

# IDENTIFICATION OF THE EXPERIMENTAL DATA OF DYE ADSORPTION ON NATURAL DISPERSED SORBENTS TO THEORETICAL MODELS

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**Abstract** The present study deals with removal of organic dyes from wastewater onto natural dispersed sorbents, namely bentonite, glauconite and paligorskyte. The obtained data were fitted to various theoretical models of adsorption and the statistical estimation of the model fit has been performed. The values of kinetic constants have been calculated.

**Keywords:** adsorption, natural dispersed sorbents, dyes, identification. Isotherm, theoretical models of adsorption

## INTRODUCTION

All methods for physical and chemical removal of dyes from wastewater that are reported in literature can be divided into three groups.

The first group implicates the methods which remove dye pollutant by its conversion to sediment via sorption on metal hydroxides particles. The last are formed during reagent treatment of wastewater [1-4]. These methods (e.g. coagulation, reagent pressure flotation, electric coagulation, etc.) are disadvantageous because of low efficiency of color removal and necessity to choose the reagents and electrode material empirically, which complicates treatment of wastewater of unstable composition. The reagent dosage automatization is also unfavorable. In addition, these processes form high volumes of wet sediments or flotation slags and since the demand in additional construction for their treatment (dehydration), storage and burial arises. In case of burial the possibility of soil and groundwater can not be excluded.

The second group involves the destructive methods [5-6], based on profound transformation of organic molecules resulting from redox-processes. The most widely used are oxidation, reagent redox, electrochemical and electrocatalytical destruction. They possess several advantages, e.g. high efficiency and processibility, compactness and simplicity of automatization and operation. However, they are also exposed to disadvantages, such as low removal efficiency of chemically stable organic pollutants, which may result in formation of more toxic substances, and intricate mounting of oxidative module. If redox destruction method is used, the wastewater aftertreatment has to be involved. Electrochemical and electrocatalytical destruction is very energy-consuming and requires application of dimensioned equipment.

The third group includes separation methods, such as adsorption on activated carbon, macropore ionites and other types of sorbents, including natural; reverse osmosis, ultrafiltration, foam separation, electroflotation [7-8]. These methods, except for the latest two, provide high efficiency for wastewater cleaning.

Sorption process is the one that could be easy monitored and controlled. It allows removing the different pollutants to any residual concentration irrespective of its chemical stability. This process does not form secondary pollution. We propose usage of the natural dispersed sorbents as the most promising ones due to several reasons. They are low-price and therefore do not require regeneration; they are widely spread in Ukraine and also effective in water treatment processes [7, 9]. We chose bentonite, glauconite and palygorskite sorbents.

### RESULTS AND DISCUSSION

We investigated the treatment of wastewater polluted with anionic red 8C, which has the following features: empirical formulae  $C_{38}H_{25}O_{13}N_6S_3Na_3$ , molar weight 938,8 g/mol.

This type of dye is chosen as it is widely used in production which generates high volume of wastewater. From the other side, it is a preproduct and contains no other dyes.

Therefore, the investigation of adsorption of anionic red allows to state that a single product adsorption takes place and the process can be described by the equation of physical sorption. The experimental investigations shown on the Fig. 1 have been performed as follows.

