal removal of sugar colorants.

**Colorants in cane sugar**

Colorants in cane sugar originate from two main sources: the sugarcane and the sugar refining process. Each cane sugar colorant is placed into one of four descriptive groups: 1) phenolics and flavonoids, 2) caramels, 3) melanoidins, and 4) alkaline degradation products of sucrose. In addition to these four groups, there are also color precursors. These are natural cane substances, which do not themselves exhibit color but will react with another non-colored compound to form a colored compound under favorable reaction conditions. Examples of these are amino acids, hydroxy acids, aldehydes, iron, and reducing sugars (Nick, 1992; Clarke et al, 1984; Carpenter, 1985). The phenolics and flavonoids come from the cane, where they exist as glycosides attached to sugar residues (Clarke et al., 1984). Smith and Gregory (1971) found that approximately two thirds of the color in raw sugar comes from the phenolics and flavonoid group. Some phenolics are not colored when they first come from the plant, but oxidize, complex, or react (sometime with an amine) to form colorants during processing. Cane colorants usually possess an electrostatic charge at high pH and, if unreacted, exhibit an average molecular weight of about 5 kDa (Clarke et al,
Molecules in the other chemical groups develop color during the refining process. These include caramels, melanoidins, and alkaline degradation products of the fructose moiety of sucrose. Caramels are known to originate from thermal degradation of glucose while melanoidins are formed through the Maillard reaction involving amine compounds and the alcoholic hydroxyl groups on the sugars.

**Removal of sugar colorants**

Decolorization has traditionally been accomplished with carbon adsorbents (bone char), although additional materials (i.e. anion exchange resins) have also been used. The removal of colorants generally employs one or a combination of the following three mechanisms:

1) Adsorption through hydrophilic bonding, such as aromatic colorants removed by activated carbon.

2) Ion exchange through ionic functional groups, such as charged colorants removed by ion exchange resins. This is appropriate for acidic colorants retained by anion-exchange resins.

3) Precipitation followed by occlusion and/or adsorption via van der Waals forces. During the precipitation process, colorants form complexes with ammonium salts or metals such as Ca(II). The remaining color is then trapped into crystal or porous adsorbents (Carpenter, 1985).
The classes of carbon adsorbents that are used at present and the materials with which they are effective are:

1. Bone char, used to remove colorants, and metals (ash).
2. Granular activated carbons, used to remove organic colorants.
3. Powdered activated carbons, used to remove colloids and colorants (Carpenter, 1985).

The adsorption of color has been shown to be an equilibrium reaction in which materials other than coloring agents assist or take part. In addition, sugar colorants are a mixture of many different components, each with a different adsorptive potential. Therefore, it is impossible remove all types of colorants with a single adsorbent. In general, colorants can be classified according to their charge and molecular structure. Four classes can be cited:

1) Ionic/aromatic colorants: These include colorants having ionic functional groups and basic aromatic structure. This type of colorant can be removed by ion exchange resins or by activated carbon.
2) Non-ionic/aromatic colorants: These, highly aromatic in nature, with no ionic groups, can be removed by activated carbon.
3) Ionic/non-aromatic colorants: This type possesses an ionic functional group and an aliphatic molecular structure. Due to its aliphatic structure, this group is most effectively removed through ion exchange.
4) Non-ionic/non-aromatic: This represents a small group of colorants that are difficult to remove unless the non-aromatic fraction is highly conjugated (Carpenter, 1985).

**Adsorption theory**

Adsorption is a process in which a molecule is transferred from solution to the surface of a solid whereon the molecule is held on the surface by physical/chemical forces. Various forces exist between molecules in proximity to a solid surface and the surface molecules, all having their origin in the electromagnetic interactions of nuclei and electrons. Two types of binding forces are commonly distinguished: physiosorption and chemosorption. A third type of binding force, electrostatic interaction, is encountered in the interaction between ions and charged functional groups on solid surfaces, as manifested in ion exchange operations (Weber and Vliet, 1980).

Physical adsorption results from the action of van der Waals forces, comprised of London dispersion forces and classical electrostatic forces. In physical adsorption, the electron distributions of adsorbate molecules and solid surface molecules undergo some distortion in mutual proximity; however, the electrons maintain their association with the original nuclei. The continuous motion of electrons in atoms and molecules effect rapidly fluctuating temporary dipole and quadripole moments. Such fluctuating dipole and quadripole moments in molecules (or atoms) approaching a solid surface can perturb the electron distribution of surface molecules to induce temporary
dipoles and quadripoles therein, and conversely. This leads to attractive interactions between the adsorbent and adsorbates. These attraction potentials are nonspecific and operate between polar and nonpolar molecules (atoms), and covalent, metallic and ionic solid surfaces (Weber and Vliet, 1980). The overall van der Waals physical adsorption interaction generally also includes the contribution of classical electrostatic interactions.

The second important category of solute-solid surface interaction is that of chemosorption. As a result of significant solute-surface affinity, molecular orbital overlap occurs between molecules in the respective phases. Transfer and sharing of electrons take place between adsorbed solute and adsorbent forming chemosorptive bonds, which can have all the characteristics of chemical bonds (Weber and Vliet, 1980). The chemosorptive bond is localized at active centers on the adsorbent and it is usually stronger than the physical forces. Chemosorption is favored by higher temperature, since chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures, while physical adsorption is usually dominant at low temperature. Unlike physicosorption, chemosorption is not reversible. The reversibility of physical adsorption depends on the strength of attractive forces between adsorbate and adsorbent and if these forces are weak, desorption is readily affected (Sing, 1989). Adsorption of solutes on solid surfaces is affected by the nature and interaction of adsorbent-adsorbate and external condition such as pH and temperature.
Adsorbents are generally characterized by high surface area, to provide sufficient active sites to allow a substantial concentration of solute to be sorbed. They usually possess high porosity to provide readily available access sites to the diffusing molecules (Jaroniec et al., 1989). Regarding the solute, there are many factors that determine the extent of adsorption. These include concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric hindrances and the nature of the competitive solutes.

**Adsorption of sugar colorants by GACs**

The mechanism by which sugar colorants are adsorbed onto a carbon surface may be divided into four consecutive steps: 1) dispersion, 2) interparticle film diffusion, 3) intraparticle diffusion, and 4) adsorption onto surface sites. The diffusion of the color components is a function of the temperature and viscosity of the sugar solution, and the molecular size of the colorants (Chou, 1982). Adsorption is achieved when a physical or chemical bond forms between the adsorbate and the internal carbon surface. The adsorption of color can be also influenced by the solution pH. This is because most colorants in raw sugar are natural dyes that increase in color intensity with increased pH and become less colored at lower pH (Hassler, 1963). In a solution at low pH, most acidic colorants are in their non-ionized form. When acidic colorants react with base, they are ionized, giving various anionic species which are adequately adsorbed by activated carbon (Chou, 1985).
The large surface area provided by activated carbon allows colorants to interact with the carbon surface by a variety of molecular forces, the primary one being van der Waals' forces. Van der Waals' forces depends on the potential energy of a molecule about to be adsorbed as it approaches the surface of an adsorbent. The size and shape of the granular activated carbon pores affects the type of molecule that will be trapped or adsorbed. Small pore size will not trap large molecules and large pores may not be able to retain small molecules (Luhr, 1991). According to Hassler (1963), the factors influencing adsorption at carbon-liquid interface are generally: 1) attraction of carbon for solute, 2) attraction of carbon for solvent, 3) solubilizing power of solvent for solute, 4) association, 5) ionization, 6) effect of solvent on orientation at an interface, 7) competition for the interface in the presence of multiple solutes, 8) interactions of multiple solutes, 9) coadsorption, 10) molecular size of other molecules in the system, 11) pore size distribution in the carbon, and 12) carbon surface area.

Adsorption of sugar colorants by activated carbon is a function of the following factors:

1) Time of contact between sugar solution and carbon. Removal of sugar colorants increases with increased time of contact. The rate of adsorption of color from a sugar solution is rapid during the first interval of contact but gradually reaches a point where increased time of contact results in no further decolorization.
Thus, the choice of an optimal time of contact is critical to achieve an efficient sugar decolorization process.

2) Temperature of treated liquor. There is an increase in color removal at temperatures up to 90°C. The color may increase with higher temperatures (> 90°C) due to the formation of heat induced colorants. Therefore, temperature of sugar liquor has to be monitored and maintained around 90°C to ensure efficient color removal and minimize new color formation.

3) Concentration of test liquor. The percentage of color removed varies inversely with increasing concentrations of the test liquor. As the concentration of sugar solution increases, its diffusion in the carbon matrix slows down causing a reduction of color removal achieved for fixed contact time and temperature.

4) Percentage of carbon used. When time of contact and temperature are fixed, the percentage of total color removed varies directly with the percentage of carbon used. Color removal continues to increase linearly with increasing carbon/sugar liquor ratios up to a ratio where the decolorization reaches a maximum after which the rate of color removal remains the same regardless of the amount of activated carbon added.

5) pH of sugar solution. The more acidic a solution is, the greater is the adsorption of caramel, negatively charged color bodies and colloids, while alkalinity favors adsorption of electropositive substances (Nakhla et al., 1994).
Measurement of sugar color

Raw sugar color is measured according to the standards of the International Commission of Uniform Methods of Sugar Analysis (ICUMSA) enumerated under method 4. Factors that affect color determination include:

1) Solution Brix. The refractive index of any solution changes with its Brix (percentage of dissolved sucrose). Refractive index is higher for low Brix sugar solutions and may induce erroneous color measurement. To minimize the refractive index impact, ICUMSA recommends the use of sugar solutions of 50 Brix or greater for color determination.

2) Sample turbidity. The scattering of light should be minimized for more reliable color readings (Carpenter, 1986). For this, ICUMSA recommends that light-colored sugar solutions be filtered through 0.45 nm membrane filters to reduce the turbidity effect on measured color.

3) Wavelength. Adsorption changes rapidly with variations in wavelength. It is, therefore, essential to specify the wavelength at which color measurements are made. ICUMSA uses 420 nm for white sugars and 560 nm for darker colored products. The use of a spectrophotometer with a very narrow band width is also recommended to minimize light absorption changes due to variations of wavelength caused by instrumental error (Chou, 1985).

4) Solution pH. Sugar colorants are sensitive to pH. Therefore, for color comparison of various sugars and sugar products, all colors should be measured at a specified pH. For this, ICUMSA recommends a pH of 7±0.03
(ICUMSA, 1994). However, in the currently used ICUMSA method for color determination, the major source of error is from pH fluctuations during the color measurement process. This is due to the existence of a pH-sensitive fraction among sugar colorants. The color intensity of the pH-sensitive fraction will vary through changes in molecular structure and association/dissociation equilibria (Smith and Gregory, 1971). Within the above pH sensitive fraction, phenolics and flavonoids have the greatest pH sensitivity because of the molecular rearrangements that can occur in alkaline conditions causing a series of conjugated double bonds responsible for visible color (Clarke et al. 1985). The necessity of pH adjustment is illustrated by the fact that an error of 0.1 pH unit in the adjustment at pH 7.0 results in an error of 5% or more in the color reading (Chou, 1985). Ahmedna et al. (1997a) also found that color measurement was affected by slight changes in pH in unbuffered solutions, which was attributed to the type of filter used. These authors proposed the use of a specific buffer to minimize pH fluctuation during color measurement.

