Use of Carbon Derived from Almond Shells to Filter Municipal Drinking Water Supplies

Project No.:   **10-WATER5-Ledbetter**

Project Leader: Craig A. Ledbetter
USDA-ARS
San Joaquin Valley Agricultural Sciences Center
9611 S. Riverbend Avenue
Parlier, CA 93648-9757
559.596.2817
559.596.2951 (fax)
craig.ledbetter@ars.usda.gov

Project Cooperators and Personnel:
K. Thomas Klasson, USDA-ARS, New Orleans, LA
Bob C. Little, Fresno Dept. of Public Utilities, Fresno, CA

Objectives:

1. Ascertain the effectiveness of using activated carbon made from almond shells to remove various concentrations of dibromochloropropane (DBCP), formerly a widely used soil fumigant, from municipal water systems.
2. Compare the effectiveness of almond shell-based activated carbon with that of the currently used standard form of activated carbon in terms of their ability to meet both US EPA and local contamination-reduction requirements.

Interpretive Summary:

The use of activated carbons for removal of DBCP from municipal water is considered best technology treatment technique by the Environmental Protection Agency, and activated carbon vessels have been used successfully to remove DBCP from water supplies in affected San Joaquin Valley cities. Activated carbons can be made from many sources, including almond shells or other agricultural by-products. The purpose of this work was to evaluate the effectiveness of almond shell activated carbons (ASAC) in removing DBCP from a contaminated well-water source as compared with the coal-based activated carbon 'F-300.' Pilot-scale columns of almond shell and F-300 activated carbons installed at a DBCP-contaminated well were challenged continuously over a six month period with water flow rates matched to full-scale filtration vessels. Flow rate changes during the period of operation were insignificant between the two carbon types, demonstrating the physical stability of ASAC under standard operating conditions. F-300 was significantly higher in physical density than ASAC, providing for more (in terms of weight) activated carbon being packed into the column, and allowing a longer filter life. DBCP was first detected in effluent from the ASAC filter after 13 weeks of continuous operation, very close to its calculated lifespan based on laboratory analyses. The ASAC filter remained in operation for another 90 days prior to effluent reaching ½ the DBCP inlet concentration. This point allows for calculation on the useful life of a full scale system.

Materials and Methods:

Almond shells were kindly donated by Pacific Ag Management Inc. (Wasco, CA) and were milled with a cutting mill (SM2000, Retsch GmbH, Haan, Germany) and sieved to retain the 0.84-2 mm (No. 10-20 sieve) and >2 mm fractions. Two-hundred gram of the material were pyrolyzed in a furnace with retort (Lindberg Type 51662-HR, Watertown, WI) at 650°C for 1 hr with a nitrogen gas flow, after which the temperature was increased to 800°C and water was introduced into the nitrogen stream to create a steam atmosphere in the furnace for 45 min. A total of eight runs were performed to generate enough material for all the studies.

Batch Studies

DBCP was obtained as 5000 mg/L solution in methanol (Sigma-Aldrich, St. Louis, MO). Batch isotherm studies were first performed by mixing 10 mL deionized water, various volumes of DBCP stock solution and activated biochar (0.01 g) in 40-mL glass vials with Teflon-lined caps. The vials were placed on an end-over-end mixer for 24 h. After contact, a portion of the content was filtered using 0.2-μm-pore-size nylon syringe filters (Whatman, Kent, United Kingdom), and a fraction of the filtrate was combined with heptane in 2-mL gas chromatography auto-sampler vials, vortexed, and the top phase was injected into a gas chromatograph (Model 6890N, Agilent Technologies, Santa Clara, CA), equipped with an electron capture detector. Batch studies were carried out with well water samples in a similar fashion. In these studies, both 10 mL and 40 mL of well water were used, to cover a greater range of the isotherm curve.

