Introduction of Process Dissection and Reintegration into Undergraduate Laboratory

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Abstract

Students often approach the engineering curriculum as discrete parcels of knowledge–knowledge identifiable only by course number. The lack of integration among courses only reinforces this tendency. To combat this tendency, we initiated a novel pedagogical approach to laboratory instruction, which we call "process dissection and reintegration". Under such an instructional methodology, we dissect a unit operation into its various physicochemical phenomena. In doing so, we pay particular attention to how such phenomena influence the equipment design. In this paper, we highlight the many ways we incorporate our novel methodology in two Unit Operations laboratory courses.

Course Setting

We practice process dissection and reintegration in our two-semester laboratory course sequence, ChE 234 and 236, Chemical Laboratory I and II. Our students take these three-credit hour laboratories in semesters six and seven. The prerequisites for ChE 234 include chemical equilibria (ChE 143), momentum (ChE 231) and heat transfer (ChE 233) while the prerequisites for ChE 236 include staged operations (ChE 235) and differential mass transfer (ChE 237).

ChE 234 involves a variety of laboratory projects that demonstrate the principles of momentum and heat transfer: *Pressure Drop Through Valves and Fittings; Two-Phase Flow Through a Packed Bed; Reboiler and Condenser Heat Duties; Turbulent Heat Transfer in Empty and Statically-Mixed Tubes;* and *Batch Heating of a Mixed Tank.* ChE 236 involves experiments that demonstrate either a chemical separation or conversion–the "bread and butter" of a chemical engineers. These experiments consist of: *Heterogeneously-Catalyzed Esterification of Acetic Acid and Ethanol; Desorption of Aqueous Ammonia Using a Packed Bed; Batch Drying of a Moist Solid; Batch Distillation of Methanol and Water;* and *Adsorptive Dehydration of Ethyl Acetate.*

Course Objectives

Since we approach ChE 234 and 236 as a two-semester sequence, they have similar learning objectives:

- reinforce and extend the principles forwarded in theory courses;
- introduce and hone methods of engineeering experimentation; and
- hone professional skills especially relative to technical communication.

These objectives therefore carry student expectations that include:

- understand underlying physicochemical phenomena involved in each laboratory experiment;
- apply statistical design of experiments and statistically interpret experimental results; and
- articulate results and theoretical concepts through oral presentations, written reports, graphical

displays of quantitative information, and visualizations of complex phenomena.

In addition, we wish to accomplish our objectives through the promotion of teamwork. This requires us to take a more integrated approach where students rely more and more on each other to acquire knowledge. The trick, therefore, becomes how do you build such a learning environment?

Course Approach

We typically start ChE 234 with an instrument calibration needed for a particular experiment so students can gain some familiarity with the project. Next, the students run a series of experiments and model the data. The students then use these data to solve a portion of a chemical process design problem posed to the entire laboratory class. This semester students must design a process to recover solvent used in an antibiotic extraction. The whole idea requires the design of a problem that uses the experiment data obtained in each semester project. In this way, the students learn how a series of physicochemical phenomena work in concert to effect a chemical separation or reaction process and the relationships and similiarities shared among the laboratory projects.

Besides process dissection and reintegration among experiments, we also promote this pedagogy in the design of the new experiments we introduce into our laboratory. We shall discuss our most recent addition, *Adsorptive Dehydration of Ethyl Acetate* , a project funded by the Camille and Henry Dreyfus Foundation and the National Science Foundation.

Example of an Integrated Experience

We use a fixed-bed adsorption process as an example of how to create an integrated laboratory experience through the practice of process dissection and reintegration. Here we have dissected the adsorption process into its individual physicochemical phenomena and created a series of experiments involving phase equilibria, pore diffusion, and elements of computer data acquisition and control. Students reintegrate the results from these lower-level experiments into a model that simulates the adsorber's performance. They then compare the simulation to actual fixed bed performance data. Thus, students see more clearly how the various physical phenomena, and process control and instrumentation work in concert to achieve a chemical separation.

Theory

In this section, we shall present the physical phenomena and theoretical equations associated with the analysis of the adsorptive dehydration of an ethyl acetate solution saturated with water. We refer the reader to work of Teo and Ruthven (1986) for additional details.

Our example separation process involves the following mass transfer steps or resistances:

- diffusion of solute molecule (water) to the external surface of solid adsorbent;
- diffusion of solute molecule through the porous solid’s macropores;
- diffusion of solute molecule into the porous solid’s micropores (molecular sieve); and
- adsorption of solute into an active site.

