

Selection of Pecan Shell–Based Activated Carbons for Removal of Organic and Inorganic Impurities from Water

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Activated carbons are a byproduct from pyrolysis and have value as a purifying agent. The effectiveness of activated carbons is dependent on feedstock selection and pyrolysis conditions that modify their surface properties. Therefore, pecan shell–based activated carbons (PSACs) were prepared by soaking shells in 50% (v/v) H_3PO_4 or 25 to 50% of KOH-NaHCO_3 followed by pyrolysis at 400 to 700°C under a N_2 atmosphere. Physically activated PSACs were produced by pyrolysis at 700°C under N_2 followed by activation with steam or CO_2 at 700 to 900°C. Physicochemical, surface, and adsorption properties of the PSACs were compared with two commercially available activated carbons. The average mass yield of PSACs with respect to the initial mass of the biomass was about 20 and 34% for physically activated and chemically activated carbons, respectively. Acid-activated carbons exhibited higher surface area, higher bulk density, and lower ash content compared with steam- or CO_2 -activated carbons and the two commercial products. Base activation led to the development of biochar with moderate to high surface area with surface charges suitable for adsorption of anionic species. Regardless of the activation method, PSACs had high total surface area ranging from 400 to 1000 $\text{m}^2 \text{g}^{-1}$, better pore size distribution, and more surface charges than commercial samples. Our results also showed that PSACs were effective in removing inorganic contaminants such as Cu^{2+} and NO_3^- as well as organic contaminants such as atrazine and metolachlor. This study showed that pyrolysis conditions and activation had a large influence on the PSAC's surface characteristics, which can limit its effectiveness as a custom sorbent for targeted water contaminants.

THE ANNUAL PRODUCTION of shelled tree-nuts in the United States in 2010 was about 1.52 million Mg ha^{-1} (USDA, 2012). The production of pecans in 2010 was 133,221 Mg ha^{-1} , amounting to 48,262 Mg ha^{-1} as nutshell byproduct (USDA, 2012). In recent years, there has been interest in producing activated carbon from agricultural byproducts such as nutshells (Hu and Vansant, 1995; Toles et al., 1997, 1998; Johns et al., 1998; Bansode et al., 2003b; Ahmedna et al., 2004).

Nutshells are inexpensive wastes that have been shown to possess natural adsorbent properties and to serve as a precursor to the production of activated carbons (Ioannidou and Zabanitoutou, 2007). Activated carbon can be used in applications such as drinking water purification, decolorization of food products, and wastewater treatment (Ferro-Garcia et al., 1988; Pendyal et al., 1999; Ahmedna et al., 2004). The advantages of nutshells as a carbon feedstock material include high density, availability as renewable resources, low cost, low ash content, and suitability of producing granular activated carbons (GACs) with high adsorption capacity (Heschel and Klose, 1995; Toles et al., 1997; Johns et al., 1998). These qualities make them a suitable choice as an adsorbent material. Hence, agricultural byproduct–based activated carbon has the potential to compete with existing water purification materials in their ability to remove water contaminants and in their cost effectiveness (Toles et al., 2000; Ahmedna et al., 2004).

Several studies have targeted the development of low-cost GACs from cheaper and readily available materials as a cost-effective and environmentally friendly alternative for the safe removal of metals from water (Bailey et al., 1999). Because of their high surface area, microporous character, and chemical ion exchange capacity, activated carbons have an excellent potential as an effective sorbent for the removal of metals from drinking and industrial wastewater. Nutshell-based activated carbon has been demonstrated to effectively remove potentially toxic trace metals such as Cu^{2+} , Pb^{2+} , and Zn^{2+} (Ahmedna et al., 2004). A recent study by Hameed et al. (2009) showed that activated carbons

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Abbreviations: GAC, granular activated carbon; MMA, macro-mesoporous area; PSAC, pecan shell–activated carbon; TSA, total surface area.

from date stone can be used as an adsorbent for the removal of 2,4-D pesticide. Jusoh et al. (2011) reported that activated carbons are capable of greatly reducing the concentrations of malathion from agricultural runoff. However, there are few studies that have critically examined if the metal and pesticide sorbent effectiveness of shell-based carbons can be optimized through pyrolysis and physio-chemical activation procedures (Bansode et al., 2003a; Fang and Huang, 2009; Chen et al., 2011; Chang et al., 2011). This study was conducted (i) to produce pecan shell-based activated carbons (PSACs) via physical and chemical activation methods for use in water purification; (ii) to evaluate physical, chemical, and surface properties of PSACs; and (iii) to determine the efficiency of PSACs in removing common pesticides, NO_3^- , and metal ions from water. The pesticides used as indicators of carbon performance in this study were atrazine and metolachlor. The maximum contaminant level admissible under USEPA regulations for atrazine in drinking water is $3 \mu\text{g L}^{-1}$ (USEPA, 2012), and the lifetime human health advisory for metolachlor is $100 \mu\text{g L}^{-1}$ (USEPA, 1995). These herbicides were chosen because of their widespread presence in water, their worldwide use in agriculture, and their prevalence as environmental pollutants that are harmful to humans even at concentrations found in the environment.

Materials and Methods

Preparation of Pecan Shell-Based Granular Activated Carbon

Physical Activation

Pecan shells were obtained from a pecan processing company (Carolina Grains). The raw pecan shells were crushed using a Retsch Mill (Retsch Inc.) and were sieved using a 1.70- to 2.00-mm sieve (U.S. Standard Sieve). Sieved pecan shells were pyrolyzed at 700°C for 1 h using a Lindberg box furnace oven equipped with an air-tight retort under a continuous stream of N_2 at a flow rate of 0.1 mL min^{-1} . After pyrolysis, activating gases (CO_2 or steam) were injected into the retort at specific flow rates, exposure times, and activation temperatures. In the case of steam activation, water was injected into the furnace at a flow rate of 2 mL min^{-1} under three different activation temperatures (700 , 800 , and 900°C). Upon completion of activation, the steam was switched off, and the activated carbon was allowed to cool overnight inside the furnace retort while maintaining a gentle stream of N_2 . The CO_2 activation was performed following a process similar to that of steam activation. The CO_2 activation was performed using a 75% CO_2 and 25% N_2 (v/v) mixture based on a prior screening trial using several CO_2 concentrations. Steam and CO_2 activations were evaluated at two process times (3 and 5 h) as described by Johns et al. (1999) and Ng et al. (2003).

