# The Five-Minute Adsorption Demonstration

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## The Five-Minute Adsorption Demonstration

### Introduction

Adsorption is an environmental engineering treatment process that is used extensively to remove contaminants from water and air. Environmental engineering faculty typically teach this topic by describing mathematical models that are used to quantify adsorption. This approach, by itself, may result in students having an incomplete understanding of adsorption because students frequently have difficulty visualizing scientific phenomena such as the mass transfer process that occurs during adsorption. A hands-on laboratory experiment (cf. Speitel, 2001) where students collect and analyze adsorption data, may enhance students' understanding of adsorption. Undeniably, hands-on experiences help students develop a deeper understanding of principles studied in and out of the classroom (Butkus et al., 2004; Pfluger et al., 2012; Wankat and Oreovicz, 2015). Unfortunately, adsorption experiments typically require 2-48 hours to reach equilibrium, vide infra, which can limit opportunities for hands-on laboratory experiments. This work presents an undergraduate classroom demonstration that replicates the adsorption experiment and data analysis, which may engage students and enhance learning without imposing substantial demands on student time. In addition, the experimental procedure presented here can be used to execute a full scale hands-on adsorption laboratory.

### Engineering Principles

Adsorption is a mass transfer process in which matter (adsorbate) accumulates at an interface between two phases e.g. a solid (adsorbent) and water (solvent). Adsorption is widely used in environmental engineering for numerous applications, especially for removing contaminants from water and air. Environmental engineers typically quantify the mass of adsorbate per mass of adsorbent (adsorption density, q) as follows.

$$q = \frac{x}{M} = \frac{(C_o - C_{aq})V}{M}$$

where,

$C_o$ = initial aqueous concentration (mg sorbate/L)
$C_{aq}$ = equilibrium aqueous concentration (mg sorbate/L)
$V$ = volume of solvent (L)
$M$ = mass of sorbent (g)

When modeling and designing adsorption treatment processes, the adsorption density is typically graphed as a function of the adsorbate's equilibrium aqueous concentration at a constant temperature; this relationship is called an isotherm. Environmental and chemical engineers use adsorption isotherm models, such as the Langmuir and Freundlich isotherm models, in the design of adsorption treatment works (see Benjamin and Lawler (2013) and Weber and DiGiano (1996) for a thorough discuss of adsorption isotherm models). The adsorption density can be determined with the Langmuir Isotherm Model (Langmuir, 1918) as follows.

$$q = \frac{Q_m K_{ad} C_{aq}}{1 + K_{ad} C_{aq}}$$

where,

$Q_m$ = Maximum adsorption density (mg sorbate/g sorbent)
$K_{ad}$ = Langmuir adsorption equilibrium constant (L/mg sorbate)

This rational function can be converted into a linear form as follows.

$$\frac{C_{aq}}{q} = \frac{C_{aq}}{Q_m} + \frac{1}{Q_m K_{ad}}$$

The linear form of the isotherm equation can be used to find $Q_m$ and $K_{ad}$ with experimental data via linear regression. There are other linear forms of this equation, which can yield different fits to experimental data (cf. Hamdaoui and Naffrechoux, 2007).

The Freundlich Isotherm Model (Freundlich, 1907) is also commonly used to quantify adsorption density as follows.

$$q = K_F [C_{aq}]^n$$

where,

$K_F$ = constant that represents adsorption densities under standard conditions
    (mg sorbate/g sorbent*[L/mg sorbate]$^n$)
n = dimensionless constant that represents distribution of binding energies

This power function can be converted into a linear form as follows.

Log (q) = n[log($C_{aq}$)] + Log($K_F$)

Linear regression can be used to find n and $K_F$ with experimental data. The choice of which isotherm to use (in addition to sundry other models that have not been discussed here) is based on the fit to empirical data as shown below in the data analysis section.