To build an integrated experience, we must take these various steps and create a separate experiments for each phenomena involved and then create a capstone experiment that uses data from the lower-level experiments. The first step listed above actually involves the convective transport of the solute molecule to a region near the external surface then followed by a diffusion through a stagnant film. We chose not to create an experiment to demonstrate this step. To estimate the external resistance, students use the correlation of Wakao and Funazkri (1978)

$$N_{Sh} = \frac{2k_f R_p}{D_m} \quad = \quad 2.0 \quad + \quad 1.1 N_{\mathrm{Sc}}^{0.33} N_{\mathrm{Re}}^{0.6} \tag{1}$$

We did, however, created experiments to measure solid/liquid equilibria, q^* and pore diffusion coefficient, D_p followed by a capstone fixed bed adsorber experiment.

Equilibrium Isotherm. The equilibrium isotherm describes how the adsorbate molecule distributes between an adsorbed state and bulk fluid phase. The familiar Langmuir isotherm model represents the solid/liquid equilibria

$$q^* = \frac{b_1 c}{1 + b_2 c} \tag{2}$$

If the adsorption becomes highly favorable, the isotherm approximates a rectangular or irreversible form ($c = 0,\ q^* = 0;\ c > 0,\ q^* = q_s$).

Batch Uptake Kinetics. Let us consider a known mass of identical spherical adsorbent particles with a pore void fraction of ε_p immersed in a well-mixed reservoir and subject these particles to a step increase in sorbate concentration from 0 to C_0. If we neglect the external or fluid-side resistance as negligible and assume the equilibrium isotherm follows a rectangular form, then the "shrinking core" model describes uptake of sorbate. Figure 1 shows general form of the sorbate concentration profile where all the adsorption occurs at the front (radius $R_f < R_p$), a front that divides the sorbate-free core from the saturated external shell.

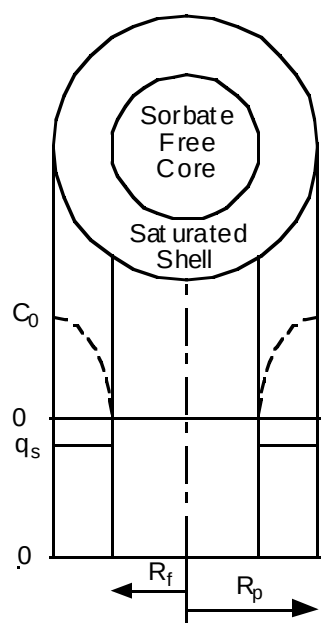

Figure 1. Concentration profile for an irreversibly adsorbed (rectangular isotherm) sorbate in a porous adsorbent particle of radius R_p.

Over the region, $R_p > R > R_f$, the total flux remains constant and the sorbate concentration drops from c_0 at the surface ($R = R_p$) to 0 at R_f by the following profile

$$c = k\left[\frac{1}{R_f} - \frac{1}{R}\right] \tag{3}$$

At the particle surface, Eq. (3) yields the following expression for c_0

$$c = k\left[\frac{1}{R_f} - \frac{1}{R_p}\right] \tag{4}$$

If we now equate the total flux with the net sorbate uptake rate, we find

$$4\pi R^2 \varepsilon_p D_p \left(\frac{\partial c}{\partial R}\right) = -4\pi R_f^2 q_s \frac{dR_f}{dt} \tag{5}$$

Substituting Eqs. (3) and (4) into Eq. (5), we obtain upon rearrangement

$$\frac{\varepsilon_p D_p}{R_p^2}\frac{c_0}{q_s} = \left(\eta^2 - \eta\right)\frac{d\eta}{dt} \tag{6}$$

where $\eta = \dfrac{R_f}{R_p}$.

Since the sorbate concentration c_0 in the reservoir changes with time, the following overall mass balance relates reservoir concentration to the variable η

$$c_0(\eta) = C_0\left[1 - \Lambda\left(q / q_s\right)\right]C_0\left[1 - \Lambda\left(1 - \eta^3\right)\right] \tag{7}$$

where C_0 represents the initial sorbate concentration, Λ the fraction of sorbate initially present that the adsorbent eventually adsorbs, and (q/q_s) fractional uptake of the adsorbent at time t. Combining Eqs. (6) and (7) and integrating, we obtain

$$\frac{\varepsilon_p D_p}{R_p^2}\frac{c_0}{q_s} t = \int_1^{\eta} \frac{\left(\eta^2 - \eta\right)d\eta}{1 - \Lambda + \Lambda\eta^3} = I_2 - I_1 \tag{8}$$