Chemical Activation

Chemical activation consisted of soaking sieved pecan shells in 50% (v/v) H_3PO_4 for 2 h. Soaked shells were then heated under a stream of N_2 gas at a flow rate of $0.1 \text{ m}^3 \text{ h}^{-1}$ at 170°C for 30 min. After this low dehydration temperature, activation was conducted by holding the temperature of the carbonized materials at one of three activation temperatures (400 , 450 , and 500°C) for 1 h under a stream of compressed air (80/20%, N_2/O_2). After 1 h of activation, the activated carbon was left overnight in the furnace to allow slow cooling under a stream of N_2 gas. After cooling, the acid-activated

carbon was sieved with a sieve size of 1.7 to 2.0 mm (U.S. Standard Sieve) and washed with boiling water to remove any residual H_3PO_4 . The material was then rinsed with distilled water until the pH of the rinsed water reached near neutral values. Washed GAC samples were redried at 110°C for at least 3 h in a vacuum oven. Mass yield was calculated using the following equation:

$$\text{Yield (\%)} = \frac{W_f}{W_0} \times 100 \quad [1]$$

where W_f and W_0 are dry mass (g) of the produced activated carbon (g) and dry mass (g) of precursor (pecan shell), respectively.

Hybrid Activation: Combining Physical and Chemical Activation

Two bases (NaHCO_3 and KOH) were used in the hybrid activation-based process for preliminary screening of several bases for judging their suitability as activating agents. Ground pecan shells were soaked before pyrolysis at the ratio of the solution mass to the shell mass (w/w) of 10, 25, or 50% for NaHCO_3 and 10, 15, or 17.5% for KOH . After soaking for 2 h, the material was pyrolyzed at 700°C as described previously. Immediately after pyrolysis, the resulting carbonaceous material was steam activated at 700 , 800 , or 900°C for 3 or 5 h as described previously. Upon completion of this last step of hybrid activation, activated carbon was cooled overnight under a gentle stream of N_2 inside the furnace retort. The hybrid GAC was washed with boiling water and rinsed with distilled water until the rinse water reached near neutral pH. The washed sample was dried at 110°C for at least 3 h in a vacuum oven. Samples were stored in a dessicator until analysis or until being used in proceeding with the experiments.

Measurement of Carbon Properties of Materials

Bulk density was determined using the method of Ahmedna et al. (1998). A 25-mL cylinder was filled to a specified volume with 10- to 30-mesh granular-activated carbon that had been oven dried at 80°C overnight. The preweighed cylinder was tapped for at least 1 to 2 min to compact the carbon and weighed (Bansode et al., 2003a). The bulk density was calculated by the following formula:

$$\text{Bulk density (g mL}^{-1}\text{)} = \frac{\text{weight of dry material (g)}}{\text{volume of packed dry material (mL)}} \quad [2]$$

The pH measurements of activated carbon were conducted using the method prescribed by Ahmedna et al. (1998). The method for pH measurement consists of preparing 1% (wt/wt) suspension of activated carbon in deionized water. The suspensions were heated to approximately 90°C and stirred for 20 min. The suspensions were allowed to cool to room temperature, and the pH was measured with a Corning pH 10 portable pH meter.

For ash content, approximately 2 g of activated carbon was placed into preweighed ceramic crucibles. Crucibles and their contents were dried overnight at 80°C and reweighed to obtain the dry carbon weight. The samples were heated in an Isotemp Laboratory Muffle Furnace (Fisher Scientific) at 760°C for at least 6 h. The crucibles were cooled in a desiccator, and the remaining solids (ash) were weighed (Bansode et al., 2003a). The percent ash was calculated as follows:

$$\text{ash}(\%) = \frac{\text{remaining solids weight}(\text{g})}{\text{original carbon weight}(\text{g})} \times 100 \quad [3]$$

Surface Area Measurement

Between 0.2 and 0.25 g of carbon that was previously degassed overnight (for at least 8 h) was placed into the evacuated sample chamber of the surface area analyzer. The Nova 2200 (Quantachrome Instruments) was equipped with automated software for acquisition of Brunauer–Emmett–Teller surface area and pore size distribution based on monolayer adsorption of nitrogen. Micro-, meso-, and macropore volumes were calculated using the Barrett, Joyner, and Halenda model, and pore surface areas were calculated using t-plots (Johns et al., 1999; Bansode et al., 2003a; Toles et al., 1997).

Surface Charge

Two different titration types were used depending on the type of activation used to produce activated carbon. For physically and chemically activated carbon, 50 mL of each base were placed in a 250-mL Erlenmeyer flask, and 0.5 g of carbon was introduced into each flask (1% w/v slurry) along with a Teflon stirring bar. In the case of hybrid activated carbon, 50 mL of 0.1 mol L⁻¹ HCl was used to prepare the 1% (w/v) carbon slurries along with the blank. A blank (i.e., a base with no carbon) was run in parallel with the carbon samples. Sealed flasks containing test samples were stirred at 150 to 200 rpm for 24 h. At the end of 24 h, carbon was separated from the base or acid solution using 0.45- μm Teflon filters. Ten milliliters of the filtrate were then pipetted into a 50-mL beaker followed by the addition of 15 mL of 0.1 mol L⁻¹ HCl. For hybrid activated carbon, there was no addition of HCl to the 10 mL of filtrate because the filtrate is made up of HCl. In each case, excess HCl concentration was determined by titration with 0.1 mol L⁻¹ NaOH. Titrations were performed using a Titrando system (Metrohm Ltd) operated by PC-controlled software and connected to a titration stand and rod stirrer. A dynamic pH titration was conducted for detection of inflection points (Ahmedna et al., 2000). The difference in 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 a standard base per gram of carbon.

Adsorption Properties

Copper Adsorption. The batch assays for Cu²⁺ adsorption consisted of placing 0.25 g of carbon in 50 mL of 0.01 mol L⁻¹ CuCl₂·2H₂O solution buffered at pH 5.05 with 0.035 mol L⁻¹ NaOAc and 0.011 mol L⁻¹ HOAc with an ionic strength of 0.076 mol kg⁻¹. Solutions with effective concentration of Cu²⁺ of 10 $\mu\text{g mL}^{-1}$ containing the carbon as well as blank were prepared in triplicate (buffer without GAC). Samples were stirred at 500 rpm for 24 h (room temperature) using 1 \times 2.5 cm stirring bars. The final slurry pH was measured after stirring to ensure that the metal solution remained buffered at pH 5. An aliquot was drawn from each sample using a disposable syringe and filtered through a 0.22- μm Teflon filter. When necessary, samples were diluted with deionized H₂O before analysis. The amount of Cu²⁺ in filtered aliquots was measured by inductively coupled plasma optical emission spectrometry using a PerkinElmer Optima 3300DV. Certified inductively coupled plasma standards were used to develop standard curves for quantitative analysis of Cu²⁺.