Field Studies

A DBCP-contaminated well on the southeast side of Fresno, CA was utilized at the study site, providing a water source averaging 0.28 μg/L DBCP during the study period. Water from this well is normally treated with activated carbon employed through a commercially manufactured 'Model 12' vessel. According to the Fresno Dept. of Public Utilities, the vessels at the site contained 740 cu. ft. of carbon and the flow rate was 650 gpm. For the field study, glass (chromatography) columns (25 mm diameter by 600 mm in length, Ace Glass, Vinland, NJ) with Teflon end caps were used. The ASAC was sieved into 10 different fractions and recombined in the same proportion as determined in the commercially used activated carbon Filtrasorb 300 (Calgon Carbon, Pittsburgh, IL). The columns were installed at the field site, next to full scale vessels and operated at the ambient conditions at the site. A slip stream from the inlet to one of the full-scale columns was diverted, allowed to flow into an open container from which water was pumped into the top of the columns. This allowed for the cool pressurized water to reach ambient conditions and degas before entering the columns. Without this degassing system, the columns filled with gas. A peristaltic pump (MasterFlex, Cole-Parmer, Court Vernon Hills, IL) was used to deliver approximately 34.5 mL/min well water to the top of the columns. This flow rate was selected to reach the same contact time as in the full-scale vessels. Samples were collected weekly and the inlet flow was adjusted to the set point as needed. Samples were kept on ice and delivered the same day to a commercial laboratory (BSK Associates, Fresno, CA) for analysis. Column effluents went directly to drain, eliminating any possible contamination of the public water system.

Results and Discussion:

Batch experiment showed that the adsorption of DBCP was not impacted by the composition of the well water (as compared with deionized water) and that the adsorption equilibrium followed a typical Langmuir isotherm (see **Figure 1** for isotherm and Langmuir equation). The predicted capacity of the almond shell based activated carbon was 0.022 mg/g according to the equation, which at the conditions at the site (0.00028 mg/L) is linear.
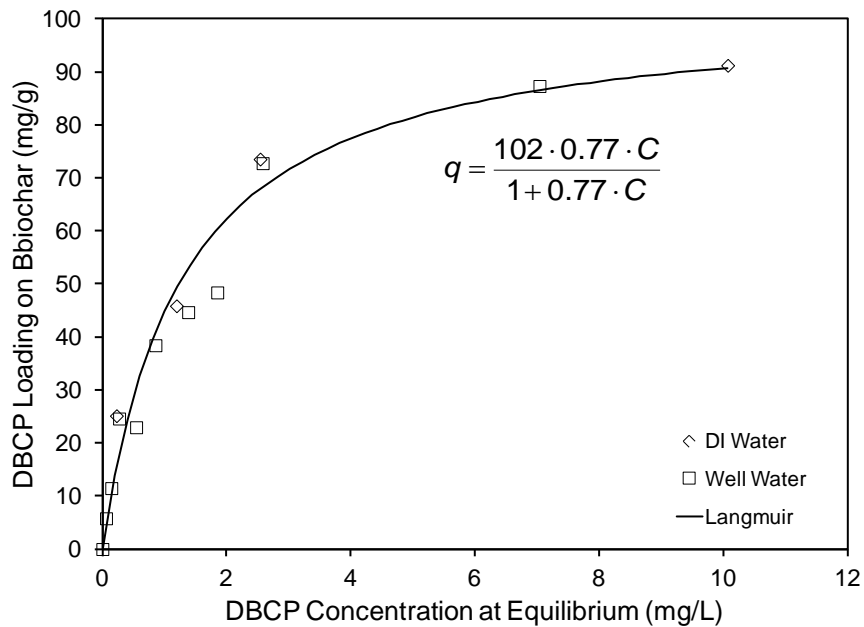

In the figure:

$$q = \frac{102 \cdot 0.77 \cdot C}{1 + 0.77 \cdot C}$$

Legend: ◇ DI Water, □ Well Water, — Langmuir

X-axis: DBCP Concentration at Equilibrium (mg/L)
Y-axis: DBCP Loading on Bbiochar (mg/g)

Figure 1. Results of batch experiment carried out in DBCP-spiked deionized water and well water.