**PROPERTIES OF ACTIVATED CARBONS RECOMMENDED FOR SUGAR DECOLORIZATION**

Physical, chemical and surface characteristics of activated carbon determine its efficiency in removing the targeted sugar colorants through the process of adsorption. Among these characteristics, the following are particularly important to sugar decolorization.
Physical properties

Particle size

The smaller the particle size of a porous carbon, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size decreases, because of the shorter mass transfer zone, causing a faster rate of color adsorption (Cookson, 1978). Powdered activated carbon mixes intimately with liquid providing a higher contact area than granular activated carbon and, therefore, has better decolorizing power. However, very fine powdered carbon, that is, the fraction that can pass through a No. 70 sieve, is undesirable and is discarded as dust because these particles adversely affect filtration flow rate and promote channeling (Carpenter, 1985). This causes shorter filter cycles and increases carbon treatment cost. Therefore, it is essential that carbon particles be of the correct size and structure to act as good filter aids and to reduce pressure drop during filtration. A carbon with proper particle size should form a good filter cake and should not require additional materials such as Fuller's earth to aid in filtration.

Bulk density

Density is particularly important in sugar decolorization where high viscosity syrup is displaced through a column of activated carbon. Bulk density is important when carbon is removed by filtration because it determines how many pounds of carbons can be contained in a filter of a given solids capacity and how much treated liquid is retained by the filter cake (Hutchins, 1988).
In addition, when two carbons differing in bulk density are used at the same
weight per liter, the carbon having higher bulk density will be able to filter more
liters before the available cake space is filled. Carbons with an adequate
density also help to improve the filtration rate by forming an even cake on the
filter surface. Generally, a carbon with a bulk density of about 0.5-0.6 g/mL
is adequate for sugar decolorization. Bone chars, currently used for sugar
decolorization, have a bulk density of about 0.6 g/mL (Carpenter, 1985).

**Hardness**

A carbon should possess sufficient mechanical strength to withstand
the abrasion resulting from continued use. In the course of carbon usage,
particle breakdown and dust formation occurs due to the continuous
mechanical friction between carbon particle and sugar liquor. Dust formed by
attrition is undesirable because it slows down the filtration rate and decreases
the amount of regenerated carbon. Therefore, carbons designed for sugar
decolorization should have enough abrasion resistance to minimize attrition.

**Chemical properties**

**pH**

Activated carbon pH may influence color by changing the pH of the
sugar solution. Such a change affects the pH-sensitive fraction of solution
colorants, causing unreliable color measurements (Ahmedna et al., 1997a).
Moreover, acid carbons, for example, may be a better decolorizer (Paton and
Smith, 1983); but a sugar refiner would seldom employ a highly acidic carbon
because the acid would cause inversion of sucrose to noncrystallizable sugars, with subsequent lower yield (Mantell, 1946). Bemardin (1985) reported that, in sugar decolorization, a distinctly acidic activated carbon may cause inversion of sucrose and a distinctly alkaline carbon may cause color development through alkaline degradation of organic impurities. Hence, a carbon pH of 6-8 is acceptable for most applications.

Ash (minerals)

Ash content of carbon is the residue which remains when the carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered an impurity. Ash leached into sugar liquor during the process of decolorization is known to cause uneven distribution of heat in the boiler during sugar crystallization. Ash may also interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. For instance, the ash content may affect the pH of the carbon since the pH of most commercial carbons is produced by their inorganic components. Usually, materials with the lowest ash content produce the most active products.

Surface properties

Because adsorption is essentially a surface or interfacial phenomenon, the surface characteristics of activated carbons are of major importance. Total surface area, pore distribution and surface chemistry are the three major
characteristics of carbon surface that greatly affect raw sugar decolorization.

**Surface area**

Activated carbon has the highest adsorptive porosity of any material known to man. Because of its large surface area (1 quart of granules = 6 football fields of area), activated carbon has a great ability to adsorb organic and inorganic molecules from liquids or vapors (Roy, 1995). Thus, activated carbons are unique and versatile adsorbents that are widely used because of their extended surface area (Bansal et al., 1988). The most widely used of commercially available carbons have specific surface area on the order of 800 to 1200 m$^2$/g. This extensive surface area is almost exclusively microporous (Weber and Vliet, 1980). Surface area is, therefore, the single most important characteristic of activated carbon designed for adsorption of compounds from liquid or gas media. Large surface area is generally a requirement for a good adsorbent. However, the total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species.

**Pore size distribution**

Activated carbon is a complex network of pores of varied shapes and sizes. The shapes include cylinders and rectangular solids, as well as many irregular shapes. As previously discussed, activated carbon pores are classified into three groups according to their diameters, namely, micropores, mesopores and macropores. The assortment of pore sizes is called pore size distribution and depends on the carbon source material and on the method
and extent of activation. An activated carbon with large surface area may absorb very rapidly, but its adsorptive capacity could be low because it lacks the right pore volume to contain the adsorbed material (Patrick, 1995). Carbons with small pores are suitable for the removal of molecules having small molecular weights and usually cannot remove high molecular weight compounds. In contrast, larger pores may not be able to bond small molecules tightly enough, but are suitable to trap large molecules. The intraparticle surface of activated carbon (micropores) consists primarily of the basal planes of the microcrystallite, exposed during activation. The basal plane is likely to be relatively uniform in nature and are not likely to contain functional groups because the electrons of the carbon atoms are involved in covalent bonding with neighboring carbon atoms. Adsorption at this type of surface occurs predominantly as a result of physical van der Waals interactions. In contrast, surface area generated by the more reactive edges of the graphitic planes of the crystallite are likely to contain functional groups to which color compound can be chemosorbed. Since molasses contains color compound that are similar in sizes and polarities to those found in raw sugar, the molasses test is generally used as an indicator of the suitability of a given carbon as sugar decolorizer. A good adsorption of molasses colorants usually indicates good sugar decolorization efficiency (Hassler, 1963; Mantell, 1946; Luhr, 1991).
**Surface chemistry**

As previously discussed, the surface area generated by the more reactive edges of the microcrystallites will contain a wide variety of functional groups which are likely to form the bases for chemosorptive interactions and also for "specific adsorption" (Weber and Vliet, 1980). The nature of the functional groups is determined to a large extent by the method of activation as well as by the type of raw material from which the carbon is produced. Operational conditions during activation of carbon, notably temperature, will have a major effect on the type of oxides that will form. Carbons activated below 500°C will develop predominantly acidic surface oxides, while those activated at temperature around 800-1000°C will develop basic surface (Weber and Vliet, 1980). The presence of surface oxygen complexes will impart a polar character to the activated carbon surface, which should affect preferential adsorption of polar organic solutes. The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption between ionic adsorbates and the activated carbon. Although raw sugar colorants are made up of a complex mixture of polydispersed compounds of differing molecular size and net charges, sugar colorant are predominantly anionic. Therefore, the diversity of functional groups on the carbon surface affect the surface behavior of carbon and thus enhance or reduce the affinity of carbon to the adsorbed raw sugar colorants via electrochemical mechanisms.
CHAPTER 2
PRODUCTION OF GRANULAR ACTIVATED CARBONS FROM AGRICULTURAL BY-PRODUCTS AND EVALUATION OF THEIR PHYSICAL, CHEMICAL AND ADSORPTION PROPERTIES

INTRODUCTION

Activated carbons can be prepared from a large variety of carbon-containing feedstocks by the activation of an initially pyrolyzed char. The most common feedstocks for the commercial production of activated carbons are wood, anthracite and bituminous coal, lignite, peat, and coconut shells (Pollard et al., 1992). Lignocellulosic waste materials have been recognized as starting materials for the preparation of activated carbons. High volume agricultural by-products such as sugarcane bagasse, rice straw, soybean hulls, rice hulls and nutshells are lignocellulosic wastes that may offer an inexpensive and renewable source of activated carbons. Such carbons may have the potential to replace existing coal-based carbons for use in many industrial applications such as the removal of color and odor compounds in aqueous systems and removal of heavy metals from wastewater.

Physical, chemical, and adsorption properties of activated carbon determine its efficacy in removing targeted compounds, e.g. sugar colorants. Physical and chemical characteristics that are important for sugar decolorization include surface area, particle size, bulk density, hardness, pH, and ash. These properties vary depending on the precursor and
pyrolysis/activation conditions used to produce activated carbons (Gergova et al., 1992; Mackay and Roberts, 1982; Mattson and Mark, 1971; Rodriguez-Reinoso and Molina-Solano, 1989). Activated carbons can be powdered or granular. Granular activated carbons (GACs) are generally considered more versatile than the powdered carbons due to their regenerability. Because of their versatility, GACs command a large percentage of the carbon market (Activated Carbon Markets, 1994), especially for raw sugar decolorization.

The type of agricultural by-product is important in determining its suitability for GAC production. Agricultural by-products used as precursors in carbon production can be classified into two groups. Group 1 materials consist of soft compressible waste products of low density, such as sugarcane bagasse, rice straw, soybean hulls, peanut shells, and rice hulls. To make a good precursor for production of GACs, group 1 materials must be mixed with suitable binder and compressed into briquettes or pellets to increase the density of the final product (Johns et al., 1998). In contrast, group 2 materials, such as nutshells from pecan and walnut, are hard, dense and not easily compressed. Group 2 by-products are also suitable as GAC precursors without binder or briquette formation.

Rice hulls, rice straw, and sugarcane bagasse, by-products from economically important Louisiana crops, have been used as a source of powdered activated carbons by several authors (Pollard et al., 1992; Youssef and Mostafa, 1992; Tecker et al., 1997; Lavarack, 1997; Bernardo et al., 1997;
Mackay and Roberts, 1982a). However, limited knowledge is available on the production of granular activated carbons from these agricultural by-products. Production of GACs from these soft materials uses binders to ensure intimate contact of the lignocellulosic particles during pyrolysis. Coal tar is the binder commonly used in the production of coal-based granular activated carbons. Sugarcane molasses, a by-product of sugar refining, has been used as a binder in various agricultural by-products to produce GACs (Arida et al., 1992; Grigis et al., 1994; Ahmedna et al., 1997b; Johns et al., 1998; Pendyal et al., 1999a). Similarly, other liquid by-products, such as sugar beet molasses and corn syrup, can also be used as binders for the production of GACs from group 1 by-products (Pendyal et al., 1999a).

One particular group 2 material, coconut shells, has been used as a commercial source of GACs for years. Recently, several studies (Toles et al., 1997; Toles et al., 1998) have demonstrated that other nutshells make excellent GACs for metals adsorption, and also show promise in removal of sugar colorants (Ahmedna et al., 1997b).

