Exercise 4.1 – Adsorption kinetics

20 ml of an antibiotic solution with initial concentration C_0 = 30.0 mg/ml were contacted with 2.5 g of an adsorption resin. The evolution of the solute concentration in the liquid phase was measured as a function of contacting time. The results are given in the table below.
Assuming the kinetics is of the second order, determine the adsorption rate constant k_2 and the equilibrium concentration q_{equ}. Please don't forget to specify the units for these parameters.

t [min]	0	2	5	10	18	30
C [mg/ml]	30	24.4	20.4	17.4	15.4	14.1
q [mg/g]	0	44.8	76.8	100.8	116.8	127.2
t/q [min*g/mg]		0.0446	0.0651	0.0992	0.1541	0.2358

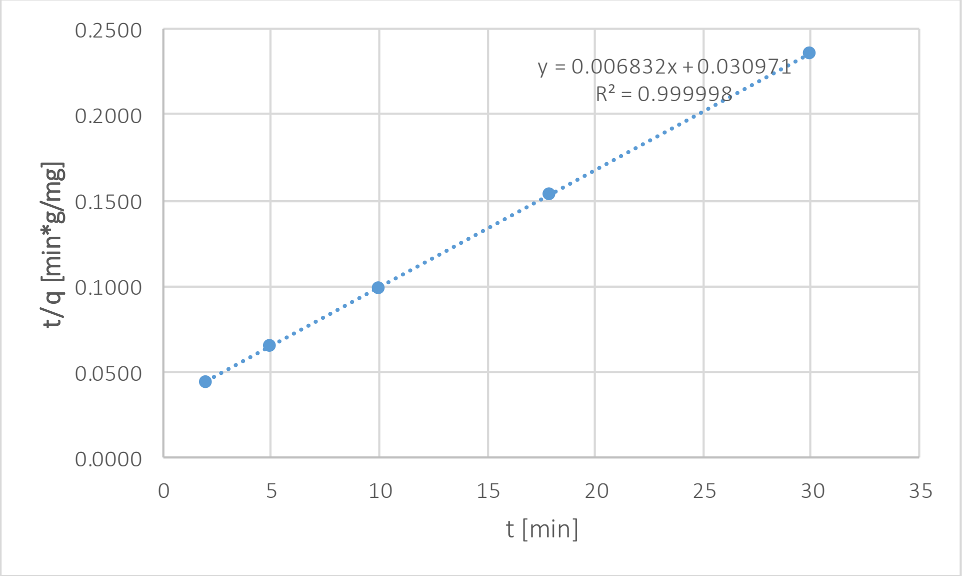
Complete the table by calculating the adsorbed concentrations q [mg/g] corresponding to the measured data points using the mass balance information:

$$q_t = \frac{V_{liq} * (C_0 - C_t)}{m_{resin}}$$

The results are given in the table above.
The linearized form of the 2nd order kinetics consists in plotting t/q as a function of t. The result is:

$$\frac{t}{q} = \frac{1}{k_2 * q_{equ}^2} + \frac{1}{q_{equ}} * t$$

The result of the regression is:



From the slope and intercept of the straight line, one gets:
q_{equ}=1/0.006832=146.37 [mg/g]
k_2 = $1.507 \cdot 10^{-3}$ [g/(mg min)]

Exercise 4.2 – Adsorption isotherm

To characterize the adsorption isotherm of an antibiotic on a resin, 20 mL of antibiotic solutions with variable initial concentrations C_0 were contacted with 2.5 g adsorbent.

The residual concentration C_{equ} was measured in the liquid phase once equilibrium was reached. The results are given in the table below. **Also, use the result of Exercise 4.1 to complete the table.** Calculate the adsorbed concentrations at equilibrium q_{equ} and treat the data according to the Langmuir model to determine the parameters of the isotherm curve.

Hint: to linearize the Langmuir model, try plotting C_{equ}/q_{equ} as a function of C_{equ}. What do you obtain? How do you extract the parameters from the obtained slope and intercept?

C_0 [mg/ml]	0	10	20	30	40	50
C_{equ} [mg/ml]	0	2.3	6	11.7	19	27.3
q_{equ} [mg/g]	0	61.6	112	146.4	168	181.6
C_{equ}/q_{equ} [g/ml]	/	0.037337662	0.05357143	0.07991803	0.11309524	0.1503304

The values for q_{equ} are calculated using the same mass balance equation as for Exercise 4.1:

$$q_{equ} = \frac{V_{liq} * (C_0 - C_t)}{m_{resin}}$$

The results are given in the table above.