The particle size distributions of the activated carbons are shown in **Figure 2**. Both carbon types have the same distribution, void volumes, packing characteristics, and contact times. A noticeable difference was the bulk density of the materials were quite different; 0.22 kg/L for the ASAC and 0.64 kg/L for the commercial carbon. Thus, approximately three times as much carbon was used in the column filter containing the commercial carbon.
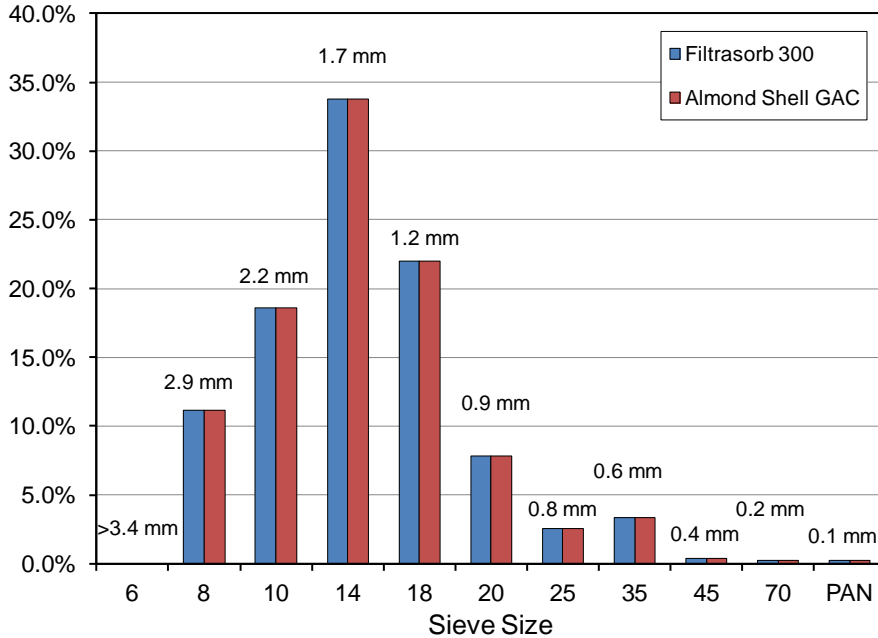
Figure 2. Particle size distribution of the commercial activated carbon and the activated carbon made from almond shells.

The results of the column study are shown in **Figure 3**. As mentioned before, the inlet concentration averaged 0.28 µg/L and varied only slightly over the duration of the study. As is noted, the effluent concentration was below the method detection limit (0.006 µg/L) for about 85 days. Then, the effluent concentration slowly increased over approximately 90 days until 50% breakthrough was reached, at which time the experiment was halted. However, it should be noted that the columns still removed DBCP to below the regulatory limit (0.20 µg/L).
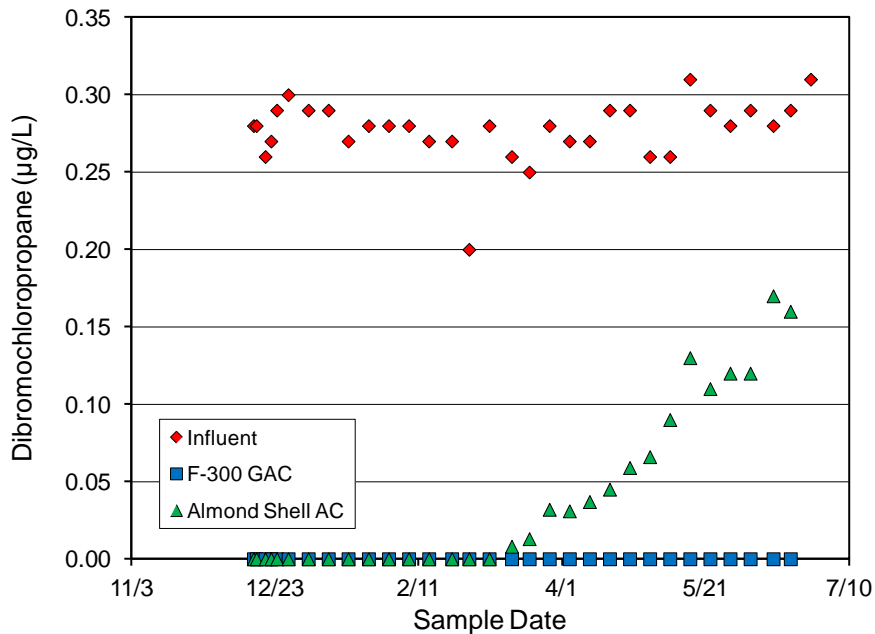

