10-WATER5-Ledbetter

Predicting performance of almond shells for cleanup of almond soil fumigants in potable water

Craig A. Ledbetter – USDA/ARS, Crop Diseases, Pests & Genetics RU, Parlier, CA
K. Thomas Klasson – USDA/ARS, Commodity Utilization RU, New Orleans, LA
Bob Little – City of Fresno, Fresno Water Division, Fresno, CA

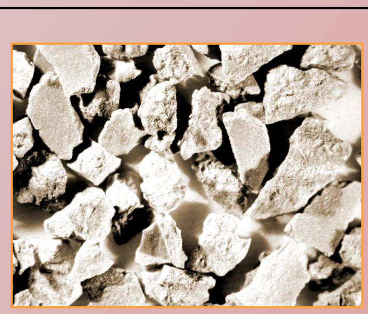
Background: DBCP (1,2 Dibromo-3-chloropropane) was an effective nematicide used throughout the San Joaquin Valley until its use was banned by the EPA in 1979. While it has not been used for the past 30 years, DBCP still persists in aquifers below formerly treated fields. Currently, a plume of DBCP in the aquifer below the Fresno, CA is being monitored and managed by Fresno Water Division personnel. With the DBCP-contaminated aquifer being Fresno's primary source of drinking water, efforts to effectively remove the DBCP have been ongoing for the last 20 years.

Granular activated carbon (GAC) filtration is being used to remove DBCP from contaminated wells. Throughout the municipality of Fresno, 27 GAC sites are used to manage the DBCP contamination, and sites are sampled regularly to monitor water quality and GAC filter longevity.

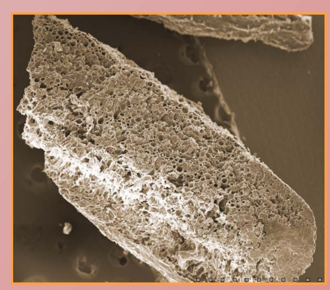
GACs are produced from a variety of starting materials (lignite and bituminous coal are common) , and materials are converted to GACs with various temperature, pressure and modified atmosphere regimes during production. Surface area of the precursor materials increases dramatically during production, providing location for chemical adsorption or reactions.

Factors such as lignin structure(s) of the starting materials, ash content and/or embedded compounds/secondary metabolites all affect adsorption characteristics of the GACs. Given the variability in almond shells from the many varieties grown in California, it behooves researchers to examine feedstock sources to identify those that are particularly suitable for GACs production and can maximize adsorption of DBCP or other organic contaminants.

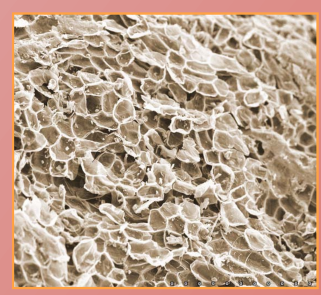
In-shell sample



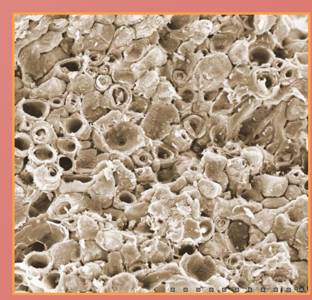
1-2 mm chunks



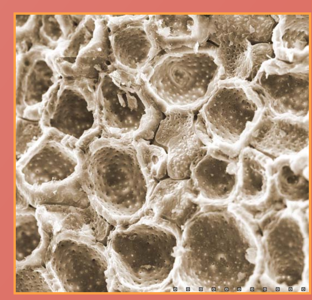
1 mm



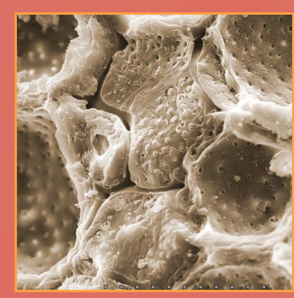
300 micron



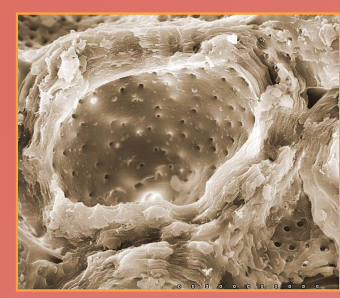
200 micron



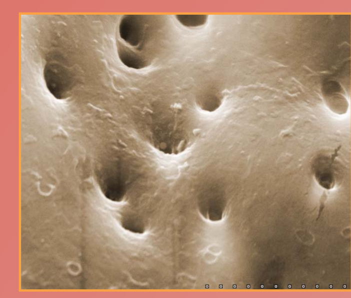
100 micron



50 micron



30 micron



5 micron

Almond shells and fragments at various magnifications (scale in lower right) to demonstrate complex pore structure, necessary for adsorption of organic contaminants in water.