**Isotherm Experiment**

*Stock solutions*

Ten mL of one percent Aqueous Crystal violet (Carolina Biological Supply Co., North Carolina), was combined with 1 L of deionized water. This suspension was filtered through a 0.2 μm, 115 mL Nalgene CN filter unit (Rochester, NY). Gravimetric analysis was used to determine the mass of crystal violet in the filtrate. Spectrophotometry (Cary-60 UV-Vis, Aligent Technologies, Germany) was used to create a standard curve relating absorbance, using 1 cm plastic UV cuvettes (Brand, Germany), to concentration (mg/L) at 590 nm. The filtrate (stock solutions) was further diluted to obtain an absorbance of less than one.

*Adsorption Isotherms*

Adsorption experiments were created by combined 200 mL of stock solution with various masses of prewashed activated carbon (-20+40 mesh, Alfa Aesar, Ward Hill, MA) in 250 mL Nalgene (Fisher Scientific, Hampton, NH) bottles. The bottles were mixed in a TCLP rotating tumbler (Analytical Testing Co., Warrington, PA) at 32 rpm for four hours. (See Appendix A for kinetics.) Concentration was quantified via absorbance following the four hour reaction period.

*Column Demonstration*

A 60 mL Luer-Lok syringe (Becton Dickinson, Franklin Lakes, New Jersey) was filled with prewashed granular activated carbon to make a flow through carbon column. The syringe was placed in a clamp on a pipette stand. While wearing gloves, a Crystal violet solution was poured into the top of the column and effluent was collected with a 250 mL glass beaker. The Crystal violet waste was managed according to local regulations.

## Results

Linear forms of the isotherm models with experimental data are presented in Figures 1 and 2.
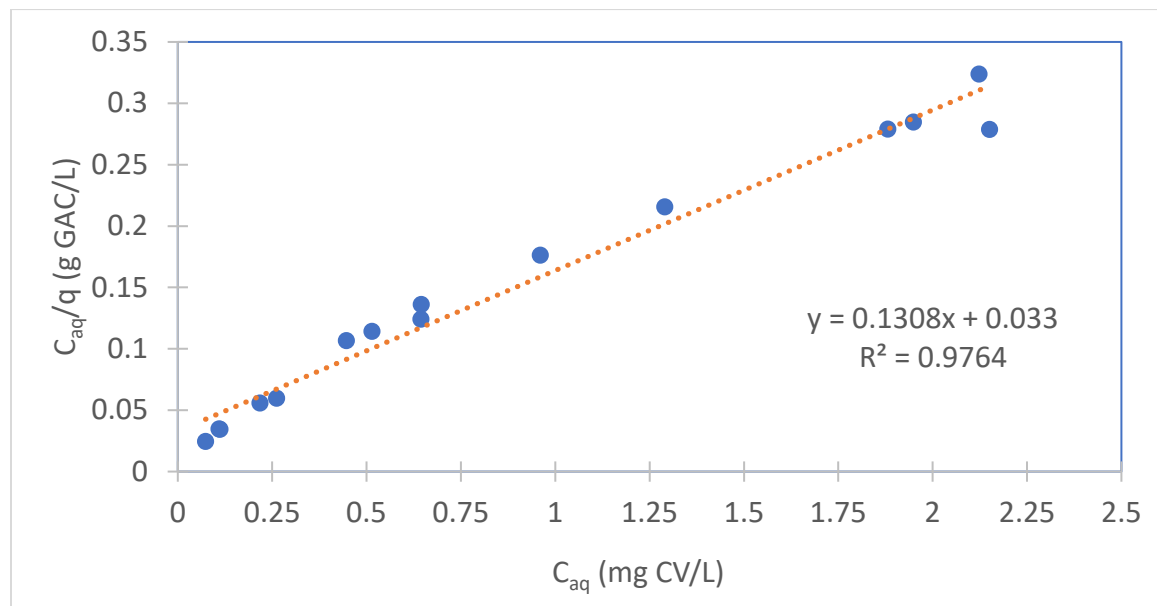


