Adsorption of volatile organic compounds by pecan shell- and almond shell-based granular activated carbons


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Abstract

The objective of this research was to determine the effectiveness of using pecan and almond shell-based granular activated carbons (GACs) in the adsorption of volatile organic compounds (VOCs) of health concern and known toxic compounds (such as bromo-dichloromethane, benzene, carbon tetrachloride, 1,1,1-trichloromethane, chloroform, and 1,1-dichloromethane) compared to the adsorption efficiency of commercially used carbons (such as Filtrasorb 200, Calgon GRC-20, and Waterlinks 206C AW) in simulated test medium. The pecan shell-based GACs were activated using steam, carbon dioxide or phosphoric acid. An almond shell-based GAC was activated with phosphoric acid. Our results indicated that steam- or carbon dioxide-activated pecan shell carbons were superior in total VOC adsorption to phosphoric acid-activated pecan shell or almond shell carbons, inferring that the method of activation selected for the preparation of activated carbons affected the adsorption of VOCs and hence are factors to be considered in any adsorption process. The steam-activated, pecan shell carbon adsorbed more total VOCs than the other experimental carbons and had an adsorption profile similar to the two coconut shell-based commercial carbons, but had greater adsorption than the coal-based commercial carbon. All the carbons studied adsorbed benzene more effectively than the other organics. Pecan shell, steam-activated and acid-activated GACs showed higher adsorption of 1,1,1-trichloroethane than the other carbons studied. Multivariate analysis was conducted to group experimental carbons and commercial carbons based on their physical, chemical, and adsorptive properties. The results of the analysis conclude that steam-activated and acid-activated pecan shell carbons clustered together with coal-based and coconut shell-based commercial carbons, thus inferring that these experimental carbons could potentially be used as alternative sources for VOC adsorption in an aqueous environment.

Keywords: Granular activated carbons; Pecan shells; Almond shells; Volatile organic compounds

1. Introduction

Activated carbon has long been recognized as one of the most versatile adsorbents to be used for the effective removal of organic contaminants in wastewater treatments. Urgent need has been exhibited by various public and health agencies for the removal of these contaminants in stream and natural water and has resulted in the emergence of activated carbon adsorption as one of the most effective methods for removing these contaminants in wastewater treatments. Although various materials are used in the production of commercial activated carbons (wood, coal, peat, lignite, coconut shells), abundant availability and low cost of agricultural by-products make them good candidates and sources of raw materials for activated carbons.

The annual harvesting and processing of various agricultural crops grown in the United States result in considerable quantities of agricultural by-products. These by-products have been shown to have potential as raw materials in the manufacture of activated carbons (Toles et al., 1997, 1998, 1999; Johns et al., 1998). The US produced 315 million lbs of pecan and 850 million lbs of almonds for the 2001 crop year (Agricultural Statistics, 2002). Production and processing of these
commodities are estimated to generate 157 million lbs of pecan shells, and 425 million lbs of almond shells, as by-products.

In recent years various applications of granular activated carbons (GACs) from agricultural by-products, especially from nutshells, have been studied for raw sugar decolorization (Ahmedna et al., 2000a,b), metal and organic adsorption (Toles et al., 1997, 1998, 2000; Johns et al., 1998; Dastgheib and Rockstraw, 2001; Wartelle and Marshall, 2001), and geoimin adsorption in water (Ng et al., 2002). The physical and chemical properties and the surface chemistry (Johns et al., 1999; Ahmedna et al., 2000a; Toles et al., 1999, 2000) of these carbons have been studied to gain a comprehensive understanding of their adsorption properties.

In recent decades the quality of many water supplies has been adversely affected by factors associated with the tremendous growth in the production of industrial chemicals, especially volatile organic compounds (VOCs). Studies have indicated that VOC contamination of groundwater supplies in the United States is widespread and that significant number of people have been exposed to VOC levels higher than their individual maximum contamination limits (Faust and Aly, 1998).