Previous work: Almond processors distinguish varieties on the basis of shell strength, being either soft or hard shelled. But within these broad classes, almond varieties exhibit varietal diversity in shell morphology and physical characters. California almond varieties differ significantly in their bulk density and cracking strength (Ledbetter, 2008). Given these physical differences, interest was expressed in determining whether shells of different almond varieties varied in their ability to adsorb organic contaminants from water.

Recently, both hard and soft shelled almond varieties were examined for their ability to adsorb DBCP from contaminated water. GACs were prepared from varietal shell samples and challenged with DBCP-laced water in the laboratory. Hard shelled (Padre, Tuono, Y120-74) and soft shelled (Nonpareil, 23-122) almond shell GACs all adsorbed significantly more DBCP from contaminated solutions than the bituminous coal-based GAC (Klasson et al., 2010) (Fig 1). Further, with the exception of GAC prepared from 23-122 shells, almond shell GACs were shown to be at least as durable as the control carbon (Fig 2).

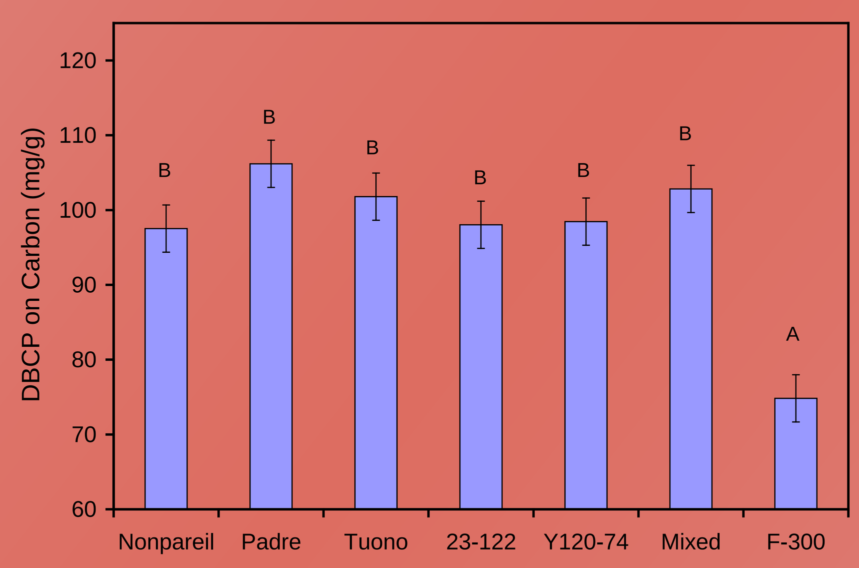


Fig. 1. DBCP uptake by commercial activated carbon and activated carbons made from different almond variety nutshells. The error bars indicate standard errors (based on pooled standard deviation) and the letters above the bars show the results of the Tukey's post-hoc statistical test.

