



SOLID-LIQUID ADSORPTION. DETERMINATION OF THE ADSORPTION ISOTHERM COEFFICIENTS

INTRODUCTION

Adsorption is a surface phenomenon associated with the existence of unsaturated intermolecular forces at the interphase surface. Particles on the surface are of a different energy state (surface energy) than the molecules in the bulk material. Adsorption is a process of increasing the concentration of particles at the surface. Thus, adsorption may be positive when that concentration is higher than in the bulk, or negative in the opposite situation. The substances able to adsorb on a surface are called surface-active substances (**Surface-active agents**, Surfactants). Substances that can the accumulation of other particles at their surface are called **adsorbents**.

Adsorbents may be natural materials (such as zeolites, and pumice), or obtained by preparative (graphite carbon black, activated carbon, silica gels, activated Al_2O_3 , synthetic and semi-synthetic ion exchangers). Adsorbents may also be nonporous (such as BaSO_4 precipitate, ground glassy or crystalline solid blacks, or graphite) and porous (active carbons).

Adsorbents - if the solvent is water – the adsorbents can be divided into:

- hydrophobic* - poorly wettable by water - such as activated carbon, organic acids, alcohols (solutes adsorb well water).
- hydrophilic* - well wettable by water - such as silica gels, electrolytes, carbohydrates, protein, glycerol.

The adsorption properties are determined by:

- The gravimetric or volumetric surface area (the surface area - for non-porous adsorbents is up to $10 \text{ m}^2/\text{g}$, Al_2O_3 - $100 - 200 \text{ m}^2/\text{g}$, activated carbons: $400 - 3000 \text{ m}^2/\text{g}$),
- Spatial structure (the diameter and the degree of homogeneity of pore: pore size of $80 - 100 \text{ nm}$, then transition around 10 nm , micropores approximately 1 nm),
- Chemical properties of adsorbent.

There are two main types of adsorption: physical and chemical adsorption (chemisorption). They differ by the nature of the binding forces of adsorbate molecules (adsorbed substances) from the surface of adsorbent particles.

In the case of physical adsorption, intermolecular van der Waals forces of hydrogen bonding bridge are responsible for the increasing concentration of molecules at the interface. Such adsorption is characterized by a relatively low heat of adsorption (of about $50 \text{ kJ}\cdot\text{mol}^{-1}$), values of the heat are of the same order of magnitude as the heat of evaporation, besides is reversible, relatively fast, multilayer, and mainly depends on adsorbate nature.

Chemisorption is determined by the presence of chemical interactions (electron transition). The heat of adsorption is in the range of $100 - 400 \text{ kJ}\cdot\text{mol}^{-1}$ (the same order of magnitude as the chemical reaction heat). Chemisorption creates a single layer (unimolecular) of adsorbed particles, depending on many factors: adsorbent and adsorbate kind, the type and size molecule, the number of active sites, etc.

Process of adsorption can occur at the interface: solid-gas, solid-liquid, liquid-liquid, liquid-gas. The adsorption process, in steady-state equilibrium, can be described quantitatively by so-called isotherms of adsorption, which are the equations describing the amount of adsorbate on the adsorbent surface as a function of its pressure (if it is gas) or concentration (in case of liquids phase) at a constant temperature. The quantity of adsorbed substance is always normalized and expressed by the mass of adsorbent (m)



In the case of monolayer adsorption, the semi-empirical **Langmuir** equation is often used (1918). It assumes that the surface of the adsorbent has several identical adsorption centers, and each center can adsorb only one molecule of the adsorbate. The binding of the adsorbent can be chemical or physical, so strong that particles cannot be moved. The state of maximum adsorption corresponds to filling all the centers, i.e. formation of a monolayer surface on the adsorbate.

Denoting the number of moles of substance adsorbed by a given mass of adsorbent as n , the number of moles when all the centers are filled n_m , you can define the surface coverage Θ :

$$\Theta = \frac{n}{n_m} \quad (1)$$

In the case of the adsorption of gases, the rate of the adsorption process is proportional to gas pressure and a fraction of the uncovered area ($1 - \Theta$), while the rate of desorption is proportional to the adsorbate surface coverage (Θ). At the equilibrium state, rates of adsorption and desorption are the same we can write an equation:

$$k(1 - \Theta)p = k'\Theta \quad (2)$$

Where k and k' are the rate constant of the adsorption and desorption processes respectively

After transformations, we obtain adsorption isotherm:

$$\Theta = \frac{bp}{1 + bp} \quad (3)$$

where: $b = k/k'$, is called adsorption coefficient.

