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An Experiment Illustrating Both the Langmuir and Freundlich Isotherms

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Adsorption and adsorption processes are important fields of study in physical chemistry. They form the basis for understanding phenomena such as heterogeneous catalysis, chromatographic analysis, dyeing of textiles, and clarification of various effluents. Activated carbon finds particular application in the clarification of effluents, including the removal of coloring matter from various types of solution and the elimination of organic substances from treated potable water (especially trihalomethanes) and waste water. However, finding simple and easily performable experiments to illustrate the quantitative aspects of adsorption can be very difficult. A number of such experiments were described in some previous issues of *this Journal* (*1–5*).

The present investigation describes the adsorption of methylene blue, a cationic organic dyestuff commonly used for tracer studies in water research, on activated carbon. Although it has been claimed (*2*) in a previous investigation using different adsorbents, that methylene blue adsorption obeys the Frumkin type of adsorption isotherm, it was found in the present case to obey both the Langmuir and Freundlich isotherms better for the specific type of adsorbent used.

Experimental Procedure

The adsorbent used in the experiment was a commercial activated carbon, the physical characteristics of which are given in Table 1. A methylene blue solution with a concentration of 25 mg/L was prepared from analytical-grade reagent and distilled water. The position of maximum absorbance (λ_{max}) of this solution was determined to be at 630 nm on a Spectronic 20 spectrophotometer. Concentrations of ≤25 mg/L of this methylene blue solution were found to obey the Beer–Lambert law.

Adsorption isotherms were obtained as follows: Accurately weighed samples of between 0.001 g and 0.100 g of adsorbent were placed in seven separate 250-mL conical flasks, each containing 100 mL of the 25 mg/L methylene blue solution. The flasks were then stoppered with rubber stoppers and shaken vigorously on a mechanical shaker for ~72 h to reach equilibrium. At the end of this time analysis of the supernatant solution in each flask was carried out by spectrophotometry at 630 nm. All the experimental runs were conducted at 25 °C.

Treatment of Results

The derivation of the Langmuir, Freudlich, and Frumkin adsorption isotherms is dealt with in most physical chemistry textbooks. It will therefore suffice to state only the final form of each equation in this discussion. The Langmuir adsorption isotherm may be written as

$$\frac{1}{x} = \frac{1}{x_m K} \cdot \frac{1}{c} + \frac{1}{x_m} \quad (1)$$

where x = amount of solute (MB) adsorbed per mass of adsorbent (act.C), x_m = limiting amount of adsorbate that can be taken up per mass of adsorbent, K = a constant, and c = concentration of the solute in the solution that is in equilibrium with the adsorbent. Thus the plot of $1/x$ against $1/c$ should be linear with a gradient of $1/x_m \cdot K$ and intercept of $1/x_m$ on the $1/x$ axis.

The equation describing the Freundlich isotherm can be defined as

$$\log x = \log K + {}^1\!/_n \log c \quad (2)$$

where K, n = constants and x, c have the same meaning as in the Langmuir isotherm. It is clear from eq 2 that a plot of log x against log c should yield a straight line with a slope of $^1/_n$ and an intercept of log K.

The equation describing the Frumkin isotherm can be written as

$$\nu = \log(\beta/55.55) + 2\alpha\theta/2.303 \quad (3)$$

where $\nu = \log(\theta(1-\theta)\text{-}c)$, $\theta = M/M_{ads}$, M = the amount of dye adsorbed at equilibrium, M_{ads} = the maximum amount of dye adsorbed at equilibrium (2.48 mg in this experiment), and α,β = constants, while c has the same meaning as before.

Plotting the first member against θ should yield a straight line if the Frumkin isotherm is obeyed. From the intercept with the ordinate β is obtained while α can be calculated from the slope.

The experimental data points summarized in Table 2 were fitted to all three isotherms, which are graphically represented in Figures 1–3. The dotted line in each figure represents a linear regression fit to the results. However, since adsorption data are of a nonlinear nature, nonlinear regression was also performed on each set of data points. These nonlinear regression fits are represented as solid lines in Figures 1–3. The correlation coefficients obtained with both kinds of regression for all three adsorption isotherms are summarized in Table 3. Except in the case of the Langmuir isotherm, nonlinear regression fits produced better correlation coefficients and thus more accurate constants than are obtained with the

Table 1. Physical Properties of the Adsorbent

BET surface area, m^2/g	950–1050
Pore volume, cm^3	0.8–0.9
Iodine number (mg/g)	900–1000
Apparent density, g/cm^3	0.460
Effective particle size, mm	0.8–1.1
Abrasion number	75–80

Table 2. Experimental Adsorption Data

Activated carbon mass (mg)	Initial MB mass before adsorption (mg)	Final MB mass after adsorption (mg)	Mass of MB adsorbed (mg)	[MB] after adsorption (mg/dm^3)
1	2.50	1.99	0.51	19.9
5	2.50	1.08	1.42	10.8
10	2.50	0.42	2.08	4.2
12.5	2.50	0.35	2.15	3.5
25	2.50	0.10	2.40	1.0
30	2.50	0.07	2.43	0.70
100	2.50	0.02	2.48	0.20