VOCs, such as low molecular weight chlorinated aliphatics and chlorinated and non-chlorinated aromatics are generally treated with air stripping or GAC. Air stripping yields 95–99% removal of VOCs. However, because of environmental issues, discharge of VOCs into the atmosphere limits its use. GAC, on the other hand, can remove volatile as well as non-volatile compounds with effective reduction of organic contaminants to undetectable limits and prevent their discharge back into the atmosphere (Stenzel and Gupta, 1995). The objective of this research was to determine the effectiveness of using pecan shell- and almond shell-based GACs in the adsorption of select VOCs and to compare their effectiveness to the adsorption efficiency of coal- and coconut-based commercial carbons in an aqueous test medium.

2. Methods

Pecan shells were obtained from Sun Diamond of New Mexico, Las Cruces, NM and almond shells were a gift of California Almond Hulls, Turlock, CA. Filtrasorb 200 (F200), a steam-activated, coal-based carbon, and GRC-20, a steam-activated, coconut shell-based carbon, were obtained from Calgon Carbon Corp. (Pittsburgh, PA). Waterlinks 206C AW is a steam-activated, coconut shell-based activated carbon procured from Barney and Sutcliffe (Solon, OH). VOCs were supplied as a mixture from Supelco (Bellevofonte, PA), where each organic compound was present at 2000 μg/ml concentration.

2.1. Preparation of granular activated carbons

Pecan and almond shells were milled to a 10 × 20 mesh size (US standard sieve) with a hammer-cutter mill (Glen Mills, Clifton, NJ). Milled samples were placed in a box furnace with retort (Lindberg, Watertown, WI). For steam or carbon dioxide activation, the pecan shells were initially pyrolyzed under a stream of nitrogen gas at a flow rate of 0.1 m³/h and a pyrolysis temperature of 700 °C for 1 h. Steam activation involved injecting water into the nitrogen gas flow entering the heated retort at a flow rate of 2 ml/min at an activation temperature of 900 °C for 6 h. A yield of 14% of the initial mass of shells was obtained. Carbon dioxide activation required exposing the pyrolyzed shells to a gas mixture of 30% carbon dioxide and 70% nitrogen (wt./wt.) at an activation temperature of 900 °C for 6 h. A yield of 22% of the initial shell mass was recorded. After activation, the carbons were cooled overnight in the retort under a nitrogen gas atmosphere and were ready for use.

For phosphoric acid activation, the milled pecan and almond shells were soaked with 50 wt.% phosphoric acid for 2 h. The soaked shells were heated in a flowing nitrogen gas environment inside the retort at a flow rate of 0.1 m³/h and at a temperature of 170 °C for 1 h. The nitrogen gas was replaced with compressed air and introduced into the retort at the same flow rate as the temperature was increased to 450 °C and held at this temperature for 1 h. After 1 h, the power supplied to the furnace was shut off and the temperature in the retort was decreased due to convection cooling. During the cooling phase in the retort, the carbons were subjected to some further air activation until the temperature in the retort decreased below approximately 150 °C.

The acid-activated carbons were cooled overnight in the retort, then washed in boiling water until free of detectable phosphate ion as evidenced by the lack of a lead phosphate precipitate upon introduction of a few drops of lead nitrate to a sample of the wash water. The washed carbons were dried at 102 °C for at least 2 h before use. Yields of 37% and 39% were determined for the almond shell and pecan shell carbons, respectively.

2.2. Measurement of carbon physical and chemical properties

Surface areas for all carbons were measured by nitrogen adsorption at 77 K using a Micromeritics Gemini 2375 surface area analyzer (Micromeritics Inc., Norcross, GA) using a 15 point BET (Braunauer et al., 1938). Bulk density was determined using the method of Ahmedna et al. (1997). A 25 ml cylinder was filled to a specified volume with 10–30 mesh GAC that had been dried in an oven at 80 °C overnight. The cylinder was tapped for at least 1–2 min to compact the carbon, then weighed. The bulk density was calculated as:
bulk density (g ml⁻¹)

\[ = \frac{\text{wt. of dry material (g)}}{\text{vol of packed dry material (ml)}} \]

