TECHNICAL TRANSACTIONS 3/2018
CZASOPISMO TECHNICZNE 3/2018
CHEMISTRY
DOI: 10.4467/2353737XCT.18.038.8300
SUBMISSION OF THE FINAL VERSION: 27/2/2018

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The effect of external mass transfer resistance on the adsorption rate in a liquid phase

Wpływ zewnętrznych oporów przenoszenia masy na szybkość adsorpcji w fazie ciekłej

Abstract

The paper presents the results of studies on the adsorption of a dye from a water solution on activated carbon. An activated carbon with the best adsorption properties for the dye used in the studies was selected experimentally. The equilibrium and kinetic measurements for the selected system were conducted. Constants of linear, Langmuir and Freundlich isotherms were determined. The obtained results have shown that increasing the flow rate of the solution in an adsorber results in increasing the adsorption rate.

Keywords: adsorption, activated carbon, dye removal

Streszczenie

W pracy zaprezentowano wyniki badań adsorpcji barwnika z roztworu wodnego na węglu aktywnym. Dokonano eksperymentalnego doboru węgla aktywnego o najlepszych właściwościach adsorpcyjnych dla stosowanego w badaniach barwnika. Wykonano badania równowagi i kinetyki adsorpcji dla badanego układu. Wyznaczono stałe w równaniu izotermy liniowej, Langmuira i Freundlicha. Otrzymane wyniki wskazują, że zwiększenie natężenia przepływu roztworu w adsorberze skutkuje zwiększeniem szybkości adsorpcji.

Słowa kluczowe: adsorpcja, węgiel aktywny, usuwanie barwnika

1. Nomenclature

A – absorbance
b – constant
C – concentration of the dye in the liquid phase
C_0 – initial concentration of the dye in the solution
C_e – equilibrium concentration of the dye in the solution
D_e – effective diffusion coefficient
k_F – constant
k_l – mass transfer coefficient on the fluid side
K – equilibrium constant
L – characteristic linear dimension
m_c – mass of activated carbon
n – rotational speed of the peristaltic pump
q – concentration of the adsorbed component in adsorbent grains
q_e – equilibrium content of the dye in adsorbent grains
q_∞ – constant
Q_v – flow rate of the liquid
t – time
V_s – volume of the dye solution
v – constant

2. Introduction

Adsorption is one of the basic surface phenomena; it is the occurrence of changes in the concentration of substances on the surface of adjacent phases. Due to the nature of the acting forces, there are two main types of it: chemical and physical adsorption. In the case of chemical adsorption, there are forces, which determine the formation of a chemical bond on the surface of a solid [1]. The chemical bond formed because of a chemical reaction involved in chemisorption makes this type of adsorption stronger than in the case of physical adsorption [2]. The heat of this process is of the same order as the heat of a chemical reaction [1]. Physical adsorption is caused by the forces of intermolecular interactions. Between the molecules of the substance, there are Van der Waals forces, which equilibrate inside of the phase. Moreover, particles located on the surface of contacting phases are subjected to unbalanced adhesion forces directed perpendicularly to the boundary surface [1].

Adsorption is a process used in various fields of chemical applications, technology and industry. It is applied for the purification of air and water, in recovering industrial solvents and in drying processes. It is also possible to measure the size of particles and pores in powdered substances using the adsorption process [3]. Adsorption on activated carbon [4–7] is primarily used to dispose of organic compounds, both natural and man-made, from water. Activated carbon as an adsorbent is also productive in terms of removal of certain types of

viruses, some inorganic impurities, and the binding of chlorine and chloramines. Adsorption allows one to remove impurities causing color, odor and taste from water.

When molecules of a gas or liquid hit the surface of a solid, some of them stick to it and are adsorbed, while other bounce off. At first, the velocity of adsorption is high, because the whole surface of the adsorbent is free from any molecules. The velocity becomes lower with time due to the increasing coverage of the surface of solid with the molecules of adsorbate. In the meantime, the velocity of desorption (a process, where previously adsorbed molecules are peeled from the adsorbent) becomes faster. In some cases, the velocity of adsorption will become so low, and the velocity of desorption so fast, that an equilibrium will be reached, and both velocities will be equal. Generally speaking, it is a dynamic equilibrium, because the number of adsorbed and desorbed molecules is the same [2]. The adsorption equilibrium state for the adsorbate-adsorbent system is dependent on the pressure of the gas and the temperature of the whole process. It can be presented as an adsorption isotherm at a constant temperature, an adsorption isobar at a constant pressure or an adsorption isostere. The widely used method, which represents the equilibrium state of the adsorption system, is the adsorption isotherm because of its simplicity and versatility.