**Figure 1. Fit of Langmuir Isotherm Model to experimental data collected at room temperature.**
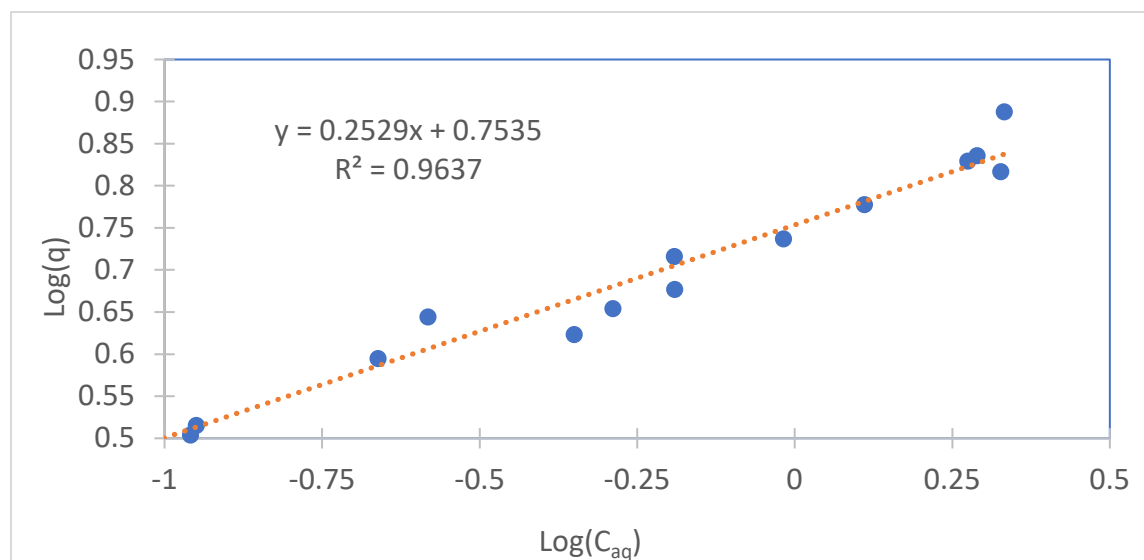


**Figure 2. Fit of Freundlich Isotherm Model to experimental data collected at room temperature.**

The Langmuir Model and Freundlich Model provided comparable fits to the data. Model constants are presented in Table 1.

**Table 1. Model parameters for adsorption of Crystal violet (CV) by activated carbon (GAC) at room temperature**.

| Langmuir Model Parameters | | |
|---|---|---|
| $Q_M$ | 7.6 | mg CV/g GAC |
| $K_{ad}$ | 4.0 | L/mg CV |
| **Freundlich Model Parameters** | | |
| $K_F$ | 5.7 | mg CV/g GAC[L/mg CV]$^n$ |
| n | 0.25 | - - - |

Adjustment of pH was not essential during the isotherm experiments because pH remained between 6.5 and 7.1.  The Crystal violet isotherm experiment, presented here, may be less complicated to execute than the 2,4-dichlorophenol student laboratory experiment described elsewhere (Speitel, 2001), because the latter method typically requires acid/base adjustment during the experiment to maintain pH (based on data from our laboratory, not shown). In addition, sodium hydroxide must be added to all samples such that the 2,4-dichlorophenol solution pH is greater than 10.2, prior to quantifying $C_{aq}$ with a spectrophotometer.