Our laboratory has recently determined the physical, chemical and adsorptive properties of GACs made from sugarcane bagasse, rice straw and rice hulls along with the binders coal tar, corn syrup, sugarcane molasses, and sugar beet molasses (Pendyal et al., 1999a; Pendyal et al., 1999b). We found that the presence of specific binders influenced the physical and chemical properties of the resultant carbons, while adsorption of sugar colorants was
dictated by the by-product, and not the binder. The by-product/binder combinations with the best physical/chemical or adsorptive properties were employed in this study, albeit under different activation conditions. Our choice of pecan shells as the group 2 representative was based on the promising results for pecan shell-based carbons as sugar decolorizers in an earlier study from our laboratory (Ahmedna et al., 1997b) and also on the fact that pecan are Louisiana number one tree nut crop.

The objectives of this study were to (1) produce GACs using representative feedstocks from groups 1 and group 2 agricultural by-products that had shown promising results in previous studies from our laboratory, (2) determine the physical/chemical and adsorption properties of by-product-based carbons along with those of two commercial carbons, and (3) select the best by-product-based carbons from each group based on their similarities to the reference carbons using principal component and cluster analyses.

MATERIALS AND METHODS

Materials

Agricultural by-products were obtained from the following sources: sugarcane bagasse (SB) from Audubon Sugar Institute, Louisiana State University Agricultural Center, Baton Rouge, LA; Rice hulls (RH), and rice straw (RS) from Supreme Rice Mill, Crowley, LA and pecan shells (PS) from Sun Diamond of New Mexico, Las Cruces, NM.
Binders were procured from the following sources: sugarcane molasses (CM) from Alma Sugar Company, Baton Rouge, LA; sugar beet molasses (BM) from American Crystal Sugar Company, Moorhead, MN; corn syrup (CS) from A. E. Staley Manufacturing Company, Decatur, IL; and coal tar pitch (CT) from Koppers Industries, Follarsbee, WV.

The reference carbons were Calgon CPG-LF and Cane Cal from Calgon Carbon, Pittsburgh, PA. The commercial GACs were made from bituminous coal with coal tar as a binder and were selected on the basis of manufacturer recommendations as excellent decolorizers of organic liquids such as raw sugar liquors (Calgon, 1987).

Methods

Preparation of granular activated carbons

Group 1 by-products (sugarcane bagasse, rice hulls and rice straw) were milled in a hammer-cutter mill (Glen Mills Inc., Clifton, NJ) to 5-10 mesh size (US standard sieve).

Sugarcane bagasse was mixed with each one of four binders (sugarcane molasses, sugar beet molasses, corn syrup and coal tar), while rice hulls were blended with sugarcane molasses or coal tar and rice straw was mixed with corn syrup or coal tar in a by-product/binder ratio of 1:0.5 (w/w). Sugarcane molasses, sugar beet molasses and corn syrup were heated to 80°C, then combined with the by-products in a laboratory mixer until homogeneous. The blends were cooled to room temperature and placed in stainless steel cylinder.
of 5.7 cm diameter and 7.0 cm height. A pressure of 5000 psi was applied to the cylinder contents by means of a laboratory press (F.S. Carver Inc., Wabash, IN) for 5 min. to form briquettes. The coal tar pitch was heated to 140°C during mixing. The hot blend was quickly added to the cylinder and pressed into briquettes before the coal tar could solidify. All briquettes were stored at room temperature for 2-3 days. Briquettes were pyrolyzed in an atmosphere of nitrogen gas at 750°C for 1 hr using an inert atmosphere furnace (Model BAF-8128, Grieve Corp., Round Lake, IL) with retort. The pyrolyzed samples were cooled overnight in the furnace in a nitrogen atmosphere. The pyrolyzed briquettes were crushed and sieved to produce samples of 12-40 mesh particle size. The granules were activated in the same furnace at 900°C using gas mixtures of 13% CO\(_2\) and 87% N\(_2\) until approximately 30% burn-off was achieved which occurred between 4 and 20 hrs depending on the binder used. The GACs were cooled overnight in the furnace under nitrogen gas then washed with 0.1 N HCl to remove surface ash particles. The GACs were water washed until the slurries reached pH 6-8. GACs were subsequently dried overnight at 50°C. Carbon yields recorded for these samples were 47% to 52%, 25% to 30%, 24% to 26%, and 25% to 31% for the GACs made from group 1 by-products using coal tar, cane molasses, corn syrup, and beet molasses, respectively.

Pecan shells were milled in a hammer-cutter mill (Glen Mills Inc., Clifton, NJ) to 10-20 mesh size (US standard sieve). Milled pecan shells were
subsequently pyrolyzed and activated by either physical activation or chemical activation as described below, using an inert atmosphere furnace with retort.

Physical activation was achieved by pyrolyzing pecan shells in an atmosphere of nitrogen gas at 700°C for 1 hr. Upon pyrolysis, the resulting char was immediately activated at 900°C using gas mixtures of 13% CO₂/87% N₂, 30% CO₂/70% N₂ or 75% CO₂/25 % N₂ for a duration of 2 to 8 hrs. The GACs were cooled overnight in the furnace under nitrogen gas, then washed and dried overnight at 50°C. Yields for carbons produced by physical activation were 14% to 26%.

Chemical activation was carried out by soaking milled pecan shells in either 25% or 50% H₃PO₄ (w/w) for 2 hrs at room temperature. Phosphoric acid-shell mixture was pyrolyzed at 170°C for ½ or 1, hr then activated at 450°C for 1 hr. Activation of the char was carried out under nitrogen gas or air. Activated carbon was subsequently cooled overnight under nitrogen gas, washed in a soxhlet extractor until no residual phosphoric acid was present as shown by the absence of a precipitate when 10 drops of 0.01 M lead acetate was added to 100 mL of the final wash water. The GACs were then dried overnight at 50°C before use. Final yields for chemically activated pecan shells were 37% to 41%.

Table 2.1 summarizes the pyrolysis and physical and chemical activation conditions for the production of pecan shell-based activated carbons.
Table 2.1: Pyrolysis and activation conditions for the production of pecan shell-based granular activated carbons

<table>
<thead>
<tr>
<th>Activated Carbons</th>
<th>Pyrolysis Conditions</th>
<th>Activation Type</th>
<th>Activation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS18</td>
<td>1 hr at 800 °C under N₂</td>
<td>Physical</td>
<td>2 hr at 800 °C under 30% CO₂</td>
</tr>
<tr>
<td>PS23</td>
<td>1 hr at 700 °C under N₂</td>
<td>Physical</td>
<td>6 hr at 800 °C under 75% CO₂</td>
</tr>
<tr>
<td>PS9</td>
<td>1 hr at 700 °C under N₂</td>
<td>Physical</td>
<td>8 hr at 800 °C under 13% CO₂</td>
</tr>
<tr>
<td>PS22</td>
<td>1 hr at 700 °C under N₂</td>
<td>Physical</td>
<td>4 hr at 800 °C under 75% CO₂</td>
</tr>
<tr>
<td>PS26</td>
<td>2 hr soak in 25% H₃PO₄ (w/w) then ½ hr at 170 °C under N₂</td>
<td>Chemical</td>
<td>1 hr at 450°C under air</td>
</tr>
<tr>
<td>PS24</td>
<td>2 hr soak in 50% H₃PO₄ (w/w) then ½ hr at 170 °C under N₂</td>
<td>Chemical</td>
<td>1 hr at 450°C under air</td>
</tr>
<tr>
<td>PS11</td>
<td>2 hr soak in 50% H₃PO₄ (w/w) then 1 hr at 170 °C under N₂</td>
<td>Chemical</td>
<td>1 hr at 450°C under N₂</td>
</tr>
<tr>
<td>PS10</td>
<td>2 hr soak in 50% H₃PO₄ (w/w) then ½ hr at 170 °C under N₂</td>
<td>Chemical</td>
<td>1 hr at 450°C under N₂</td>
</tr>
</tbody>
</table>
Measurement of physical properties: Apparent (bulk) density, hardness, and surface area

Apparent (bulk) density was determined by filling a 10-mL tube with dry activated carbon. The tubes were capped, tamped to a constant (minimum) volume by tapping on a table, and weighed. The apparent density of 30-mesh size activated carbon was calculated by:

\[
\text{Apparent density (g/cm}^3\text{)} = \frac{\text{Weight of dry sample (g)}}{\text{Volume of packed dry material (cm}^3\text{)}}
\]

To determine hardness of the carbons, 2 g of 30-mesh activated carbon was weighed, placed in a 250-mL Erlenmeyer flask, and 10 glass marbles (15 mm diameter, 5.41 g each) were then introduced into each flask. The flasks were capped and placed in an Aquatherm water bath shaker (New Brunswick Scientific Co., Edison, N.J.). The samples were shaken at 200 rpm for 20 minutes at 25°C and then screened through a 30-mesh screen. The material retained by the screen was weighed and the hardness number calculated as follows:

\[
\text{Hardness number} = \frac{\text{Weight of carbon retained by screen (g)}}{\text{Initial sample weight (g)}} \times 100
\]

Two hundred to 300 mg of both commercial and experimental carbons were dried under vacuum at 110°C for 3 hr to remove moisture from the carbon pores.

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Surface area measurements using the BET method were obtained from nitrogen adsorption isotherms at 77° K using a Micromeritics Gemini III 2375 Surface Area Analyzer (Micromeritics, Inc., Norcross, GA).

**Measurement of chemical properties: ash, pH and conductivity**

Total ash was determined using crucibles containing a known amount of carbon placed overnight in a circulating air oven set at 115°C. After cooling in a desiccator, crucible and contents were weighed and placed in a Jelrus furnace (Jelrus Technical Products, NY.). The samples were heated to 950°C for 1.5 hr with a current of air circulating over them. The crucibles were then allowed to cool in a desiccator and weighed. The residue weight was calculated and reported as percentage of ash.

One percent (w/w) suspensions of activated carbons in water were heated to 90°C and were subjected to continuous stirring for 20 minutes then cooled to room temperature. The pH of the suspension was subsequently determined with an Orion Research Digital Ionanalyzer, Model 601/A (Cambridge, MA.).

The presence of water leachable minerals were determined by electrical conductivity. To measure electrical conductivity, a 1% (w/w) carbon-water suspension was prepared. The mixture was stirred for 20 minutes, then the electrical conductivity of the suspension was recorded using a CDM3 conductivity meter (Radiometer, Copenhagen).
Measurement of adsorption properties: molasses test and raw sugar decolorization

The molasses test used was described by Ahmedna et al. (1997b). Ten g of blackstrap molasses together with 15 g of disodium phosphate was dissolved in 500 mL of water and sufficient phosphoric acid was added to give a pH of 6.5. The mixture was diluted to 1 L, then filtered through a thin layer of filter aid in a Buchner funnel.