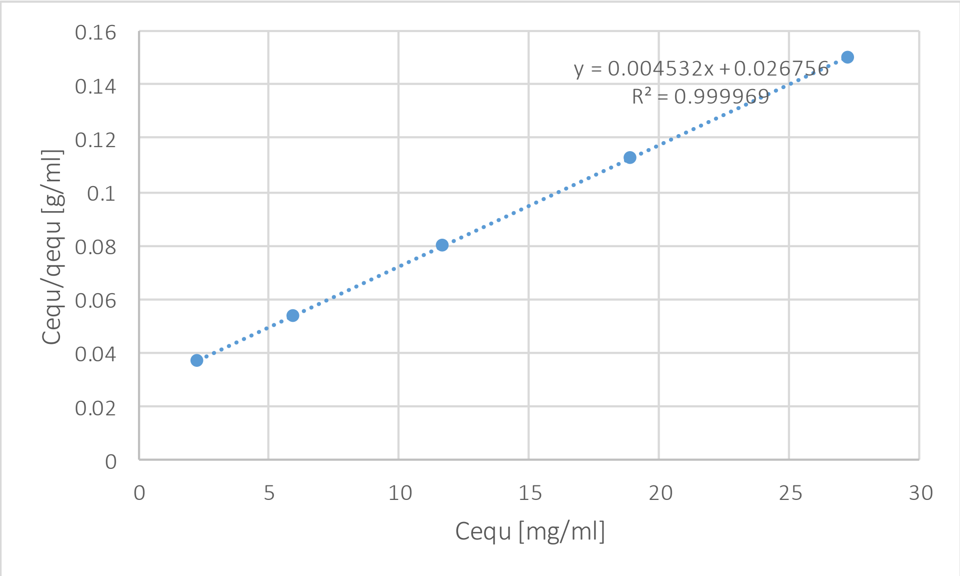
The Langmuir model has the following form:

$$q_{equ} = V_{liq} * \frac{C_{equ}}{(K_L - C_{equ})}$$

From this equation one gets a straight line if plotting C_{equ} / q_{equ} as a function of C_{equ}. The equation of the straight line is:

$$\frac{C_{equ}}{q_{equ}} = \frac{K_L}{q_{max}} + \frac{1}{q_{max}} * C_{equ}$$

The resulting plot effectively yields a straight line which equation is:



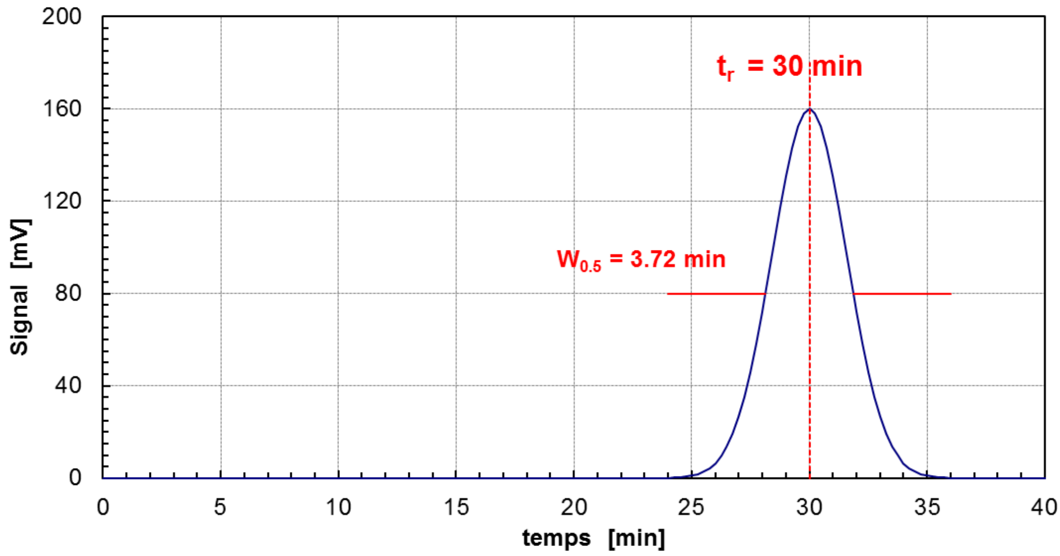
From the slope and intercept of the straight line, one gets:

q_{max} = (slope)$^{-1}$ = 220.6 [mg/g]

k_L = (intercept/slope) = 5.89 [mg/ml],

Exercice 4.3 - NPT and HEPT for a preparative column

A pulse injection was performed at time t=0 to determine the packing efficiency of a preparative chromatography column (diameter 5 cm, bed length 36 cm). The resulting peak is shown in the figure below.



Determine the number of theoretical plates NTP and the height equivalent to a theoretical plate HETP.

This exercise is a simple application of the formulas that has been given in the course. They are an expression of the mathematic properties of Gaussian peaks.

Since injection was done at t=0, the retention time of the peak is clearly 30 min.

To determine the number of theoretical plates one can use either the peak width at half height $W_{0.5}$, or the peak width at its base, W_{base}.

$W_{0.5}$ as measured from the graph is ca. 3.7 min

Hence NEPT = $5.54 \cdot (t_r/W_{0.5})^2$ = 364 plates

The peak width at its base W_{base} is around 6.4 min.

Hence NEPT = $16 \cdot (t_r/W_{base})2$ = 352 plates

Both calculated values of NEPT are not identical. This is largely due to the fact that they are based on geometric constructions and measurements on a small graph. Using your ruler and pencil you have probably found (slightly) different values as well and this is absolutely normal.

Based on these results, the height equivalent to a theoretical plate HETP is equal to the column length L divided by the number of plates N.

The result is 989 µm for the calculation with $W_{0.5}$ and 1023 µm (or 1.023 mm) for the calculation with W_{base}