



# Copper and strontium adsorption by a novel carbon material manufactured from pecan shells

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## Abstract

A novel carbon material (PS276a) was produced from pecan shells, a waste product of the agricultural industry. Preparation of this material involved the impregnation of the pecan shell feedstock with a phosphoric acid solution. Activation was followed by a water wash and a sodium hydroxide treatment. The carbon produced was characterized by adsorption of N<sub>2</sub> and revealed a pore structure with an average pore diameter of 74.8 Å. Equilibrium sorption isotherms prepared for this carbon demonstrate that it has a significantly higher capacity for copper and strontium sorption than that of a commercial material used for comparison. A maximum of 95 mg Cu<sup>2+</sup> and 180 mg Sr<sup>2+</sup> are adsorbed per gram of this carbon at pH 3.6 and 8.5, respectively. Demonstrated process advantages of this carbon material and preparation technique include low temperature manufacture, in-situ regeneration potential, and adsorbate recovery capability. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Commercial activated carbon (CAC) is a common adsorbent that can be used for the removal of various species from gas phase mixtures and aqueous solutions. CAC can be produced from different types of raw materials, including wood, coal, fruit stones, and nutshells. The feasibility of producing carbon from agricultural wastes depends on a number of factors, including the adsorption capacity and mechanical strength of the product, the availability of the raw material, and the cost of production.

Researchers have studied the production of activated carbon from coal [1,2], coconut shells [3], almond shells [4–6], olive stones [7,8] and other agricultural products [9] using physical [10–12] and/or chemical processes [5,13–15]. However, the adsorption capacity of the activated carbon for a specific adsorbate varies strongly with the type of raw material and the processing techniques used.

This paper discusses the use of pecan shells as a raw material for the production of an activated carbon using a novel activating technique. The activated carbon produced is then characterized by its adsorption equilibrium capacity toward copper and strontium.

## 2. Experimental

Pecan shells were obtained from farms located along the Rio Grande River in southern New Mexico. These materials were combined, crushed, and sieved to a particle size ranging from 75 µm to 1 mm. The crushed pecan shells were then treated in a 4-l batch reactor. Activation was achieved by mixing 20 g of the crushed shells with 82.6 g of (85 wt.%) phosphoric acid solution. The mixture was heated to 260°C while being agitated. Air was sparged into the mixture during the heating process to assure complete oxidation as well as to assist with the agitation process. The resulting carbon was allowed to cool to ambient temperature, washed with distilled water, soaked in dilute

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sodium hydroxide solution for 30 min, washed a second time with distilled water, dried, and finally classified by particle size. A patent is pending on this process and state-of-matter [15].

Samples of the dried PS276a were tested using a Micrometrics ASAP 2010 gas adsorption surface area analyzer to study the adsorption of nitrogen at 77 K, and as a result to determine the surface area of the carbon samples using the Brunauer–Emmett–Teller (BET) equation [16].

Aqueous solutions of copper sulfate and strontium chloride of initial concentrations ranging between 10 and 500 mg/l were prepared (all chemicals were analytical grade reagents supplied by Sigma Chemical Company). Batch adsorption tests for copper and strontium were performed for a fixed particle size ( $<75 \mu\text{m}$ ) of adsorbents of PS276a and a resin of type SR-5 (supplied by Sybron Chemicals Inc.) selective to these metals. Using two sets of stopper bottles, equal weights of PS276a of 0.1 g were added to 100 ml of copper and strontium solution with different initial concentrations for each metal of interest. A similar procedure was also performed for comparison in which 1.0 g of the resin was added to 100 ml metal solution. The mixtures were placed in an isothermal shaker ( $25 \pm 1^\circ\text{C}$ ) for 3 days to allow complete equilibration. Based on differences in the acidic nature of the adsorbent, the pH was adjusted by adding a few drops of 0.5 N sodium hydroxide. Samples of the solutions equilibrated with the carbon were analyzed using a 5000 Perkin-Elmer atomic absorption spectrophotometer.