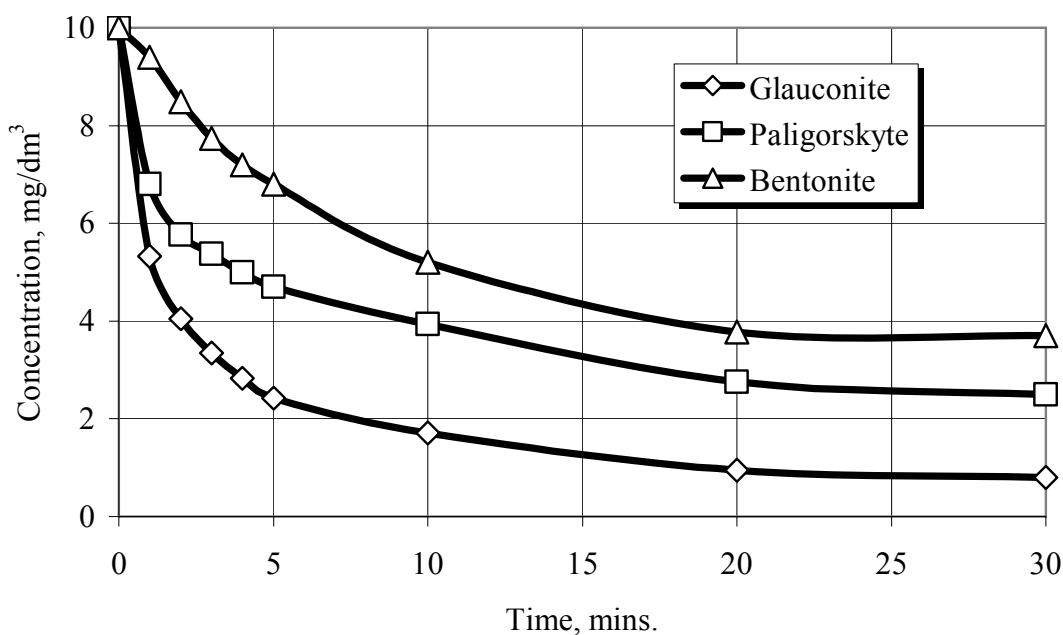


Figure 1. Kinetic of the anionic red 8C sorption by natural dispersed sorbents

A volume of 1000 ml of solution with varying initial concentration 1, 5 and 10 mg/dm<sup>3</sup> was placed into a stirred reactor. The reactor was kept in thermostat for some time till the working temperature

was reached. The effect of temperature was studied for the temperatures 12, 20 and 30°C. The chosen temperature range correspond the real temperatures applicable during the sorption treatment of wastewater polluted by dyes. After the necessary temperature has been reached, the sorbent was added. While the solution was stirring, the samples were thieved and analyzed for dye content using photocolorimetry. The sorbents used were paligorskyte and bentonite of Dashukiv mine and glaucinite of Adamiv mine with degree of fineness +0.5-1 mm. The first stage of experiments was carried out with all the studied sorbents.

Fig. 1 depicted the effectiveness of dye removal on three sorbents. It can be seen that the most effective sorbents for the studied process are glaucinite and palygorskite. Therefore these sorbents have been chosen for the further investigation.

The aim of investigation was to find the dependence of kinetic on the initial concentration and temperature. The obtained data will be used for isotherm fitting.

The results of investigation for different initial concentration are shown on Fig. 2 and 3.