Carbon hardness was determined using a wet attrition test as described by Toles et al. (2000). About 10-30 mesh carbons were used. One gram of GAC was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid, pH 4.8) in a 150 ml beaker. The solution was stirred for 24 h at 25 °C on a VarioMag Electronic Ruhrer Multipoint HP 15 stirrer (Daytona Beach, FL) at 500 rpm using 1/2 inch stir bars. The samples were then poured onto a 50 mesh (0.30 mm) screen, and the retained carbon was washed with 250 ml of deionized water. After washing, the retained carbon was transferred to a preweighed aluminum weighing dish and dried at 90 °C under vacuum for 4 h. The samples were removed and allowed to cool in a desiccator and weighed. The attrition (wt. % attrition) was calculated as:

\[ \% \text{ attrition} = \left( \frac{\text{initial wt. (g)} - \text{final wt. (g)}}{\text{initial wt. (g)}} \right) \times 100 \]

Ash content (%) was determined by the method of Ahmedna et al. (1997). Approximately 2 g of powdered activated carbon was placed into weighed ceramic crucibles. Carbon and crucibles were dried overnight at 80 °C and reweighed to obtain the dry carbon weight. The samples were heated in a Jelrus 250 muffle furnace (Hicksville, NY) at 1400 °F (760 °C) for at least 6 h. The crucibles were cooled in a desiccator, and remaining solids (ash) were weighed. Percent ash was calculated by:

\[ \% \text{ ash} = \left( \frac{\text{remaining solids wt. (g)}}{\text{original carbon wt. (g)}} \right) \times 100 \]

The pH was measured using the method of Ahmedna et al. (1997). A 1% (wt./wt.) suspension of activated carbon in deionized water was prepared. The suspensions were heated to approximately 90 °C and stirred for 20 min. The suspensions were then allowed to cool to room temperature and the pH was measured with a Corning pH 10 portable pH meter (Acton, MA). The pH meter was initially calibrated with pH 4 and pH 7 buffers. If the pH was found to be above pH 7, the pH meter was recalibrated with pH 7 and pH 10 buffer solution. The calibration was confirmed by analysis of a pH 7 buffer after every five analyses, and a recalibration done if the value of the pH 7 buffer varied by more than ±0.1 pH unit.

Conductivity measurements were carried out by the method of Ahmedna et al. (1997). A 1% (wt./wt.) solution of GAC in water was stirred at room temperature for 20 min. Electrical conductivity was measured using a HACH CO 150 Conductivity Meter (Loveland, CO) with values given in microSiemens (μS).

2.3. Adsorption of volatile organic compounds

The six VOCs selected to test the adsorption effectiveness of the experimental and commercial GACs were 1,1-dichloroethane, chloroform, benzene, 1,1,1-trichloroethane, carbon tetrachloride, and bromo-dichloromethane. They were chosen because of their known occurrence in municipal wastewater, proven toxicity and health hazardousness under USEPA’s listed toxic water pollutants potentially available in petroleum refinery wastewater (Liu and Liptak, 2000). A simulated test medium was selected to minimize experimental errors caused by interfering components during adsorption.

The method developed and used in this study employed 0.01 g of carbon in contact with a solution containing 100 ppb each of the six analytes listed above. Forty milligrams of the carbons were added to environmental sample vials, and 40 ml of distilled deionized water were added and spiked with 40 μl of the stock solution containing 50 ppm of each analyte to get a final concentration of 100 ppb of each analyte in the test medium for the adsorption experiment. The samples were run in triplicates, along with blanks, which were run concurrently with the samples. The carbons were left in contact with the analytes for 24 h at room temperature with constant agitation at 500 rpm. After the contact time, an aliquot of the solution (15 ml) was drawn off and preserved in an environmental sample vial under refrigeration temperature until analyzed by gas chromatography for residual organics in the samples.