### 3. Results

Table 1 lists the measured physical properties of PS276a obtained using ASTM tests (D2854-96, D2866-94, D2867-95, and D3838-80), and those of a Norit SA Plus CAC [1]. Sample PS276a has a lower ash content and a bulk density 1.5 times that of the CAC. The nitrogen adsorption isotherm for PS276a at 77 K is shown in Fig. 1. The surface area calculated from the BET equation is  $13 \text{ m}^2/\text{g}$  carbon, while that by the Langmuir equation is  $18 \text{ m}^2/\text{g}$  carbon. Similar results were obtained for the sample by Dr. Christopher Toles (United States Department of Agriculture, Southern Regional Research Center, New Orleans, LA) and Dr. Evan Koslow (KX Industries, Inc., Orange,

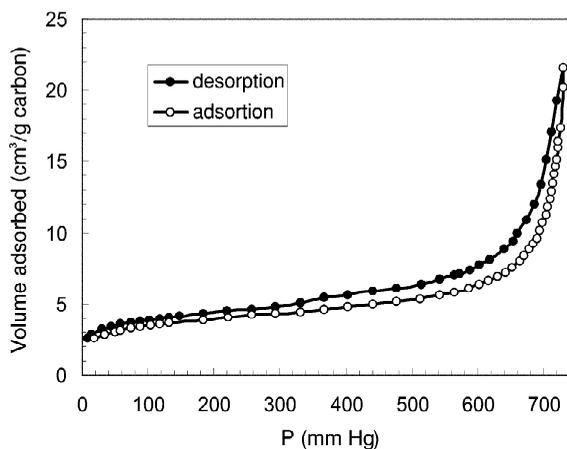


Fig. 1. Nitrogen gas adsorption isotherm for PS276a at 77 K.

CT). A scanning electron microscope image of the surface of the sample PS276a was generated using a JEOL 6300FX high-resolution scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS), and is presented in Fig. 2. This image shows the surface topography to be very undulating.

Adsorption isotherms for copper and strontium by



Fig. 2. Scanning electron microscope image of PS276a surface.

Table 1  
Selected properties of activated carbon samples PS276a and CAC

Property	ASTM method	PS276a	CAC
Total ash content (wt.%)	D2866-94	4	10
Apparent density ( $\text{g}/\text{dm}^3$ )	D2854-96	495	340
pH	D3838-80	6.5	$>9$
Moisture (wt.%)	D2867-95	2	2

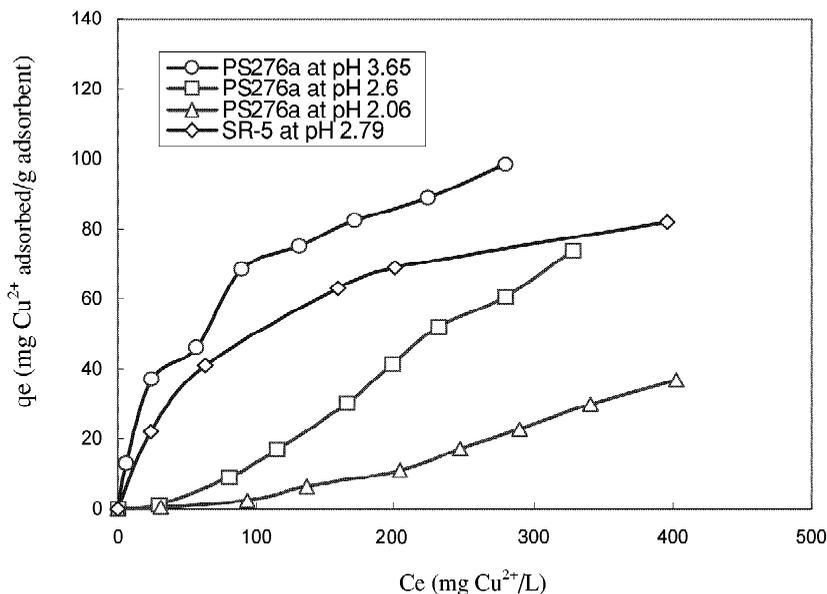


Fig. 3. Adsorption isotherm of Cu<sup>2+</sup> onto PS276a and SR-5.

PS276a and SR-5 at various pH levels are shown in Figs. 3 and 4, respectively. Within the concentration ranges studied, a maximum adsorption capacity of 95 mg Cu<sup>2+</sup> and 180 mg Sr<sup>2+</sup> per gram of PS276a was observed at pH 3.6 and 8.5, respectively. The adsorption capacity of PS276a toward Cu<sup>2+</sup> was higher than that of the amount adsorbed by the resin, which showed an adsorption capaci-

ty of 80 mg Cu<sup>2+</sup> per gram of SR-5 obtained at pH 2.79. On the other hand, the adsorption capacity of resin for Sr<sup>2+</sup> was 250 mg Sr<sup>2+</sup> per gram of SR-5 at pH 2.79. At a higher pH value of 8.5, PS276a shows an adsorption capacity as high as 180 mg/g carbon. From the trends observed, it appears that as the pH is increased, the cation adsorption capacity of PS276a also increases. At a fixed