Teo and Ruthven incorrectly reported the integrals I_1 and I_2, which we have corrected to give

$$I_1 = \frac{1}{3\Lambda\lambda}\left\{\tfrac{1}{2}\ln\left[\frac{\left(1 - \Lambda + \Lambda\eta^3\right)\left(\lambda + 1\right)^3}{\left(\eta + \lambda\right)^3}\right] + 3^{1/2}\tan^{-1}\left\{\frac{2\eta - \lambda}{\lambda 3^{1/2}}\right\} - 3^{1/2}\tan^{-1}\left\{\frac{2 - \lambda}{\lambda 3^{1/2}}\right\}\right\} \tag{9}$$

$$I_2 = \frac{1}{3\Lambda}\ln\left[1 - \Lambda + \Lambda\eta^3\right] \tag{10}$$

where $\lambda = \left[(1 - \Lambda)/\Lambda\right]^{1/3}$. Since we can express the two integrals in Eq. (8) as function of Λ and Q , we can rewrite Eq. (8) as

$$\frac{D_e t}{R_p^2} = \frac{\varepsilon_p D_p}{R_p^2}\frac{c_0}{q_s} t = I_2(Q,\Lambda) - I_1(Q,\Lambda) \tag{11}$$

where Q = $1 - \eta^3$.

Equation (11) suggests that if we plot $(I_2 - I_1)$ versus t the result should yield a straight line that passes through the origin with a slope of D_e / R_p^2.

Fixed Bed Adsorber Simulation. We shall consider the isothermal adsorption of a single solute (sorbate) from a liquid in plug flow through a bed of void fraction ε, length z, cross section area A, and packed with uniform spherical particles of radius R_p The liquid flows at a superficial velocity v and the bed initially contains no solute. At time zero, the inlet concentration of solute changes from zero to c_0.

Assuming negligible axial dispersion, the differential fluid phase mass balance for the solute becomes

$$v\frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial \overline{q}}{\partial t} = 0 \tag{12}$$

For the case of a rectangular isotherm system and the mass transfer rate controlled by a combined effect of external and internal pore diffusional resistances, Weber and Chakravorti (1974) presented the following solution to Eq. (13) for the constant pattern region $\left(\theta \geq 5/2 + N_p/N_f\right)$

$$\begin{aligned}\theta - N_p &= \frac{15}{\sqrt{3}}\tan^{-1}\left[\frac{2(1-Q)^{1/3}+1}{\sqrt{3}}\right] + \frac{15}{2}\ln\left[1+(1-Q)^{1/3}+(1-Q)^{2/3}\right] \\ &+ \frac{5}{2} - \frac{5\pi}{2\sqrt{3}} + \left(\frac{N_p}{N_f}\right)(\ln Q + 1)\end{aligned} \tag{13}$$

where Q represents the fractional uptake and θ, N_p, and N_p represent dimensionless parameters with respect to contact time, pore resistance, and film resistance. We define these parameters as follows

$$\theta = \left(\frac{15\varepsilon_p D_p}{R_p^2}\right)\left(\frac{c_0}{q_s}\right)(t - z\varepsilon/v) \tag{14}$$

$$N_p = \left(\frac{15\varepsilon_p D_p}{R_p^2}\right)\left(\frac{z}{v}\right)(1-\varepsilon) \tag{15}$$

$$N_f = k_f\left(\frac{3z}{vR_p}\right)(1-\varepsilon) \tag{16}$$

To simulate the fixed-bed adsorber response, students use their equilibrium and pore diffusion results and solve Eq. (13) for Q or c/c_0 at various times, thus generating the "breakthrough curve" or how the effluent concentration changes with time.

Experimental

Equilibrium Experiment. For the equilibrium isotherm experiments, the students weigh known amounts (1 to 3 g) of preconditioned, 4A molecular sieve on an analytical balance. The pre-conditioning procedure involves heating the adsorbent for 24 h at 300°C. They then place a known volume (10 to 25 cc) of ethyl acetate/water solution (approx. 3 wt percent H_2O) into a 50 ml sealed Erlenmeyer flasks. The prepared samples are then placed in a precision temperature bath for 72 hours. Initial and final water concentrations are measured with a Mitsubishi CA-06 Moisture Meter. The mass of water adsorbed is found by performing a mass balance.

Adsorption Isotherm. Figure 2 shows the equilibrium isotherm data at 20 and 30°C. Students would first linearized Eq. (2) as follows

$$\frac{c}{q^*} = \frac{b_2}{b_1} c + \frac{1}{b_1} \tag{17}$$

and fit the data to Eq. (17) using linear regression. Figure 3 shows the results of a linear fit to the 30°C isotherm data. From these results, we can see that data follows Eq. (2). But as Figure 2 shows the data closely approximates the rectangular form. Therefore, the students can analyze their batch uptake and fixed-bed adsorber data assuming a rectangular isotherm.