Fifty mL of the test solution was put into a 250-mL beaker, 0.5 g of carbon (1% w/v) was added and the suspension stirred. Beakers were placed on a heating plate and the contents brought to a boil. A blank to which no carbon was added was prepared. The heated mixture was filtered through Whatman No. 5 filter paper and the color of the filtrate measured using a Gilford Response-II (UV, VIS) spectrophotometer with a 10-mm cell. The wavelength used was 420 nm at a band width of 0.5 nm.

The percent of adsorption was calculated by

\[
P. M. C. R. = \frac{\text{Absorbance of blank} - \text{Absorbance of sample with carbon}}{\text{Absorbance of blank}} \times 100,
\]

Where P.M.C.R. = Percent Molasses Color Removed.

The decolorization test was a modified version of the batch-type decolorization assay used by Domino Sugar (Amstar Corporation, 1993) as described by Ahmedna et al. (1997b).
Test liquors of 60 ± 0.2 Brix were prepared by dissolving a sufficient quantity of white sugar in 0.1 M 3-(N-morpholino)-2-hydroxypropane sulfonic acid (MOPSO) buffer, previously adjusted to pH 7.00 (Ahmedna et al., 1997a). The liquor's color was adjusted by addition of blackstrap molasses to reach an absorbance reading of 0.5 at 420 nm. Finally, the pH of the test liquor was checked to ensure that it was maintained at pH 7.00.

Samples of 50 g of 60 Brix sugar liquor were weighed into 100-mL beakers. A Teflon stirring bar was placed in each beaker. Beakers containing the test liquor were covered with watch glasses and placed in a water bath at 80° ± 1°C. Samples were subjected to moderate stirring at 160 rpm and heating until the test liquor reached 80° ± 1°C. At this point, 0.5 g of granular activated carbon was added to each sample (1% w/w). Stirring was continued for 20 minutes, maintaining the liquor temperature at 80 ± 1°C. At the end of 20 minutes, samples were removed and filtered through a buchner plastic funnel containing Reeves Angel 202 filter paper. About 1% (w/w) of filter aid (No.3 diatomaceous earth) was added to the filtrate. Filtrates containing filter aid were moderately stirred and heated until they reached 70°C. The samples were then filtered through a membrane filtration assembly containing Reeves Angel 202 filter paper. The filtrates were transferred to 250-mL beakers, their Brix measured, and their pH adjusted to 7.00, if necessary. Prior to color measurement, filtrates were passed through a 0.45-μm membrane to eliminate the black color caused by suspended carbon particles generated by
carbon attrition. The color of all samples was then measured at 420 nm by a Gilford Response-II (UV-VIS) spectrophotometer using a 10-mm cell. Along with the activated carbon samples, a blank containing the test liquor alone was subjected to the same experimental conditions. The color of the blank after stirring and filtration represents the original color of the standard test liquor and was used for the calculation.

The percent color removed by activated carbons was calculated by,

\[
\text{Percent color removed} = \frac{\text{Color of blank} - \text{Color of sample with carbon}}{\text{Color of blank}} \times 100
\]

Where, in each case color is calculated as follows:

\[
\text{Color} = \frac{(1000 \times \text{Sample absorbance})}{(\text{Corrected RDS} \times \text{Corrected RDS density})} \text{ ICUMSA Units}
\]

Where: RDS = Refractometric Dry Substance or Percentage of soluble solids (Brix);
Corrected RDS density = Relative density of sugar solution (20°C vs. 4°C);
Corrected RDS = Sample RDS * Correction factor, and

\[
\text{Correction Factor} = \frac{\text{Raw sugar Weight}}{\left(\frac{\text{Solvent RDS}}{100} \times \text{Solvent Weight}\right) + \text{Raw sugar Weight}}
\]
**Statistical analysis**

All experimental data were analyzed using the generalized linear model procedure of the Statistical Analysis System (SAS, 1988). Principal component analysis (SAS, 1989) was performed on the data to determine which experimental carbons were similar to the commercial GACs in terms of their combined physical, chemical and adsorption properties. The first and second principal components were used as the criteria for carbon ratings. In addition, cluster analysis (SAS, 1989) was used. Experimental carbons were divided into 3 clusters based on similarities with the reference carbons in terms of their individual properties (physical, chemical or adsorption) or combined properties.

**RESULTS AND DISCUSSION**

**Physical properties: Apparent (bulk) density, hardness, and surface area**

The highest bulk density among the experimental carbons was observed in carbons using coal tar (CT) as a binder (Figure 2.1). Regardless of the by-product, carbons using sugarcane or sugar beet molasses (CM or BM) or corn syrup (CS) as binders exhibited relatively low bulk densities. Carbons derived from pecan shell had bulk densities slightly lower than those of the reference carbons, with the chemically activated carbons generally showing the lowest bulk densities among the pecan shell-based carbons. The high bulk density of carbons containing coal tar can be attributed to coal tar’s high carbon content.
Figure 2.1: Bulk density of experimental and commercial carbons.
SB-BM, SB-CM, SB-CS, SB-CT = Sugarcane Bagasse with Beet Molasses, Cane Molasses, Corn Syrup, and Coal Tar, respectively; RH-CM and RH-CT = Rice Hulls with Cane Molasses and Coal Tar, respectively; RS-CS and RS-CT = Rice Straw with Corn Syrup and Coal Tar, respectively; CCAL and CPGLF are commercial reference carbons, and PS = Pecan Shells. The bars represent the means of duplicate determinations where the standard error for each measurement was less than 5%.
Coal tar has higher carbon content than molasses or corn syrup and, therefore, would be volatilized to a much lesser extent and undergo less weight loss than these binders (Pendyal et al., 1998a) yielding more compact (dense) material.

Physically activated pecan shell-based carbons and carbon samples containing coal tar as the binder showed the highest hardness numbers (Figure 2.2). Hardness of these carbons was similar to the commercial GACs. As with bulk density, the high carbon content of coal tar could have resulted in low volatilization of the briquettes containing coal tar, yielding a more compact carbon material with high hardness and limited porosity. The softest carbon was made with sugar beet molasses as binder. Similar observations were reported by Pendyal et al. (1998a), who found that carbons made with sugar beet molasses were soft and friable. These authors concluded that such soft carbons would not be suitable for decolorization because of their high attrition that could reduce the yield of carbon after regeneration and reduce the rate of filtration. The hardness of pecan shell-derived carbons varied depending on the conditions of activation. Physical activation appeared to consistently produce the hardest GACs, while chemical activation yielded relatively softer carbons.

Regardless of the binder used, group 1 by-products yielded carbons with limited surface area (Figure 2.3).
Figure 2.2: Hardness number for experimental and commercial carbons. See Figure 2.1 for carbon identification.
Figure 2.3: Total BET surface area of experimental and commercial carbons. See Figure 2.1 for carbon identification.
In contrast, carbons prepared from the group 2 by-product by chemical activation exhibited surface areas larger than for the reference carbons. Physical activation of pecan shells produced GACs with relatively lower surface area. The observed difference in surface area among the carbons investigated might be attributed to the nature of the precursor, the pyrolysis temperature and the type of activation (Mattson and Mark, 1971; Girgis et al., 1994). Mackay and Roberts (1982a) reported that different classes of lignocellulosic precursors are known to develop microporosity to different extents during pyrolysis. The same authors found that the components (lignin, cellulose) of lignocellulosic materials yield chars of similar microporosity, while inorganics (ash) may fill or block some portion of the existing micropore volume. This may partially explain the low surface area observed in carbons with high ash content. Furthermore, it is well known that the lignocellulosic composition of the precursors determines char yield and porosity due to the difference in thermal stability of the major components (lignin, cellulose, hemicellulose) (Mackay and Roberts, 1982a; Mackay and Roberts, 1982b; Mattson and Mark, 1971). In our case, the composition of by-products and binders would have affected the final surface characteristics of the experimental GACs. The method of activation is also another potential cause for the observed differences in surface area among the by-product-based carbons. When using the same precursor, carbons obtained by physical activation had lower surface areas than carbons obtained by chemical
activation. This is probably due to the mechanism by which pore formation is achieved by each activation method. Physical activation relies on diffusion of gases (CO₂) through the carbon matrix to drill, deepen, clear and/or volatilize impurities. In chemical activation, the chemical is introduced into the precursor, where it produces physical and chemical changes modifying the thermal degradation process (Rodríguez-Reinoso and Molina-Sabio, 1992). The chemical used in our case was phosphoric acid which is impregnated into the raw material to influence the pyrolysis such that the tar formation and volatilization are kept to a minimum (Pollard et al., 1992). Chemical activation is carried out at lower temperatures than physical activation. Carbon produced at lower temperatures is likely to possess an extensive surface area and a well-developed microporosity (Girgis et al., 1994).

Chemical properties: ash, pH and conductivity

The ash content of by-product-based carbons is dependent on the ash content of the materials which comprise the carbon. The ash contents of all by-product-based carbons made from group 1 materials were considerably higher than for any of the carbons (Figure 2.4). Specifically, GACs with cane and beet molasses as binders produced the highest ash contents among all the carbons. This is due to the high ash content of these binders. The high ash content of GACs made from rice straw and rice hulls can be explained by their high specific mineral content, especially their richness in silica (Mantell, 1946) and the addition of high ash binders such as sugarcane and sugar beet molasses.
Figure 2.4: Ash contents of experimental and commercial carbons. See Figure 2.1 for carbon identification.
Carbons from pecan shells, on the other hand, exhibited ash contents lower than the reference carbons. The low ash content of shell-based carbons is due to the inherently low mineral content of the shells (Mattson and Mark, 1971), and to the absence of binder in their preparation.