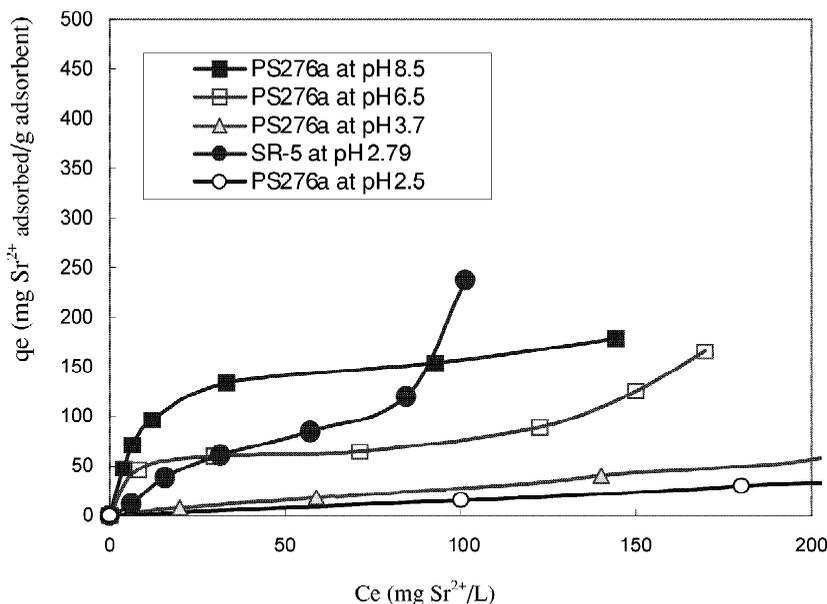


Fig. 4. Adsorption isotherm of Sr<sup>2+</sup> onto PS276a and SR-5.

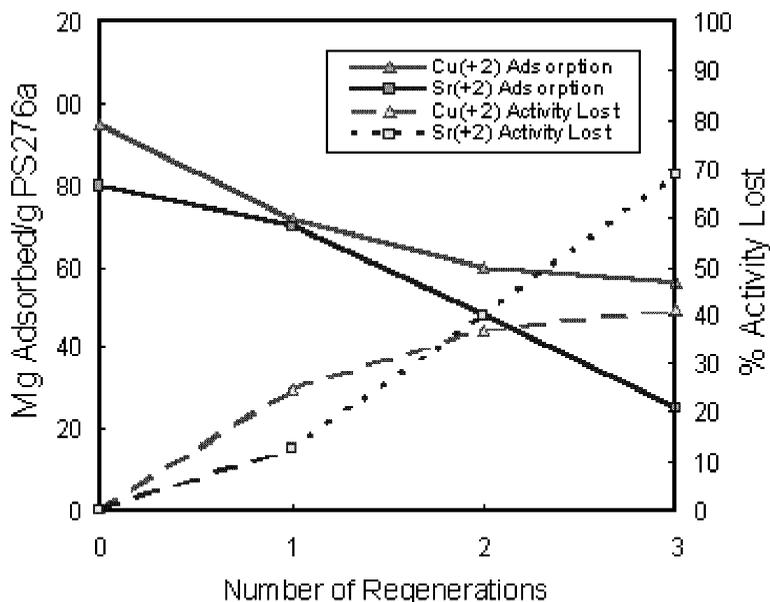


Fig. 5. PS276a adsorptivity after successive regenerations.

pH and initial solution concentration, the amount of solute adsorbed by PS276a is higher for  $\text{Cu}^{2+}$  than that observed for  $\text{Sr}^{2+}$ .

The regeneration tests consisted of filtering out the adsorbent after a first sorption cycle up to pH 12, then washing it with 100 ml of concentrated acid (75 wt.% HCl/25 wt.%  $\text{HNO}_3$ ). After washing was performed, the adsorbent was neutralized with NaOH solution, dried, and then re-immersed in adsorbate solution at the same initial condition. The present loss in sorption activity (that is, the fraction of adsorbate that could no longer be adsorbed relative to that adsorbed during the first cycle) was calculated as:

$$\% \text{ activity lost} = 100 \times \left[ \frac{(A - I)}{A} \right]$$

where  $A$  is the amount adsorbed during the first cycle, and  $I$  is the amount adsorbed during each subsequent cycle. The results of these regeneration tests are provided in Fig. 5.