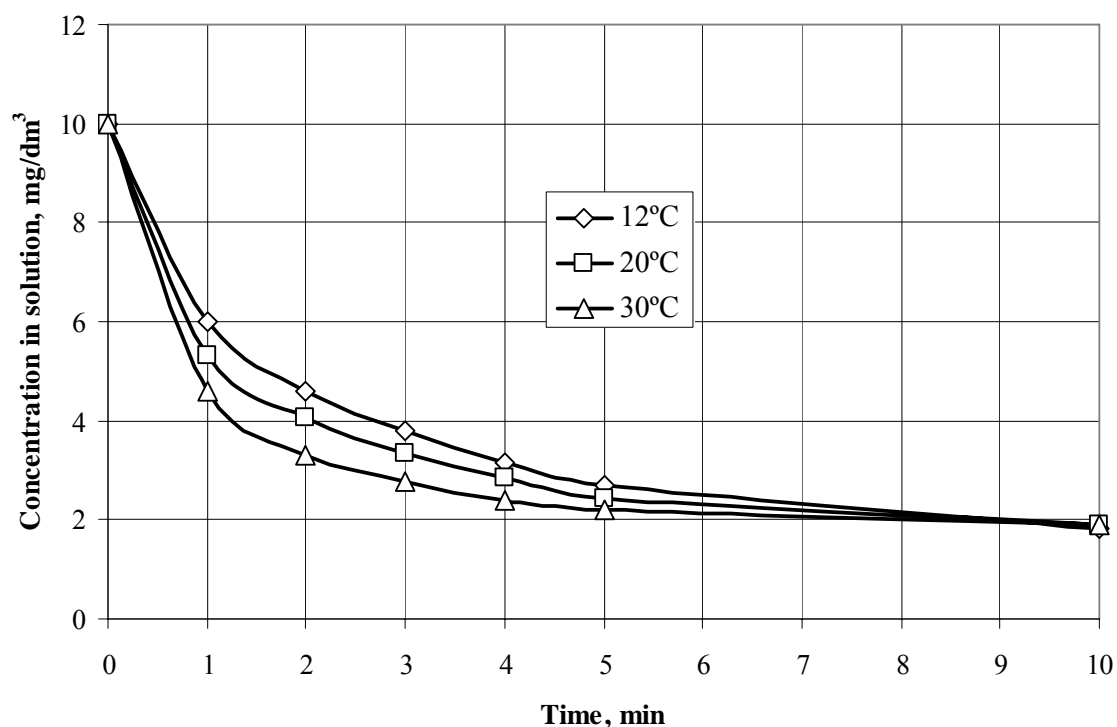


Figure.2. Kinetic of adsorption of anionic red 8C onto glaucinite. Initial concentration of dye is 10 mg/l.

The experimental data prove that the adsorption of dye in the studied range is rather effective and finishes when the adsorption capacity of the sorption is reached. Providing the correct dosage of the adsorbent, which contributes the sufficient adsorption capacity, the high efficiency of dye removal (up to LOD residual concentration) can be achieved. This would enable wastewater discharge to surface water basins without threat to environment.

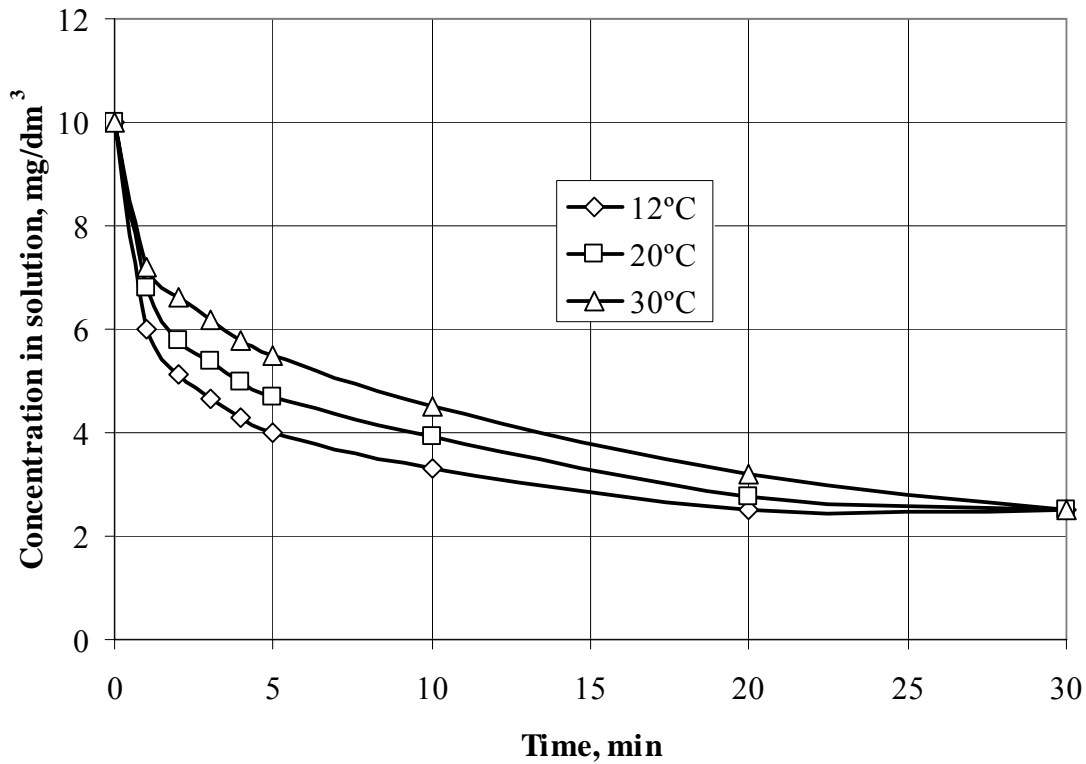


Figure 3. Kinetic of adsorption of anionic red 8C onto paligorskyte. Initial concentration of dye is 10 mg/l.

Modeling and equilibrium of physical sorption has been carried out via fitting of experimental data to model of adsorption. As a result, we chose the isotherm that best fits the process.

For modelling and description of the physical sorption equilibrium the following isotherms have been tested. The equations are given below.