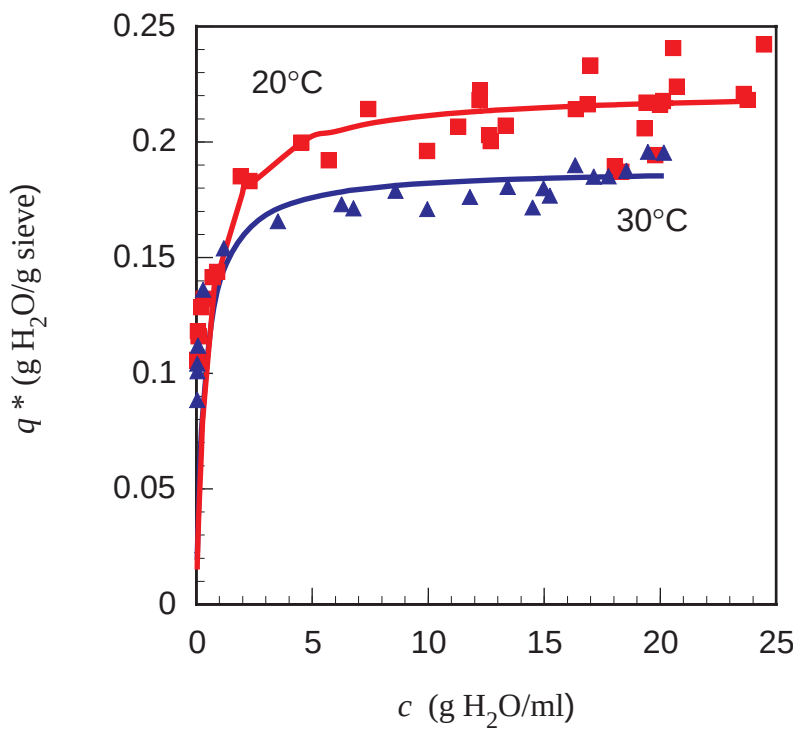

Figure 2. Equilibrium isotherms for water adsorbed from ethyl acetate/water solutions on 4A Molecular Sieve at 20 and 30°C. The solid lines represent the fit to the Eq. (2). The adsorbent was regenerated for 24 h at 300°C. Equilibrium assumed after 72 h.

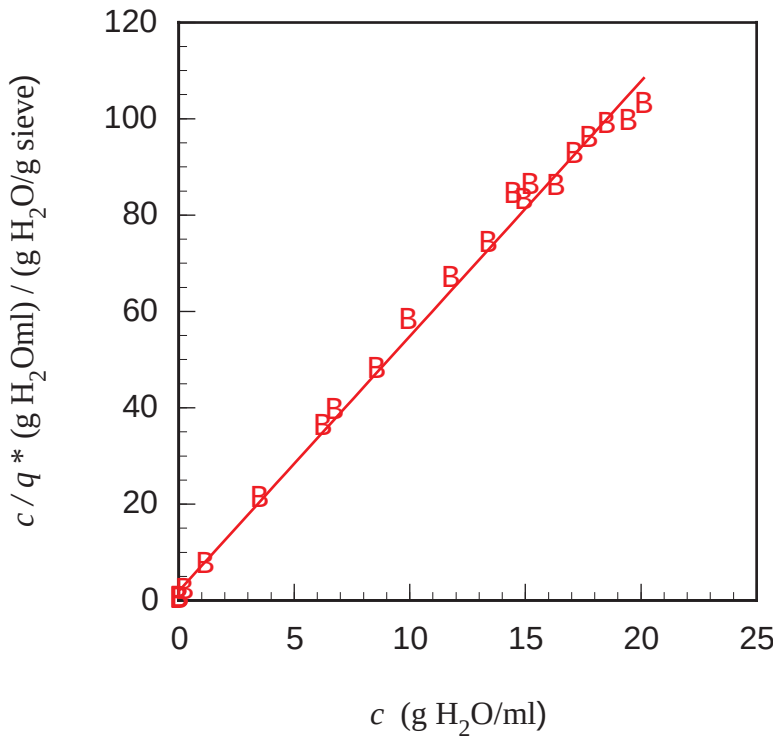

Figure 3. Equilibrium isotherm for water adsorbed from ethyl acetate/water solutions on 4A molecular sieve at 30°C. The adsorbent was regenerated for 24 h at 300°C. Equilibrium assumed after 72 h. The solid lines represent the fit to the Eq. (17) where $1/b_1 = 1.9$ and $1/b_2 = 5.3$.