Activated carbons prepared from pecan shells had pH values similar to or slightly lower than the commercial carbons (Figure 2.5). The carbons in which cane molasses or beet molasses were used as binders were alkaline with pH values above 9. The pH variation among experimental carbons may be explained by variation in their ash content. Ash and pH values were positively correlated ($r = +0.83$, $p<0.05$, data not shown). Carbons with pH of 6-8 (group 2 precursors) had relatively low ash contents while those with a pH of 7-11 (group 1 precursors) had high ash contents. Hassler (1963) reported that the pH of most commercial carbons is due to inorganic constituents originating from the precursor or added during manufacture. Therefore, the high ash binders (cane and beet molasses) used with group 1 by-products may explain their richness in minerals, which in turn may have contributed to their relatively high pHs. A neutral pH range of 6-8 is recommended for sugar decolorization (Hassler, 1963). According to Hassler (1963), an acidic carbon would be a better sugar decolorizer but its efficiency may be offset by the losses due to the conversion of sucrose into non-crystallizable sugars.
Figure 2.5: pH of experimental and reference carbons. See Figure 2.1 for carbon identification.
With the exception of the carbon derived from sugarcane bagasse with coal tar as the binder, all the experimental carbons exhibited conductivity values significantly higher than those of the reference carbons (Figure 2.6). The highest conductivity was observed in carbons prepared with cane or beet molasses. This was expected given the high ash content of these binders. In comparison to the commercial carbons, most of the experimental carbons exhibited high conductivity values indicating that an acid or water wash was not enough to reduce leachable ash to the level observed in commercial carbons. The results of electrical conductivity indicated that even though the tested samples were acid or water washed, substantial amounts of water-soluble minerals remain in the carbons. Such high leachable mineral contents are unacceptable when the carbons are to be used for commercial sugar decolorization. This is because, ash, especially leachable ash, in activated carbon is not desirable and is considered an impurity. Ash leached into sugar liquor during the process of decolorization is known to cause uneven distribution of heat in the boiler during sugar crystallization. Ash may also interfere with carbon adsorption through competitive adsorption, catalysis of adverse reactions, and blockage of carbon pores. Consequently, more extensive washing with acid would be necessary to reduce the amount of water-soluble minerals to a level similar to that of the reference carbons. Reducing the soluble mineral contents of the carbons would also reduce any deleterious effects on pH.
Figure 2.6: Conductivity of experimental and commercial carbons. See Figure 2.1 for carbon identification.
**Adsorption properties: molasses test and raw sugar decolorization**

The amount of colorants that can be removed from a solution by activated carbon depends on factors, such as contact time, carbon dosage, temperature, concentration or viscosity of the solution, and the intrinsic features of the carbon itself. These factors were controlled in a standardized batch test that was designed to allow direct comparison of the decolorization efficiency among the experimental carbons and reference carbons. Of all the above factors, carbon dosage is particularly important because it determines the extent of decolorization and may also be used to predict the cost of carbon per unit of sugar solution to be treated. In our case, carbon dosage could not exceed 1% (w/v), since only limited quantities of experimental carbons were available. However, adsorption of color bodies from aqueous solutions (e.g. sugar solution) as a function of carbon dosage follows a logarithmic model that can be used to predict the amount of color that would be removed at higher carbon dosages. In Figure 2.7, one of the commercial carbons (Calgon CPG-LF) was used as typical example to show the relationship between the percent molasses color removed and carbon dosage.

The molasses test is generally an indicator of an activated carbon’s ability to adsorb color bodies, especially sugar colorants. Carbons with high molasses color removal are potentially good decolorizers. The carbon prepared from sugarcane bagasse using corn syrup as binder was the most efficient in removing molasses color (Figure 2.8).
Figure 2.7: Removal of sugar colorants as a function of carbon dosage (Calgon CPG-LF used as typical example).
Figure 2.8: Percent molasses color removed for experimental and commercial carbons.
See Figure 2.1 for carbon identification.
Percent color removed was similar to or better than the reference carbons. The remaining group 1-based carbons exhibited relatively low percent molasses color removal. Carbons derived from pecan shells had decolorization efficiencies that varied with activation conditions. Among the pecan shell-based carbons, two physically activated (PS23 and PS9) and two chemically activated (PS10 and PS11) carbons exhibited the best molasses color uptakes, achieving decolorization efficiencies close to the reference carbons.

As observed in the molasses test, carbons prepared from sugarcane bagasse and corn syrup along with the two commercial carbons were the best sugar decolorizers (Figure 2.9). The remaining carbons from group 1 materials had lower decolorization capacity than the commercial GACs. Decolorization efficiency of carbons prepared from pecan shells by physical activation was closest to that of the reference carbons. Chemical activation reduced the decolorization capacity. In general, similarities between the results of the molasses test and those of the sugar decolorization assays were observed. This was expected since the molasses test is normally considered as an indicator of an activated carbon's ability to remove colorants from aqueous solutions (Hassler, 1963).

Since molasses and raw sugar decolorization of GACs did not appear to vary directly with their total surface areas, their pore size distribution as well as their surface charges may have played a role in the observed differences.
Figure 2.9: Raw sugar decolorization efficiency of experimental and commercial carbons. See Figure 2.1 for carbon identification.
For instance, the carbon produced from sugarcane bagasse and corn syrup (SB-CS) exhibited a relatively low surface area, but high decolorization efficiency. In contrast, PS26 (a chemically activated pecan-based carbon) had a relatively large surface area, but poor ability to remove sugar colorants in both molasses and raw sugar tests. Because surface properties may have played a key role in the observed differences in the decolorization capacity of by-product-based carbons, their effects will be investigated in the next chapter, entitled “Surface properties of granular activated carbons from agricultural by-products and their effects on raw sugar decolorization.”

Grouping of experimental GACs based on their similarities to the reference carbons

Principal component analysis was used to produce a scatter plot of the relationship between the commercial reference carbons and experimental carbons in terms of their physical, chemical, and adsorption properties (Figure 2.10). Four quadrants were separated by the intersection of the zero values along the x- and y-axes. The experimental carbons most similar to the reference carbons are expected to cluster in the quadrant containing the latter. With the exception of PS26, all pecan shell-based carbons clustered around the two reference GACs (upper and lower right quadrants), while GACs produced from group 1 materials (except SB-CS) did not cluster in these two quadrants. Carbons containing cane or beet molasses as binders were the least similar to the commercial references, probably because of their low
Figure 2.10: Grouping of GACs based on the first two principal components. See Figure 2.1 for carbon identification.
surface area, high ash, high conductivity, low bulk density, and brittleness. A combination of sugarcane bagasse and corn syrup produced the best overall GAC among group 1-based carbons. This carbon showed good decolorization capacity and its chemical properties were similar to those of the commercial carbons.

Cluster analysis is another multivariate technique that allows grouping of GACs based on similarities using several variables simultaneously. Cluster analysis was used to classify the activated carbons into three groups based on their individual or combined physical, chemical or adsorption properties (Table 2.2). Three clusters were chosen under the assumption that if there were no similarities between the commercial carbons, and the GACs from group 1 and group 2 by-products, separate clusters would naturally form. Otherwise, those experimental carbons that cluster with the commercial references would be considered similar to the latter. Based on a combination of all properties, four group 2-based carbons (PS10, PS11, PS24, and PS26) but no group 1-based carbons clustered with the reference GACs (Table 2.2). However, clustering based on adsorption properties classified one group 1-based GAC (SBCS) along with three pecan shell-based GACs (PS9, PS10, and PS 23) as similar to the reference carbons. Cluster analysis appeared more selective than principal component analysis when all properties were considered, selecting only three of sixteen experimental carbons while principal component analysis selected eight of sixteen as similar.

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Table 2.2: Clustering of GACs based on their individual or combined physical, chemical or adsorption properties

<table>
<thead>
<tr>
<th>Basis of clustering</th>
<th>Cluster 1</th>
<th>Cluster 2</th>
<th>Cluster 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical Properties</td>
<td>PS10</td>
<td>CCAL</td>
<td>RH-CM</td>
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<tr>
<td></td>
<td>PS11</td>
<td>PS26</td>
<td>SB-CS</td>
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<td>PS24</td>
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<td>RS-CT</td>
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<td></td>
</tr>
<tr>
<td>All Properties</td>
<td>CCAL</td>
<td>RH-CT</td>
<td>PS18</td>
</tr>
<tr>
<td></td>
<td>CPG-LF</td>
<td>RS-CT</td>
<td>PS9</td>
</tr>
<tr>
<td></td>
<td>PS10</td>
<td>RH-CM</td>
<td>PS22</td>
</tr>
<tr>
<td></td>
<td>PS11</td>
<td>SB-CM</td>
<td>PS23</td>
</tr>
<tr>
<td></td>
<td>PS24</td>
<td>SB-CT</td>
<td>SB-CS</td>
</tr>
<tr>
<td></td>
<td>PS26</td>
<td>RS-CS</td>
<td>SB-BM</td>
</tr>
</tbody>
</table>

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The one group 1-based GAC (SB-CS) found similar to the reference carbons by principal component analysis was not viewed as similar with cluster analysis because of its poor physical properties. The greater selectivity of cluster analysis over principal component analysis is attributable to the difference in algorithm used by each method. Principal component uses the first two principal components (linear combinations) which account for most (and thus less than 100%) of the variability of the data, while cluster analysis groups carbons based on similarity using the original data without loss of information. In contrast, regardless of the basis of analysis, carbons made from by-products using cane or beet molasses as binders did not cluster with the reference carbons and would be, therefore, inferior to the commercial carbons. Clustering of GACs on the basis of physical properties revealed that none of the group 1-derived carbons could match the characteristics of the reference carbons, mainly because of their low surface area and low hardness. Generally, results of cluster analysis were in agreement with those of principal component analysis with the exception of PS26 and SB-CS. Both techniques revealed that three physically activated pecan shell-based carbons (PS9, PS10, and PS23) were similar to the two commercial reference carbons in all properties and, thus would make good alternate choices to commercial carbons for use in raw sugar decolorization.
CONCLUSIONS

The type of agricultural by-product and binder as well as the activation conditions appeared to determine the properties of the experimental carbons. Combination of group 1 by-products with either sugarcane molasses or sugar beet molasses generated brittle GACs possessing low surface area, low bulk density, high pH and excessive ash content. The use of coal tar, on the other hand, yielded GACs with good physicochemical properties, but with very limited surface area and, thus poor adsorption capacity. Sugarcane bagasse showed a better potential than rice straw or rice hulls as precursor of GACs with the desirable properties of a good sugar decolorizer, especially when combined with corn syrup. Pecan shells (group 2 by-products) yielded GACs that were similar to the commercial references. Chemical activation of pecan shells generated GACs with large surface area, but with sugar decolorization efficiency lower than those produced by physical activation. Since pecan shell-based GACs were the closest to the reference carbons, they would make good candidates for use as sugar decolorizers. Their commercial production would, however, require optimization of their activation conditions and characterization of their surface properties; for instance selection of activation conditions (e.g., use of steam) that induce a large surface area and optimize pore size distribution and surface chemistry of GACs to adsorb sugar colorants. The next chapter will study the relationship of the surface properties of these by-product-based GACs to their ability to remove sugar colorants.
CHAPTER 3
SURFACE PROPERTIES OF GRANULAR ACTIVATED CARBONS
FROM AGRICULTURAL BY-PRODUCTS AND THEIR
EFFECTS ON RAW SUGAR DECOLORIZATION

INTRODUCTION

The adsorption capacity of activated carbon is determined, not only by its total surface area, but also by its internal porous structure and the presence of functional groups on the pore surface. Carbon surfaces have a pore size which determine its adsorption capacity, a chemical structure which influences its interaction with polar and nonpolar adsorbates, and active sites which determine the type of chemical reactions with other molecules (Bansal et al., 1988). For instance, carbons with small pore size will not trap large adsorbate molecules and those with large pores may not be able to retain small adsorbate molecules. The electrical charge of the surface groups may also enhance or hinder the adsorption of the target molecules on the carbon surface; if the adsorbate has the same electrostatic charge as that of the carbon surface, repulsion would occur, thereby inhibiting the process of adsorption. However, the adsorption of such molecules would be enhanced if they and the carbon surface carry opposite charges. Thus, the adsorption behavior of activated carbon cannot be interpreted on the basis of the surface area alone.
Carbons having equal surface area but prepared by different methods or given different activation treatments often show markedly different adsorption characteristics. As a result, an effective carbon should have a large surface area with the proper pore size to trap the targeted species and a surface charge opposite that of the adsorbate.