1. Langmuir:

$$q_K = \frac{K \cdot C_K \cdot \Gamma}{1 + K \cdot C_K} \quad (1),$$

$q_K$  – equilibrium amount adsorbed of adsorbate by the adsorbent mg/g;

$K$  – Langmuir constant  $\text{m}^3/\text{mg}$ ;

$C_K$  – equilibrium concentration of dye in solution,  $\text{mg}/\text{m}^3$ ;

$\Gamma$  – sorption capacity,  $\text{mg}/\text{g}$ .

2. Langmuir – Freundlich:

$$q_K = \frac{(K \cdot C_K)^n \cdot \Gamma}{1 + (K \cdot C_K)^n} \quad (2),$$

$n$  – constant that takes the surface heterogeneity into account

3. Reciprocal Langmuir:

$$q_K = \frac{C_K}{\frac{C_K}{\Gamma} + \frac{1}{K \cdot \Gamma}} \quad (3).$$

4. Redlich-Peterson:

$$q_K = \frac{K \cdot C_K \cdot \Gamma}{1 + (K \cdot C_K)^n} \quad (4).$$

5. Dubinin-Radushkevitch:

$$\log q_K = -n(\log^2(K \cdot C_K)) + \log \Gamma \quad (5).$$

6. Modified Dubinin-Radushkevitch:

$$\log q_K = -n \left( \log^2 \left( \frac{K \cdot C_K}{1 + K \cdot C_K} \right) \right) + \log \Gamma \quad (6).$$

7. Toth

$$q_K = \frac{K \cdot C_K \cdot \Gamma}{\left(1 + (K \cdot C_K)^n\right)^{1/n}} \quad (7).$$

8. bi-Langmuir:

$$q_K = \frac{K_1 \cdot C_K \cdot \Gamma_1}{1 + K_1 \cdot C_K} + \frac{K_2 C_K \Gamma_2}{1 + K_2 C_K} \quad (8).$$

Identification of the experimental data has been carried out using the specific software. The data fitting to Langmuir for glauconite (a) and paligorskite (b) is shown on Fig. 4.

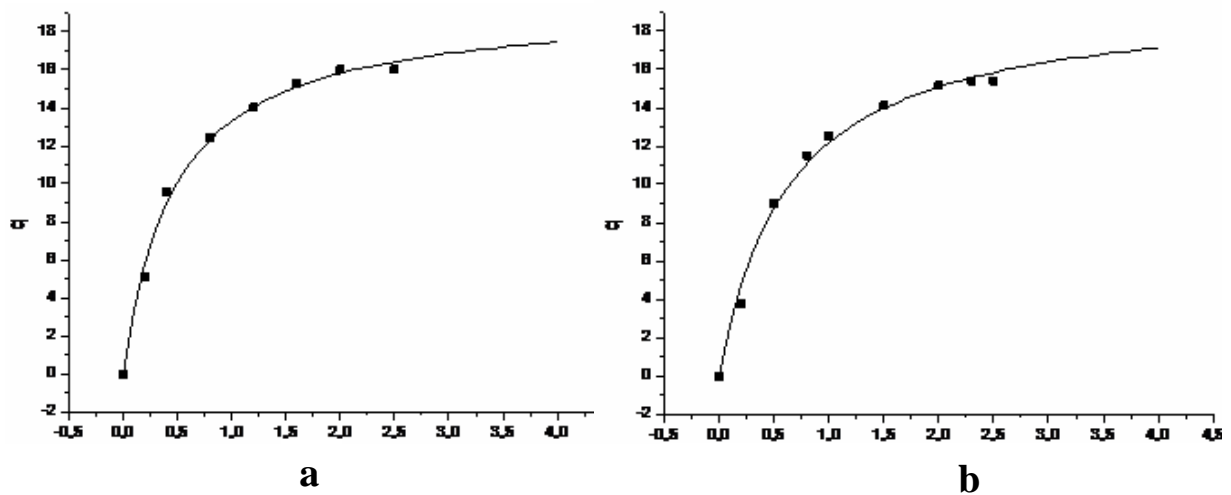


Figure 4. Identification of experimental isotherm of anionic red 8C sorption onto glauconite (a) ra paligorskite (b) to Langmuir model

For evaluation of the experimental data fitting to the tested theoretical models the sum of the squares of the errors (SSE), variance, Fisher test and coefficient of determination have been applied. Identification allowed calculating the values of kinetic constants, such as equilibrium constant, sorption capacity and constants that takes the surface heterogeneity into account. The obtained values are given in Table 1.