Batch Uptake Experiment. Figure 4 shows a schematic of the batch uptake experiment. Instead of placing the sieve in an agitated vessel, we opted to place the adsorbent in a cell and pump liquid passed the sieve. We have assembled six adsorption cells containing about four grams of 4A molecular sieve. Each cell contains a different mesh size of particles (8-12, 12-16, 16-20, 20-30, 30-40, and 40-50 mesh) so the students can study the possible effect of particle size. The metering pump also allows the students to study recirculation rate (negligible external resistance assumption) as well.

Before placing the adsorption cell into the circulation loop, the sieve undergoes a 24-hour preconditioning at 300°C in external oven. The students would then place the cell containing the preconditioned adsorbent into the circulation loop and charge the fluid reservoir with 250 ml of an ethyl acetate/water solution of known concentration. The fluid reservoir is jacketed so its contents can be heated or cooled with a circulation temperature bath. The by-pass loop located off the main circulation loop allows the agitation of the fluid to bring the system to a constant temperature before introducing the adsorbate-laden solution to the adsorption cell. Once a steady temperature has been reached, air-actuated, three-way valves are repositioned to initiate a run. Samples of the fluid reservoir are periodically taken through a syringe port located at the top of the reservoir and analyzed for water concentration with the moisture meter. The amount of sorbate uptake is then determined by a mass balance.

Batch Uptake Kinetics. Figure 5 shows typical batch uptake curves for two particle sizes, 12-16 and 20-30 mesh. From these data, students can clearly see a dependence on particle size. They then fit the uptake data to Eq. (11). Figure 6 shows the fit of a typical set of batch uptake data.

From the linear fit, the students calculate the pore diffusivity and check the validity of the negligible external resistance assumption.