The mass transfer process under consideration may be divided into five stages, which are theoretically important from the kinetics point of view [8]:

1. Transport of the molecules of the adsorbate in the solution to the boundary layer solution-adsorbent.
2. Diffusion in the boundary layer near the surface of the adsorbent.
3. Diffusion in the pores of the adsorbent to its active sites.
4. Surface diffusion.
5. Proper adsorption, during which the adsorbate molecules are placed at active adsorbent sites.

The rate of each stage is dependent on the velocity of the individual components. In this case, the slowest step limiting the rate of adsorption is the process of multistage diffusion, which is the transport of adsorbate molecules to adsorbent active sites.

In this paper, particular attention was paid to the process of adsorption of the dye on activated carbon [9]. The purpose of this work was to determine the equilibrium and kinetics of the adsorption of the dye Direct Fast Navy Blue BR 200% from an aqueous solution on the active carbon ORGANOSORB 10. The study of adsorption equilibrium was aimed at determining the equilibrium curve, i.e. adsorption isotherm. The dependence of the dye content in the solid phase on its concentration in the liquid phase was obtained by measurements. Constants of the linear, Freundlich and Langmuir models were found. In the case of adsorption kinetics, the measurements focused on the temporal changes of dye concentration in the aqueous solution for different flow rates of the solution in the adsorber filled with activated carbon grains. The purpose of these studies was to determine the effect of the flow rate on the changes of dye concentration in the liquid and solid phase over time.

3. Materials and Methods

3.1. Adsorbate – Direct Fast Navy Blue BR 200%

The adsorbate used for the study was the Direct Fast Navy Blue BR 200% (Granat bezpośredni BR 200%) produced by the Boruta company. It is applied primarily in the textile industry for dyeing mainly cellulose fibers, such as cotton, wool, viscose or sisal and silk [10]. Its properties are given in Table 2.1 [10] and structure is shown in Fig. 1 [11].

Table 1. General characteristic of Direct Fast Navy Blue BR 200%

General look	Dark gray powder
pH	9.5–10.5
Solubility at 20°C	30 g/dm^3
Solubility at 60°C	40 g/dm^3
Bulk density	650 kg/m^3

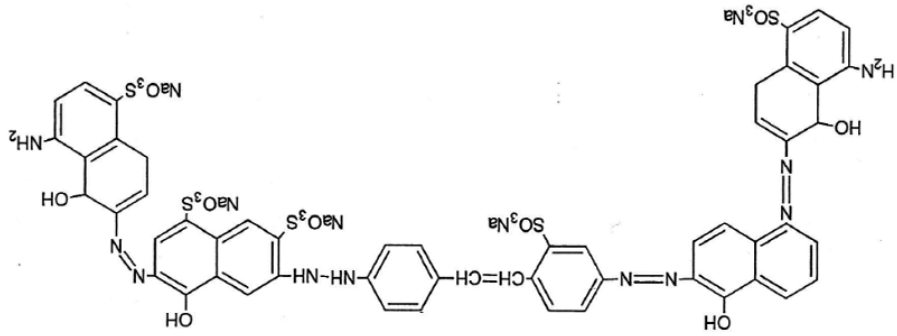

Fig. 1. Chemical structure of Direct Navy Blue BR 200%

3.2. Adsorbent – choosing the best

Four solutions of Direct Fast Navy Blue BR 200% with distilled water with a concentration of 5 mg/dm^3 were made in flat-bottom flasks. The volume of the solutions was equal to 100 cm^3. Different types of active carbon were added to each flask in the amount of 0.5 g:

- BA 10 – produced from hard coal using the vapor-gas method. The diameter of the granulate is about 3 mm. It is characterized by a large surface area, very good mechanical strength and high sorption capacity [12].
- BA 20 – formed activated carbon made from hard coal by the vapor-gas method. The diameter of the granules is 3-4 mm. It has a basic character. It is characterized by high adsorption capacity and very good mechanical strength. It is widely used in water and wastewater treatment [13].
- ORGANOSORB 10-CO – made from coconut shells. Its grain size is 2.36–0.6 mm. It is used to remove impurities of organic origin and in liquid filtration [14].

- ORGANOSORB 10 – made from coconut shells [15] and specially prepared for the purification of water (drinking, process) and sewage. High adsorption capacity eliminates organic pollutants to trace amounts [16].

