

## An experiment in . . .

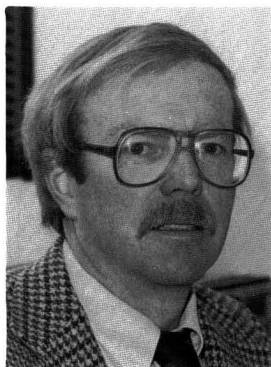
# LIQUID-PHASE ADSORPTION FUNDAMENTALS

DAVID O. COONEY  
University of Wyoming  
Laramie, WY 82071

**A**DSORPTION PROCESSES ARE important in the removal of organic contaminants from wastewaters and municipal drinking water supplies, in the removal of solvents and odor compounds from gas streams, in the drying of air, *etc.* The adsorbent employed may be activated carbon, synthetic resins, silica gel, *etc.*

An adsorption experiment has been developed and successfully run in our unit operations laboratory course at the University of Wyoming. It involves the liquid-phase adsorption of an organic compound from aqueous solution on activated carbon, but is relevant to adsorption processes in general.

In designing the experiment several goals were set: (1) it had to be capable of being completely run in four hours or less, (2) it should demonstrate the applicability of both the Langmuir and Freundlich isotherm equations to equilibrium data, and (3) it



David Cooney is Head of the Chemical Engineering Department at the University of Wyoming. His research has focused mainly on liquid-phase adsorption topics. He is the author of approximately 70 research papers and two books.

should familiarize the student with both batchwise and continuous fixed-bed types of operations. In addition, the component to be adsorbed should be reasonably water-soluble so that aqueous solutions could be employed, and it should be colored so that its removal by batch adsorption and its breakthrough behavior in fixed-bed operation be *visible* to the student. This requirement also allowed for easy measurement of the solute's concentration colorimetrically. One problem often encountered with colored solutes, however, is that their color intensity is a function of solution pH. And, since contact with activated carbon can change the pH of an aqueous solution and thereby alter the solute's color intensity (even at constant solute concentration), buffering of the aqueous solution to be used was considered to be necessary.

After some trial-and-error, the stock solution for the experiment was chosen to be a 0.30 g/liter solution of 2,4 dinitrophenol (DNP) in distilled water, buffered to a pH of 7.4 by the addition of 1.184 g/liter  $\text{KH}_2\text{PO}_4$  and 4.289 g/liter  $\text{NaHPO}_4$ . The DNP (Eastman Kodak Chemicals brand) contained around 15% moisture, which was *included* in the 0.30 g/L portions weighed out. A Pye Unicam Model 6-550 UV/Visible spectrophotometer was used in the visible mode at a wavelength of 480 nm with standard 1 cm  $\times$  1 cm  $\times$  4.5 cm matched glass sample cells (one cell was a reference cell containing distilled water; the other was the "sample" cell) to analyze all samples generated in the experiment for DNP concentration (the stock solution absorbance was around 0.600). Beer's Law was found to be obeyed for DNP sufficiently well over the range of concentrations involved in the experiment, *i.e.*, the DNP concentrations were proportional to the visible light absorbance values given by the spectrophotometer. The stock solution was deep-yellow in color.

The carbon used was Pittsburgh CPG activated

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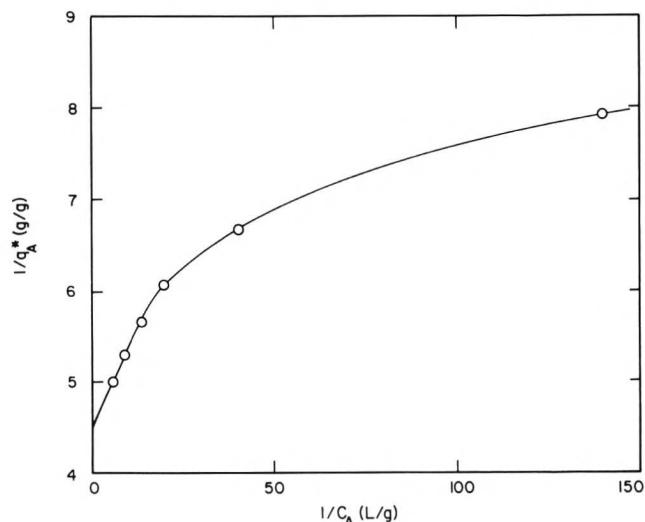
carbon, sieved to 28/40 mesh for the fixed-bed experiments and ground to less than 325 mesh for the batch (equilibrium) experiments. The carbon was heated in an oven at 150°C for 24 hours prior to use and then kept in closed glass jars (this prevents contamination by stray gas-phase adsorbates).