The solution sample vials were used for headspace sampling by a Micro-Fast gas chromatograph with an FID detector and a 1.2 m DB-170 column with 0.4 μm film thickness and 0.1 mm i.d. Hydrogen was used as the carrier gas, and the sorption trap consisted of 5 mg tenax GR (80 × 100 mesh size). Injection time was set at 1000 ms, and the desorption temperature was adjusted to 250 °C. The column temperature was ramped from 30 to 180 °C at 5 °C/s. A calibration curve was constructed by using standard solutions of 25, 50, and 100 ppb for each analyte. The calibration curves were deemed acceptable when \( r > 0.95 \) for each analyte.

2.4. Statistical analysis

Analysis of variance (SAS, 1989) was conducted on the data with 95% confidence level to determine the significant differences between the physical and chemical properties of the experimental carbons and the commercial carbons. Multivariate techniques such as principal component analysis and cluster analysis were carried out to interpret the data to group the carbons based on their physical and chemical properties, adsorptive properties, and overall properties. Principal component analysis (SAS, 1989) uses a scatter plot with four quadrants along the x- and y-axes. The distribution
of carbons based on their overall adsorptive properties was studied. For cluster analysis (SAS, 1989), both hierarchical and non-hierarchical techniques were analyzed.

3. Results and discussion

3.1. Physical and chemical properties of experimental and commercial carbons

The physical properties (surface area, bulk density, attrition) and chemical properties (ash, pH, conductivity) of experimental and commercial carbons are presented in Table 1. The adsorption of VOCs onto activated carbon is usually related in a direct manner to the surface area of the carbon. Normally, large surface areas signify high adsorption of organic compounds, especially non-polar organic compounds. Hence, surface area is an important attribute while considering the selection of adsorbents in the separation process.

Among the shell-based experimental carbons, ALA had the largest surface area of any carbon at 1340 m²/g (Table 1). PSS had the next largest surface area among the experimental carbons at 917 m²/g, followed by PSA at 902 m²/g and PSC at 435 m²/g. Acid activation appeared to result in carbons with high surface area and under the same activation conditions, almond shells produced a higher surface area than pecan shells. This indicates that the starting material may dictate the surface area of a carbon to some degree. Carbon dioxide activation produced a carbon with the lowest surface area among all the carbons. This method appears to be a less effective method for imparting surface area at specific time and temperature conditions compared to steam activation. The results may indicate why acid and steam activation are preferred activation methods for commercial processes compared to carbon dioxide activation. Carbon dioxide is more expensive than steam in addition to yielding a lower surface area under the same activation conditions of time and temperature.

From the data on total surface area shown in Table 1, among the three commercial carbons used, GRC-20 had the largest total surface area with 1038 m²/g, followed by 206C AW with 898 m²/g, and F200 at 835 m²/g. Since these carbons were steam activated, their surface areas were comparable to the surface area of PSS.

Bulk density is an important characteristic of the carbon and is related to the starting material. Bulk density is one of the variables in the design of adsorption columns and it also affects the overall cost of the adsorption process. A higher density carbon will generally not have to be regenerated as frequently because it will hold more adsorbate per unit volume (US Environmental Protection Agency, 1973).

The data on bulk density of the almond and pecan shell-based experimental GACs and the commercial carbons (Table 1) indicate that of the three commercial carbons used in this investigation, 206C AW had the highest bulk density (0.54 g/m³) followed by F200 with 0.49 g/m³ and GRC-20 with a value of 0.47 g/m³. In regard to the bulk density of the experimental carbons, the data indicate that PSC had the highest value (0.57 g/m³) followed by PSA (0.51 g/m³), PSS (0.49 g/m³), and ALA (0.30 g/m³). Almond shells are considered softer and less dense than pecan shells (Wartelle and Marshall, 2001) and produced carbons of lower density at the same particle size. Statistical analysis of the bulk density data (Table 1) indicated that the bulk density of ALA was significantly less than the bulk density of the three commercial carbons. Also, the bulk density of PSS was significantly less than the bulk density of 206C AW and significantly greater than the bulk density of GRC-20.