After a few days, the concentration in each solution was measured. It was observed that the concentration of the solution with ORGANOSORB 10 was the lowest. This meant that this type of active carbon adsorbent had the best adsorption properties for the considered dye and that is why it was chosen for further experiments. Its physical and chemical properties are given in table 2.2 [14].

Table 2. Physical and chemical properties of ORGANOSORB – 10

Basic material	**Bituminous coal – granulated**
Specific surface area	Min. 950 m^2/g
Iodine number	Min. 950 mg/g
Moisture	Max. 5 %
Grain	0.6–2.36/0.425–1.70 mm

3.3. Adsorption Equilibrium Measurements

The adsorption equilibrium was examined by the static method. For this purpose, 8 flat-bottom flasks were prepared, to which 100 cm^3 of a solution of a known concentration of the dye Direct Fast Navy Blue BR 200% and 0.3 g of the pure adsorbent ORGANOSORB 10 were introduced. The samples were maintained at room temperature (20°C) and were regularly shaken mechanically (Fig. 2). The frequency of the shaker was set to 300 rpm. Before and after each shaking, the absorbance of solutions was measured in a spectrophotometer Shimadzu UV-2600 in a measuring cell with an optical path length of 50 mm. After about 10 days, the concentration of the solutions in flasks stopped changing, which can be assumed as being equivalent to an equilibrium between the adsorbate and the adsorbent.

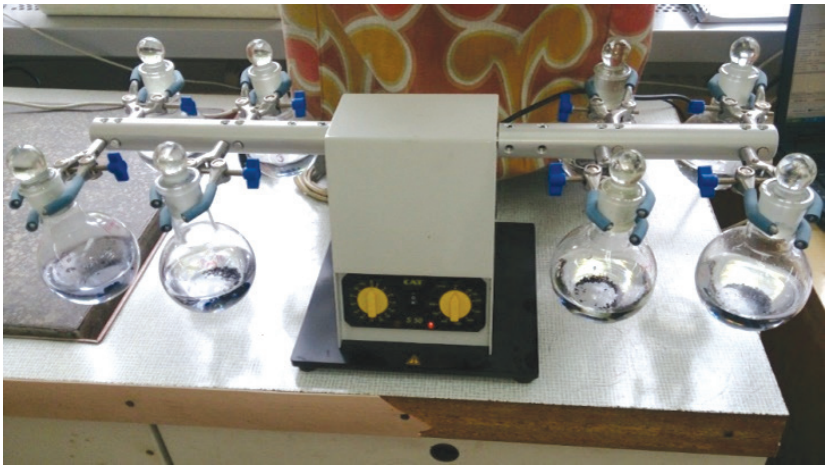

Fig. 2. Flat bottom flasks placed in a shaker during equilibrium measurements

3.4. Adsorption Kinetics Measurements

The test stand (Fig. 3) at which the dye adsorption kinetics studies were performed consisted of a 600 cm^3 beaker, a magnetic stirrer and a peristaltic pump together with the adsorber and connecting pipes forming a closed circuit. The peristaltic pump was set to the appropriate value. The examined solution was continuously mixed in a beaker with a magnetic stirrer to make the concentration uniform in the entire volume of the tank. Subsequently, the solution was pumped by the peristaltic pump to the adsorber. After passing through the adsorber filled with activated carbon, the solution returned to the beaker. Ten series were made, with changing the flow rate, as presented in Tab. 3. In each measurement, the amount of active carbon in the adsorber was about 2 g. Each measurement took an hour including a sample zero, that is the solution before any contact with active carbon. Every 5 minutes, 15 cm^3 of the solution was pipetted from the beaker, placed in a measuring cell of the spectrophotometer in order to measure the absorbance of the solution. All measurements were made for a wavelength equal to 584 nm. After measuring the absorbance, the solution from the measuring cell was poured back into the stirrer tank. The results were reported using the Shimadzu UV Probe program and saved to the hard disk.