#### BATCH (EQUILIBRIUM) EXPERIMENTS

Approximately six samples containing roughly 0.005 to 0.030 grams of the powdered carbon (at essentially equally spaced weight intervals) were weighed into new dust-free liquid scintillation vials (Wheaton 20 mL borosilicate glass vials, from Cole-Parmer Instrument Co., Chicago, Cat. No. J-8918-02) using a Mettler AE 160 digital balance capable of weighing to 0.1 mg. Then 10 mL of the stock DNP solution was added to each vial using a standard volumetric pipette. The vials were capped with the caps that came with them (these had Poly-Seal conical seals in them) and taped (with cellophane tape) onto the bed of a shaker bath (Precision Scientific, Model 25, Chicago) (water omitted) set at 100 oscillations/minute. Any other suitable shaking device would work just as well. After one hour of shaking, the vials were removed and let stand for about ten minutes to allow most of the powdered carbon to settle. (It was proved separately that equilibrium is reached in about twenty minutes, for < 325 mesh carbon.)

Meanwhile, six filter units each consisting of a 13 mm diameter Millipore HAWP 0.45 μm pore size membrane filter in a 13 mm size Swinny filter holder (both available from the Millipore Corporation, Bedford, MA) were prepared. About 15 mL of each sample supernatant solution was taken up into a 20 mL plastic syringe which was then attached to a filter holder, and the solution was filtered to remove the remaining carbon particles. The first few mL were discarded (membrane "debris" sometimes flushes off into the first portion of the filtrate) and the remainder was collected in a small beaker (covered) or clean capped scintillation vial for subsequent colorimetric analysis.

For each sample, the DNP concentration was computed from: concentration (g/L) = 0.30 x (sample absorbance at 480 nm/stock solution absorbance at 480 nm). This concentration,  $C_A$ , was used in the mass balance  $q_A^* W = V (C_{AO} - C_A)$  where  $W$  = grams of



**FIGURE 1. "Linearized" Langmuir equation plot of the equilibrium data, which should yield a straight line if  $K$  and  $Q$  are constant.**

powdered carbon used,  $V$  = volume of solution used (0.01 liter), and  $C_{AO}$  = initial DNP concentration (0.30 g/liter), to compute the equilibrium carbon-phase concentration  $q_A^*$  (g DNP/g carbon).

#### BATCH (EQUILIBRIUM) RESULTS

Since the Langmuir isotherm equation

$$q_A^* = KQ C_A / (1 + K C_A) \quad (1)$$

can be linearized to the form

$$\frac{1}{q_A^*} = \frac{1}{Q} + \frac{1}{KQ C_A} \quad (2)$$

the data were plotted in the form of  $1/q_A^*$  versus  $1/C_A$  in the hopes that they could be fit with a straight line to give an intercept of  $1/Q$  and a slope of  $1/KQ$ , from which  $K$  and  $Q$  (the value of  $q_A^*$  reached as  $C_A \rightarrow \infty$ , *i.e.*, the monolayer adsorption capacity of the carbon for DNP) could be determined. As Figure 1 shows, such a straight-line fit was impossible (*i.e.*, the data simply do not fit the Langmuir model).