#### 4. Discussion

Activation using phosphoric acid followed by sodium hydroxide treatment produces a carbon (PS276a) with a large adsorption capacity toward solutes in aqueous solution. This adsorption capacity has been compared with that of a commercial adsorbent resin and found to be competi-

tive with this material. PS276a shows some unique qualities for an activated carbon that will be further explored.

The gas adsorption tests indicate that the novel material has a low surface area. Nonetheless, the novel material also displays a relatively high capacity for reversibly adsorbing divalent metals from water, with the adsorption capacity being strongly affected by the pH of the solution. Such behavior suggests that a potential ion exchange or acid/base reaction may be occurring, rather than a purely physical adsorption process. If such an adsorption mechanism were assumed, both the adsorptive behavior of the carbon toward divalent metals and the relatively low nitrogen adsorption observed during the gas adsorption tests could be explained. If PS276a lacks a substantial pore structure, there would be relatively few sites for nitrogen gas to adsorb in the pore capillaries. Being neither ionic nor polar, nitrogen would not have a tendency to chemically adsorb to the PS276a surface either. Thus, we believe that gas sorption measurements for the evaluation of the surface area available to liquid phase adsorbates are meaningless for assessing the cation adsorption potential of PS276a. Others have commented on the use of gas adsorption as a means of comparing carbons, indicating that the adsorption capacity of the carbon is best obtained experimentally with the solute of concern [17]. We believe that this is the case with PS276a.

The adsorption of metal ions onto PS276a may be considered an ion exchange mechanism in which the adsorption capacity of the carbon is large when the charge-to-volume ratio of the metal ion is large. The higher

positive charge-to-volume ratio of the metal ion, the more strongly attracted is the ion to the negatively charged carbon surface. Copper (+2) ions have a relatively large electronegativity of 2.0 with a small ionic radius of 0.72 Å, while strontium (+2) has an electronegativity of 1.0 and an ionic radius of 1.13 Å. Consequently, at a fixed initial concentration and operating conditions, the order of increasing adsorptivity is expected and observed to be  $\text{Cu}^{2+} > \text{Sr}^{2+}$ .

Energy dispersive X-ray spectrometry (EDS) analysis of PS276a on the Los Alamos National Laboratories (LANL) SEM further supports the notion of the ion-exchange mechanism in that the elemental distribution of species shows high concentrations of phosphorous on the surface of the carbon, thus providing the required acidic sites for the suggested reaction to occur.

The adsorption capacities of  $\text{Cu}^{2+}$  and  $\text{Sr}^{2+}$  by PS276a are also strongly dependent on pH. As pH increases, the efficiency of the separation is increased as there is a decrease in the degree of competition between hydrogen ion and  $\text{Cu}^{2+}$  or  $\text{Sr}^{2+}$  for the exchange sites.

Washing the spent PS276a with a diluted mixture of HCl/ $\text{HNO}_3$  then neutralized with sodium hydroxide can refresh the surface of the carbon from the adsorbed  $\text{Cu}^{2+}$  and  $\text{Sr}^{2+}$  to be reused many times. Fig. 5 shows the maximum amount of  $\text{Cu}^{2+}$  and  $\text{Sr}^{2+}$  adsorbed at the surface of PS276a at pH 3.6 and 6.1, respectively. It appears that as the number of regeneration cycles increases, there is an increase in the activity losses for both copper and strontium. At the condition studied, the activity losses for strontium are much more than that of copper. This could be attributed to a partial collapse of the PS276a structure.

## 5. Conclusion

It has been demonstrated that pecan shells, a high-volume agricultural waste product, represent a potential feedstock for the production of a novel carbon material with desirable physical properties for use in separating metal ions from aqueous solution. Based on the differences between this process technique and the traditional methods of carbon production, it is expected that this material will have a relatively low manufacturing cost. The activation process used produces a material with a relatively high capacity for adsorption of  $\text{Cu}^{2+}$  and  $\text{Sr}^{2+}$ .

The adsorption capacity of PS276a toward aqueous solutes is enhanced by increasing the pH of the solution. The adsorptive capacity of PS276a toward a number of contaminants of commercial interest is being investigated, and future work from this lab will discuss those results.

The low energy demand of production and the low raw material cost provide a strong potential for commercial

production if it is found that PS276a has a high adsorptive capacity toward these other materials. Evaluation of the economics of manufacture and application of PS276a is underway by this lab in conjunction with the Waste-Management Education and Research Consortium (Las Cruces, NM) and the Center for Plant Biotechnology Research (St. Simons Island, GA).

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