Fig. 3. Laboratory equipment for adsorption kinetics measurements

Table 3. Pump speed and the flow rate of the liquid through the adsorber

Measurement No.	Pump rotations [rpm]	Q_v [cm^3/min]
1	35.625	19.688
2	67.742	35.806
3	110.901	58.638
4	136.341	72.128
5	169.780	89.617
6	203.220	107.107
7	236.660	124.597
8	270.100	142.087
9	303.540	159.576
10	336.980	177.066

4. Results

4.1. Equilibrium Studies

The graph in Fig. 4 shows how the concentration of the dye changed over time. As can be seen, the concentration lowers with time for all the considered water solutions of the dye. After some time, the lines stabilize and it can be assumed that the equilibrium was reached. For the lowest concentrations of the dye in water, after a few days, the concentration was so low that it was not possible to measure the absorbance accurately. Possibly, if the spectrophotometer was equipped with a measuring cell with an optical path length of 100 mm, such small concentrations could be measured. The graph also shows that mechanical shaking greatly influences the rate of adsorption. Only few hours of shaking can result in a similar decrease in concentration as can be observed after 24 hours for solutions without shaking.

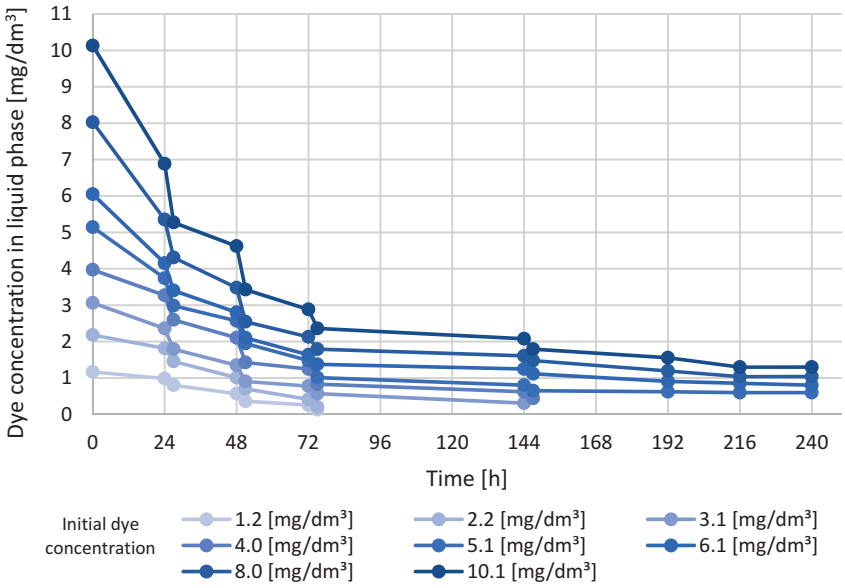

Fig. 4. Temporal concentration changes for all equilibrium measurements

The graph in Fig. 5 shows the relationship between dye concentration in adsorbent grains q_e and in the solution C_e. The points mark experimental results. The dye concentration values in the adsorbent grains q_e were calculated from the mass balance:

$$q_e = \frac{v_s(c_0 - c_e)}{m_c} \tag{1}$$

The lines in Fig. 5 refer to adsorption isotherms: linear, Freundlich and Langmuir. Parameters of these models were calculated by linear regression on the basis of the experimental results and are given in Table 4. As can be seen in Fig. 5, the experimental points correspond most to the Freundlich isotherm.