Attrition is a measure of the mechanical strength of the carbons and is an important parameter for understanding its relative loss during transportation, han-

<table>
<thead>
<tr>
<th>Physical and chemical properties</th>
<th>Experimental carbons</th>
<th>Commercial carbons</th>
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<tr>
<td></td>
<td>Phosphoric acid activation</td>
<td>Carbon dioxide or steam activation</td>
</tr>
<tr>
<td></td>
<td>ALA</td>
<td>PSA</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>1340</td>
<td>902</td>
</tr>
<tr>
<td>Bulk density (g/m³)</td>
<td>0.30±0.10a,b,c</td>
<td>0.51±0.20a,b,c</td>
</tr>
<tr>
<td>Attrition (%)</td>
<td>31.7±1.0a,b,c</td>
<td>7.10±0.45a,b,c</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>3.50±0.10a,b,c</td>
<td>1.42±0.01a,b,c</td>
</tr>
<tr>
<td>pH</td>
<td>6.08±0.01a,b,c</td>
<td>5.70±0.52a,b,c</td>
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<tr>
<td>Conductivity (µS)</td>
<td>21.7±1.8a,b,c</td>
<td>46.0±0.3a,b,c</td>
</tr>
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</table>

Abbreviations: ALA = phosphoric acid-activated almond shell; PSA = phosphoric acid-activated pecan shell; PSC = carbon dioxide-activated pecan shell; PSS = steam-activated pecan shell; F200 = coal-based, Calgon Filtrasorb 200; GRC-20 = coconut shell-based activated carbon from Calgon; 206C AW = coconut shell-based activated carbon from Barneby and Sutcliffe.

a Significantly different from F200 at 5% significance level.
b Significantly different from GRC-20 at 5% significance level.
c Significantly different from 206C AW at 5% significance level.
dling, and regeneration. The results (Table 1) indicate that commercial carbons generally displayed lower attrition than the nutshell-based carbons. F200, with a value of 3.26%, had the lowest attrition among the commercial carbons. Both GRC-20 and 206C AW showed comparable attrition values to each other. All the commercial carbons displayed attrition values below 10%; only one of the nutshell-based carbons (PSA) was below 10% attrition. The percent attrition observed in carbons is the result of the density or hardness of the starting material.

PSA showed the lowest attrition (7.10%) among experimental carbons, followed by PSC (12.8%), PSS (22.2%) and ALA (31.7%). ALA showed the highest attrition value, making it undesirable because of its susceptibility to abrasion losses during commercial use. Among the experimental carbons, only PSA (7.10%), was not significantly different from GRC-20 (7.27%) and 206C AW (7.26%). The other experimental carbons (ALA, PSC, and PSS) were significantly different from all the commercial carbons.

Since pecan shells have higher density than almond shells, almond shell carbons would be softer with higher attrition values, which was the case in this study. The surface area appeared to have little effect on attrition for both the commercial and experimental samples (Wartelle and Marshall, 2001). Ash content is a measure of the minerals as impurities in the carbons, mainly derived from the carbon precursor. GRC-20 had the highest ash content (9.60%) when compared to F200 and 206C AW with ash contents of 6.50% and 2.00%, respectively. Among experimental carbons, PSC had the highest ash content (6.00%) followed by PSS with 5.53%, ALA with 3.35%, and PSA with 1.42%. Ash content in the experimental carbons may be traced to the presence or absence of acid and/or water washes the carbons undergo during processing. In the present case, PSC and PSS were not washed after activation as was PSA and ALA. This probably influenced the ash values. Statistical analysis showed (Table 1) that all experimental carbons were significantly different from the commercial carbons in their ash content.

The pH of a carbon directly impacts the adsorption process and may affect the final pH of the treated wastewater. Therefore a neutral pH is generally preferred. The pH values of the commercial carbons (F200, GRC-20, and 206C AW) were 7.40, 8.63, and 8.15, respectively. The pH of the experimental carbons depended on the wash treatment received after activation. Acid-activated carbons such as ALA and PSA had acidic pH values of 6.08 and 5.70, respectively. The carbon dioxide and steam-activated carbons, PSC and PSS, had basic pH values of 10.1 and 10.0, respectively. The alkaline pH values are the result of the absence of an acid and water wash after activation for these carbons. Acid and water washes are effective in removing alkaline ash from the carbons, thus lowering the carbon pH. Statistical analysis showed that all the experimental carbons had statistically different (p < 0.05) pH values than the commercial carbons.

