Exercise 11

Determination of specific surface area of activated carbon

Topics: Physical and Chemical Adsorption. Heat of Adsorption. Freundlich, Langmuir, and BET Adsorption Isotherms. Capillary Condensation. Applications of Adsorption Phenomenon. Adsorptive Chromatography.

Adsorption is a fundamental and ubiquitous phenomenon that occurs at the interface between a solid material and a fluid (gas or liquid). It plays a crucial role in numerous natural and industrial processes, making it an essential topic of study in various scientific disciplines, including chemistry, chemical engineering, environmental science, and materials science. The process of adsorption involves the accumulation of molecules or ions from the fluid phase onto the surface of a solid, resulting in a concentration gradient at the interface.

Throughout history, adsorption has captivated the attention of scientists and researchers due to its wide-ranging applications and its importance in understanding molecular interactions. From ancient times, humans observed the adsorption of dyes onto fabrics, which laid the foundation for dyeing techniques. With advancements in scientific knowledge and analytical techniques, the exploration of adsorption expanded beyond traditional practices, revealing its significance in environmental remediation, gas separation, drug delivery, and catalyst design, among other fields.

The fascination with adsorption has led to the development of various theoretical models that attempt to describe and predict the behavior of adsorbate molecules on solid surfaces. Among these models, the Langmuir adsorption model and the Freundlich adsorption model are two of the most widely used and influential representations of adsorption processes.

To comprehend the complexities of adsorption, it is essential to delve into the underlying molecular forces and mechanisms driving this process. When a solid material is brought into contact with a fluid containing adsorbate molecules, interactions occur between the adsorbate molecules and the surface atoms or functional groups of the solid. These interactions can be broadly categorized as physical or chemical adsorption, depending on the nature of the forces involved.

Physical adsorption, also known as physisorption, involves weak van der Waals forces, dipole-dipole interactions, and hydrogen bonding between the adsorbate molecules and the surface of the solid. It is a reversible process that occurs at relatively low temperatures and high fluid pressures. Physisorption is often observed in the adsorption of gases on solid surfaces. The forces involved are generally weaker and do not lead to significant changes in the chemical structure of the adsorbate or the solid surface.

Chemical adsorption, or chemisorption, is a more substantial and irreversible process involving the formation of chemical bonds between the adsorbate and the surface. This type of adsorption requires a higher activation energy and is favored at higher temperatures and lower fluid pressures. Chemisorption plays a critical role in catalysis, where reactant molecules adsorb on the catalyst surface, leading to chemical reactions with altered pathways and enhanced reaction rates.

Adsorption is a dynamic process, meaning it continues until an equilibrium is established between the adsorbate molecules in the fluid phase and those adsorbed on the solid surface. The adsorption equilibrium is characterized by an adsorption isotherm, which relates the equilibrium concentration of the adsorbate (*c*) in the fluid phase to the degree of adsorption (θ) or the amount of adsorbate adsorbed on the surface (q).

The adsorption isotherm is often obtained through experimental measurements under specific conditions of temperature and pressure. It provides valuable insights into the nature of the adsorption process and the interactions between adsorbate molecules and the solid surface.

In 1916, the American chemist Irving Langmuir introduced a revolutionary adsorption model based on his studies of gas adsorption on solid surfaces. The Langmuir adsorption model was groundbreaking for its time and represented a significant advancement in understanding the surface chemistry of adsorbates. Langmuir's model stemmed from his belief that adsorption occurred on discrete, localized sites on the solid surface, each capable of binding a single adsorbate molecule.

The Langmuir model makes several key assumptions, which have formed the basis for further research and the development of more complex adsorption models:

- Homogeneous Surface: The model assumes that the solid surface is homogeneous, with each adsorption site being identical in nature and energetic properties. This assumption simplifies the mathematical treatment of the adsorption process.
- Monolayer Adsorption: Langmuir proposed that adsorption occurred in a monolayer fashion, meaning that only one layer of adsorbate molecules can be accommodated on the surface. This assumption is valid at low adsorbate concentrations.
- Non-Interacting Adsorbate Molecules: The Langmuir model assumes that the adsorbate molecules do not interact laterally with one another once adsorbed on the surface. Consequently, the adsorption process is seen as a series of individual adsorption events.

The Langmuir adsorption model can be mathematically represented by the Langmuir isotherm equation:

$$\theta = \frac{K c}{1 + K c}$$

where:

- θ represents the fraction of the surface covered by adsorbate molecules, often referred to as the degree of adsorption.
- *K* is the Langmuir adsorption equilibrium constant, a parameter related to the energy of adsorption at the surface.
- *c* is the equilibrium concentration of the adsorbate in the fluid phase.