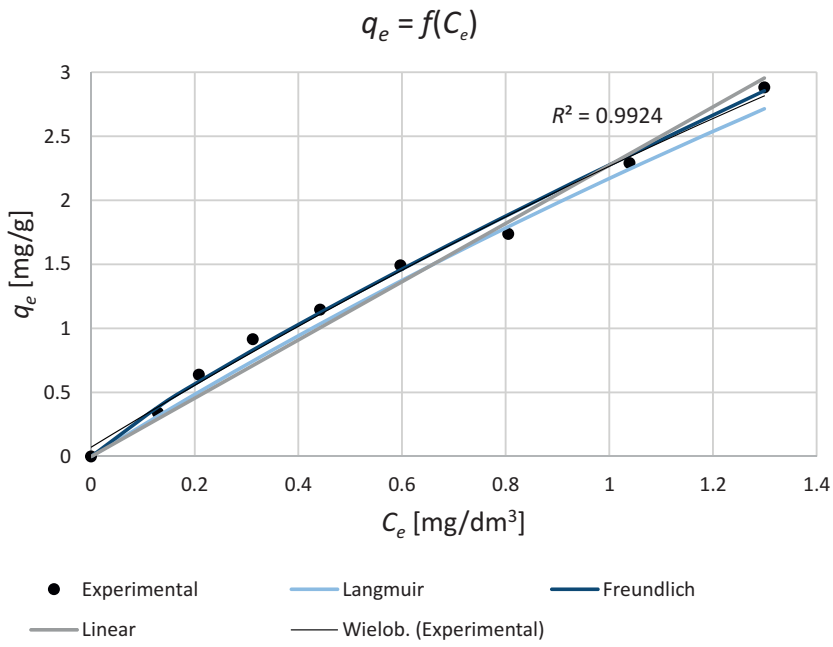

Fig. 5. Adsorption isotherm of Direct Fast Navy Blue BR 200%

Table 4. Constants of adsorption isotherms

Adsorption isotherm				
Linear $q_e = KC_e$	Langmuir $q_e = q_\infty \frac{bC_e}{1+bC_e}$		Freundlich $q_e = k_F C_e^{\nu}$	
K	q_∞	b	k_F	ν
2.275	16.556	0.151	2.278	0.865

4.2. Kinetics Studies

Table 5 as well as graphs 6 and 7 show the results of the adsorption kinetics studies. They refer to measurement 5 (according to Tab. 3), i.e. to fluid velocity equal to 89.617 cm^3/min. The dye concentration in the liquid decreases during the adsorption (Fig. 6), while concentration in the solid phase increases (Fig. 7). Both concentrations seek to achieve equilibrium values, respectively C_e and q_e.

The graphs in Figs. 8 and 9 show a comparison for all the performed kinetics measurements. It can be concluded that the flow rate influences the adsorption rate. When the flow rate of liquid phase, which bathes the adsorbent, is increased, the liquid phase concentration decreases for a given time (Fig. 8). When the liquid phase flow rate is increased, the solid phase concentration also increases for a given time (Fig. 8). As we increase the turbulence of the liquid around the grains, the mass transfer coefficient k_l increases and the external resistance of the mass transport decreases. Adsorption occurs more intensively and effectively.

Table 5. Results of experiment No. 5: values for the flow rate equal to 89.617 cm^3/min

TIME [min]	ABSORBANCE [–]	C [mg/dm^3]	q [mg/g]
0	0.183	4.753	-
5	0.163	4.233	0.061
10	0.153	3.974	0.092
15	0.138	3.584	0.139
20	0.130	3.376	0.163
25	0.118	3.064	0.201
30	0.111	2.883	0.222
35	0.104	2.701	0.244
40	0.099	2.571	0.259
45	0.092	2.389	0.281
50	0.087	2.259	0.296
55	0.081	2.104	0.315
60	0.077	2.000	0.327