Since surface properties of GACs are a function of the precursor and pyrolysis and activation conditions, it is essential to characterize them with respect to the number and type of the chemical groups on the surface, the polarity of the surface, pore size distribution and total surface area. Many investigators have studied the porous structure (Wigmans, 1989; Rodriguez-Reinoso and Molina-Sabio, 1992; Mackay and Roberts, 1982; Atkins, 1965; Rodriguez-Reinoso et al., 1985; Rodriguez-Reinoso et al., 1989; Dubinin, 1985; McEnaney, 1988) and surface chemistry (Contescu et al., 1997; Mortera and Low, 1985; Reed and Matsumoto, 1991; Arico et al., 1989; Bandoz et al., 1993; Papirer et al., 1991; Molina-Sabio et al, 1991; Coughlin and Esra, 1968; Matsumura et al., 1976; Rositani et al., 1987) of activated carbons made from a variety of precursors and activation conditions. This extensive research effort has led to the development of several methods for the determination of the surface properties of activated carbons and demonstrated the importance of surface properties in the commercial use of activated carbons. Among the accepted techniques, the Brunauer, Emmet and Teller (BET) method (Rodriguez-Reinoso and Solano, 1989) and titration with bases of different
degree of alkalinity or Boehm method (Boehm, 1966) remain the most popular techniques used to quantify an activated carbon’s surface area and surface oxides, respectively.

Based on the study presented in chapter 2, pecan shells, a group 2 by-product, and sugarcane bagasse, a group 1 by-product, along with two binders (corn syrup and coal tar) were selected as precursors of GACs.

The objectives of this work were to (1) determine the surface properties (surface area, pore size distribution, surface functional groups), of granular activated carbons prepared from sugarcane bagasse and pecan shells, (2) determine the efficiency of these carbons in removing sugar colorants compared to the commercial carbons and (3) study the relationship between carbons’ surface properties and their ability to remove sugar colorants from aqueous solutions.

MATERIALS AND METHODS

Materials

Sugarcane bagasse (SB) was provided by the Audubon Sugar Institute, Louisiana State University Agricultural Center, Baton Rouge, LA, and pecan shells (PS) by Sun Diamond of New Mexico, Las Cruces, NM. Corn syrup (CS) was supplied by A. E. Staley Manufacturing Company, Decatur, IL, and coal tar pitch (CT) by Koppers Industries, Follarsbee, WV.
Methods

Preparation of granular activated carbons

The production of GACs from sugarcane bagasse and pecan shells followed the same procedures described in Chapter 2. However, in this study, two binder (corn syrup, coal tar)/by-product ratios (1:1 and 1:2) were used with sugarcane bagasse and the inclusion of steam activation of pecan shells. Carbon yields for the bagasse- and pecan shell-based GACs were similar to the carbons described in Chapter 2.

Steam activation was carried out by pyrolysis of pecan shells at 700°C for 1 hr under a nitrogen atmosphere. After pyrolysis, the resulting char was steam activated at 850°C by metering water into the retort chamber at a rate of 120 mL/hr for 6 hr using nitrogen gas as a carrier for the water. After activation, the GAC sample was cooled overnight in the furnace under nitrogen gas, then water washed and dried overnight at 50°C. Carbon yield was 24%.

Table 3.1 illustrates pyrolysis and activation conditions of various GACs obtained from sugarcane bagasse (with binders) and pecan shells (by physical or chemical activation).

Measurement of select physical, chemical and adsorption properties

The physical (bulk density and hardness) and chemical (ash content, and pH) properties of the experimental GACs were determined as described in Chapter 2.
Table 3.1: Precursors, pyrolysis and activation conditions of agricultural by-product-based granular activated carbons

<table>
<thead>
<tr>
<th>Carbon Labels</th>
<th>Precursor (P)</th>
<th>Binder (B)</th>
<th>P/B ratio</th>
<th>Pyrolysis Conditions</th>
<th>Activation Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBCS11</td>
<td>Sugarcane bagasse</td>
<td>Com Syrup</td>
<td>1/1</td>
<td>700°C for 1h under N₂</td>
<td>Physical: 900°C for 4hrs under 13% CO₂</td>
</tr>
<tr>
<td>SBCS21</td>
<td>Sugarcane bagasse</td>
<td>Com Syrup</td>
<td>2/1</td>
<td>700°C for 1h under N₂</td>
<td>Physical: 900°C for 4hrs under 13% CO₂</td>
</tr>
<tr>
<td>SBCT11</td>
<td>Sugarcane bagasse</td>
<td>Coal Tar</td>
<td>1/1</td>
<td>750°C for 1h under N₂</td>
<td>Physical: 900°C for 20hrs under 13% CO₂</td>
</tr>
<tr>
<td>SBCT21</td>
<td>Sugarcane bagasse</td>
<td>Coal Tar</td>
<td>2/1</td>
<td>750°C for 1h under N₂</td>
<td>Physical: 900°C for 20hrs under 13% CO₂</td>
</tr>
<tr>
<td>PS23</td>
<td>Pecan Shells</td>
<td>None</td>
<td>N/A</td>
<td>700°C for 1h under N₂</td>
<td>Physical: 800°C for 6hrs under 75% CO₂</td>
</tr>
<tr>
<td>PS9</td>
<td>Pecan Shells</td>
<td>None</td>
<td>N/A</td>
<td>700°C for 1h under N₂</td>
<td>Physical: 800°C for 8hrs under 13% CO₂</td>
</tr>
<tr>
<td>PS63</td>
<td>Pecan Shells</td>
<td>None</td>
<td>N/A</td>
<td>700°C for 1h under N₂</td>
<td>Physical: 850°C for 6 hrs under steam</td>
</tr>
<tr>
<td>PS10</td>
<td>Pecan Shells</td>
<td>None</td>
<td>N/A</td>
<td>2 hr soak in 50% H₃PO₄</td>
<td>Chemical: 1hr at 450°C under N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>½ hr at 170°C</td>
<td></td>
</tr>
</tbody>
</table>
Adsorption properties (Percent molasses color removed and percent sugar decolorization) were also performed as described in chapter 2; the only modification was the use of a carbon dosage of 4% (w/v) instead of 1% (w/v).

**Determination of surface properties**

Total surface area and pore size distribution. Granular activated carbons were dried under vacuum at 110°C for 3 hr to remove moisture from carbon pores.

Approximately 250 mg of dry carbon were then placed in a Micrometrics Gemini 2375 Surface Area Analyzer (Micrometrics, Inc., Norcross, GA) and nitrogen adsorption isotherms were run at 77°K. From these isotherms, micro-, meso-, and macropore volumes were calculated using the BJG model and pore surface areas were calculated using t-plots (Gregg and Sing, 1982).

**Surface chemistry.** Two methods were used to study the nature of the oxygen groups on the surface of activated carbons. These methods were titration with bases of varying strength and Fourier Transform Infrared Spectroscopy (FT-IR).

**Titration method.** One-tenth N solutions of sodium bicarbonate (pKₐ=6.37), sodium carbonate (pKₐ=10.25), sodium hydroxide (pKₐ=15.74) and sodium ethoxide (pKₐ=20.58) were prepared along with a 0.1N solution of HCl. Fifty mL of each base was placed in a 250-mL Erlenmeyer flask and 0.5g of carbon was introduced into each flask with a teflon stirring bar. A blank (base with no carbon) was run in parallel with the carbon samples. Flasks containing 1% (w/v) carbon slurries along with the blanks were sealed and continuously
stirred for 24 hr. At the end of 24 hr, carbon was separated from the solution using 0.45μm filters. Ten mL of the filtrate was pipeted into a 50 mL beaker and 15 mL of 0.1N HCl was added to it. Excess HCl was subsequently determined by titration with 0.1N NaOH. Titrations were carried out using a PC Titrate Autotitrator (Man-Tech Associates, Inc., Tonawanda, N.Y.) equipped with a 50 mL burette and a Coming pH Meter probe. The titrant volume was automatically controlled at 0.3 pH unit increments. This option allowed good control of the volume of titrant around inflexion points of the titration curves, where pH change is most rapid, thereby ensuring accurate detection of the inflexion points. The volume of NaOH necessary to reach the equivalent point was recorded for the blank and the carbon samples. The difference in volume of NaOH consumed by the blank and by the carbon sample was calculated and converted into H⁺ equivalents neutralized by standard base per gram of carbon.

**Fourier Transform Infrared Spectroscopy (FT-IR).** Each carbon was mixed with an appropriate amount of KBr (analytical grade IR) in order to prepare a 0.5% (w/w) dispersion of carbon in KBr. The dispersions were dried overnight in a vacuum oven at 100°C. To prevent contamination with water, KBr-carbon disks were made in a glove bag under nitrogen atmosphere. Disks were prepared using a Delta Press (Tetragon Scientific, Elbridge, N.Y.). Infrared spectra of the disks were determined using a Prospect FT-IR (Midac Corporation, Irvine, California) and automatically corrected for an air
background. For each run, 32 scans were taken at a resolution of 4 cm\(^{-1}\). During the scans, the FT-IR chamber was continuously purged with a flow of nitrogen to remove moisture.

**Statistical Analysis**

Analysis of variance (ANOVA) was used to compare the mean values of physicochemical and adsorption properties among various GACs. Multiple regression was used to select models relating carbon surface properties to the decolorization efficiency of GACs. The selected models were employed to generate 3-dimensional plots of the decolorization capacity as a function of carbon surface properties. Finally, Principal component and cluster analyses served as tools by which the experimental and commercial carbons were grouped based on their similarities in terms of all the properties investigated.

**RESULTS AND DISCUSSION**

**Physical and chemical properties**

The physical and chemical properties of GACs may not relate directly to their effectiveness in removing sugar colorants, but they are important for their commercial utilization. As a result, they are usually given as a part of the commercial specification of industrial carbons.