High conductivity of the carbons is undesirable because it interferes in the adsorption process because of the leachable minerals associated with the carbon surface. From Table 1, F200 had the lowest conductivity of 5.85 μS, followed by GRC-20 (9.08 μS) and 206C AW (11.95 μS). PSC and PSS had high conductivity values consisting of 331 μS and 753 μS, respectively. ALA and PSA showed lower conductivity than PSC and PSS with conductivity values of 27.1 μS and 46.0 μS, respectively. Conductivity of PSC and PSS was probably influenced by the presence of ash (Table 1) generated from the activation process, since ALA and PSA were extensively washed and have much lower conductivity values. Conductivity of all the experimental carbons was significantly (p < 0.05) higher than conductivity of the commercial carbons.

3.2. Adsorption of volatile organic compounds

Data on the adsorption of VOCs consisting of one aromatic compound (benzene) and five halogenated aliphatic compounds (bromo-dichloromethane, 1,1,1-trichloroethane, chloroform, and 1,1-dichloroethane) by experimental carbons and commercial carbons are presented in Fig. 1 and Table 2. The data from Fig. 1 indicate that, in terms of total VOC adsorption, 206C AW showed the highest performance (516 ppb) followed by PSS (506 ppb), GRC-20 (502 ppb), F200 (476 ppb), PSC (430 ppb), PSA (407 ppb), and ALA (347 ppb). Within the three commercial carbons, the two coconut shell-based carbons, 206C AW and GRC-20, showed better adsorption than the coal-based carbon, F200. Among the four experimental carbons, the three-pecan shell-based carbons PSA, PSS, and PSC exceeded the almond shell-based carbon, ALA, in adsorption performance. The carbon dioxide- and steam-activated pecan shell carbons were superior in their adsorption to acid-activated pecan and almond shells. These results indicate that the carbons with high surface area, namely, ALA and PSA, do not always have high VOC adsorption. Therefore, high surface area is not always indicative of good organic adsorption. In the present case, acid-activated nutshell carbons have a high negative surface charge and this surface charge may impede the adsorption of the VOCs (Johns et al., 1999).

These data infer that the method of activation and precursors selected for the preparation of activated carbons may affect the adsorption of VOCs and hence are factors to be considered in any adsorption process. All the carbons studied exhibited efficiently adsorbed benzene (Table 2), possibly because of its zero dipole
moment. PSA showed higher adsorption (93.1%) of 1,1,1-trichloroethane when compared to all the carbons studied. PSS showed higher adsorption (85.4%) of bromo-dichloromethane compared to all the other carbons. It can be inferred that the adsorption of the VOCs mainly depends not only on the carbon precursor but also on the method of activation, which influences the surface chemistry of the carbons.

### 3.3. Statistical analysis of physical and chemical properties of GACs

The statistical analysis based on non-hierarchical clustering is presented in Table 3. With respect to the physical properties of carbons (surface area, bulk density, attrition), PSS and PSA grouped with the commercial carbons (cluster 1) whereas PSC and ALA grouped in clusters 2 and 3, respectively. PSA and ALA grouped closely with commercial carbons (F-200, GRC-20, and 206C AW) with respect to chemical (ash, pH, conductivity) and overall properties. PSA grouped with the commercial carbons (F200, GRC-20, and 206C AW) in all the parameters analyzed, thus emphasizing its closeness to the commercial carbons. It is noteworthy that all commercial carbons grouped together in all three parameters studied.

For principal component analysis of combined physical and chemical properties of both experimental and commercial carbons, four quadrants were separated by the intersection of the zero values along the x- and y-axes as shown in Fig. 2. ALA and PSA grouped in the same quadrant as F200 and 206C AW. GRC-20, PSC and PSS occupied separate quadrants.