Figure 3. Results of column field experiment.

The commercial carbon continued to remove DBCP to below detection throughout the experiment. This was expected as this column contained a larger weight of carbon (due to its higher density) and thus will last longer. However, it is anticipated that the type (shape) of breakthrough curve seen for the ASAC would be the same for the commercial carbon due to its similarity in particle size.

The shape of the curve, representing the effluent, can be described by modeling the breakthrough based on the adsorption of DBCP and the fluid transport in the adsorber column; e.g., Rosen (1954) describes numerical solutions for adsorbers. The general expression derived by Rosen is:

$$\frac{C_{out}}{C_{in}} = 0.5\left[1 + erf\left(\frac{\frac{3y}{2x} - 1}{2\sqrt{\frac{1 + 5v}{5x}}}\right)\right] \tag{1}$$

This equation describes the breakthrough as a function of three dimensionless variables (x, y, v). When the adsorption rate is limited by diffusion of the adsorbate inside the particles, the equation was simplified to

$$\frac{C_{out}}{C_{in}} = 0.5\left[1 + erf\left(\frac{\frac{3y}{2x} - 1}{\sqrt{\frac{4}{5x}}}\right)\right], \tag{2}$$

or, when the adsorption rate was limited by the transport of the adsorbate through the liquid film surrounding the particles, Equation 1 was simplified to

$$\frac{C_{out}}{C_{in}} = 0.5\left[1 + erf\left(\frac{\frac{3y}{2x} - 1}{\sqrt{\frac{4v}{x}}}\right)\right], \tag{3}$$

In the above equations, the following nomenclature was used:
$3y/2x$ = $[\varepsilon / (K_D \rho_s)] [(v_s t / \varepsilon z) - 1]$
$4/5x$ = $[1/15] [(v_s d^2)/(D_s K_D \rho_s z)]$
$4v/x$ = $[4v_s / (k_f z)] [1 / (1-\varepsilon)]$
C_{in} = inlet concentration (0.00028 g/m^3, average over study)
C_{out} = outlet concentration (g/m^3)
d = effective particle diameter [0.0009 m, same as for F-300]
D_s = effective diffusion coefficient of DBCP in the solid [8.98×10^{-12} m^2/s, calculated from particle porosity (ε_p=10.5%) and water diffusivity (D_L) and $D_s = \varepsilon_p^2 D_L$ (Chang et al. 2004)]
ε = void volume in bed (0.62 m^3/m^3, measured)