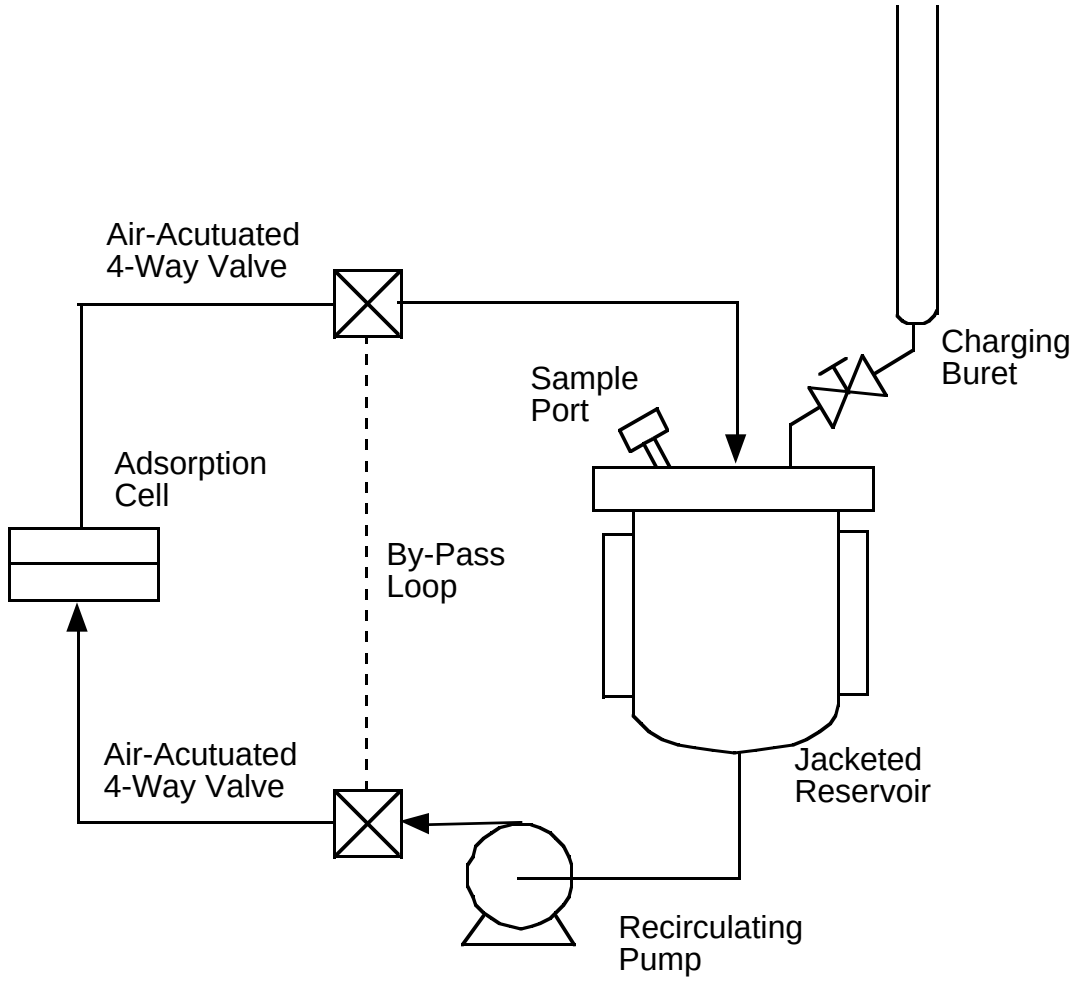

Figure 4. Schematic of batch uptake apparatus

Fixed Bed Adsorber. Figure 7 shows a schematic of the fixed bed adsorber experiment. We have configured the adsorbers such that one can be running while the another is regenerating. This experiment is interfaced to a personal computer (P2-200 MHz) that controls a Keithley Series 500 Data Acquisition System. The data acquisition system has four modules: AMM1A Master Analog Module (8 channel, 12-bit A/D, 0-10 V input); AIM7 Thermocouple Input Module (16 channels of thermocouple input); AOM3 Current Loop Module (4 channel, 12-bit D/A, 0-20mA output); and PCM2 (16 channels of solid state relays). Version 10.1, LabTech ControlPro software drives the data acquisition and control. The computer controls the switching between the adsorbers of both the feed and regeneration gas; controls the feed into the column; controls *in situ* the nitrogen regeneration of molecular sieve adsorbent; monitors temperatures with Type-T thermocouples at various locations around the adsorption process; and monitors the effluent flow rate and concentration with a MicroMotion CMF 10 Elite© Sensor coupled to an RFT 9739 Remote Flow Transmitter.

Both adsorbers are constructed of three-inch, Schedule 10, SS316 pipe and jacketed for temperature control. The bed's useable length is 18.5 in. Each adsorber has six themocouples

mounted along its length. A 1kW electric heater is used to heat the nitrogen purge that regenerates the adsorbent. We can sample the effluent stream for analysis or use a recently-donated densimeter (MicroMotion CMF 10) to determine concentration on-line.

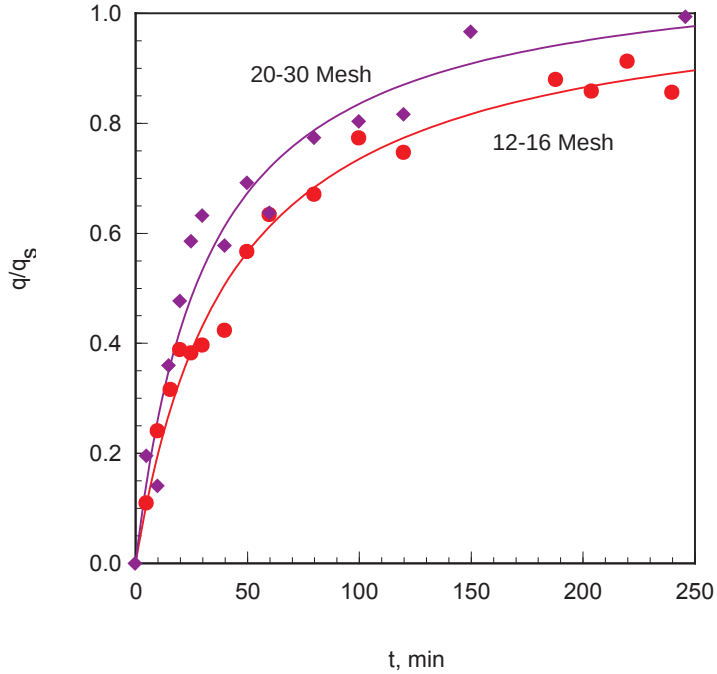

Figure 5. Batch uptake curves for 12-16 and 20-30 mesh particles.