**The Five Minute Demonstration**

The five-minute demonstration introduces students to the concept of adsorption and the Freundlich and/or Langmuir Isotherms models in our undergraduate physicochemical treatment and introduction to environmental engineering courses.  Students observe removal of Crystal violet (or food coloring as discussed below) by activated carbon in real time as the solution passes through a column (syringe) filled with granular activated carbon (Figure 3). The mass transfer process, which occurs during adsorption, is unmistakable as the water enters the column with a dark purple color and exits colorless (to the naked eye) for columns that contain activated carbon.  Recently, we have replaced Crystal violet with food coloring because the former is a carcinogen.  Food coloring is more soluble in water than Crystal violet, which implies that it is less likely to be adsorbed by activated carbon.  However, satisfactory adsorption of food coloring can be attained by using fresh activated carbon or reducing the effluent flowrate from the column to increase mass transfer to the solid phase.  The column on the right side of Figure 3 contains sand (only), which results in breakthrough of the food coloring due to sand's limited ability to adsorb this solute.
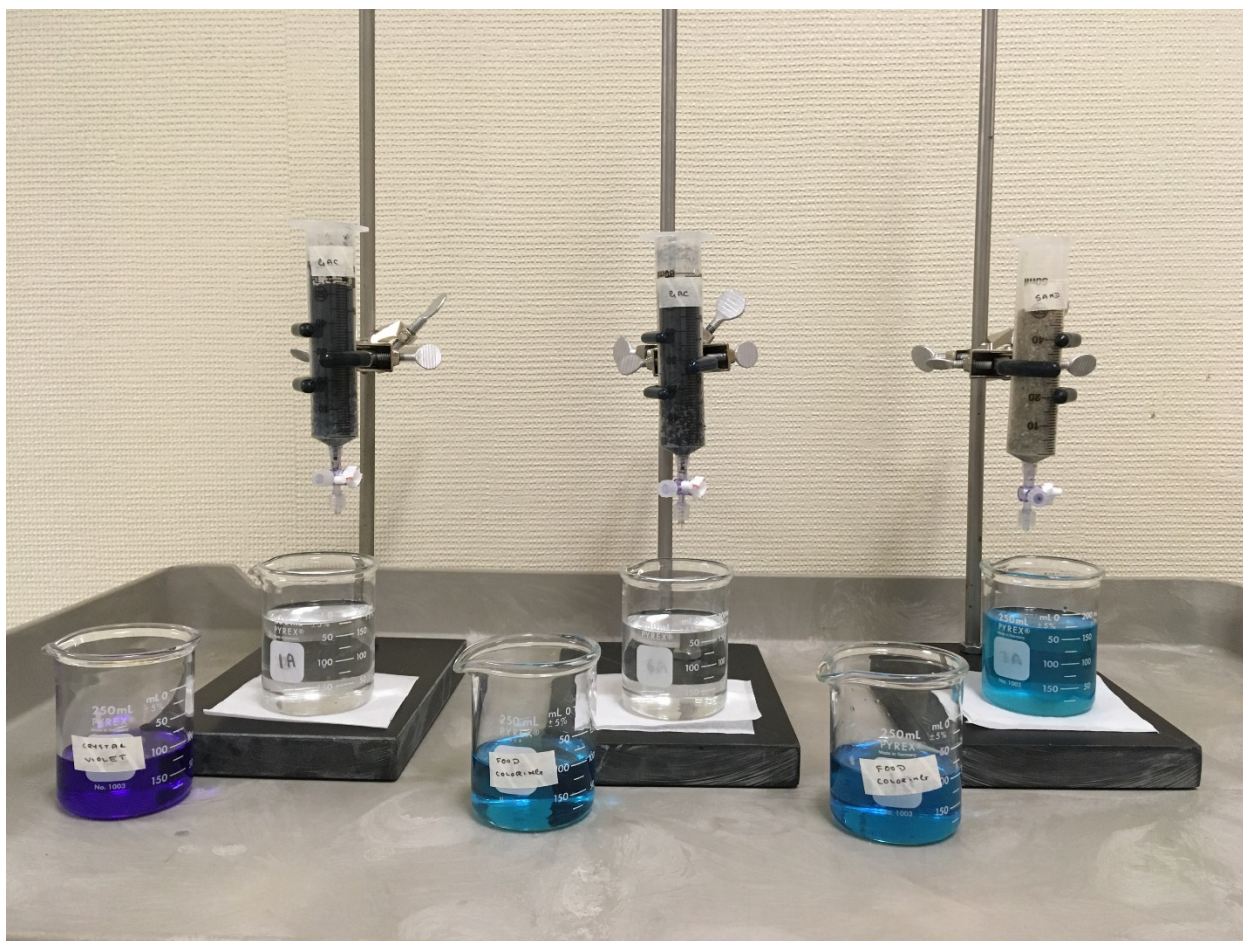
**Figure 3**. **Adsorption column classroom demonstration. The column on the left side and center contain granular activated carbon. The column on the right side contains only sand. A solution of Crystal violet (left) or food coloring (center and right) is added to the top of the columns.**

Data from the adsorption experiment presented above have been added to an animated video-PowerPoint presentation (see Appendix B for slides). This multimedia presentation takes the students from experimental set up through data analysis using the Crystal violet adsorption data. Once the presentation is complete, the instructor can complete the introductory example problem, presented in Appendix C, to reinforce the concepts and application of adsorption in engineering systems.

