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ROMANIAN (MĂCICAŞ) ZEOLITIC VOLCANIC TUFF FOR MALACHITE GREEN REMOVAL

RALUCA PLEŞA CHICINAŞ[a], HOREA BEDELEAN[b], ANDRADA MĂICĂNEANU[a,c*]

ABSTRACT. Zeolitic volcanic tuff was tested as a potential adsorbent for malachite green (MG) dye removal from aqueous solutions. The influences of contact time, temperature, dye initial concentration, solid:liquid ratio, and adsorbent grain size over the adsorption capacity and efficiency were considered. Removal efficiencies up to 99% and a monolayer capacity (Langmuir) of 4.05 mg MG/g were calculated. The equilibrium and kinetic study showed that the experimental data were best fitted on the Temkin model and that the intra-particle diffusion could be the rate determining step. Thermodynamic analysis showed that MG adsorption onto ZVT is an endothermic, non-spontaneous process.

Keywords: *natural zeolite, malachite green, adsorption, efficiency, equilibrium, kinetic, thermodynamic*

INTRODUCTION

Natural zeolite is an abundant resource available all over the world, is usually regarded as a low-cost material and has been used as an adsorbent to remove heavy metals, dyes and ammonia ions [1-3]. Zeolites are able to exchange ions with external medium, having a high ion exchange capacity, which is their significant characteristic. The ion exchange behaviour depends on framework structure, ion size and shape, and charge density of the anionic framework. These properties make zeolites attractive materials that can be successfully used for pollutants removal from wastewaters [4-5].

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[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania*

[b] *Babeş-Bolyai University, Faculty of Biology and Geology, 44 George Bilaşcu St., 400015, Cluj-Napoca, Romania*

[c] *Indiana University of Pennsylvania, Department of Chemistry, Indiana, PA 15705, USA*

** Corresponding author: Sanda.Maicaneanu@iup.edu*

Dyes are important pollutants of water, which are discharged from textile, printing, paper, plastics, food and leather industries. It is estimated that more than 100,000 commercially available dyes with over $7 \cdot 10^5$ tons of dyestuff are produced annually [6]. They affect the nature of the water, reducing the photosynthetic reaction. Also some dyes are toxic and even carcinogenic [5-6]. Malachite green is a basic dye used in ceramic industry, textile industry, leather industry, as a cytochemical dye and in paints manufacturing. Because of its toxicity is used to treat parasites, fungal infections, and bacterial infections in fish and fish eggs [7].

In order to remove dyes from wastewaters, physical, chemical, and biological methods were reported. Between the various methods tested, adsorption proved to give the best results in terms of initial cost, flexibility, simplicity of design and very important does not result in the formation of harmful substances [6].

The purpose of this work was to study the possible use of zeolitic volcanic tuff (ZVT) as an adsorbent for malachite green (MG) removal from aqueous solution. The influence of the reaction parameters such as temperature, adsorbent quantity, MG initial concentration, and adsorbent grain size were considered. Equilibrium (Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin) and kinetic (pseudo-first-, pseudo-second-order, liquid film diffusion, and intra-particle diffusion) models were used to evaluate the adsorption mechanism. Also the thermodynamic parameters ΔG^0, ΔH^0, and ΔS^0 were calculated.

RESULTS AND DISCUSSION

Zeolitic volcanic tuff characterization

The zeolitic volcanic tuff sample used in this work is included in the Dej Formation of Badenian age, located in the north-western part of the Transylvanian Depression. The tuff may be characterized as a vitric tuff. The glass shards in tuffs are replaced by zeolite minerals, clinoptilolite type. Quartz, plagioclases, micas and opal-CT are also present.

X-ray diffraction (XRD) analysis confirms the presence of the clinoptololite as the main zeolite mineral phase [8].

The whole rock chemical analysis showed the acid character of the tuff with SiO_2 >60% [9]. The loss of ignition value (over 13%) indicates that zeolites represent between 60% and 80% of the crystallized fractions of the tuff [8-10].

MG adsorption results

The results obtained for MG removal from aqueous solution using ZVT are presented further and discussed in terms of removal efficiency and adsorption capacity.

