Institute of Science and Technology

Department of Process Engineering / First Year of Master's in Chemical Engineering/ Second Semester

Practical Work N: 03

Study of the Adsorption Kinetics of Methyl Orange and Methylene Blue in a Binary Solution

Objective

- Evaluate the adsorption kinetics of methylene blue and methyl orange from a binary solution.

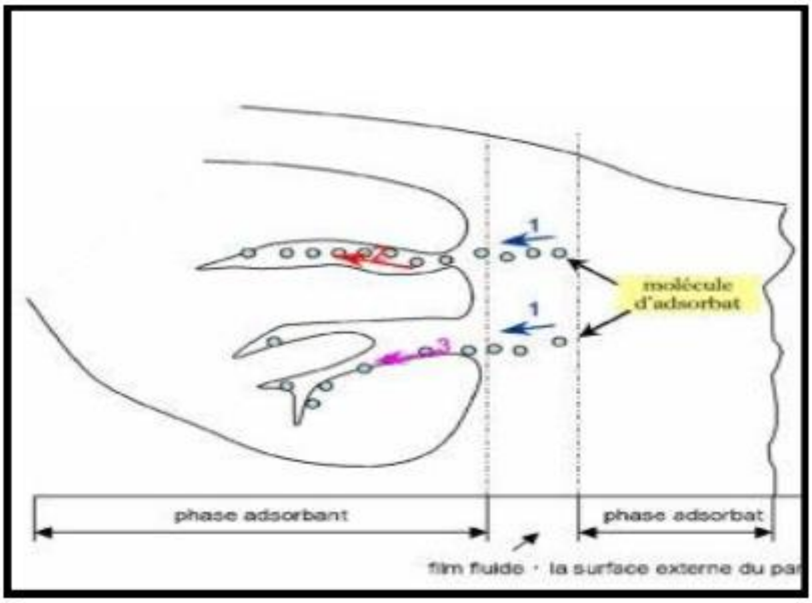
- Understanding the competitiveness of dyes in solution.

1/ Introduction to Adsorption

Adsorption is a surface phenomenon by which molecules of a fluid (gas or liquid) accumulate on the surface of a solid or a liquid (the adsorbent), forming a molecular layer.

This process is crucial in many environmental and industrial applications, notably for wastewater treatment, air purification, and chemical compound separation.

The adsorption is divided into two main categories: **physisorption**, which involves van der Waals forces and is reversible, and **chemisorption**, which forms chemical bonds between the adsorbate and the adsorbent, and is generally irreversible.



2/Adsorbents

Activated carbon (AC), with its high specific surface area and high porosity, is the most commonly used adsorbent.

Other materials, such as clays, zeolites, and synthetic polymers, are also used depending on specific applications. The selection of the adsorbent is crucial and depends on its ability to specifically adsorb the solutes of interest.

3/Adsorption Kinetics

Understanding adsorption kinetics, through models such as the pseudo-first-order and pseudo-second-order, is essential for optimizing treatment processes. These models allow the description of adsorption rates and the identification of the mechanisms controlling the process.

Pseudo-First-Order Model (Lagergren Model)

This model is often used to describe the adsorption of solutes at low concentrations on adsorption sites. It is based on the assumption that the adsorption rate is proportional to the number of available adsorption sites.

The equation of the pseudo-first-order model is:

$$\log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t$$

Where q_e is the amount of solute adsorbed at equilibrium (mg/g), q_t is the amount of solute adsorbed at time *t* (mg/g), k_1 is the pseudo-first-order adsorption rate constant (min^{-1}), and t is the time (min).

Pseudo-Second-Order Model

This model assumes that the adsorption rate is proportional to the square of the number of available adsorption sites, which implies that the rate-limiting step may be chemical adsorption involving sharing or exchange of electrons between the adsorbate and the adsorbent. The equation of the pseudo-second-order model is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Where q_e and qt have the same meanings as in the pseudo-first-order model, k_2 is the pseudo-second-order adsorption rate constant (g/(mg·min)), and t is also the time (min).

The absorbance spectrum graph of methylene Methyl Orange illustrates the differences in the compound's maximum absorption wavelengths, thereby facilitating the selection of the appropriate wavelength for specific absorbance measurements.