It is important to recognize that the isotherm models presented in this work are commonly used in design of batch adsorption systems and not flow through column absorbers, such as the demonstration columns presented in Figure 3. Flow through absorbers are typically designed using other approaches (see Hutchins, 1974), which are often studied after isotherm models.

**Conclusion**

Visual aids and video demonstrations that show an adsorption experiment and data analysis, can engage students and enhance learning without imposing substantial demands on student time. Adsorption of Crystal violet by activated carbon is a suitable system for studying the adsorption process via multimedia demonstrations. However, Crystal violet can be replaced by a food coloring-water solution for classroom demonstrations, which is a much safer and environmentally friendly alternative.

# References

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**Appendix A: Kinetics Experiment on Adsorption of Crystal violet Dye with Granular Activate Carbon**

A kinetics study was conducted to determine the time needed for a suspension of Crystal violet dye and granular activated carbon (GAC) to reach equilibrium via adsorption. The study was conducted in triplicate at room temperature with an initial dye concentration of $0.9262 \text{ cm}^{-1}$ and a GAC concentration of $0.2 \pm 0.003$ g. Samples were prepared in 250 ml Nalgene containers and mixed in a TCLP rotating tumbler at 32 rpm. The initial and equilibrium aqueous dye concentrations were quantified by absorbance (590 nm) in one-cm cuvettes.

The rate of adsorption, presented in Figure 4, implies that adsorption isotherm experiments should run for at least 240 minutes (4 hours) to ensure that equilibrium is reached. This equilibrium time is comparable to values reported in the literature for adsorption of Crystal violet by activated carbon (Senthilkumaar et al., 2006).
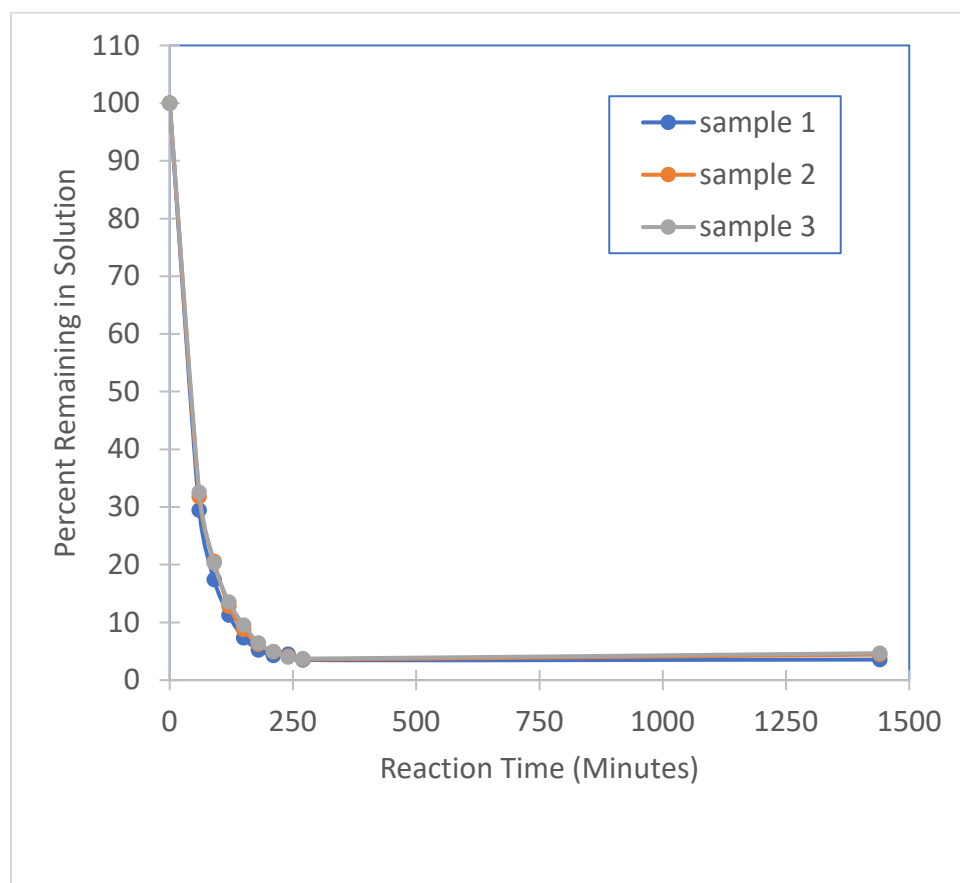