Multilayer adsorption can be described by the B.E.T equation, introduced by **Brunauer, Emmett, and Teller** (1938). In the case of gas-solid adsorption, the BET equation can be described:

$$a = \frac{a_m c \cdot \frac{p}{p_o}}{\left(1 - \frac{p}{p_o}\right) \left[1 + (c - 1) \cdot \frac{p}{p_o}\right]} \quad (4)$$

In this equation, a , and a_m are constants, p_o is the saturated vapour pressure of the adsorbate at the temperature at which adsorption takes place, and c is an exponential function of temperature, determined by the difference between the heat of adsorption in this layer - ΔH^o and heat (assumed that condensation) in the further layer - ΔH_k :

$$c = e^{(\Delta H^o - \Delta H_k)/RT}$$

The BET isotherm may take different shapes depending on many factors, including the difference $\Delta H^o - \Delta H_k$.

Adsorption on the solid-solution interface is a more complicated process than adsorption of gases. Both components of the solution: solute particles and the solvent molecules adsorb on the surface.



At constant temperature, the volume and rate of adsorption depend on:

- The quantities of the ingredients in the solution,
- The type, size, and structure of the molecules of the solvent,
- The type and condition of the surface of the adsorbent.

Large particles adsorb strongly, as well as substances that dissolve less in the solution. If the adsorbed substance contains functional groups, it may have a high affinity to a particular solid phase.

A characteristic feature of adsorption from the solution is an arrangement of component particles in the adsorption layers.

The rate of adsorption is influenced by the rate of diffusion of molecules in the solution and by the pore length of porous material. Stirring or shaking the solution with the adsorbent accelerates the process.

Adsorption from solutions describes well the aforementioned Langmuir equation, and the middle sections of the Langmuir isotherm, formerly known as an empirical equation, called the **Freundlich** equation (1906) can be applied. This equation is first used for the description of the adsorption of gases on solid, however, it can also be used for adsorption from solution. Then has the form:

$$\frac{x}{m} = kp^{\frac{1}{n}} \quad \text{or} \quad \frac{x}{m} = kc^{\frac{1}{n}} \quad (5)$$

where:

x - number of moles of the substance adsorbed,

m - mass of adsorbent,

p - pressure of the substance adsorbed in the gas phase in the equilibrium process,

c - molar concentration of the substance adsorbed in solution at equilibrium process,

k and n – coefficients of the Freundlich equation,

The factor x/m is a measure of the surface concentration of adsorbed substances, relative to the unit weight of the adsorbent. the logarithm form of the equation (5) is a linear correlation:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \quad (6)$$

Adsorption of the components of the solution on a solid adsorbent can be determined by static or dynamic methods.

The static method is based on the determination of differences in concentrations of the adsorbed substance in the solutions before and after adsorption. For this purpose, a known amount of the adsorbent is treated by the solution of a particular concentration at a constant temperature until the achieving of the equilibrium.

The composition of the solution before and after adsorption is determined by the analytical or physicochemical method. Measurements are carried out for several solutions (at different concentrations). The difference in concentration before and after adsorption lets to calculate the amount of the substance adsorbed. The dependence of the concentration of the adsorbed substance on its concentration in the solution in equilibrium constants determines the coefficients of the isotherm adsorption equation

The dynamic method is based on passing the multi-component solution through the stationary solid adsorbent phase. The components that are poorly adsorbed quickly penetrate the solid phase flowing through the



adsorbent and components of stronger effects saturate the adsorbent surface centers. Multicomponent mixtures are split along the adsorbent layer. This method is based on the adsorption chromatography process.

PURPOSE OF EXERCISE

The object of the exercise is to determine the coefficients of the equation of Freundlich adsorption isotherm for the adsorption of the selected dye on the active carbon surface.

APPARATUS

- Spectrophotometer SPECOL - the basic adapter and cuvettes (thickness 1 cm).
- Shaker.
- Centrifuge.
- Analytical balance.
- Hairdryer.