The Langmuir isotherm equation suggests that the degree of adsorption (θ) increases with increasing equilibrium concentration (*c*) of the adsorbate until a saturation point is reached. At high concentrations, the surface becomes fully covered, and the degree of adsorption remains constant, approaching unity.

The derivation of the Langmuir adsorption model begins with considering that the number of molecules adsorbed within a certain time is directly proportional to the gas pressure (or adsorbate concentration) and the fraction of the surface not covered:

$$N_1 = k_1 c (1 - \theta)$$

In contrast, the number of molecules undergoing desorption in the same time is proportional to the number of adsorbed molecules and, therefore, to the degree of surface coverage:

$$N_2 = k_2 \theta$$

From the equilibrium condition:

$$N_1 = N_2$$

We obtain:

$$\theta = \frac{K c}{1 + K c}$$

where $K = \frac{k_1}{k_2}$.

The Langmuir adsorption model has proven to be a valuable tool for understanding the interactions between adsorbate molecules and solid surfaces, especially in situations where the adsorption process is limited to a monolayer and does not involve significant lateral interactions.

If n represents the number of moles of substance adsorbed on the surface of an adsorbent with unit mass, and n_j - represents the number of moles of the same substance required for complete coverage of the surface of the same amount of adsorbent with a monolayer, then the degree of coverage can be expressed as:

$$\theta = \frac{n}{n_j}$$

By substituting this equation into equation $\theta = \frac{K c}{1 + K c}$ and performing the appropriate transformation, we obtain a linear equation:

$$\frac{c}{n} = \frac{1}{n_j} c + \frac{1}{K n_j}$$

If the area S occupied by a molecule adsorbed in a monolayer, known as the 'sitting' or seating area, is known, it's possible to determine the specific surface area A of the adsorbent. This is the actual surface area participating in adsorption per unit mass of the adsorbent:

$$A = n_j N_A S$$

where N_A is Avogadro constant. The value of n_j can be calculated from equation $\frac{c}{n} = \frac{1}{n_j} c + \frac{1}{K n_j}$. Most commonly, the value of specific surface area is expressed in m^2/g.

Exercise Execution

The aim of the exercise is to determine the specific surface area of activated carbon from measurements of acetic acid adsorption on its surface. In the case of acetic acid adsorption from diluted aqueous solutions, conditions for the formation of a monolayer are appropriate, so it can be assumed that the studied adsorption follows the Langmuir theory. The surface coverage, S, of acetic acid on activated carbon is 21×10^{-20} m^2.

To prepare six solutions with the following concentrations: 0.15, 0.12, 0.09, 0.06, 0.03, and 0.015 M, dilute 0.2 M acetic acid with water (M = mol dm^{-3}). Then, using titration with a standardized sodium hydroxide solution in the presence of phenolphthalein, determine the exact concentration of the initial acetic acid.

Next, place accurately weighed (*m*) amounts of activated carbon (approximately 1 g) into six conical flasks, and to each flask, add precisely measured volumes (50 cm^3) of acetic acid solutions with different concentrations (c_0). Leave the bottles with the content for 20 minutes, shaking them frequently. Then, separate the activated carbon from the solution by filtration. Determine the equilibrium concentration of acetic acid, *c*, in the filtrate by titration with the standardized sodium hydroxide solution. Record the results in a table.

Table 1.Results of measurements

The CH_3COOH volume taken for titration [cm^3]	The NaOH volume used for titration [cm^3]	*m* [?]	c_0 [?]	*c* [?]	*n*	*c/n* [?]

Data analysis

Based on the obtained titration results, calculate the concentrations of acetic acid before and after adsorption (denoted as c_0 and *c*, respectively) in each sample. Then, using the material balance, find the number of moles of acetic acid, *n*, that have been adsorbed per unit mass of activated carbon.

Using the obtained results, apply the method of least squares to find the values of the slope (equal to the reciprocal of n_j) and the *y*-intercept of the line described by equation:

$$\frac{c}{n}=\frac{1}{n_j}c+\frac{1}{K n_j}$$

Plot the function *c/n* = *f(c)* on the graph by placing empirical points and the regression line. From equation: $A=n_j N_A S$, determine the specific surface area of activated carbon, *A*. Estimate the standard error of the determination by applying the law of propagation of standard errors.