K_D = slope of linear isotherm (true for low levels of DBCP) (m^3/g)
ρ_s = bulk density of sorbent (221,000 g/m^3, measured)
t = time of operation (s)
v_s = empty bed superficial velocity (0.0011 m/s, based on volumetric flow rate and cross-sectional area of column)
z = length of column (0.593 m, measured)
k_f = mass transfer coefficient for the fluid film surrounding the particles (0.120 1/s, calculated from the relationship = [11.1 D_f /d^2] [(1 − ε) / ε]$^{2/3}$ [(Sc Re) / (1 − ε)] from Kawamura et al. (1997)]
D_f = diffusion coefficient of DBCP in the fluid (water) [8.15×10^{-10} m^2/s, based on Hayduk and Minhas relationship (Reid et al. 1987)]
Re = Reynolds number, $\rho_f v_s d$ / μ (1.0, dimensionless)
Sc = Schmidts number, μ / (ρ_f D_f) (1231, dimensionless)
ρ_f = bulk density of fluid (water) (997,000 g/m^3)
μ = absolute viscosity for fluid (water) [1 g/m,s from Perry et al. (1984)]

In **Figure 4**, the data in **Figure 3** has been re-plotted to show breakthrough (C_{out}/C_{in}) as a function of time of column operation together with the prediction according to Equations 2 and 3 for internal (particle) and external (film) mass transfer limitations. The only variable
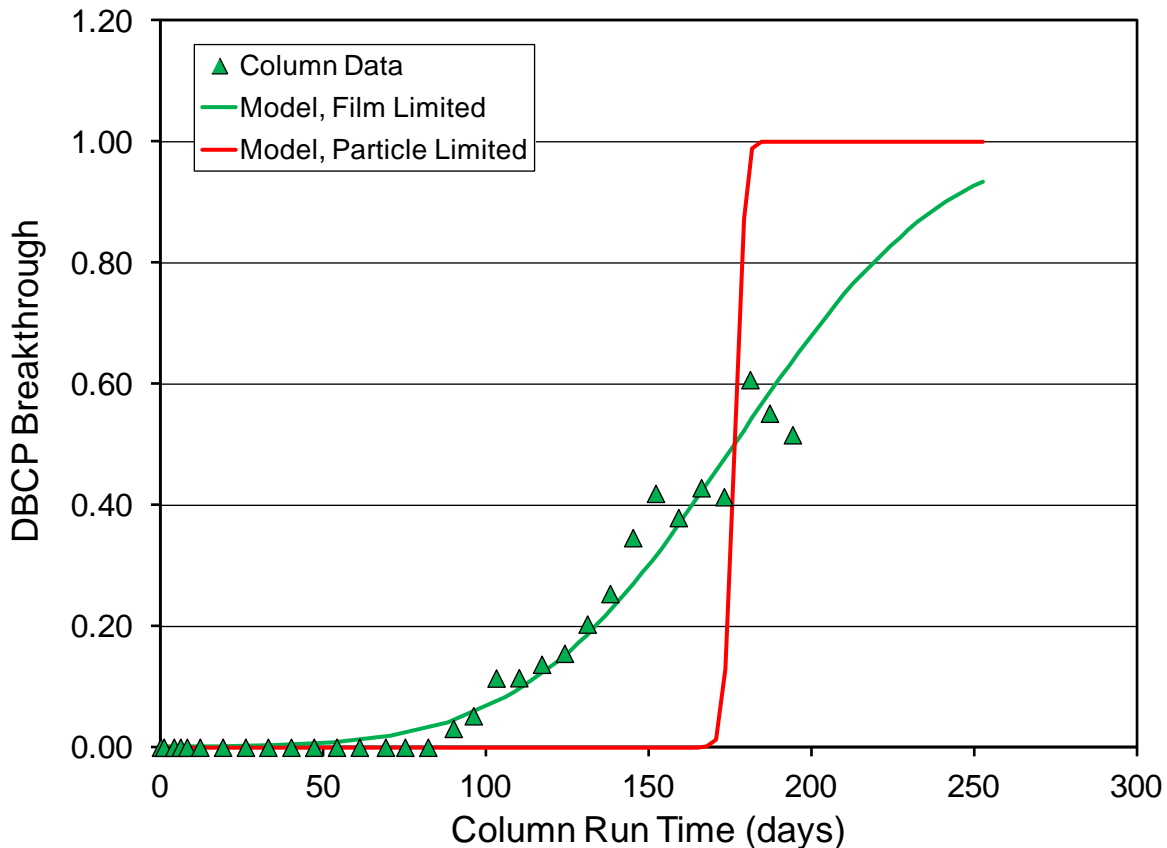

