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Laboratory Worksheet P3: **Adsorption Isotherm Test**.

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Objective : To understand the fundamentals of the commonly used adsorption models; practice to apply the models to quantify the performances of adsorption of activated carbon.

Introduction

Adsorption is an essential physical-chemical reaction to affect the transportation of pollutants in the soil-water environment. The processes of adsorption are usually described by both the adsorption rate and capacity. Adsorption isotherms (applicable to most solid-water interfaces, i.e. soil and activated carbon) are simply the relations between the moles of sorbate adsorbed per unit mass of sorbent and the concentration of sorbate remaining in solution at equilibrium at a constant condition, usually temperature. Experimental determination of an isotherm is usually accomplished by mixing a known amount of adsorbent with a given volume of liquid of known initial sorbate concentration. The system is allowed to achieve equilibrium at a selected temperature, and the final liquid-phase sorbate concentration is measured. The concentration change is then used to calculate the mass of sorbate adsorbed, x (mg) as follows:

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

where C_i, C_e = initial and equilibrium molar concentrations of sorbate respectively; and V = liquid volume.

Mass adsorbed are then divided by the mass of sorbent m (g), and the result is plotted against the equilibrium concentration C_e. Most equilibrium data follow either one of the following models:

1. The Brunauer, Emmett, Teller (BET) isotherm.
2. The Langmuir isotherm.
3. The Freundlich isotherm.

Both BET and Langmuir isotherms are based on theoretical developments, while he Freundlich isotherm is an empirical relationship. The BET isotherm is based on the concept of multi-layer adsorption while the Langmuir model assumes that only a single layer can be adsorbed.
The Freundlich isotherm is an exponential model expressed as:

$$\frac{x}{m} = K_f C_e^{\frac{1}{n}}$$

where K_f is the Freundlich adsorption coefficient. Usually the Freundlich isotherm is plotted on log-log paper to facilitate determination of the model's validity and the values of K_f and n.

Study of the adsorption rate of a sorbent aims to determine the time required for the adsorption to reach equilibrium. Many adsorption processes proceed at relatively slow rates, thus valuable information for process design can be obtained. A quantity of the sorbate is placed in contact with the sorbent of interest and mixed. With time, small portions of the sorbate solution are periodically removed and the sorbate concentrations are determined. The decay curve of the sorbate can then be constructed.

The adsorption rate is based on an analogy to Fick's first law as follows:

$$\frac{dC}{dt} = -k(C - C_e)$$

where C = Concentration of sorbate at time t; C_e = equilibrium concentration of sorbate; and k = adsorption coefficient.

The driving force for adsorption is due to a liquid sorbate concentration that is higher than the concentration that would be in equilibrium with the amount of mass adsorbed on the sorbent.

Apparatus and Materials

- Spectrophotometer
- Volumetric flasks
- Activated Carbon
- Electrical Mixer/Stirrer
- Methylene Blue Solution

- Stopwatch

Procedure

Standard Curve calibration

1. Prepare 1, 2, 5, 8, 10, 15 and 20 ppm of standard methylene blue solutions.
2. Measure the absorbance of the standards at 660 nm using a spectrophotometer.
3. Plot absorbance against standard methylene blue concentrations to obtain a calibration curve for unknown methylene blue concentration measurements.

Freundlich Isotherm and Adsorption Rate Determination

1. Determine the initial methylene blue concentration of the influent sample.
2. Prepare six beakers each with different carbon dosage of 0g, 0.5g, 1.5g, 3g, 5g, and 10g respectively.
3. Wash the carbon with distilled water to rinse away the very fine carbon particles.
4. Mix each prepared breakers with 300 mL of influent sample.
5. Start the stirrer at 80 rpm.
6. Collect 3 mL of sample from each beaker at an interval of 10 min.
7. Filter the samples if necessary and measure the concentration of sorbate in them.
8. After a sufficient contact period (usually 24 hours), filter the mixtures and determine the final concentration of sorbate in the solutions.
9. Use the data obtained to plot the Adsorption Decay Curve and the Freundlich Isotherm, thus determine the adsorption rate constant and the isotherm characteristic coefficients.

Results and Discussion

1. Determine the adsorption coefficient k and equilibrium concentration C_e based on the experimental data of each test.

2. Plot the adsorption isotherm in a linear scale based on the Freundlich model.

3. Determine a minimum daily requirement of activated carbon to treat a dyeing wastewater containing methylene blue only from 50 mg/L to 1 mg/L, if a flow rate is 100 m^3/d.

4. Discuss the meanings of concave and convex isotherms.