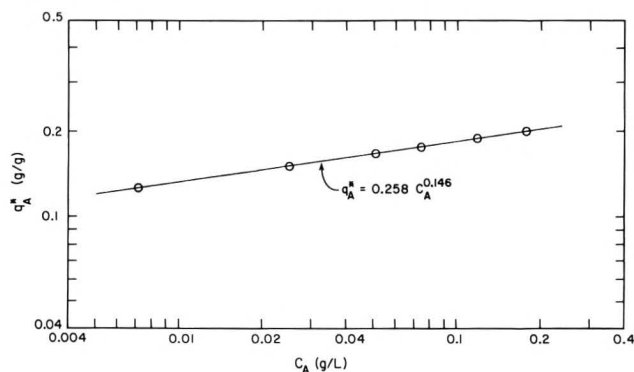
The  $q_A^*$  versus  $C_A$  data were also plotted on log-log paper, since the Freundlich isotherm equation is

$$q_A^* = k C_A^{1/n} \quad (3)$$

hence

$$\log q_A^* = \log k + (1/n) \log C_A \quad (4)$$

Students always try to get an "intercept" on such a plot, but this is impossible, of course. They should



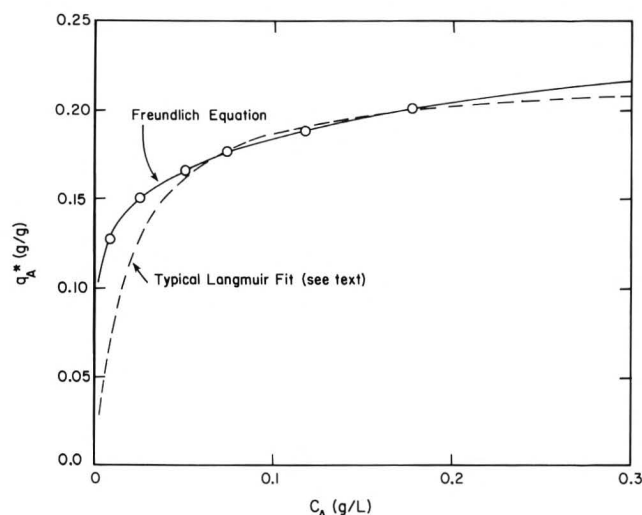
**FIGURE 2. Linearized Freundlich equation plot of the equilibrium data.**

simply pick two points near the ends of the best fit straight line, and insert these two ( $q_A^*$ ,  $C_A$ ) pairs into the last equation, thereby generating two equations from which the two unknown parameters  $k$  and  $1/n$  can be determined. As Figure 2 shows, the data fit the Freundlich expression extremely well. This is consistent with the author's and other investigators' previous experience in measuring liquid-phase equilibria for organic compounds adsorbing on activated carbon, in which it has been repeatedly observed that the Freundlich equation fits such data very well (see the references listed at the end of this paper).

Although the Langmuir equation obviously does not fit the equilibrium data, the data for the four highest  $C_A$  points (*i.e.*, for the four lowest  $1/C_A$  points in Figure 1) can be fit reasonably well to a straight line, from which one obtains  $Q = 0.221$  and  $K = 53.7$ . Figure 2, for the Freundlich equation, gives  $k = 0.258$  and  $1/n = 0.146$ . Plots of Eqs. (1) and (3) with these parameter values give the comparison to the equilibrium data shown in Figure 3. Obviously, the Freundlich equation fits essentially exactly, while the Langmuir equation fits somewhat well at high  $C_A$  and poorly at low  $C_A$ , as one would expect considering how  $Q$  and  $K$  were obtained.

## FIXED BED EXPERIMENT

Four grams of the 28/40 mesh Pittsburgh CPG carbon were loaded into a 0.9 cm I.D. by 15 cm long chromatography column (type K 9/15 from Pharmacia Fine Chemicals, Inc., Piscataway, NJ). The empty column, with the top inlet header unscrewed, was filled with distilled water (with the outlet line clamped), and small portions of the carbon were dropped into the column successively until the column was packed with the full 4 grams of carbon. This technique prevents any trapping of air bubbles in the bed. While some classification of the carbon particles occurs as they fall through the water, gross classification of the bed is avoided by adding the carbon in small batches with a spatula and waiting for each batch to settle. The water level in the column rises as one does this, so the clamp on the column outlet line must be periodically opened to drain off some of the water and keep it from overflowing out of the top of the column. Once



**FIGURE 3. Comparison of equilibrium data with the Freundlich equation, and with a Langmuir equation derived from fitting the high  $C_A$  data.**

the column was packed, the top inlet header was screwed onto the column. The stock DNP solution, 3 liters of which were contained in a standard one-gallon glass jug, was pumped to the column at 25 mL/minute using a Masterflex Unified Variable Speed Model 7523-10 tubing pump drive fitted with a number 7014 Standard Pump Head, and number 14 silicone rubber tubing (Cole-Parmer Instrument Co., Chicago).

The pump was turned on briefly enough to bring the DNP solution to the end of the tubing, which was

then attached to the column inlet header. At "time zero," a stopwatch was started and the pump was re-started. Effluent from the column was collected in a 1000 mL graduated cylinder and, as each successive 100 mL mark was reached, a spectrophotometer cell was held under the effluent line for long enough to collect about 2.5 mL of effluent. The sample absorbance was then measured colorimetrically (any drops of sample on the cell outside surfaces were first dried off using Kimwipes). The reference cell was checked

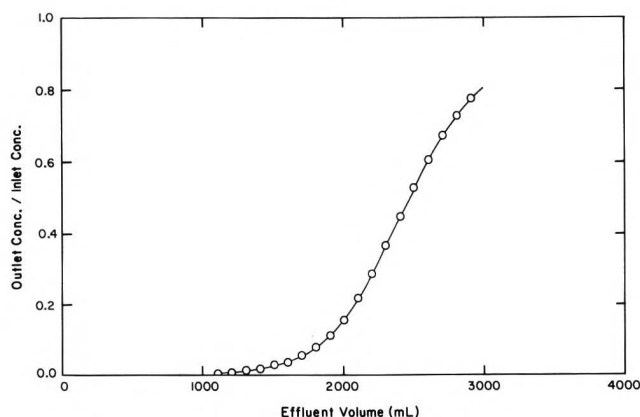


FIGURE 4. Effluent curve behavior for the experiment.

each time to see that its absorbance read 0.000. The sample was then dumped back into the collection cylinder. When the first 1000 mL cylinder was full, a second one was used to replace the first one, and the first one was dumped. The cylinders were alternated this way, with sample measurements each 100 mL, until the effluent concentration exceeded 75% of the inlet concentration. The fixed bed experiment was then shut down and the data were plotted as  $C_A$  versus total effluent volume.

#### FIXED BED RESULTS

Figure 4 shows the breakthrough curve obtained from the fixed-bed part of the experiment. If ideally-sharp breakthrough behavior were to exist, a step function would have been obtained at a point where a vertical line passes through the point  $C_A = 1/2 C_{A,feed}$  (assuming a symmetrical breakthrough curve). The total effluent volume corresponding to this step function can be seen to be about 2460 mL, and hence the total column capacity for DNP is thus (2.46 liters) (0.30 g/liter)/4.0 g carbon = 0.185 g DNP/g carbon. However, inserting  $C_A = 0.30$  g/liter into the Freundlich equation gives a  $q_A^*$  value of 0.235. The

reason why the 0.185 is about 21% too low is that the effluent curve is actually *not* symmetrical but would show significant "tailing" if it had been followed further. Hence, the proper position to place the step function for the ideal case would be at an effluent volume greater than 2460 mL. This would raise up the calculated 0.185 value and give better agreement with the "ideal saturation capacity" value calculated from the Freundlich equation.

Nevertheless, the step-function replacement of the actual breakthrough curve does give a rough approximation to the column's ideal capacity. Of course, in actual operation, a fixed-bed system would be shut down as soon as the outlet concentration is just a few percent (*e.g.*, 5%) of the inlet concentration. The only reason we followed the breakthrough curve so far in this experiment was to allow the students to see what the curve looks like at later stages, and to allow them to compare (at least approximately) the total DNP capacity from this dynamic column technique to values predicted by batch equilibrium experiments.

#### COMMENTS

With a group of three students performing this experiment, we start the batch sample part first. Then, while the samples are shaking (one hour) we begin the column part. Sometime during the column run, the batch samples are ready for filtration, so the filtration is carried out by one of the students, and the filtrates are kept aside for analysis after the column run is over.

In their reports, the students are asked to discuss general principles of adsorption, particularly low temperature physical adsorption (*via* van der Waals type forces) on activated carbon. They are also asked to discuss how activated carbon is usually made, and its properties (internal surface area, pore-size distribution, *etc.*).

Overall, the experiment and subsequent student reports are effective in conveying most of the basic principles of physical adsorption processes.

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