**Figure 4. Rate of Crystal violet adsorption on GAC at room temperature. Percent remaining values are based on absorbance readings at 590 nm.**
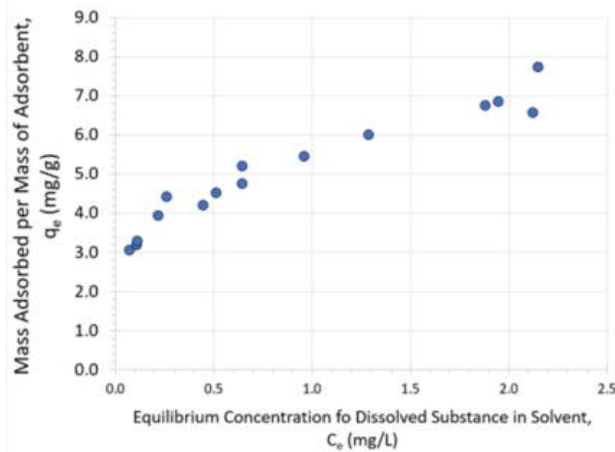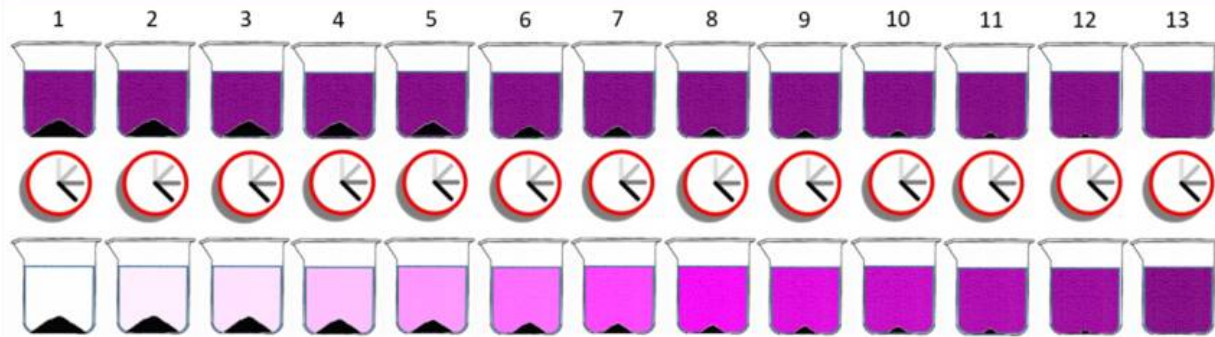
**Appendix B: PowerPoint Slides**

A video, which shows the adsorption experiment, is available to accompany these slides.