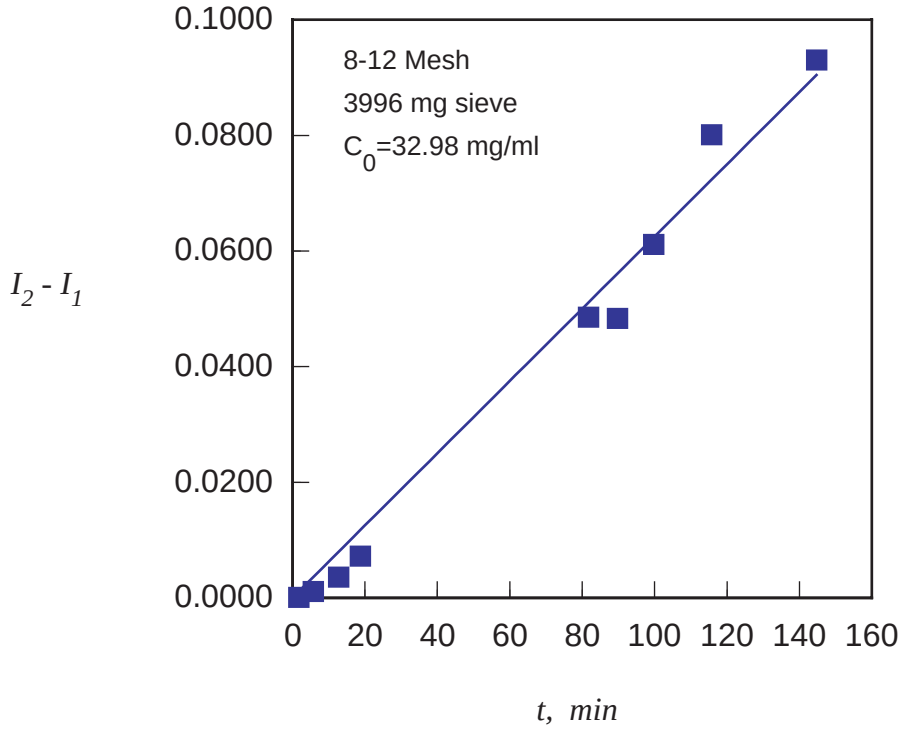

Figure 6. Uptake data for 8-12 mesh particles evaluated according to Eq. (11). The slope equals $\varepsilon_p D_p / R_p^2 = 6.25 \times 10^{-4}\ \mathrm{min}^{-1}$.

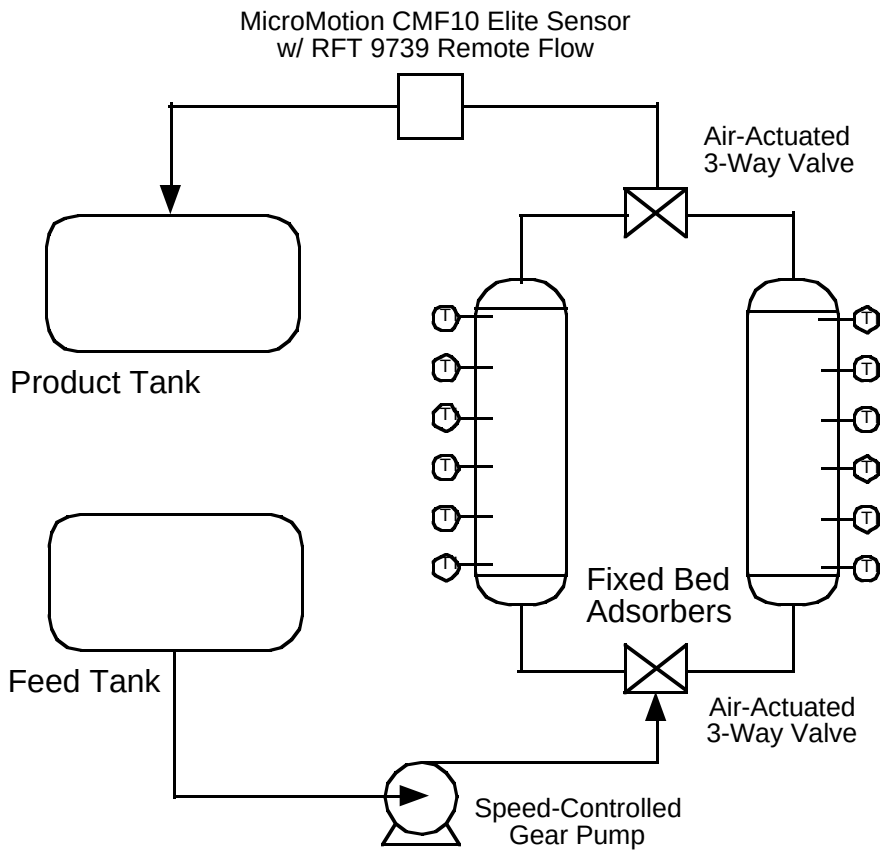

Figure 7. Schematic of fixed bed adsorbers.