4/ Adsorption in a Binary Solution

Adsorption in a binary solution introduces additional complexity due to competition between different adsorbates for the limited adsorption sites on the adsorbent. This competition can significantly affect the adsorption efficiency of each compound.

The graph below compares the absorbance spectra of methyl orange and methylene blue. This representation clearly illustrates the difference between the maximum absorption wavelengths of the two compounds, thereby facilitating the selection of the appropriate wavelength for absorbance measurements specific to each compound.

Absorption spectrum of methyl orange and methylene blue.

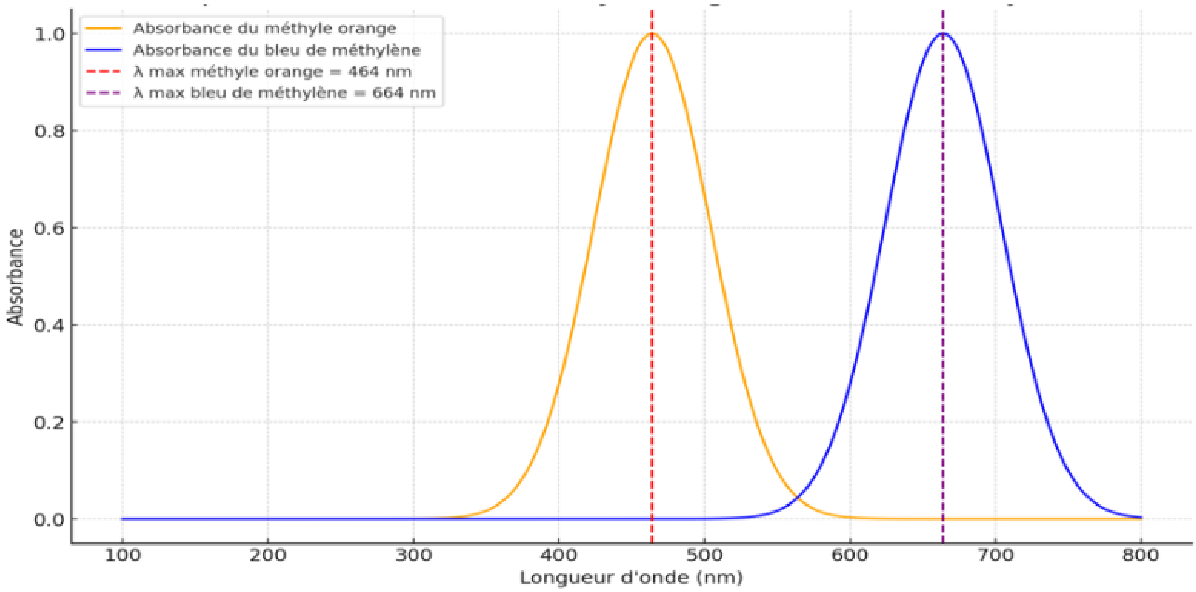


Figure I: Absorbance spectrum of methyl orange and methylene blue.

The calibration curves of the two dyes established during the previous practical sessions are shown in the following figure:

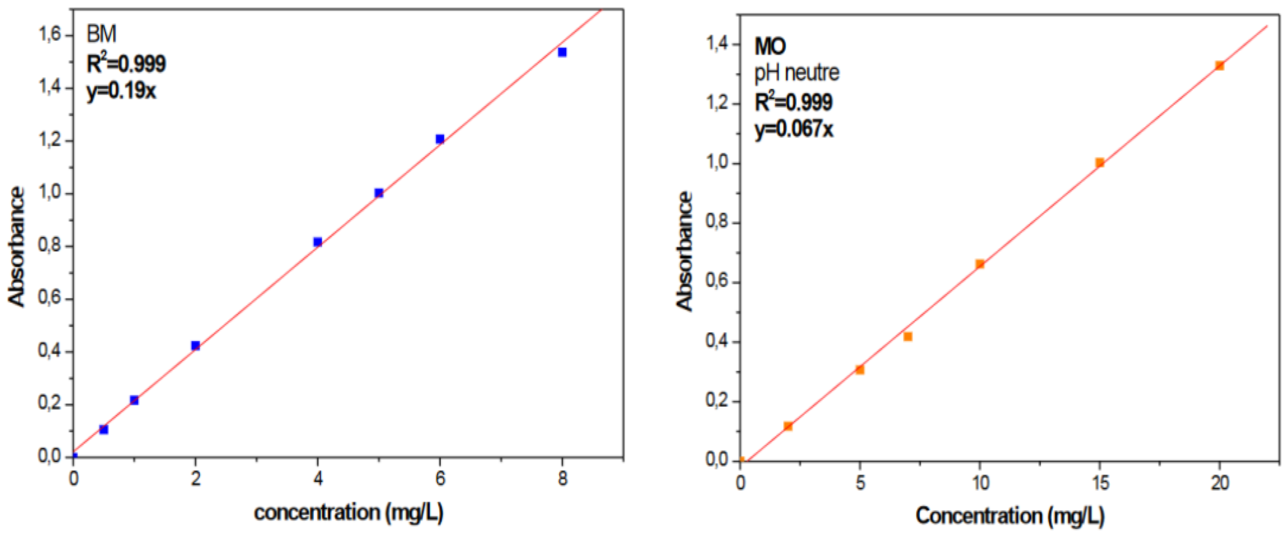


Figure II: Calibration curves of methyl orange and methylene blue

5/ Experimental

a/ Preparation of the Binary Solution

Prepare 500 mL of a binary solution by dissolving 20 mg of methylene blue and 20 mg of methyl orange in distilled water to obtain a total dye concentration of 40 mg/L, with each dye at a concentration of 20 mg/L.

b/ Adsorption

- Add 0.5 g of activated charcoal to the 500 mL of the prepared binary solution.
- Stir the mixture at room temperature at a constant speed to ensure uniform dispersion of the activated charcoal.

c/ Sampling

- At predetermined time intervals (e.g., 5, 10, 20, 30, 60 minutes, etc.), take a sample of the solution.
- Immediately filter to separate the activated charcoal from the solution.

d/ Spectrophotometric Measurements

- Measure the absorbance of the filtered samples at the maximum absorption wavelength for each dye (see Figure I).
- Use the previously established calibration curves (Figure II) to calculate the concentrations CtC_tCt.
- Calculate the amount of each dye adsorbed per unit mass of activated charcoal at each time interval according to the following law:

$$q_t = \frac{(C_0 - C_t)v}{m}$$

where: qt is the amount of dye adsorbed per unit mass of activated carbon at time t (mg/g), C0 is the initial dye concentration in the solution (mg/L), Ct is the dye concentration in the solution at time t (mg/L), V is the volume of the solution (L), m is the mass of activated carbon used (g).

- fill in the following tables:

Table 1: MO

Time(min)	**0**	**5**	**10**	**20**	**30**	**40**	**60**	**70**	**90**
absorbance									
Ct (mg/L)									
qt(mg/g)									

Table 2: MB

Time(min)	**0**	**5**	**10**	**20**	**30**	**40**	**60**	**70**	**90**
absorbance									
Ct (mg/L)									
qt(mg/g)									

Table 3: MO+MB

Time(min)	**0**	**5**	**10**	**20**	**30**	**40**	**60**	**70**	**90**
absorbance									
Ct (mg/L)									
qt(mg/g)									

e/ Data Analysis

- **Kinetic Curve Plotting:** Plot the adsorbed amount of the dyes (qt) as a function of time for each dye.
- **Kinetic Modeling:** Apply the pseudo-first-order and pseudo-second-order kinetic models to the data for each dye to determine the kinetic constants and identify the model that best describes the adsorption process.
  - For the **pseudo-first-order model**, plot log(qe−qt) versus t and determine k1 from the slope of the resulting line.
  - For the **pseudo-second-order model**, plot t/qt versus t and determine k2 and qe from the slope and the intercept of the fitted line.

- Compare the calculated qe values from the models with the experimental data to determine which of the two models best describes the adsorption process.

f/ Discussion

- Compare the adsorption kinetics of BM and MO to evaluate the selectivity of the activated carbon.
- Analyze the impact of the simultaneous presence of the two dyes on the adsorption efficiency of each.

g/ Conclusion

- Conclude on the effectiveness of activated carbon in adsorbing the dyes in a binary solution and on the competition between the dyes for adsorption.
- Propose recommendations to optimize dye removal in binary solutions based on the obtained results.

6. Lab report

After each lab session, the student must write a report including:

1. Cover page.
2. Bibliographic section.
3. Objectives and aims of the lab.
4. Materials and methods.
5. Answers to the questions.
6. Conclusion.