1   2   3   4   5   6   7   8   9   10   11   12   13
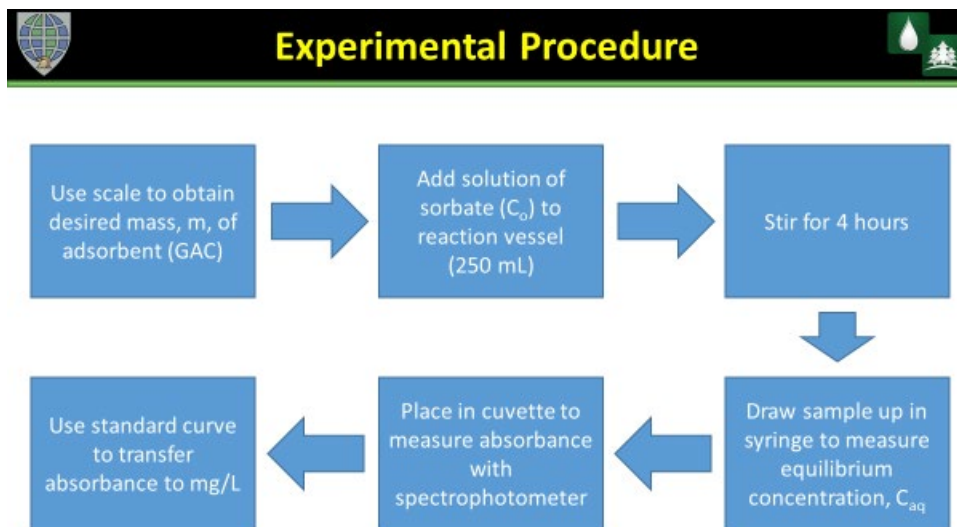
Steps per Batch Reactor:

1) Add a weighed mass of adsorbent (m) to a beaker

2) Add an initial concentration of dissolved substance ($C_o$) in a solvent (250 mL of water) with a known volume ($V$)

3) Stir for 4 hours based on kinetics study to reach equilibrium

4) Measure equilibrium concentration of dissolved substance in solvent ($C_e$)

5) Calculate the mass adsorbed (x), where

$$x = (C_o - C_e)V$$

6) Calculate the ratio of mass adsorbed per mass of adsorbent ($q_e$), where $q_e = \frac{x}{m}$

7) Plot $q_e$ vs. $C_e$

**Plot:** Mass Adsorbed per Mass of Adsorbent, $q_e$ (mg/g) vs. Equilibrium Concentration fo Dissolved Substance in Solvent, $C_e$ (mg/L)

| Experiment | m (g) | $C_o$ (mg/L) | $C_e$ (mg/L) | $V$ (L) | x (mg) | $q_e$ = x/m (mg/g) |
|---|---|---|---|---|---|---|
| 1 | 0.223 | 2.785 | 0.074 | 0.25 | 0.678 | 3.043 |
| 2 | 0.210 | 2.785 | 0.110 | 0.25 | 0.669 | 3.192 |

# Determining Model Parameters & Modelling
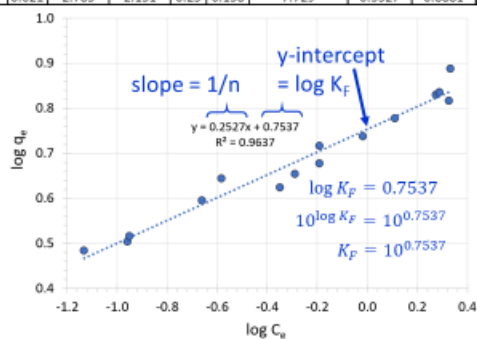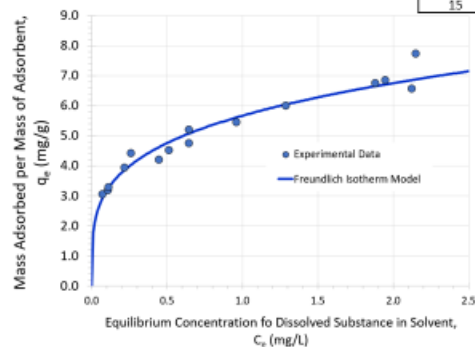
Determine Model Parameters ($K_F$ and $1/n$) for Freundlich Isotherm:
1) Calculate log $C_e$
2) Calculate log $q_e$
3) Plot log $q_e$ vs. log $C_e$
4) Fit a linear trend line to identify the slope ($1/n$) and y-intercept (log $K_F$)
5) Solve for $K_F$
Model Data using Freundlich Isotherm
1) Calculate Freundlich Isotherm modeled value ($q_e = K_F C_e^{1/n}$) for full range of equilibrium concentrations ($C_e$)