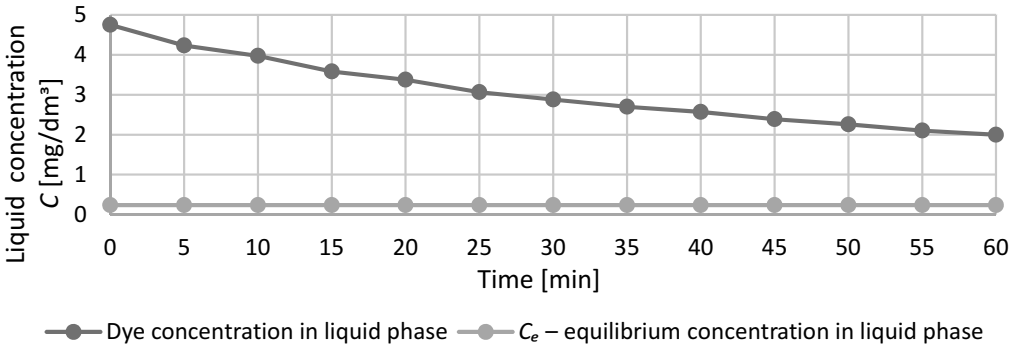

Fig. 6. Concentration of dye in the liquid phase vs. time for measurement 5

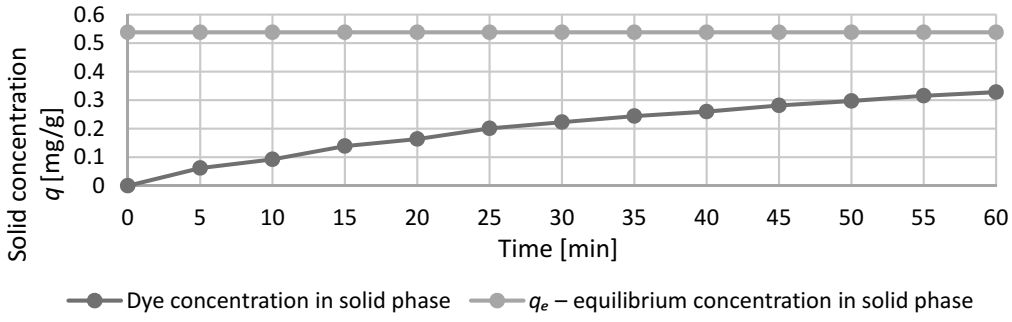

Fig. 7. Concentration of dye in solid phase vs. time for measurement 5

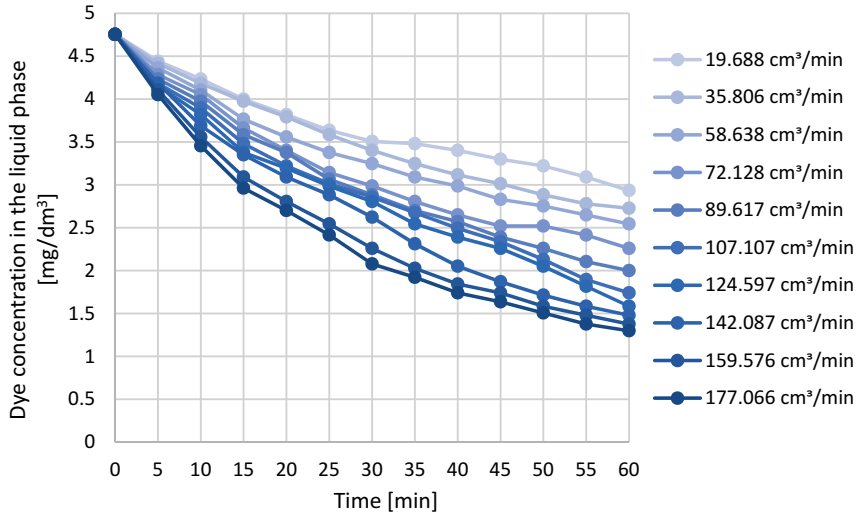

Fig. 8. Temporal changes of concentration in the solid phase for all the kinetics measurements

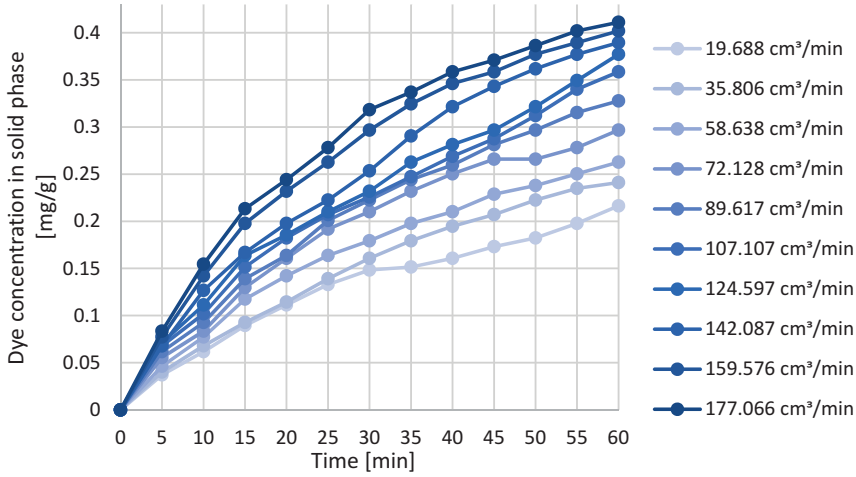

Fig. 9. Temporal changes of concentration in the liquid phase for all the kinetics measurements

5. Summary

- The results of the studies presented in this work show that the activated carbon ORGANOSORB 10 effectively removes the dye Direct Navy Blue BR 200% from its aqueous solution.
- As a result of the adsorption equilibrium analysis, it was shown that experimental points correspond the most to the Freundlich isotherm.
- Achieving equilibrium in the adsorption systems under investigation is greatly accelerated by mechanical shaking, which increases the speed of the liquid phase

movement and the mass transfer coefficient, and intensifies the transfer of matter between the fluid and the adsorbent. Short shaking causes a much greater decrease in the dye concentration in the solution than longer-lasting adsorption without the use of external factors.

- With increasing the flow rate of the solution in the adsorber, the concentration of the dye in the liquid phase decreases and its concentration in the solid phase increases for a given time. This can be explained by the fact that a higher flow rate causes the solution to be in contact with the adsorbent particles faster. Large fluid turbulence allows for an easier exchange of mass. This results in a higher mass transfer coefficient and lower external mass transfer resistance. However, the maximum flow speed is limited by residence time adequate for efficient adsorption and pressure drop of the fluid.

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