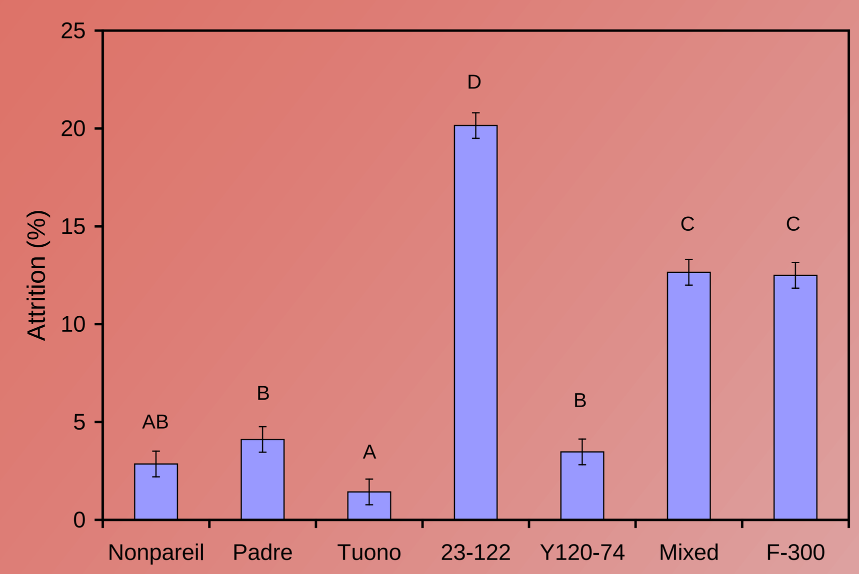


Fig. 2. Results from attrition studies. The experiments were conducted in duplicates. The error bars indicate standard errors (based on pooled standard deviation) and the letters above the bars show the results of the Tukey's post-hoc statistical test.

Fresno Water Division, Site T1 in SE Fresno. Well # 184 (center) will be used to challenge almond shell GAC with DBCP removal from contaminated water.

Planned studies: We will be conducting a pilot study of almond shell GAC performance at the Fresno Water Division's 'T1' site in southeast Fresno, CA. Well # 184 pumping to this GAC vessel site have DBCP levels averaging 0.25 – 0.30 µg/L. A manifold will be installed for two experimental filter columns to compare almond shell GAC with that of the coal-based control.

Clean almond shells have been secured during harvest from a mixture of California varieties. The shells are currently being carbonized and steam-activated to enhance their adsorptive ability. Column filters will be loaded with almond shell or coal-based GACs and plumbed into inflow pipes to receive DBCP-contaminated groundwater. After preparing column beds to remove fine particles and enhance GAC packing, water flow rate through the experimental columns will be adjusted to match actual flows from well # 184.

Column filters at the T1 site will be installed and run for an extended period of time to determine the useful service life of almond shell GAC. Water samples from the experimental columns will be obtained weekly and tested for DBCP levels according to EPA method # 504.

A 'Model 12' vessel filled with 740 ft^3 of GAC for DBCP removal. Almond shell GAC filter columns will be installed at the inflow to this vessel.

Box furnaces are used to produce the activated carbons. In this process, appropriately sized almond shells are heated to 700C in a N_2 atmosphere for 1 hr, after which the temp is bumped to 800C, and steam is injected along with the N_2 for an additional 45 min for activation.

Almond shell GAC as a value-added product

Current market value of almond shell material is no more than 10 – 20 USD per ton for uses as animal bedding or in a variety of industrial applications. Annual usage of GAC in the US has been estimated at 300 million lb. Based on data from Almond Board of California Position Reports (July 2010), nearly 370,000 metric tons of clean shells would be available from the 2009 harvest alone for the top 5 producing varieties (Nonpareil, Carmel, Monterey, Butte & Padre).

Production cost for steam-activated almond shell GAC has been estimated previously at 1.54 USD per kg (Toles et al., 2000), well below the current commercial price of ~ 4.40 USD per kg for coal-based carbons. Thus, it appears that almond shell GACs would have potential in a commercial market as long as they prove being both physically durable and have sufficient service life as compared to current commercial GACs.

A gas chromatograph equipped with electron capture detection is used to analyze halogenated compounds, such as DBCP in water.

Literature Cited

Ledbetter, C.A. 2008. Shell cracking strength in almond (*Prunus dulcis* [Mill.] D.A. Webb.) and its implication in uses as a value-added product. *Bioresource Technology* 99: 5567 – 5573.

Klasson, K., Ledbetter, C.A., Wartelle, L. and S. Lingle. 2010. Feasibility of dibromochloropropane (DBCP) and trichloroethylene (TCE) adsorption onto activated carbons made from nut shells of different almond varieties. *Industrial Crops and Products* 31: 261 – 265.

Toles C.A., Marshall, W.E., Wartelle, L.H. and A. McAloon. 2000. Steam- or carbon dioxide-activated carbons from almond shells: physical, chemical and adsorptive properties and estimated cost of production. *Bioresource Technology* 75: 197 – 203.