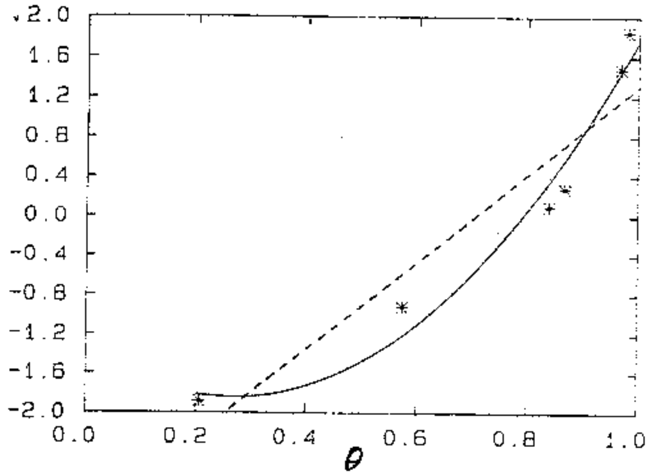

Figure 1. Application of the Frumkin equation to the experimental data points determined for the adsorption of methylene blue on an activated carbon at 25 °C.

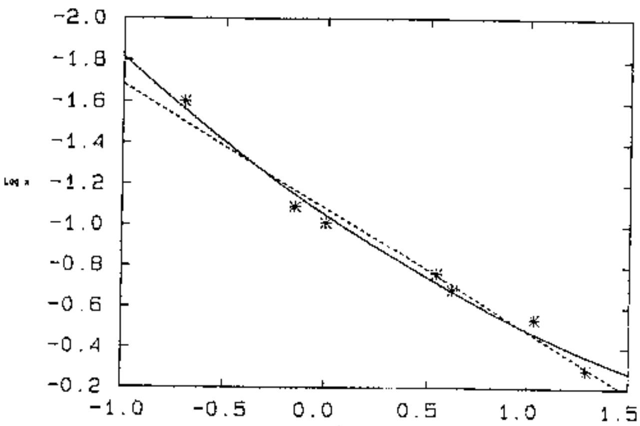

Figure 3. Application of the Freundlich equation to the experimental data points determined for the adsorption of methylene blue on an activated carbon at 25 °C.

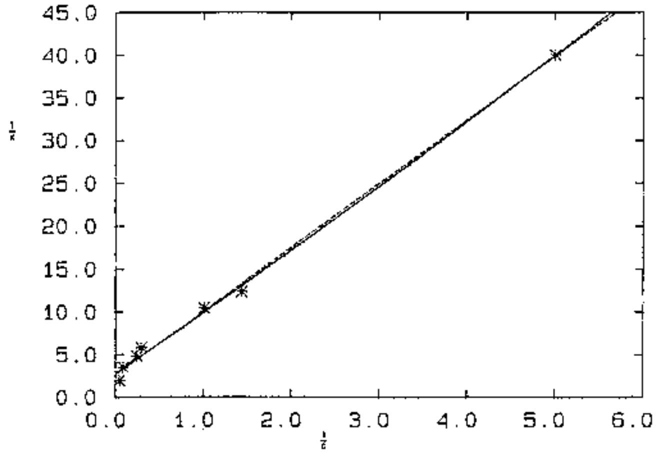

Figure 2. Application of the Langmuir equation to the experimental data points determined for the adsorption of methylene blue on an activated carbon at 25 °C.

Table 3. Correlation Coefficients for Linear and Nonlinear Regression Fits of Different Adsorption Isotherms

Type of adsorption isotherm	Correlation Linear regression	Coefficient Nonlinear regression
Frumkin	0.940	0.984
Langmuir	0.998	0.998
Freundlich	0.987	0.992

Table 4. Langmuir and Freundlich Isotherm Constants

	Langmuir		Freundlich	
Type of regression	x_m	K	K	n
Linear	0.376	0.358	0.0834	1.66
Nonlinear	0.355	0.401	0.0897	1.50

ordinary linear regression. From these values it is clear that although the adsorption of methylene blue on Pyrex beads and Ta_2O_5 can be described by the Frumkin isotherm (*2*), this is not the case for activated carbon. The correlation coefficient values in Table 3 also indicate that the data fit the Langmuir isotherm better than the Freundlich isotherm, both in the case of linear and nonlinear regression. It is furthermore evident that both the Langmuir and Freundlich isotherms describe the adsorption process very well and are better adhered to than the Frumkin isotherm. The values of the constants obtained for the Langmuir and Freundlich isotherms from both types of regression are given in Table 4.

Calculation of the Specific Surface Area of the Activated Carbon

One can also determine the approximate specific area, S, of the activated carbon, using the value of x_m obtained from the Langmuir isotherm in Figure 2:

$$S = x_m \cdot N \cdot a \quad (4)$$

where N = Avogadro's number and a = the area of the dye molecule. In this case the value of "a" for methylene blue can be taken as 120 Å^2 (*6*).

This simple experiment brings to the student's attention the basic principles of adsorption as well as the application of more than one isotherm to describe the whole process. It also enables the student to judge the suitability of different types of regression fits to experimental data, to become acquainted with the measurement of specific surface area of the adsorbent, and to estimate an approximate value for it.

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