Table 1 The statistical estimation of identification of experimental data to theoretical adsorption models.

Model	Statistical parameter			
	SSE	Dispersion	Fisher test	Coefficient of determination
Glaucosite				
Langmuir	1,2079760	0,4486973	168,33214	0,9975037
Redlich-Peterson	0,8242999	0,4060295	205,56959	0,9982695
Reciprocal Langmuir	1,2080172	0,4487050	168,32639	0,9975059
Langmuir-Freundlich	0,6196052	0,3520242	273,48218	0,9986953
Toth	0,7404391	0,3848218	228,85202	0,9984426
Dubinin-Radushkevitch	0,7898287	0,3974490	214,54143	0,9983376
Modified Dubinin-Radushkevitch	0,5995182	0,5590598	282,64526	0,9987365
bi-Langmuir	1,2501915	0,5590598	108,43202	0,9973670
Palygorskite				
Langmuir	1,6935387	0,4918679	128,36912	0,9967499
Redlich-Peterson	2,3297035	0,6231243	79,984946	0,9957150
Reciprocal Langmuir	1,6928241	0,4917641	128,42331	0,9967520
Langmuir-Freundlich	0,0970524	0,1271825	1920,0060	0,9998028
Toth	0,2743156	0,2138206	679,29482	0,9994626
Dubinin-Radushkevitch	0,2386318	0,1994291	780,87318	0,9995175
Modified Dubinin-Radushkevitch	0,0728151	0,5871847	2559,0981	0,9998519
bi-Langmuir	1,7239294	0,5871847	90,075814	0,9966671

The investigation showed that data of adsorption of dye onto glaucosite are best fitted to Redlich-Peterson, Toth, modified Dubinin-Radushkevitch and Langmuir-Freundlich. The adsorption onto palygorskite the Toth, modified Dubinin-Radushkevitch and Langmuir-Freundlich provide best fits.

During the identification the values of kinetic constants have been calculated for the studied models. These values are given in Table 2.

The obtained values allow calculating the adsorption process in the stirred reactor.

Table 2. The kinetic constants of the studied adsorption equations

Model	Kinetic constants				
	k	$\Gamma$	n		
<b>Glauconite</b>					
Langmuir	2,155	19,480	-		
Redlich-Peterson	1,457	23,690	1,140		
Reciprocal Langmuir	2,158	19,470	-		
Langmuir-Freundlich	2,655	17,510	1,292		
Toth	1,814	17,290	1,467		
Dubinin-Radushkevitch	0,350	16,080	0,349		
Modified Dubinin-Radushkevitch	0,596	17,110	0,535		
	$k_1$	$\Gamma_1$	$k_2$	$\Gamma_2$	$\Gamma_1+\Gamma_2$
bi-Langmuir	2,059	19,73	0,628	8,6E-07	19,73
<b>Palygorskite</b>					
Langmuir	1,591	19,820	-		
Redlich-Peterson	2,060	17,500	0,945		
Reciprocal Langmuir	1,592	19,800	-		
Langmuir-Freundlich	2,137	16,850	1,445		
Toth	1,295	16,360	1,865		
Dubinin-Radushkevitch	0,370	15,390	0,461		
Modified Dubinin-Radushkevitch	0,630	16,690	0,712		
	$k_1$	$\Gamma_1$	$k_2$	$\Gamma_2$	$\Gamma_1+\Gamma_2$
bi-Langmuir	1,694	15,10	1,239	4,787	19,887

## CONCLUSIONS

The kinetic of adsorption of organic dye anionic red 8C has been determined on natural dispersed sorbents, namely glauconite and palygorskite. The identification of the experimental data to the theoretical models has been performed. The statistical estimation of adequateness of identification allows stating that if glauconite is used as sorbent, sorption follows the models of Redlich-Peterson, Toth, Dubinin-Radushkevitch, modified Dubinin-Radushkevitch and Langmuir-Freundlich. If palygorskite is used as sorbent then the sorption fits best with the models Dubinin-Radushkevitch and Langmuir-Freundlich. The values of kinetic constants for anionic red 8C adsorption onto glauconite and palygorskite are calculated. These data might be used for calculation of industrial processes of adsorption treatment and adsorption facilities.

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