Figure 4. Experimental data as compared to model prediction for the case of external (film) limiting mass transfer case and for the intra particle diffusion mass transfer limited case.

adjusted was K_D to allow the 50% breakthrough of the model(s) to coincide with the experimental data. This value was set to 0.130 m^3/g. The value of K_D based on the batch data isotherm was 0.0785 m^3/g (calculated as q/C at 0.28 µg/L from **Figure 1**). Thus, the batch data under-predicted the performance of the column by 66%. The likely reason for this difference is that the isotherm model describes the equilibrium over a larger range of liquid concentrations and may not be as accurate at the lower DBCP concentrations.

As is noted from the result in **Figure 4**, the performance was favorably described by the model assuming mass transfer limitation in the film surrounding the particle (Equation 3). If the adsorption rate had been limited by the diffusion in the particle, a much steeper breakthrough curve would have been expected.

Overall the results were very encouraging, showing excellent performance of the almond shell activated carbon. Also encouraging was that the breakthrough followed published relationships derived for different systems. This allows for easy predictability of performance in larger scale columns. In **Figure 5**, we have included the predicted breakthrough in a full-scale column.
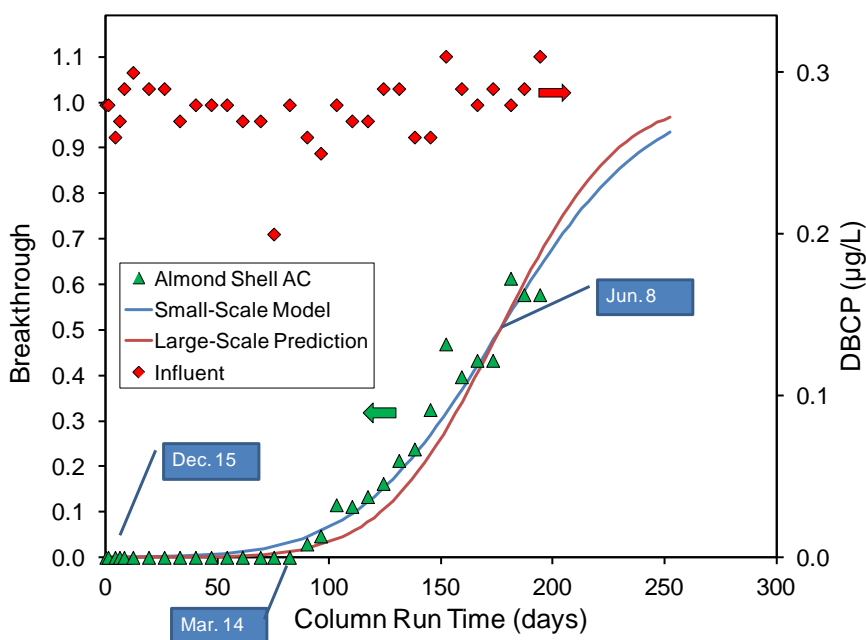

Figure 5. Experimental data, small-scale model, and large- (full-) scale performance prediction.

At the end of the experiment, both columns were backwashed and the fines (<40 mesh) were collected. Both beds contained approximately 1 gram of fines. Further, bed volume did not change during the column run, once the initial startup period was completed. The stability of the almond shell activated carbon through-out the study was adequate.

Research Effort Recent Publications:

A manuscript is in preparation with the results of the laboratory and field studies. The results were presented as a poster presentation at the US Biochar Conference at Sonoma State University in Rohnert Park, CA, July 29-August 1, 2012.

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