GACs prepared from sugarcane bagasse and corn syrup had relatively low bulk density, low hardness, similar pH and high ash contents when compared to the reference carbons (Table 3.2).
Table 3.2: Physical and chemical properties of experimental granular activated carbons

<table>
<thead>
<tr>
<th>Activated Carbons</th>
<th>Bulk Density (g/cm³)</th>
<th>Hardness (% survival)</th>
<th>pH</th>
<th>Ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBCS21</td>
<td>0.25±0.01³</td>
<td>74.25±4.99³</td>
<td>8.26±0.22³</td>
<td>26.96±1.14³</td>
</tr>
<tr>
<td>SBCS11</td>
<td>0.25±0.01³</td>
<td>70.00±10.60³</td>
<td>8.07±1.16³</td>
<td>26.88±2.87³</td>
</tr>
<tr>
<td>SBCT11</td>
<td>0.47±0.01³</td>
<td>93.25±2.75³</td>
<td>6.60±0.24³</td>
<td>17.79±1.37³</td>
</tr>
<tr>
<td>SBCT21</td>
<td>0.47±0.01³</td>
<td>83.25±1.50³</td>
<td>6.44±0.25³</td>
<td>23.39±0.62³</td>
</tr>
<tr>
<td>PS23</td>
<td>0.42±0.01³</td>
<td>91.50±1.29³</td>
<td>8.10±0.53³</td>
<td>7.33±1.49³</td>
</tr>
<tr>
<td>PS9</td>
<td>0.44±0.01³</td>
<td>91.50±1.29³</td>
<td>8.11±0.22³</td>
<td>3.61±1.41³</td>
</tr>
<tr>
<td>PS63</td>
<td>0.38±0.02³</td>
<td>92.00±1.15³</td>
<td>7.74±0.13³</td>
<td>1.70±0.27³</td>
</tr>
<tr>
<td>PS10</td>
<td>0.34±0.02³</td>
<td>70.75±2.75³</td>
<td>7.66±0.41³</td>
<td>3.30±1.72³</td>
</tr>
<tr>
<td>CCAL²</td>
<td>0.48±0.01³</td>
<td>83.25±3.59³</td>
<td>8.25±0.15³</td>
<td>9.08±0.52³</td>
</tr>
<tr>
<td>CPG-LF²</td>
<td>0.54±0.01³</td>
<td>94.00±1.41³</td>
<td>7.38±0.19³</td>
<td>4.70±0.45³</td>
</tr>
</tbody>
</table>

¹ = Means with different letters are significantly different at 5% significance level.
² = Commercial Carbons, manufactured by Calgon Corp.
Sugarcane with coal tar as binder had similar bulk density and hardness but lower pH and higher ash content than the reference GACs. Physical activation of pecan shells produced carbons with physical and chemical characteristics (bulk density, hardness, pH and ash) that were generally similar to the reference carbons. Chemical activation of pecan shell (PS10) appeared to reduce bulk density and hardness.

As discussed in Chapter 2, the observed differences in physical and chemical characteristics among the experimental carbons are attributable to the precursors and activation conditions used in their manufacture. For instance, the low ash, and high hardness values of pecan shell-based carbons can be explained by high lignin and low ash contents of the shells in comparison to sugarcane bagasse and the absence of high ash binders.

**Surface area and pore size distribution**

In comparison to the reference carbons, sugarcane bagasse-based carbons, especially with coal tar as binder, exhibited limited surface area, while the GACs derived from pecan shells showed relatively larger surface area (Table 3.3). The highest surface area (1200 m²/g) among pecan shell-based carbons was achieved by chemical activation (PS10) and the lowest surface area (522 m²/g) by carbon dioxide activation (PS9). Steam activation yielded a carbon (PS63) with the closest surface area (852 m²/g) to the reference carbons. The proportion of meso- plus macropore/total surface area ranged from 8 to 50% of the total surface area.
Table 3.3: Surface properties of experimental and commercial GACs*

<table>
<thead>
<tr>
<th>Activated Carbons</th>
<th>TSA(^1) (g/m(^2))</th>
<th>MSA(^2) (g/m(^2))</th>
<th>MMSA/TSA(^3)</th>
<th>TSC(^4) (meq H(^+)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBCS21</td>
<td>314</td>
<td>261</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>SBCS11</td>
<td>337</td>
<td>267</td>
<td>0.21</td>
<td>0.19</td>
</tr>
<tr>
<td>SBCT11</td>
<td>78</td>
<td>39</td>
<td>0.50</td>
<td>0.07</td>
</tr>
<tr>
<td>SBCT21</td>
<td>180</td>
<td>120</td>
<td>0.34</td>
<td>0.12</td>
</tr>
<tr>
<td>PS23</td>
<td>641</td>
<td>588</td>
<td>0.08</td>
<td>0.34</td>
</tr>
<tr>
<td>PS9</td>
<td>522</td>
<td>477</td>
<td>0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>PS63</td>
<td>852</td>
<td>645</td>
<td>0.24</td>
<td>0.31</td>
</tr>
<tr>
<td>PS10</td>
<td>1203</td>
<td>942</td>
<td>0.22</td>
<td>1.12</td>
</tr>
<tr>
<td>CCAL(^5)</td>
<td>920</td>
<td>783</td>
<td>0.15</td>
<td>0.47</td>
</tr>
<tr>
<td>CPG-LF(^5)</td>
<td>904</td>
<td>802</td>
<td>0.11</td>
<td>0.49</td>
</tr>
</tbody>
</table>

* Values are means of duplicate determinations where the standard deviations are less than 10% of the mean values.

\(^1\) = Total Surface Area
\(^2\) = Micropore Surface Area
\(^3\) = Ratio of Macro- plus Mesopore Surface Area to Total Surface Area.
\(^4\) = Total Surface Charge
\(^5\) = Commercial carbons, manufactured by Calgon Corp.
Pecan shells activated with carbon dioxide (PS9, PS23) were predominantly microporous, while carbons from sugarcane bagasse and coal tar had the highest meso- plus macroporosity. Both the type of precursor and the method of activation appear to affect pore size distribution. Carbon dioxide activation produced larger meso- plus macropore surface area when applied to sugarcane bagasse chars (17-50%) than when used to activate pecan shell chars (8-9%). The latter showed more meso- plus macropore development when activated with either steam or phosphoric acid. These observations can be explained by the fact that steam is more reactive than carbon dioxide at a given temperature (Rodriguez-Reinoso and Molina-Sabio, 1992). The water molecule has a smaller molecular dimension than carbon dioxide, which leads to faster diffusion into the porous structure of the char and, therefore, a faster reaction rate. The reaction rate of steam is approximately three times faster than for carbon dioxide at 800°C (Gergova et al., 1992). Phosphoric acid, on the other hand, is impregnated into the raw material to influence the pyrolysis such that the tar formation and volatilization are kept to a minimum (Pollard et al., 1992). The bubbling of phosphoric acid through the by-product matrix and the reduction of tar formation result in a well developed surface area. The total surface charge did not appear to significantly impact sugar decolorization efficiency of GACs. However, the charge contributed by dissociation of the most acidic groups (groups ionizable at neutral pH) lowered the sugar decolorization efficiency of GACs.
This is probably due to charge repulsion between predominantly negatively charged sugar colorants and carbon surface.

**Surface chemical groups**

The titration method revealed that many, but not all of the carbons evaluated contained four classes of surface oxides (surface groups): carboxyls, lactones, phenols and carbonyls (Figure 3.1). The concentration of surface groups varied depending on the precursor and activation conditions. Among the 10 carbons investigated, chemically activated pecan shell (PS10) showed the highest concentration of surface groups. In contrast, GACs prepared from sugarcane bagasse and coal tar exhibited the lowest concentrations. Phenols and carbonyls were the dominant surface oxides for most of the GACs. Carboxyls were absent in one of the commercial carbon (CCAL) as well as in the steam activated pecan shell-based carbon.

The results of FT-IR studies were generally consistent with those of the titration method as shown by the representative examples of FT-IR spectra given in Figures 3.2-3.4. For instance, the carbon derived from pecan shells through chemical activation (PS10) had the most intense peaks among all the experimental carbons (Figure 3.3). These peaks covered the absorption bands corresponding to all the functional groups revealed by titration. The two commercial carbons (Figure 3.2) and the steam activated pecan-based carbon (Figure 3.3) exhibited relatively weak FT-IR absorption peaks, indicating a low concentration of oxides on their surface.
Figure 3.1: Concentration of surface oxides for GACs.
SB-CS and SB-CT = Sugarcane Bagasse with Corn Syrup and Coal Tar, respectively; and PS = Pecan Shells; CCAL and CPGLF are the commercial reference carbons. SB-CS and SB-CT = Sugarcane Bagasse with Corn Syrup and Coal Tar, respectively; and PS = Pecan Shells; CCAL and CPGLF are the commercial reference carbons. Bars represent the means of two replications where the standard error for each measurement was less than 5%.
Figure 3.2: FT-IR spectra of the reference carbons (a) CPG-LF and (b) CCAL.

**Band assignments:**

**Band 1:** Stretching of C=O in carbonyls (aldehyde and ketones), carboxylic acids, and lactones.

**Band 2:** C-O stretching and O-H bending in alcohols (phenols, lactones), and carboxylic acids.

*Absorption of each group may shift within each band depending on molecular structure and environment.
Figure 3.3: FT-IR spectra of granular activated carbons from pecan shells produced by (a) chemical activation (PS10), (b) carbon dioxide activation (PS23), and (c) steam activation (PS63). See Figure 3.2 for band assignments.
Figure 3.4: FT-IR spectra of granular activated carbons made from (a) sugarcane bagasse and coal tar (SBCT21), (b) sugarcane bagasse and corn syrup (SBCS21). See Figure 3.2 for band assignments.
Approximate FT-IR band assignments indicated the presence of carbonyls, carboxylics, lactones and phenols. The 1800-1540 cm\(^{-1}\) band (band 1) was associated with the C=O stretching mode in carbonyls, carboxylic acids and lactones, while the 1440-1000 cm\(^{-1}\) band (band 2) was assigned to the C-O stretching and O-H bending modes, such as in phenols and carboxylic acids, (Mortera and Low, 1983; Mortera and Low, 1985; Zawadzki, 1981; Laine et al., 1989). The assignment of a specific wave number to a given functional group was not possible because the absorption bands of various functional groups overlap and shift depending on their molecular structure and environment. Shifts in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, stearic effect, and degree of conjugation. For instance, within its given range, the position of C=O stretching band (common to carbonyls, carboxylic acids and lactones) is determined by many factors. These include: (1) the physical state, (2) electronic and mass effects of neighboring substituents, (3) conjugation, (4) hydrogen bonding, and (5) ring strain (Kendall, 1966; Smith, 1979). The IR absorption bands of oxygen groups on the surface of solid GACs are likely to be affected by some or all of the factors listed above. The presence of peaks in Band 1 is indicative of the presence of carbonyls and/or lactones. Coexistence of peaks in both Band 1 and Band 2 are indicative of carboxylic acids (C=O, C-O stretching and O-H in plan bending), phenols (O-H bending) lactones and carbonyls (C=O stretching). The absence of distinct peaks in one
or two bands indicates absence of the corresponding surface oxides. Most of the carbons activated at high temperature (800-900°C) showed absorption peaks in band and no peaks in band 2 suggesting a predominance of carbonyls and lactones. Chemical activation of pecan shells (PS10), showed strong absorption peaks in both bands indicating the presence of carboxylic acids and phenols along with carbonyls and lactones. The same pattern was also revealed by titration (Figure 3.1). These results are in agreement with the findings of many investigators (Bansal, 1988; Molina-Sabio; 1991; Zawadzki, 1981) who reported that carbons produced at lower temperature have a variety of surface oxides, including carboxylic acids, but the majority of these surface structures, especially carboxylic acids and lactones decompose in the temperature range 600-800°C. Similarly, FT-IR spectra of sugarcane bagasse-based carbons (Figure 3.4) showed peaks of intermediate intensity in both regions.