### 3.4. Statistical analysis of VOC adsorption

Principal component analysis was used to produce a scatter plot of the relationship between the commercial carbons (F200, GRC-20, and 206C AW) and experimental carbons (ALA, PSA, PSS, and PSC) in terms of
their combined physical and chemical properties and adsorption of VOCs (Fig. 3). The experimental GACs most similar to the commercial GACs are expected to cluster in the quadrant containing the latter. Only one experimental carbon (PSA) clustered around the two commercial GACs, F200 and 206C AW, in the lower left quadrant. ALA and GRC-20 occupied the lower right quadrants, whereas PSC and PSS occupied upper right and upper left quadrants, respectively. The dissimilarity of the GRC-20 against the other two commercial GACs can be mainly attributed to higher adsorptive capacity, higher surface area, and ash content.

Cluster analysis is another multivariate technique that allows grouping of GACs based on similarities using several variables simultaneously. For cluster analysis, both hierarchical (Fig. 4) and non-hierarchical analysis (Table 4) was used. The non-hierarchical clustering presented in Table 4 indicates that the grouping of adsorptive and overall properties were very much similar, inferring that adsorptive properties greatly influenced the overall properties. Furthermore, the experimental carbons, PSS and PSA, with respect to the overall and adsorptive properties, grouped with two commercial carbons, F200 and 206C AW, in cluster 3.

Groups of physical and chemical properties of carbons varied substantially in that only F200 and PSA clustered similarly in cluster 3. The PSS separately clustering in cluster 1 is attributed to its high
conductivity and high pH. Similarly, groups of PSC in cluster 2 can be attributed to its low surface area and low bulk density.

The hierarchical clustering presented in Fig. 4 was more selective than either of the other two statistical analyses (principal component analysis and non-hierarchical clustering). The hierarchical clustering represented in the left wing of Fig. 4 was similar in adsorption characteristics of VOCs and overall properties to grouping of F200, 206C AW, PSS and PSA presented in cluster 3, Table 4, and grouping of GRC-20 and PSC presented in cluster 2, Table 4. The dissimilarity between hierarchical and non-hierarchical grouping was primarily the formation subgroups in hierarchical cluster of PSS and PSA in one sub-group and F200 and 206C AW in the second sub-group.
4. Conclusions

Physical, chemical and adsorptive properties were determined for four experimental carbons made from pecan shells or almond shells by three different activation methods. These carbons were compared to the physical, chemical and adsorptive properties of three reference or commercial carbons. Two statistical techniques, namely principal component analysis and cluster analysis, both non-hierarchical and hierarchical, were applied to the data to determine which of the experimental carbons were closest to the reference carbons based on the three properties. The results of the statistical analysis show that two pecan shell carbons, phosphoric acid-activated and steam-activated carbons, clustered together with two commercial carbons, namely F200 and 206C AW, thus inferring that these experimental carbons could be used as alternative sources of carbons in the adsorption of VOCs from an aqueous medium.

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Table 4
Non-hierarchical clustering of GACs based on their physical, chemical, and/or VOC adsorptive properties

<table>
<thead>
<tr>
<th>Basis of clustering</th>
<th>Cluster 1</th>
<th>Cluster 2</th>
<th>Cluster 3</th>
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<tr>
<td>Physical and chemical properties</td>
<td>PSS</td>
<td>PSC</td>
<td>F200</td>
</tr>
<tr>
<td>VOC adsorption</td>
<td>ALA</td>
<td>GRC-20</td>
<td>F200</td>
</tr>
<tr>
<td>Overall properties</td>
<td>ALA</td>
<td>GRC-20</td>
<td>F200</td>
</tr>
</tbody>
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Abbreviations: ALA = phosphoric acid-activated almond shell; PSA = phosphoric acid-activated pecan shell; PSC = carbon dioxide-activated pecan shell; PSS = steam-activated pecan shell; F200 = coal-based, Calgon Filtrasorb 200; GRC-20 = coconut shell-based activated carbon from Calgon; 206C AW = coconut shell-based activated carbon from Barneby and Sutcliffe.

References