Breakthrough Data. Figure 8 shows a typical breakthrough curve for a fixed-bed adsorber. We had hoped to use the simulation model described by Eq. (13) to compare the simulation results to the experimental data. However, we used too short (11.7 cm) of an adsorption bed for Eq. (13) to apply. In the future, we hope to test longer beds but that will require our students to make substantially longer runs (greater than six hours).

Other Possible Experiments. Some other possible experiments that students can perform with on the equipment presented in this paper include:

- the calibration of a mass flow meter;
- the calibration of a densimeter;
- tuning of temperature control loop; and
- tuning of flow control loop.

These all represent good first experiments to acquaint students to process instrumentation, and computer data acquisition and control software and hardware–the tools of the practicing process engineer.

Concluding Remarks

We have made but a small step toward creating a laboratory experiences that build upon previous experiments. We do, however, encourage educators to strongly consider how a new experiment

they might add to their undergraduate laboratory reinforces and extends the student's knowledge base. Without such consideration, we believe the experiment will not accomplish what we truly want our engineering graduates to possess–vision, the ability to see the total picture and how individual phenomena or pieces of process equipment work in concert to achieve the end product. We further recommend the laboratory experiment or experience should possess various levels of sophistication, such as an instrument calibration followed by a more extensive experiment. If possible, the experiments run on newly-purchased equipment should span two or more laboratory courses and conclude with a capstone experience, such as a design problem or simulation and comparison of experimental data to the simulation results.

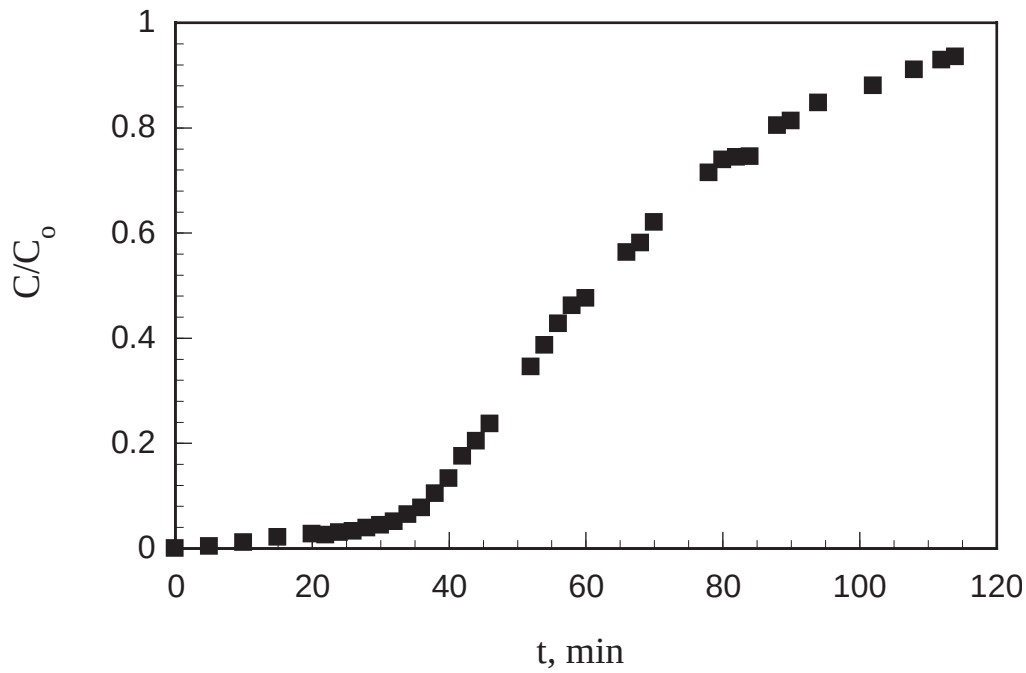

Figure 8. Breakthrough curve for an ethyl acetate/water with an initial water concentration of 22.7 mg/ml flowing a superficial velocity of 1.07 cm/min through a bed packed with 4A molecular sieve. The bed length is 11.7 cm

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Bibliography

1. Teo, W. K., and D. M. Ruthven, "Adsorption of Water from Aqueous Ethanol Using 3-Å Molecular Sieves," *Ind. Eng. Chem. Process Des. Dev.*, **25**, 17 (1986).

2. Wakao, N., and T. Funazkri, "Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Mass Transfer Coefficients in Packed Beds," *Chem. Eng. Sci.*, **33**, 1375 (1978).

3. Weber, T. W., and R. K. Chakravorti, "Pore and Solid Diffusion Models for Fixed-Bed Adsorbers," AIChE J., **20**, 228 (1974).

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