**Adsorption properties of GACs and their relationship to surface properties**

Based on both molasses color removed and sugar decolorization, GACs made from sugarcane bagasse using corn syrup as a binder (SBCS 21 and 11) and two pecan shell-based carbons (PS63, steam activated and PS10, chemically activated) were as effective as the commercial carbons in removing sugar colorants (Figure 3.5 and 3.6).
Figure 3.5: Percent molasses color removed for experimental and commercial carbons. See Figure 3.1 for carbon identification. Bars represent the means of four replications where the standard error for each measurement was less than 5%. Bars with different letters are significantly different at p<0.05.
Figure 3.6: Sugar decolorization efficiency of experimental and commercial carbons. See Figure 3.1 for carbon identification. Bars are means of four replications where the standard error for each measurement was less than 5%. Bars with different letters are significantly different at p<0.05.
GACs produced from sugarcane bagasse with coal tar as a binder and those prepared from pecan shells using CO$_2$ activation were the least effective decolorizers. The superior decolorization efficiency of the carbons produced with corn syrup is probably due to their relatively well developed surface area compared to carbons made with coal tar. The limited surface area of coal tar carbons may be attributed to the fact that coal tar has a higher carbon content than corn syrup and, therefore, would be volatilized to a much lesser extent (Pendyal et al., 1998a) yielding less developed surface area.

Overall, three characteristics of activated carbon can be used to explain the observed differences in molasses and raw sugar color adsorption among the carbons. These properties are: 1) total surface area, 2) pore-size distribution (relative proportion of micro-, meso-, and macropores) and 3) chemical reactivity, which depends on the types and concentrations of the surface oxides on the carbon surface (Mattson and Mark, 1971; Dubinin, 1987). Large surface area is generally a requirement for a good adsorbent. However, the total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species. An activated carbon with large surface area may absorb very rapidly, but its adsorptive capacity could be low because it lacks the proper pore size to contain the adsorbed material (Patrick, 1995). The presence of large and small pores implies a favorable pore size distribution for adsorption of polydispersed colorants. The system of macropores would serve as avenues for the rapid diffusion of color bodies to the
smaller pores where they are adsorbed. These structures favorably enhance both the adsorption and reactivation characteristics (Calgon, 1987). The presence of surface oxygen complexes also imparts a polar character to the activated carbon surface, which can affect preferential adsorption of polar organic solutes. Pore structure and chemistry of activated carbons made from agricultural by-products are strongly dependent on pyrolysis temperature, composition and structure of the raw materials, and method of activation (Girgis et al., 1994; Gergova et al., 1994; Rodríguez-Reinoso and Molina-Sabio, 1992).

Since percent molasses color removed and percent sugar decolorization did not seem to be directly proportional to surface area, pore size distribution as well as total surface charge may have played a role in the observed differences.

Modeling of the removed color as a function of total surface area and pore ratio that percent molasses color removal followed a curvilinear relationship (Figure 3.7). Such a curvilinear relationship predicts that optimal decolorization by GACs would occur around a macro- plus mesopore area/total surface area (MMSA/TSA) ratio of 0.25 and a total surface area exceeding of about 1000 m²/g. The low MMSA/TSA ratio of 0.08-0.09 for carbons made from pecan shells activated with CO₂ (PS9 and PS23) may, in part, explain why they failed to achieve good decolorization efficiency, despite their relatively high surface area.
Figure 3.7: Percent molasses color removed as a function of total surface area and pore ratio.
The high microporosity of these carbons would make adsorption of larger molecules, as found in sugar colorants, problematic. These large molecules would have difficulty entering and navigating through the micropores with the possibility that the micropores could become clogged, thereby effectively stopping further adsorption (Pendyal et al., 1999b). According to Wigmans (1989), an activated carbon with a high percentage of micropores will tend to adsorb low molecular weight compounds and as the percentage of micropores decreases, the carbon can adsorb compounds with a broader range of molecular sizes. The presence of macro- and mesopores may adsorb the larger colorant molecules while allowing the smaller molecules access to the micropores where they are adsorbed.

The negatively charged surface formed by the dissociation of specific types of surface oxides appears to reduce color removal by GACs. The highest percent color removal was achieved by carbons having no carboxylic groups (or no negative charge at pH 7) (Figure 3.8). A carbon’s efficiency in removing sugar colorants decreased with increasing amount of negative charges on the surface, probably because of charge repulsion of sugar colorants which are predominantly negatively charged. Electrostatic repulsion would explain why the carbon made from pecan shells with chemical activation (PS10) exhibited decolorization capacity lower than expected, despite its extensive surface area (1200 m²/g) and its favorable pore size distribution (0.22).
Figure 3.8: Percent molasses color removed as a function of total surface area and surface charge (groups ionizable at neutral pH).
The steam activated pecan shell-based carbon was a good sugar decolorizer because it possessed a good surface area (850 m$^2$/g), an optimal pore size distribution (0.24) and no carboxylics (negligible surface charge). This set of surface properties appears to favor the adsorption of sugar colorants and would, therefore, be recommended for carbons designed for use in sugar refineries.

Carbons prepared from sugarcane bagasse and coal tar exhibited low decolorization efficiency mainly because of their very low surface area (78-180 m$^2$/g). The combination of sugarcane bagasse and corn syrup yielded GACs with moderate surface area (300 m$^2$/g), good pore size distribution and a relatively low surface charge which explain their good sugar decolorizing capacity.

**Grouping of experimental GACs based on similarities to the commercial carbon references**

The results of principal component analysis (Figure 3.9) and cluster analysis (Table 3.4) revealed that two by-product-based carbons, namely PS10 (chemically activated pecan shells) and PS63 (steam activated pecan shells) were similar to the reference carbons in terms of surface and adsorption properties. The two CO$_2$ activated pecan shell-based carbons (PS9 and PS23) did not cluster with the reference carbons mainly due to unfavorable pore size distribution.
Figure 3.9: Grouping of GACs based on the first two principal components.
See Figure 3.1 for carbon identification.
Carbons prepared with coal tar (SBCT11, SBCT21), on the other hand, were not classified with the reference carbons because of their low surface area. GACs derived from sugarcane bagasse with corn syrup (SBCS11, SBCS21) were close to being included with the commercial carbons, but were excluded by their relatively low surface area. Otherwise, they showed good sugar decolorization potential.

Table 3.4: Grouping of experimental GACs based on their surface and adsorption properties

<table>
<thead>
<tr>
<th>Cluster 1</th>
<th>Cluster 2</th>
<th>Cluster 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCAL</td>
<td>SBCS105</td>
<td>PS23</td>
</tr>
<tr>
<td>CPGLF</td>
<td>SBCS11</td>
<td>PS9</td>
</tr>
<tr>
<td>PS63</td>
<td>SBCT21</td>
<td></td>
</tr>
<tr>
<td>PS10</td>
<td>SBCT11</td>
<td></td>
</tr>
</tbody>
</table>

CONCLUSIONS

Raw sugar decolorization was favored in carbons possessing high surface area, a preponderance of micropores and low negative surface charge, as evidenced by few carboxyl groups. Modeling of percent molasses color removed with surface area, pore ratio, and surface charge predicted that carbons with surface areas above 300 m²/g, pore ratios of 0.25 and no carboxylic groups were most effective in removing sugar colorants. Even with a large surface area, carbons with high negative surface charge and/or low
pore ratio exhibited relatively poor decolorization efficiency, because of charge repulsion between predominantly negatively charged sugar colorants and the negatively charged carbon surface and/or poor diffusion of sugar liquor in the carbon matrix. Pecan carbons produced by chemical activation with phosphoric acid showed promise as sugar decolorizers if their surface chemistry is altered to reduce the amount of carboxyl groups and, therefore, enhance their surface affinity to sugar colorants. Steam activation showed the best potential for producing activated carbons with high surface area, good pore ratio and few carboxyl groups, which are good characteristics for sugar decolorizers. Since GACs made from pecan shells were very similar to the commercial carbons in terms of raw sugar decolorization as well as most other characteristics, they may provide a lower cost alternative to the existing coal-based commercial carbons for use in the sugar refining industry.
GENERAL CONCLUSIONS AND RECOMMENDATIONS

This work has demonstrated that granular activated carbons can be produced from hard or soft agricultural by-products. The type of agricultural by-products and to a lesser extent, the binder used, influenced the physical, chemical, and surface properties of GACs and thus their adsorptive properties. Low density group 1 materials required the use of binders to produce GACs. Of the soft materials and binders, combination of sugarcane bagasse and corn syrup produced carbons with the best sugar decolorization capacity, but unsatisfactory physical properties. These GACs would be desirable only in “gentle” applications such as filtration through carbon-packed filters (e.g. aquarium filters) and systems designed for purification of gases (e.g. deodorization). In contrast, pecan shells, a representative of group 2 materials with high density and high hardness, were excellent GAC precursors and did not require the use of a binder. Physical, chemical and surface properties of GACs made from pecan shells were, however, dependent on the type of activation.

Modeling of sugar decolorization as a function of surface properties revealed that larger total surface area, a well-developed macro- and mesoporosity along with a minimal surface charge (few carboxyl groups) were desirable in GACs designed for sugar decolorization.
Steam activation of pecan shells carbon was the only byproduct-activation combination that produced GAC with all the above three desirable characteristics of a good sugar decolorizer. Chemical activation of pecan shell-derived carbons with phosphoric acid yielded GACs with high surface area and adequate pore size distribution, but with large surface charge. However, the latter can be further improved by subjecting these carbons to higher activation temperature treatment to eliminate some of the surface oxides, especially carboxylic acids.

Since pecan shells produced GACs that were very similar to the reference carbons, they are worthy of further investigation. Future work should focus on ways to optimize the properties of pecan shell-based carbons to meet all the standards of quality required by sugar refineries. Scale up of carbon production from bench-type to pilot plant trials, where conditions in sugar refineries could be simulated, would be the next phase. This will undoubtedly lead to a successful production of GACs from pecan shells offering a cheap and renewable source of carbons for sugar refiners in place of the existing coal-based carbons.
REFERENCES


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VITA

Mohamed Ahmedna received his bachelor of science degree in General Food Science and Technology from the Institut Agronomique et Veterinaire Hassan-II, Rabat-Morocco in November, 1989. He held the position of technical manager of the SOMAPECHE-RAJA Company, Nouadhibou-Mauritania, from 1990 through 1992. In August 1993 he joined Louisiana State University for full-time graduate study in the Department of Food Science where he received the degree of Master of Science in May 1995. Mr. Ahmedna is currently a candidate for the degrees of Doctor of Philosophy in Food Science and Master in applied statistics, which he will receive in December 18, 1998 commencement. He is a member of the Institute of Food Technologists, the American Statistical Association, and Sigma Gamma Delta honor society of agriculture.
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Candidate: Mohamed Ahmedna

Major Field: Food Science

Title of Dissertation: Granular Activated Carbons from Agricultural By-products: Carbon properties and Their Relationship to Sugar Decolorization Potential

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

October 26, 1998