LAB GLASS

- Glass vials with polyethylene stoppers - 6 pcs
- Volumetric flask vol. 100 ml - 1 pcs
- Volumetric flask vol. 10 ml - 5 pcs
- Beaker - 2 pcs
- Pipette 10 ml - 2 pcs,
- Pipette 5 ml - 2 pcs
- Wash bottle.
- Laboratory spatula.
- Polyethene vials with stoppers - 8 pcs

CHEMICALS

- Bromocresol green solution $5 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$,
- The active carbon of surface area *c.a.* $400 \text{ m}^2/\text{g}$.

EXPERIMENT PROCEDURES

Determination of the coefficients k and n in the Freundlich adsorption isotherm equation consists of measuring the amount of adsorbed dye (x) and its concentration after adsorption (c) and expressing it per known mass of adsorbent (m).

For this purpose, six samples of active carbon of different masses should be placed in vials and filled with the solution of adsorbed substance (in this case bromocresol green dye) of the same concentration. The samples are shaken to speed up the adsorption process. Then, the concentration of the dye remaining in the solution is determined by the spectrophotometric method. The total, initial concentration of dye and the concentration in the solution after the adsorption process let to determine the number of moles of dye (x), which has been adsorbed on the active carbon surface and expressed per mass on the adsorbent (m).

Determination of the solution concentration takes place by measuring the absorbance spectrophotometer SPECOL. For this purpose, the calibration curve - the concentration dependence of the absorbance $A = f(c)$ should be determined.

1. Determination of calibration curve



- a) Preparation of a **primary solution**:
pipet 5 ml of $5 \cdot 10^{-4}$ M bromocresol green to the 100 ml volumetric flask. Fill it with distilled water and shake well.
- b) Preparation of **working solutions**:
Prepare the samples of the dye of different concentrations. Pipet 10 ml, 8 ml, 4 ml, 2 ml, and 1 ml of the basic solution to the 10 ml volumetric flasks and fill it with distilled water.
- c) Measuring the absorbance
Set the wavelength, for bromocresol green, it is $\lambda = 615$ nm. Measure the absorbance values for all working solutions.
- d) Plot the diagram absorbance dependence on concentration $A=f(c)$.

2. Determination of the amount of adsorbed dye:

Prepare 6 samples of active carbon. Place the carbon samples in 6 cleaned, dried glass vials. Masses of the samples will be pointed out by the instructor. Fill each vial with 10 ml of **primary** dye solution. Close the vials with stoppers and shake about 10 minutes in a shaker. Therefore, transfer them into plastic test tubes, put them into centrifuge holders, and centrifuge (speed and time will be given by the operator). Next, carefully take clear solution (supernatants) using a syringe transfer all solutions into the cuvette, and measure the absorbance values at the same wavelength that the calibration curve was made. Based on the calibration curve, determine the values of concentration of the dye adsorption process.

PREPARATION OF RESULTS

1. Draw a calibration curve $A = f(c_0)$.
2. From this curve, determine the concentrations of solutions after adsorption.
3. The results are summarized in the table:
 - The initial concentration of dye in the samples before adsorption (c_0),
 - The concentration of samples after adsorption (c),
 - The concentration of the substance adsorbed $x = c_0 - c$,
 - The masses of active carbon m , x/m , $\log c$, $\log x/m$.
4. Plot the function $x/m = f(c)$ and in logarithmic coordinates $\log(x/m) = f(\log c)$.
5. Determine coefficients k and n by the linear regression method. Formulate the adsorption equation.



Template of the table and draft of the study

<p>..... <i>Faculty</i></p> <p>..... <i>Field of study</i> <i>Full-time/ part-time studies</i></p>	<p>..... <i>Name and surname</i></p>	<p>..... <i>Date:</i></p>
<p><i>Group no.:</i></p> <p><i>Team no.:</i></p>	<p>..... <i>Exercise no.:</i></p>	<p>..... <i>Instructor:</i></p>

<p>..... <i>Wydział</i></p> <p>..... <i>Kierunek</i> <i>Studia stacjonarne/niestacjonarne</i></p>	<p>..... <i>Imię i Nazwisko studenta</i></p>	<p>..... <i>Data wykonywania ćwiczenia:</i></p>
<p><i>Nr grupy:</i></p> <p><i>Nr zespołu:</i></p>	<p>..... <i>Nr ćwiczenia:</i></p>	<p>..... <i>Nazwisko Prowadzącego:</i></p>

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiar:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: