1. Interphase adsorption

Adsorption is a process where particles (sorbent) presented in the gas phase or solution above the solid phase (adsorbent) accumulate on the interface as a result of an existence of surface attraction forces. The total number of sorbent active sites on the adsorbate surface is limited. The fraction of the active sites θ_i occupied by sorbent i is ranging from 0 to 1 and depends on the temperature, pressure and phase composition above the adsorbent. At a constant temperature, the adsorption is described by the so-called "adsorption isotherm". Adsorption plays an important role in numerous chemical and physical processes. Examples include chemical reactions on surfaces of catalysts or substance accumulation on the surfaces of porous materials.

1.a. Determination of parameters of adsorption isotherm in methylene blue – water - activated carbon system

A model example of the physical sorption of the dissolved substance in liquid on solid phase surface is adsorption of dyes on activated carbon by the action of Van der Waals's attractive forces. The adsorption isotherm is in this case the dependence of the amount of the adsorbed dye n_a on its equilibrium concentration c in the solution.

When adsorbing the methylene blue dye on activated carbon, the equilibrium between carbon surface and solution is established after 24 hours. We can obtain values that will allow getting the isotherm to be practically identical to the true equilibrium after 30 minutes of shaking if we choose the constant adsorbent weights.

The theoretical description of adsorption uses different adsorption models that leads to mathematically different descriptions. The most famous are:

Langmuir isotherm:

$$n_a = n_{a,\max.} \cdot \frac{\omega c}{(1 + \omega c)} \tag{1.1.}$$

where $n_{a,\max}$ is the maximum amount of the adsorbed substance ($\theta = 1$), ω is the so-called adsorption parameter equal to the reciprocal value of concentration at which the half degree of coverage ($\theta = 0.5$) is reached, ie $n_a = n_{a,\max}/2$.

Freundlich isotherm:

$$n_a = k \cdot c^{\left(1/n\right)} \tag{1.2.}$$

where k and n are empirical parameters specific for different adsorption systems.

Temkin isotherm:

$$n_a = k_1 \cdot \ln\left(k_2 c\right) \tag{1.3.}$$

where k_1 a k_2 are empirical parameters of Temkin isotherm for adsorption system.

TASK: Measure the amount of methylene blue adsorbed on activated carbon at different dye concentration in solution at constant temperature (ie the experimental adsorption isotherm). Determine the parameters of Langmuir, Freundlich and Temkin isotherms for this adsorption system. Obtain the best fit of the experimental results using theoretical isotherms in one common graph. Decide what theoretical

isotherm describes the best the sorption of methylene blue on activated carbon. Use the sum of quadrates of deviation between experimental and fitted values as criterion what isotherm fits the best the experiment.

LABORATORY AIDS AND CHEMICALS: Spectrophotometer, laboratory scales, laboratory shaker, *6 flasks (250 cm³), 6* funnels and funnel stand, *6* Erlenmayer flasks, 1 graduated flask *(50 cm³)*, 1 graduated flask *(25 cm³)*, scale pipettes (*1, 5, 10* a *25 cm³*), weighing boat, spoon, filter paper, activated carbon, stock solution *2 mg/cm³* methylene blue (CAS 122965-43-9).

INSTRUCTIONS: Pour up 6 flasks (250ml), each to final volume 50ml by *7.5; 8; 9; 10.5; 12; 14 cm³* of stock solution of methylene blue and pure water. Add the weight 90 mg of the activated carbon into each flask (discuss the weight with the superior). Close flasks with stoppers and shake for *30 min* on the laboratory shaker to obtain the adsorption equilibrium.

Use a dry filter for adsorbent separation. Remove the first portion of the filtrate (about *20 cm³*) until the filter paper is saturated with dye then collect only the remaining part of the dye filtrate. Use the final part of the dye filtrate to spectrophotometrically determination the dye concentration.

At the end of the work, clean the cuvettes and laboratory aids with ethanol.

Determination of calibration curve. Take the save dye solution and prepare *50 cm³* by diluting with water using ratio 1:40. Pour 7 flasks (25 ml) using *7.5; 8; 9; 10.5; 12; 14 cm³* of dilute stock solution of methylene blue and by water up to the mark. Set a spectrophotometer to measure absorbance at a wavelength of 660nm. If the absorbance measurement is outside the calibration curve, dilute the dye solution appropriately and record the dilution factor which will be used to calculate the equilibrium dye concentration.

5.a-b

DATA ANALYSIS: Each theoretical isotherm (1.1.), (1.2.) and (1.3.) has the form $y = f(x)$ where independent variable x is the equilibrium concentration c and the dependent variable y is the weight of the dye sorbent per unit weight of the adsorbent. There are two experimental adsorption parameters in each of the relations. Adsorption parameters can be determined for individual isotherm using one of the following procedures.

Procedure A (Use of the none-linear regression): Make the best fit of the experimentally measured adsorption isotherm by an assumed non-linear theoretical adsorption function. Use the appropriate numerical method which can be found in the "Solver" function in MS-EXCEL software.

Procedure B (Use of the linear regression): Transform the dependencies (1.1.), (1.2.) and (1.3.) into linearized formulas. The results are:

$$\frac{1}{n_a} = \frac{1}{n_{a,\max}} + \frac{1}{\omega n_{a,\max}} \cdot \frac{1}{c} \tag{1.4.}$$

$$\ln n_a = \ln k + \frac{1}{n} \cdot \ln c \tag{1.5.}$$

$$n_a = k_1 ln k_2 + k_1 \ln c \tag{1.6.}$$

where you can find the new couples of coordinates: $\frac{1}{n_a}$ and $\frac{1}{c}$, $\ln n_a$ and $\ln c$, n_a and $\ln c$.

Plot the graphs using new coordinates. For each dependence, make linear regression

and find the intercept and slope. Calculate the isotherm parameters from intercept and slope for each linear dependence.

   ✍   **REPORT: Calibration table 1:** concentration of dye standard [mg/cm^3] and its absorbance. **Calibration graph 1:** Dependence of dye standard absorbance on its concentration. **Table 2:** for each adsorption experiment: no of dye solution, weight of activated carbon in *[mg]*, the amount of dye *[mg]* in the solution before and after adsorption, solution dye loss in *[mg]*, equilibrium concentration *c [mg/cm³]* evaluated from Calibration graph 1, amount of dye adsorbed per 1 gram of activated carbon *[mg dye / g act. carbon]*; values: $\frac{1}{n_a}$, $\frac{1}{c}$, $\ln n_a$, $\ln c$, and n_a . **Graph 2-4:** linear dependences (1.4.), (1.5.), and (1.6.). **Table 3:** adsorption parameters of Langmuir, Freundlich and Temkin isotherms. **Table 4:** 10 equilibrium dye concentrations used as input for calculation n_a for all isotherms (apply parameters given in Table 3). **Common graph 5:** Experimental dependence (plotted by symbols) of adsorbed amount *[mg dye / g act. carbon]* on the equilibrium concentration *c [mg/cm³]* together with the theoretical adsorption isotherms obtained by best fit (plotted by lines).