| Experiment | m (g) | $C_0$ (mg/L) | $C_e$ (mg/L) | ∀ (L) | x (mg) | $q_e$ = x/m (mg/g) | log $C_e$ | log $q_e$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.223 | 2.785 | 0.074 | 0.25 | 0.678 | 3.043 | -1.1324 | 0.4834 |
| 2 | 0.210 | 2.785 | 0.110 | 0.25 | 0.669 | 3.192 | -0.9588 | 0.5041 |
| 3 | 0.202 | 2.760 | 0.112 | 0.25 | 0.662 | 3.277 | -0.9496 | 0.5154 |
| 4 | 0.161 | 2.760 | 0.218 | 0.25 | 0.635 | 3.937 | -0.6609 | 0.5951 |
| 5 | 0.142 | 2.760 | 0.262 | 0.25 | 0.624 | 4.410 | -0.5818 | 0.6444 |
| 6 | 0.058 | 1.419 | 0.447 | 0.25 | 0.243 | 4.202 | -0.3496 | 0.6235 |
| 7 | 0.050 | 1.419 | 0.515 | 0.25 | 0.226 | 4.511 | -0.2885 | 0.6543 |
| 8 | 0.102 | 2.760 | 0.644 | 0.25 | 0.529 | 5.200 | -0.1908 | 0.7160 |
| 9 | 0.041 | 1.419 | 0.645 | 0.25 | 0.193 | 4.752 | -0.1904 | 0.6769 |
| 10 | 0.082 | 2.760 | 0.961 | 0.25 | 0.450 | 5.458 | -0.0174 | 0.7371 |
| 11 | 0.061 | 2.760 | 1.290 | 0.25 | 0.367 | 5.993 | 0.1107 | 0.7777 |
| 12 | 0.033 | 2.760 | 1.882 | 0.25 | 0.219 | 6.753 | 0.2746 | 0.8295 |
| 13 | 0.031 | 2.785 | 1.949 | 0.25 | 0.209 | 6.851 | 0.2898 | 0.8357 |
| 14 | 0.025 | 2.785 | 2.123 | 0.25 | 0.165 | 6.562 | 0.3270 | 0.8170 |
| 15 | 0.021 | 2.785 | 2.151 | 0.25 | 0.158 | 7.729 | 0.3327 | 0.8881 |



$y = 0.2527x + 0.7537$, $R^2 = 0.9637$
slope = $1/n$; y-intercept = log $K_F$
$\log K_F = 0.7537$
$10^{\log K_F} = 10^{0.7537}$
$K_F = 10^{0.7537}$

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**Appendix C: In-Class Problem**

A manufacturing process generates a waste stream of Crystal violet (CV) dye in dilute solutions which they store in 55 gallon drums. Based on local regulations, the CV waste can't be discharged to the wastewater collection system. You agree to help calculate the amount of Granular Activated Carbon (GAC) they will need to obtain a final CV concentration equal to 1.0% of the initial concentration (per drum of waste).

Given: The initial concentration of CV, $C_o$ = 500 mg/L

Assume: The Freundlich Isotherm Model is applicable

$K_F$ = 5.7 (mg CV/g GAC)[L/mg CV]$^n$

n = 2.5

Solution:

$$C_{aq} = \frac{1\%}{100\%}\left(500\ \frac{mg}{L}\right) = 5\ \frac{mg}{L}$$

Freundlich Isotherm equation is $q = K_F(C_{aq})^n$

$q$ = (5.7 (mg CV/g GAC)[L/mg CV]$^{2.5}$ ) (5 mg CV/L)$^{2.5}$

q = 318.6 mg CV/ g GAC

Determine the carbon usage rate (CUR)

$$CUR = \frac{C_o - C_{aq}}{q} = \frac{(500mg/L - 5\ mg/L)}{318.6\ mg\ CV - gGAC}$$

CUR = 1.55 g GAC / Liter of waste

c. Find the mass of carbon need to treat the entire drum.

$$Mass = (Volume\ of\ waste)*CUR = \left(55\ al\ \left|\frac{3.785L}{Gal}\right)\frac{1.55\ g\ GAC}{L} = 323\ or\ 300\ g\ AC\right.$$

➜ 300 g of GAC are required for the entire drum.