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

A model example of the physical adsorption of a substance dissolved in liquid on a solid phase surface is the adsorption of dyes on activated charcoal due to Van der Waals's attractive forces. In this case, the adsorption isotherm is the dependence of the amount of the adsorbed dye n_a on its equilibrium concentration *c* in the solution.

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

The theoretical description of adsorption uses different adsorption models that lead to mathematically different descriptions. The most well-known are:

Langmuir isotherm:

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

where $n_{\mathrm{a,max}}$ 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, i.e., $n_{\mathrm{a}} = \frac{1}{2} n_{\mathrm{a,max}}$.

Freundlich isotherm:

$$n_a = k\, c^{\left(\frac{1}{n}\right)} \qquad (2.)$$

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

Temkin isotherm:

$$n_a = k_1\, ln(k_2\, c) \qquad (3.)$$

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

TASK: Measure the amount of methylene blue adsorbed on activated charcoal at different dye concentrations in solution at constant temperature (i.e., the experimental adsorption isotherm). Determine the parameters of the 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 best describes the adsorption of methylene blue on activated charcoal. Use the sum of quadrates of deviation between experimental and fitted values as the criterion to determine which isotherm best fits the experiment.

LABORATORY AIDS AND CHEMICALS: Spectrophotometer, laboratory scales, laboratory shaker, *6* flat bottom flasks *(250 cm³)*, *6* funnels and funnel stand, *6* Erlenmeyer flasks, *1* volumetric flask *(50 cm³)*, *7* graduated flasks *(25 cm³)*, scale pipettes (*1*, *5*, *10* and *25* cm³), weighing boat, spoon, filter paper, activated charcoal, stock solution *2 mg/cm³* methylene blue (CAS 122965-43-9).

INSTRUCTIONS: Fill 6 flat bottom flasks (*250 cm³*) with *7.5; 8; 9; 10.5; 12; 14 cm³* of methylene blue stock solution. Fill each flask with water to the final volume of *50 cm³*. Add *90 mg* of the activated charcoal into each flask (discuss the weight with the laboratory assistant). Close flasks with stoppers and shake for *30 min* on the laboratory shaker to obtain the adsorption equilibrium.

For each equilibrium system. Put a dry filter in the funnel. Start filtration. Discard the first portion of the filtrate (about *20 cm³*) to be sure that the filter paper is saturated with dye. Subsequently collect the remaining part of the dye filtrate. Use the final part of the dye filtrate to determine the dye concentration by spectrophotometer.

Determination of the calibration curve. Take volumetric flask (*50 cm*^{3}), fill with *1.25 cm*^{3} of the stock dye solution, and dilute with water up to the mark.

Take 7 volumetric flasks (*25 cm*^{3}) and add *0.5; 1; 1.5; 2; 3; 4, and 5 cm*^{3} of dilute dye solution of methylene blue. Fill flasks with water up to the mark.

Set up the spectrophotometer in absorbance mode 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.

When finished, clean the cuvettes and laboratory aids with ethanol.

DATA ANALYSIS: Each theoretical isotherm (70.), (71.) and (72.) has the form $\mathrm{y} = \mathrm{f}(\mathrm{x})$ where the 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 an individual isotherm using one of the following procedures.

Procedure A (Use of the non-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 the MS-EXCEL software.

Procedure B (Use of the linear regression): Transform the dependencies (70.), (71.) and (72.) into linearized forms, as follows:

$$\frac{1}{n_a} = \frac{1}{n_{a,max}} + \frac{1}{\omega\, n_{a,max}}\ \frac{1}{c} \tag{4.}$$

$$\ln n_a = \ln k + \frac{1}{n} \ln c \tag{5.}$$

$$n_a = k_1 ln(k_2) + k_1 \ln c \tag{6.}$$

where you can find the new variable pairs: $\frac{1}{n_a}$ and $\frac{1}{c}$, $\ln n_a$ and $\ln c$, n_a and $\ln c$. Plot the graphs using the new variables. For each isotherm dependence, make a linear regression and find the intercept and slope. Calculate the isotherm parameters from the 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: the number of the dye solution, weight of activated charcoal in** *[mg]*, the amount of dye *[mg]* in the solution before and after adsorption, solution dye loss in *[mg]*, equilibrium concentration c *[mg/cm*^{3}*]* evaluated from Calibration graph 1, amount of dye adsorbed per 1 gram of activated charcoal *[mg dye / g act. charcoal]*; values: $\frac{1}{n_a}$, $\frac{1}{c}$, $\ln n_a$, $\ln c$, and n_a . **Graphs 2-4:** linear dependences (73.), (74.), and (75.). **Table 3:** adsorption parameters of Langmuir, Freundlich and Temkin isotherms. **Table 4:** about 10 chosen dye concentrations and their calculated values n_a for all isotherms (apply parameters given in Table 3). **Common graph 5:** Experimental dependence (plotted using symbols) of adsorbed amount *[mg dye / g act. charcoal]* on the equilibrium concentration c *[mg/cm*^{3}*]*

together with the theoretical adsorption isotherms (Table 4) obtained by best fit (plotted using lines).