The amount of Cu²⁺ adsorbed was determined by using the following equation (Johns et al., 1998):

$$\text{Cu}_{\text{abs}} = \text{Cu}_{\text{blank}} - \text{Cu}_{\text{sample}} \quad [4]$$

where Cu_{abs} is the concentration of Cu²⁺ adsorbed, Cu_{blank} is the concentration of Cu²⁺ in the blank, and Cu_{sample} is the concentration of Cu²⁺ in the sample after treatment with activated carbon.

Nitrate Adsorption. A fixed amount of dry adsorbent (0.25 g) was added to a volumetric flask containing 50 mL of 10 mg L⁻¹ solution of NaNO₃. The flask was shaken at 500 rpm for 24 h using a continuous agitation platform shaker. After 24 h of agitation, the samples were filtered with 0.45- μm Teflon filters, and the concentrations of NO₃⁻ in the supernatants were determined by Ion-selective electrode analysis using a flow injection analyzer (Lachat's Quick Chem. 8000 series). Measurements were performed in duplicate at pH 7.0. To ensure that NO₃⁻ was converted, a Cd rod was used to reduce NO₃⁻ to NO₂⁻. Calibration was performed with a series of standard solutions prepared from stock NaNO₃ solutions. The final NO₃⁻ concentration was expressed as mg N L⁻¹ (Ozturk and Bektas, 2004).

Pesticide Removal by Activated Carbons

The experiment consisted of placing 0, 0.05, 0.1, 0.2, 0.5, 0.75, 1.0, and 1.5 g activated carbon in flasks containing 50-mL aliquots of 25 and 40 mg L⁻¹, respectively, of atrazine or metolachlor solutions. Carbon and herbicide slurries were stirred for 24 h at room temperature using a platform shaker. After 24 h of stirring, samples were filtered through 0.45- μm Teflon filters to remove the carbon and to obtain filtrates for contaminant analysis. Aliquots of the filtered solutions were analyzed by a high-performance liquid chromatograph equipped with a 1525 binary pump and a diode array detector (Waters Inc.). The injection loop volume was 10.0 μL . An Alltima HP C₁₈ column (4.6 i.d. \times 250 mm, 5.0 μm) (Alltech Associates, Inc.) was used for separations. The mobile phase was a mixture of CH₃CN:H₂O (15:85, v/v) at a flow rate of 1 mL min⁻¹. Retention times for atrazine and metolachlor were determined for standard solutions of atrazine and metolachlor at 221.6 and 195.8 nm, respectively. Retention times obtained from standard solutions were used for monitoring atrazine and metolachlor in experimental samples. The commercial carbons F300 and USO3 were used as controls.

Determination of Optimum Conditions for Activated Carbon Production

The influence of activation conditions (temperature, time, and type of activating chemical) on activated carbon properties (yield, density, and total surface area [TSA]), ratio of macroporous area (MMA) to TSA, surface charge, and Cu²⁺ and NO₃⁻ uptake was evaluated and used to select the optimum conditions for carbon production.

A selection matrix was developed for unbiased evaluation of activated carbon produced under these various conditions. Criteria were applied to each of the five types of activated carbon individually, and the best carbon was selected from within each category of activation method. Physicochemical and surface characteristics and adsorption performances were normalized to produce a maximum composite score for each carbon. For each category of activated carbon, a composite score was calculated based on the selected carbon properties. Each variable was assigned an equal weight of 1 based on its actual or normalized values. Because

the total weight for each variable does not exceed 1, the sum of all the scores across the seven carbon properties (variables) yields a maximum composite score of 7 for each carbon within a given category. Normalization of score consisted of dividing the value of each variable by 1, 100, or 1000, depending on the nature of each particular variable. Within each of the five categories of activated carbon, individual carbon scores were obtained by summing up the normalized scores of each characteristic or property for each carbon. The carbons with the highest performance score (sum) were considered the best performing carbons, and the conditions used in their production were selected for optimized production of PSAC within the corresponding activation type.

Statistical Analysis

All experimental data were analyzed using the generalized linear model procedure of the Statistical Analysis System (SAS

Institute, 2008). Multivariate ANOVA was used to compare the mean values of physicochemical and adsorption properties among various GACs. A Tukey's post-ANOVA test was used in multiple comparisons of the experimental carbons against commercial carbon. Pearson's correlation coefficient was used to assess the correlation among major carbon properties for each category of activated carbon.

Results and Discussion

Properties of Pecan Shell–Based Activated Carbon

Mass Yield

Physical, chemical, and surface properties of the PSAC are presented in Tables 1 and 2. The activation conditions had significant effect on carbon properties. The yield values of PSAC materials ranged from 9 to 43%, depending on the type

Table 1. Properties of pecan shell–based carbons activated by physical and chemical activation.†

Carbon	Ratio‡	A _{temp}	A _{time}	Carbon acronym	Yield	Density	TSA	MA	MMA	MV	Surface charge	Cu ²⁺ §	NO ₃ ⁻ ¶
		°C	Hr		%	kg m ⁻³	m ² g ⁻¹				mmol H ⁺ eq g ⁻¹ C	%	
NaHCO ₃	10	900	3	BS109003	22.2 ± 0.9	526.5 ± 2.1	725.7 ± 14.9	682.6 ± 9.6	43.2 ± 5.1	0.34 ± 0.01	0.61 ± 0.01	74.5 ± 1.2	11.3 ± 1.5
			5	BS109005	10.3 ± 1.3	409.0 ± 15.6*	826.5 ± 116.1	762.7 ± 47.9	63.8 ± 68.2	0.37 ± 0.01	0.04 ± 0.00	24.8 ± 8.2*	8.9 ± 3.4
	25	700	3	BS257003	38.4 ± 0.5	494.9 ± 61.9*	340.8 ± 43.1*	334.0 ± 41.3*	47.9 ± 75.1	0.17 ± 0.01*	0.62 ± 0.09	34.8 ± 3.9	6.9 ± 0.5
			5	BS257005	18.0 ± 12.1	397.1 ± 56.0*	390.1 ± 38.9	333.5 ± 53.4*	56.6 ± 14.8	0.17 ± 0.03*	0.06 ± 0.01	19.4 ± 7.5*	14.4 ± 4.1
		800	3	BS258003	21.1 ± 2.0	414.0 ± 4.6	575.2 ± 61.5	398.1 ± 7.1*	177.2 ± 54.8	0.23 ± 0.02	0.63 ± 0.03	73.4 ± 1.6*	9.5 ± 2.2
			5	BS258005	11.4 ± 8.8	338.3 ± 19.3*	518.3 ± 84.2	359.0 ± 53.5*	159.3 ± 30.8	0.20 ± 0.01	0.06 ± 0.01	39.0 ± 12.7	13.4 ± 7.4
	50	900	3	BS259003	15.9 ± 0.7	459.8 ± 55.2*	814.3 ± 110.5	739.8 ± 69.1	74.6 ± 41.5	0.37 ± 0.07	0.60 ± 0.06	86.2 ± 2.1*	8.3 ± 2.6
			700	3	BS507003	38.6 ± 0.9	488.8 ± 37.9*	411.3 ± 7.6	311.9 ± 6.7*	99.3 ± 13.0	0.19 ± 0.02*	0.60 ± 0.07	49.0 ± 4.3
		5		BS507005	16.3 ± 11.0	366.8 ± 12.5*	498.5 ± 42.8	325.5 ± 63.1*	173.0 ± 105.9	0.17 ± 0.03*	0.07 ± 0.01	21.1 ± 11.4*	7.7 ± 3.2
			800	3	BS508003	21.6 ± 3.4	414.8 ± 10.2*	752.6 ± 111.0	512.9 ± 32.4	231.5 ± 90.7	0.30 ± 0.08	0.64 ± 0.01	89.1 ± 3.1*
		5		BS508005	11.0 ± 9.8	330.2 ± 24.3*	395.3 ± 379.8	222.1 ± 196.5*	199.3 ± 162.5	0.13 ± 0.11*	0.05 ± 0.01	26.0 ± 4.5	14.1 ± 6.2
		900	3	BS509003	16.7 ± 0.5	462.8 ± 53.5*	811.1 ± 81.1	723.5 ± 42.3	88.4 ± 38.1	0.37 ± 0.06	0.62 ± 0.03	83.6 ± 5.3	7.9 ± 2.3
KOH	10	800	3	KH108003	25.8 ± 1.1	504.6 ± 7.6	600.9 ± 13.3	559.2 ± 5.5	41.7 ± 7.8	0.21 ± 0.00	0.55 ± 0.01	91.8 ± 10.9*	2.4 ± 0.9
			3	KH109003	33.5 ± 0.7	413.0 ± 0.4*	621.4 ± 3.0	568.0 ± 5.8	53.4 ± 2.8	0.23 ± 0.00	0.52 ± 0.01	84.2 ± 1.7*	2.0 ± 0.00
	15	800	3	KH158003	32.4 ± 0.9	307.4 ± 0.8	756.9 ± 4.3	688.8 ± 6.7	68.2 ± 2.4	0.34 ± 0.00	0.63 ± 0.00	99.4 ± 0.0*	4.4 ± 0.4
			3	KH178003	32.6 ± 3.5	296.0 ± 33.9*	852.0 ± 7.9	816.8 ± 5.6	35.2 ± 2.3	0.42 ± 0.00	0.47 ± 0.01	100.0 ± 0.0*	2.9 ± 0.1
	17.5	800	3	KH179003	33.5 ± 2.1	275.0 ± 0.0*	883.0 ± 9.3	828.6 ± 10.5	54.5 ± 1.3	0.43 ± 0.00	0.46 ± 0.01	81.9 ± 0.7*	2.1 ± 0.4
F300	NA	–	–	F300	–	610.3 ± 10.9	740.7 ± 23.0	721.8 ± 68.0	43.8 ± 24.8	0.37 ± 0.03	0.18 ± 0.02	51.1 ± 10.4	5.4 ± 0.9

* Significantly different from F300 reference carbon at $p < 0.05$ according to Tukey's HSD range test.

† A_{temp}, activation temperature; A_{time}, activation time; MA, microporous area; MMA, meso-microporous area; MV, microporous volume; TSA, total surface area.

‡ The ratio of the solution mass to the shell mass.

§ Adsorption of Cu²⁺ consisted of placing 0.25 g of carbon in 50 mL of 0.01 mol L⁻¹ CuCl₂·2H₂O solution buffered at pH 5.05 for 24 h.

¶ Adsorption of NO₃⁻ consisted of placing 0.25 g of carbon in 50 mL of 10 mg L⁻¹ solution of NaNO₃.

of activation and the process conditions used. The highest yield was obtained via H₃PO₄ activation, and the lowest yield was observed in steam-activated carbon, especially when activated at the highest temperature (900°C) and time (5 h).

Bulk Density

The lowest bulk density was observed in carbon activated with KOH, which exhibited an average bulk density value of 275.00 kg m⁻³ (Table 1). The highest biochar bulk density was observed in the H₃PO₄-activated carbon, which averaged 629.75 kg m⁻³ (Table 2). With the exception of H₃PO₄-activated carbon, PSACs had bulk densities slightly lower than that of the reference carbon material (F300). Overall, hybrid activated carbon generally showed the lowest bulk density, probably due to physical processing from the extra physical activation step.

Surface Area Measurements

Surface properties (surface area, pore size distribution, and surface charge) of activated carbon usually play significant roles in the adsorption process (Mangun et al., 2001). Here, the PSAC production conditions have shown their significant effect on surface properties (TSA and micropore area). Although H₃PO₄-

activated carbon exhibited higher surface area (maximum surface area value of 1058 m² g⁻¹) than all experimental carbons and the reference carbon (F300), the CO₂-activated carbon material possessed the lowest surface area (Table 2). The highest total surface area was achieved using CO₂ activation; values ranged up to 622 m² g⁻¹ after 900°C activation for 3 h.

Most of the PSACs had about a 10% ratio of macro-mesoporous area to TSA, indicating a tight network of microporous area with MMA as conduits for adsorbates. Only hybrid activation with NaHCO₃ yielded a MMA to TSA ratio of 30%, indicating a less extensive network for trapping smaller-sized adsorbates and potential suitability for applications such as color removal (Hung-Lung et al., 2007).

Surface Charge

Charged active surface sites determine the adsorption behavior of activated carbon (Park and Jang, 2002). The surface charges of PSACs were found to be dependent on activation conditions such as temperature, time, and concentration of chemical agent. Although negative surface charges are suitable for the electrostatic removal of positively charged adsorbates,

Table 2. Properties of pecan shell-based carbons activated by physical or chemical activation.†

Carbon	Ratio‡	A _{temp}	A _{time}	Carbon acronym	Yield	Density	TSA	MA	MMA	MV	Surface charge	Cu ²⁺ §	NO ₃ -¶
		°C	Hr										
Steam	NA	700	3	S7003	18.3 ± 0.5	590.0 ± 0.0	546.1 ± 31.7	398.8 ± 33.2	147.3 ± 1.5	0.24 ± 0.03	0.38 ± 0.03	51.4 ± 1.2	7.9 ± 0.3
			5	S7005	14.5 ± 7.8	570.0 ± 70.7	690.3 ± 129.5	537.7 ± 181.1	152.6 ± 51.6	0.29 ± 0.1	0.33 ± 0.01	15.1 ± 2.8*	17.8 ± 1.0
		800	3	S8003	17.8 ± 0.7	540.0 ± 42.4	774.1 ± 6.8	664.0 ± 5.5	110.2 ± 1.3	0.35 ± 0.0	0.43 ± 0.02	73.3 ± 0.3	13.1 ± 0.1
			5	S8005	11.5 ± 2.1	407.0 ± 116.0*	794.8 ± 42.3	767.0 ± 40.3	27.8 ± 2.0	0.38 ± 0.0	0.44 ± 0.02	83.8 ± 0.3*	10.5 ± 1.0
		900	3	S9003	17.1 ± 0.4	570.0 ± 14.1	856.7 ± 4.4	701.1 ± 3.8	155.6 ± 8.2	0.36 ± 0.01	0.42 ± 0.02	53.0 ± 0.5	7.9 ± 0.3
			5	S9005	11.5 ± 2.1	407.0 ± 116.0*	794.8 ± 42.3	767.0 ± 40.3	27.8 ± 2.0	0.38 ± 0.0	0.44 ± 0.02	83.8 ± 0.3*	10.5 ± 1.0
75%CO ₂	NA	700	3	CO2N7003	38.7 ± 1.0	609.0 ± 1.4	351.8 ± 10.6	341.5 ± 8.7*	10.2 ± 2.1*	0.17 ± 0.01	0.23 ± 0.00	21.6 ± 0.5*	7.0 ± 0.1
			5	CO2N7005	28.7 ± 0.0	543.2 ± 31.4	517.2 ± 57.6	477.2 ± 46.2	40.0 ± 11.5	0.23 ± 0.03	0.25 ± 0.01	17.1 ± 2.9*	46.2 ± 1.0*
		800	3	CO2N8003	37.0 ± 1.3	601.5 ± 2.1	514.1 ± 7.8	485.1 ± 6.0	29.0 ± 1.8	0.25 ± 0.00	0.30 ± 0.00	27.3 ± 0.3	21.1 ± 0.6
			5	CO2N8005	23.8 ± 1.1	561.5 ± 17.8	516.8 ± 115.8	472.9 ± 109.9	44.0 ± 6.0	0.24 ± 0.04	0.21 ± 0.00	8.8 ± 1.2*	61.9 ± 1.0*
		900	3	CO2N9003	34.2 ± 1.1	610.0 ± 14.1	622.1 ± 73.8	566.1 ± 61.0	55.7 ± 13.3	0.28 ± 0.03	0.26 ± 0.02	50.7 ± 0.4	29.6 ± 1.0
			5	CO2N9005	18.0 ± 1.4	540.0 ± 84.9	497.7 ± 27.2	477.3 ± 13.5	20.4 ± 13.7	0.24 ± 0.00	0.19 ± 0.01	29.7 ± 1.7	16.7 ± 1.0
H ₃ PO ₄	50	400	1	PA504001	43.8 ± 7.2	629.8 ± 24.8	859.6 ± 69.1	819.6 ± 50.9	41.9 ± 28.4	0.40 ± 0.04	0.71 ± 0.21	64.1 ± 21.1	32.3 ± 20.5*
			1	PA504501	40.0 ± 4.7	600.5 ± 25.5	1057.8 ± 222.1	934.1 ± 144.5	125.0 ± 83.5	0.47 ± 0.08	0.81 ± 0.11	48.7 ± 7.6	39.6 ± 13.6*
			1	PA505501	39.9 ± 4.7	594.6 ± 15.8	969.9 ± 132.6	834.9 ± 68.4	135.0 ± 82.3	0.43 ± 0.04	0.66 ± 0.34	45.2 ± 4.3	45.1 ± 27.0*
F300	NA	-	-	F300	-	610.3 ± 10.9	740.7 ± 23.0	721.8 ± 68.1	43.8 ± 24.8	0.37 ± 0.03	0.18 ± 0.02	51.1 ± 10.4	5.4 ± 0.9

* Significantly different from F300 reference carbon at $p < 0.05$ according to Tukey's HSD range test.

† A_{temp}, activation temperature; A_{time}, activation time; MA, microporous area; MMA, meso-microporous area; MV, microporous volume; TSA, total surface area.

‡ Ratio of the solution mass to the shell mass.

§ Adsorption of Cu²⁺ consisted of placing 0.25 g of carbon in 50 mL of 0.01 M CuCl₂·2H₂O solution buffered at pH 5.05 for 24 h.

¶ Adsorption of NO₃⁻ consisted of placing 0.25 g of carbon in 50 mL of 10 mg L⁻¹ solution of NaNO₃.

they are more than likely to hinder the adsorption of negatively charged compounds. For example, a negatively charged carbon surface would attract positively charged ions such as Cu^{2+} and Zn^{2+} but will not be favorable for the adsorption of negatively charged NO_3^- ions. The largest surface charge was observed in H_3PO_4 -activated carbon (0.8 mmol H^+ eq g^{-1}), followed by hybrid activation with NaHCO_3 (0.6 mmol H^+ eq g^{-1}). The lowest surface charge was exhibited by steam-activated carbon (0.2 mmol H^+ eq g^{-1}). These differences in surface charge are expected to affect each carbon's ability to adsorb negatively and positively charged adsorbates (Kandah et al., 2006).

Effect of Carbon Dosage on Adsorption of Copper Ion and Nitrate

A summary of the percent Cu^{2+} uptake amounts by PSACs is provided in Tables 1 and 2. Uptake of Cu^{2+} ranged from 15% to complete adsorption within the detection limits, depending on the type of activation used to produce activated carbon. At a dosage of 0.5% of (w/v), some of the PSACs exhibited Cu^{2+} uptake twice that of commercial carbon F300 (51%). Pecan shell-based carbons activated with KOH exhibited the highest metal adsorption efficiency but showed relatively low NO_3^- uptake (Table 1). The highest NO_3^- removal (62%) was achieved by CO_2 activation at 800°C for 5 h (Table 2). With the exception of carbon activated with KOH, NO_3^- uptake by PSAC was significantly higher than that of the reference carbon (F300). The low NO_3^- removal exhibited by F300 and KOH may be explained by the limited concentration of anionic exchange sites on the surface of activated carbon leading to lower affinity to the negatively charged compounds such as NO_3^- and greater affinity toward positively charged compounds such as Cu^{2+} and Zn^{2+} . Surface charges of all PSACs were higher than the commercial carbon except the 5 h NaHCO_3 activated carbons (Tables 1 and 2).

Correlation Matrix Carbon Properties

Table 3 presents the correlation values among major carbon properties for each category of activated carbons. For KOH-activated carbon, the negative correlation coefficient ($r^2 = -0.66$) for Cu^{2+} and NO_3^- was expected because these compounds have opposite charges and these two elements would not compete for the same surface sites. The correlation matrix indicates that KOH-activated carbon favors Cu^{2+} ($r^2 = 0.48$) over NO_3^- (0.08) sorption. The TSA of carbons generally increased as the density decreased due to carbonization of organic structures ($r^2 = -0.97$), leading to higher Cu^{2+} uptake ($r^2 = 0.77$). In the case of H_3PO_4 -activated carbon, there was a negative correlation between surface charge and Cu^{2+} (-0.04) and NO_3^- (-0.22) adsorption. A previous study by Kalavathy et al. (2005) has shown that activated carbon prepared using H_3PO_4 as the activating agent was effective at Cu^{2+} ion adsorption. Also, the TSA was negatively correlated to the material's density (-0.82). This is expected because higher pyrolysis temperature yields lower density and thus increases the surface area of the carbon material. Our results are in agreement with observations by other researchers because high surface areas are usually only obtained through higher pyrolysis temperatures. This leads to a larger percentage of feedstock loss and thus a lower yield of activated carbon (van Krevelen, 1993; Speight, 1994; Lizzio and DeBarr, 1997).

The correlation matrix for PSAC activated with NaHCO_3 (Table 3) reveals that the surface chemistry of this carbon material is likely to have amphoteric charge properties (i.e., a mix of positively and negatively charged functional groups). This is supported by the positive correlations between Cu^{2+} uptake and surface charge ($r^2 = 0.69$). Furthermore, this carbon is the only carbon in which adsorption of Cu^{2+} and NO_3^- was positively correlated ($r^2 = 0.57$).

Generally, uptake of Cu^{2+} and NO_3^- increased with higher surface area. The results presented in Table 3 suggest that

Table 3. Correlation matrix among carbon properties of carbons activated with physical and chemical methods.

Paired carbon properties†	Activation agent					
	Hybrid‡		Acid	Physical		
	KOH	NaHCO_3	H_3PO_4	CO_2	Steam	
BD-TSA	-0.97*	0.16	-0.82*	-0.08		0.32
BD-MMA/TSA	-0.49	-0.67	-0.99*	-0.09		0.94*
BD-Charge	-0.14	0.77	-0.06	0.58*		-0.16
BD- Cu^{2+}	-0.77*	0.35	0.99*	0.48		-0.39
BD- NO_3^-	0.55*	-0.09	-0.96*	-0.45		-0.29
TSA-MMA/TSA	0.36	-0.46*	0.77*	0.82*		0.02
TSA-Charge	0.004	0.28	0.62*	0.29		0.60*
TSA- Cu^{2+}	0.75*	0.73*	-0.80*	0.52		0.35
TSA- NO_3^-	-0.59*	0.47	0.62*	0.46		-0.40
MMA/TSA-Charge	0.72*	-0.30	-0.01	0.22		-0.39*
MMA/TSA- Cu^{2+}	0.69*	-0.29	-0.99*	0.11		-0.55
MMA/TSA- NO_3^-	-0.55*	0.01	0.98*	0.82*		-0.22
Charge- Cu^{2+}	0.48	0.69*	-0.04	0.37		0.94*
Charge- NO_3^-	0.08	0.23	-0.22	-0.14		-0.68*
Cu^{2+} - NO_3^-	-0.66*	0.57*	-0.96*	-0.45		-0.54

* Data with significant correlation at $p < 0.05$ within each carbon properties.

† BD, bulk density; MMA, meso-macropore area; TSA, total surface area.

‡ Hybrid activation using steam as second step after soaking in a base.

the surface charge of CO₂-activated carbon is composed of functional groups that have weak negative charge, as indicated by the low positive correlation with Cu²⁺ adsorption and the negative correlation with NO₃⁻ uptake. Among all the physicochemical properties of the carbon materials, TSA was most correlated with carbon uptake of Cu²⁺ and NO₃⁻. The data showed that Cu²⁺ adsorption by steam-activated carbon was highly correlated ($r^2 = 0.94$) with carbon charge, suggesting a predominantly negatively charged surface. This is also supported by the negative correlation between surface charge and NO₃⁻ uptake and between NO₃⁻ and Cu²⁺ uptake.

Selection Criteria for Carbon Ranking Based on Properties

This study was aimed at optimizing the production of PSAC for use in the purification of water. Tables 4 and 5 summarize the selection criteria for carbon within each of the three activation types. The composite score achieved by each carbon is considered as the sum of an individual carbon's properties scoring. The composite scores and the weight and rank are given in the last two columns of the matrix. The selection matrix for NaHCO₃-based activated carbon (Table 4) shows that the

Table 4. Relative ranking of activated carbons activated by physical and chemical activation.

Activation agent	Ratio†	A _{temp} ‡	A _{time}	Carbon acronym	Weight	Rank§		
		°C	h					
NaHCO ₃	25%	900	3	BS109003	2.94	5		
		900	5	BS109005	1.74	11		
		700	3	BS257003	2.63	7		
		700	5	BS257005	1.6	12		
		800	3	BS258003	2.96	4		
		800	5	BS258005	1.95	9		
		900	3	BS259003	3.13	2		
	50%	700	3	BS507003	2.68	6		
		700	5	BS507005	1.73	8		
		800	3	BS508003	3.33	1¶		
		800	5	BS508005	1.25	10		
		900	3	BS509003	3.13	3		
		KOH	10	800	3	KH108003	2.87	3
				900	3	KH109003	2.77	5
15	800		3	KH158003	3.08	1¶		
	17		800	3	KH178003	2.98	2	
			900	3	KH179003	2.81	4	

† Ratio of the solution mass to the shell mass.

‡ A_{temp} activation temperature; A_{time} activation time.

§ Ranking is based on their physicochemical and adsorption properties.

¶ Best activated carbon within each activation agent group.

Table 5. Relative ranking of activated carbons activated by physical or chemical activation.

Activation agent	Ratio†	A _{temp} ‡	A _{time}	Carbon acronym	Weight	Rank§
		°C	h			
Steam	NA	700	3	S7003	2.54	4
		700	5	S7005	2.25	5
		800	3	S8003	2.86	1
		800	5	S8005	2.7	3¶
		900	3	S9003	2.75	2
75%CO ₂	NA	700	3	CO2N7003	1.87	6
		700	5	CO2N7005	2.25	4
		800	3	CO2N8003	2.28	3
		800	5	CO2N8005	2.26	2¶
		900	3	CO2N9003	2.67	1
H ₃ PO ₄	50%	900	5	CO29005	1.88	5
		400	1	PA504001	3.61	3
		450	1	PA504501	3.81	1¶
		550	1	PA505501	3.6	2

† Ratio of the solution mass to the shell mass.

‡ A_{temp} activation temperature; A_{time} activation time.

§ Ranking is based on their physicochemical and adsorption properties.

¶ Best activated carbon within each activation agent group.

highest composite score (weight = 3.33) was achieved by soaking shells in 50% NaHCO₃ followed by activation at a pyrolysis temperature of 800°C for 3 h (BS508003). For KOH-activated carbon, the selection matrix (Table 4) revealed that activated carbon produced by soaking shells in 15% KOH, and pyrolysis at 800°C for 3 h (KOH158003) was the best performing activated carbon, with a selection weight score of 3.08.

For steam-based activated carbon, the best activated carbon was produced by activation at a pyrolysis temperature of 800°C for 3 h (S8003), with a composite score of 2.86. However, this slightly lower scored sample was not selected for additional use. Instead, the third-ranked carbon produced by activation at 800°C for 5 h (S8005) was selected for further characterization and used in water purification. The rationale for this was that the composite score for the third-ranked carbon was nearly similar to that of the top-ranked carbon (S8003) and exhibited the highest Cu²⁺ uptake among all steam-activated carbons.

A similar situation was encountered in CO₂ activation where the second-best carbon was selected for use in filtration systems because of its high affinity for NO₃⁻ (Table 5). This consideration was especially important because none of the activation types produced carbon with NO₃⁻ uptakes comparable to that of CO2N8005 (62%). The CO₂-activated carbon with the highest composite score (CO2N9003) achieved only about 30% NO₃⁻ uptake.

The scoring matrix for H₃PO₄-activated carbons revealed that the best activated carbon was produced by soaking shells

in 50% H₃PO₄ solution followed by activation at 450°C for 1 h (PA504501). The processing conditions produced material with a composite score of 3.8.

Effect of Carbon Dosage on Adsorption of Pesticides

The adsorption performances of the best PASCs derived from the previous selection criteria were compared against two commercially available activated carbons (F300 and USO3). Because activated carbon is effective at removing pesticides from water, we evaluated the adsorption performance of PSACs against two commonly used herbicides (atrazine and metolachlor). Among the selected PSACs, carbon activated with KOH (KOH158003) exhibited the highest adsorptive performance for atrazine and metolachlor (Fig. 1 and 2). Atrazine removal was generally a function of the amount of carbon added to the volume of solution containing herbicides (carbon dosage). The data obtained on the removal of atrazine clearly showed that all PSACs had excellent affinity for atrazine removal. Atrazine removal increased in a dose-dependent manner (Fig. 1). This suggests that PSACs are effective at removing atrazine from water. Even though CO₂-activated (CO2N8005) and H₃PO₄-activated (PA504501) showed the lowest pesticide uptake, they did show complete removal of atrazine at higher carbon dosages. Carbons activated with KOH and NaHCO₃ showed complete removal of atrazine within the detection limit, comparable to commercial carbon at similar carbon dosage (50 µg g⁻¹ C). Subsequently, steam-

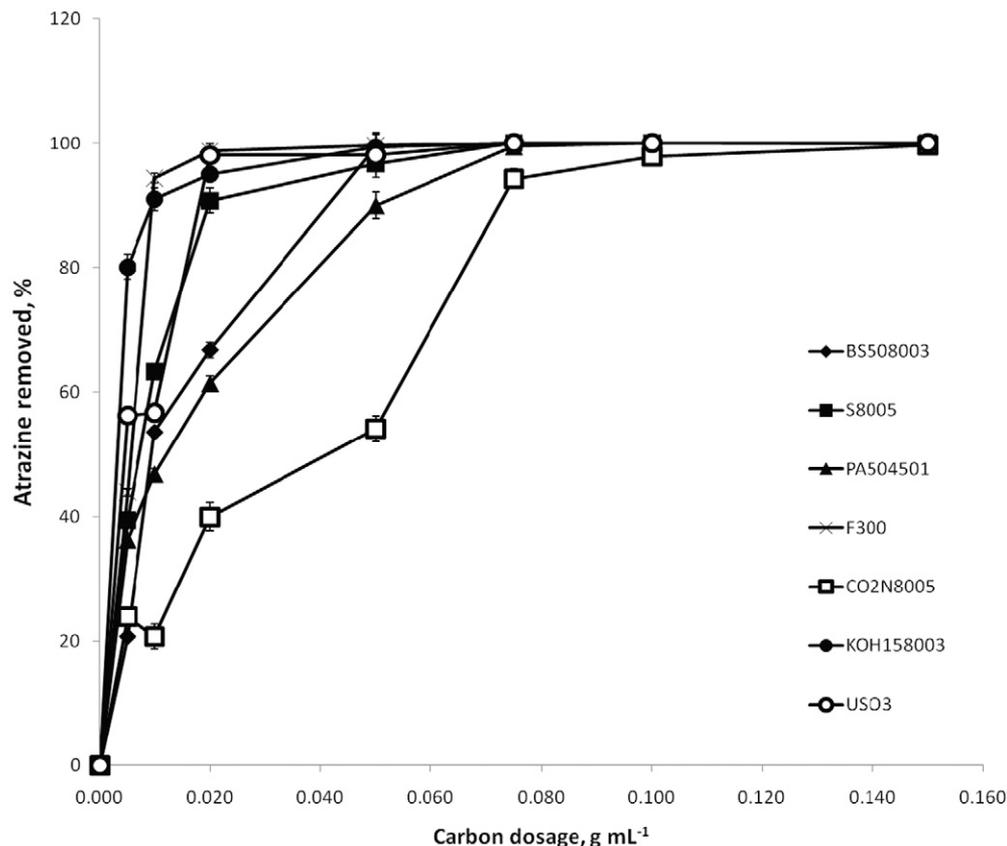


Fig. 1. Percentage atrazine removed by best performing experimental activated carbons against commercial activated carbon. The y axis represents the amount atrazine removed (%), and the x axis represents carbon dosage (i.e., the amount of carbon per 1 mL of solution). Pecan shell-based activated carbons at dosages of 0, 0.05, 0.1, 0.2, 0.5, 0.75, 1.0, and 1.5 g were placed in 50 mL each of atrazine solution at a concentration of 25 mg L⁻¹ for 24 h. ♦, NaHCO₃-activated carbon; ■, steam-activated carbon; ▲, H₃PO₄-activated carbon; ×, F300 reference carbon; □, CO₂-activated carbon; ●, KOH-activated carbon; ○, USO3 reference carbon.

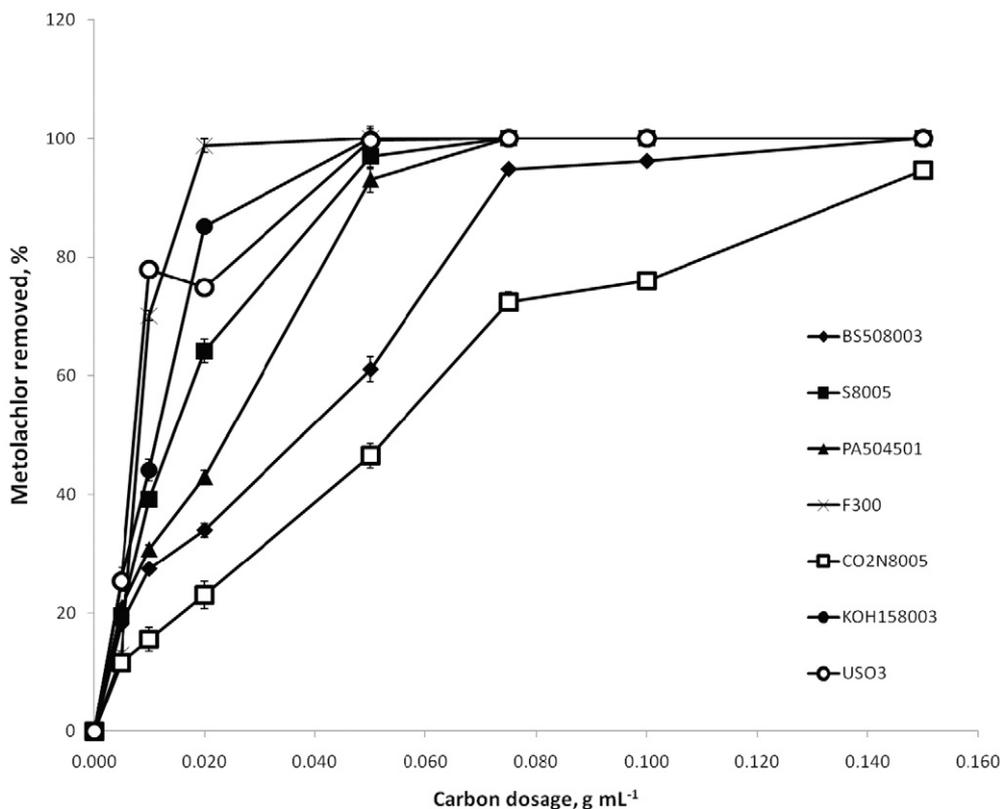


Fig. 2. Percentage metolachlor removed by best performing experimental activated carbons against commercial activated carbon. The y axis represents the amount of metolachlor removed (%), and the x axis represents carbon dosage (i.e., the amount of carbon per 1 mL of solution). Pecan shell-based activated carbons at dosages of 0, 0.05, 0.1, 0.2, 0.5, 0.75, 1.0, and 1.5 g were placed in 50 mL each of metolachlor solution at a concentration of 40 mg L⁻¹ for 24 h. ♦, NaHCO₃ activated carbon; ■, steam-activated carbon; ▲, H₃PO₄-activated carbon; ×, F300 reference carbon; □, CO₂-activated carbon; ●, KOH-activated carbon; ○, USO3 reference carbon.

H₃PO₄⁻, and CO₂-activated carbons showed atrazine adsorptive performance of 32.2, 30.0, and 9.0 μg g⁻¹ carbon, respectively. Both hybrid activated carbons showed greater affinity to atrazine adsorption, which is probably related to their higher surface charge and the higher MMA to TSA ratio achieved by the hybrid-activated carbons.

In the case of metolachlor removal, three experimental activated carbons achieved complete adsorption within the detection limits of metolachlor at a carbon dosage of 75 mg mL⁻¹ (Fig. 2). Steam-activated carbon (S8005) and H₃PO₄-activated carbon (PA505501) were the next best performing carbon materials in terms of metolachlor removal (66.7 and 62.0 μg g⁻¹ C, respectively). Sodium bicarbonate (BS508003) and CO₂-activated carbon (CO2N8005) had the lowest metolachlor adsorption capacity (20.4 and 15.5 μg g⁻¹ C, respectively). Potassium hydroxide-activated carbon showed adsorption capacity similar to the two commercial activated carbons (100 μg g⁻¹ C) (Fig. 2). Overall, Fig. 1 and 2 show that PSACs are effective adsorbers of atrazine and metolachlor at all of the tested carbon dosages.

Conclusions

Pecan shells can be converted into value-added activated carbons for water purification applications. The PSACs developed in this project showed high effectiveness in removing inorganic and organic water contaminants due to optimization of their physicochemical and surface properties. Adsorption performances of PSACs were dependent on pyrolysis and

activation conditions. Development of low-cost water filters from a renewable agricultural waste product has the potential to alleviate environmental issues caused by their disposal, adds value to the agricultural sector, and provides consumers with inexpensive material to purify their water. The use of PSACs as a water purifier could reduce the incidence of water-borne illnesses linked to the inorganic and organic chemicals investigated in this study.

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