The influence of temperature on MG adsorption was investigated using the following reaction conditions: solid:liquid ratio 0.50:10 g/mL, 50 mg MG/L, 0.6-1.0 mm adsorbent grain size, and a reaction time of 360 min. The acquired results, Figure 1, showed that an increase of the contact time has as result a gradually increase of the MG uptake with a higher rate for temperatures between 35 and 55°C in the first 100 min and then slower towards the equilibrium. Adsorption equilibrium was reached in about 300, 240, and 120 min as the temperature increased from 25 to 55°C. Removal efficiency increases from 72 to 93% as the temperature increases from 25 to 55°C.

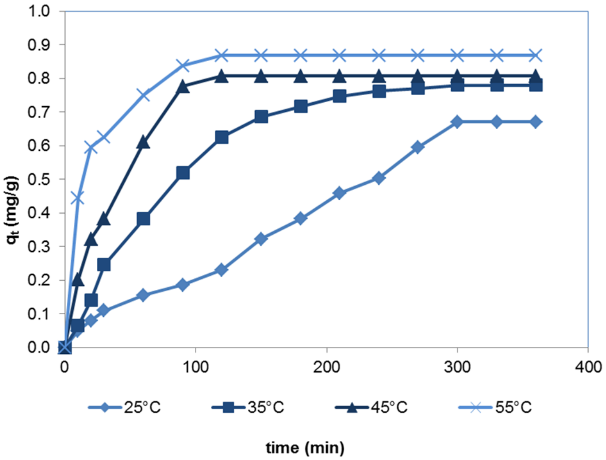

Figure 1. Time evolution of MG uptake for different temperatures (50 mg MG/L, 0.50:10 g/mL, 0.6-1.0 mm grain size, 360 min).

The results obtained for various initial concentrations of MG solution (10-250 mg/L) are presented in Figure 2. An increase of MG initial concentration led to an increase in the ZVT adsorption capacity, proving that the considered material has a high ability to retain MG even at high concentrations.

The study of the solid:liquid ratio influence upon MG adsorption process was conducted using solid:liquid ratios in 0.25:10-1.00:10 g/mL interval. The results obtained are presented in Figure 3. Thus, an increase in adsorbent quantity led to a decrease in adsorption capacity value due to the fact that for the same initial concentration, a higher surface or adsorbent quantity is available for adsorption. The highest removal efficiency calculated in this case was about 97% for 1.00:10 mg/L.

The influence of the ZVT grain size upon the adsorption capacity in the MG adsorption process was studied for a range of grain sizes in 0.2-0.4 to 1.25-1.6 mm interval. Adsorption capacities values thus obtained for all grain sizes are presented

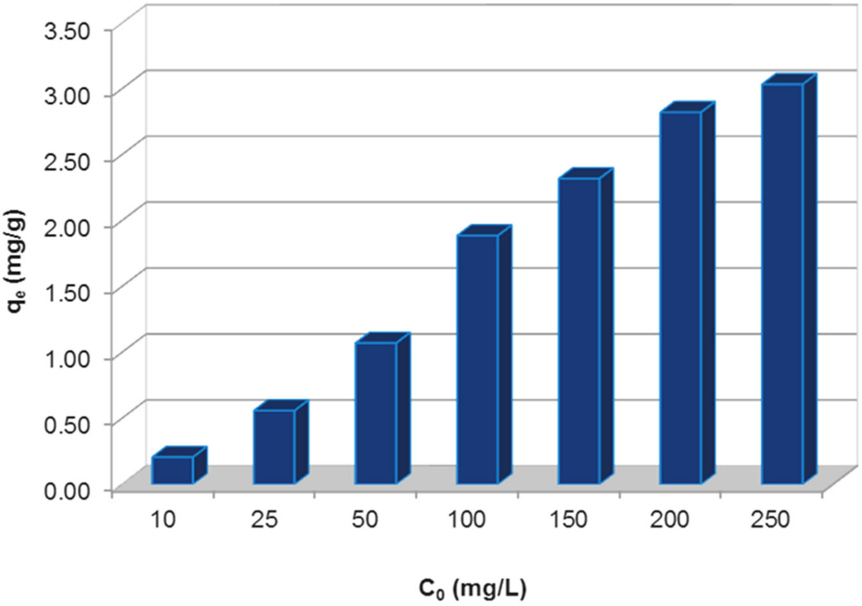

Figure 2. MG initial concentration influence over the adsorption capacity (25°C, 0.50:10 g/mL, 0.6-1.0 mm grain size and 420 min).

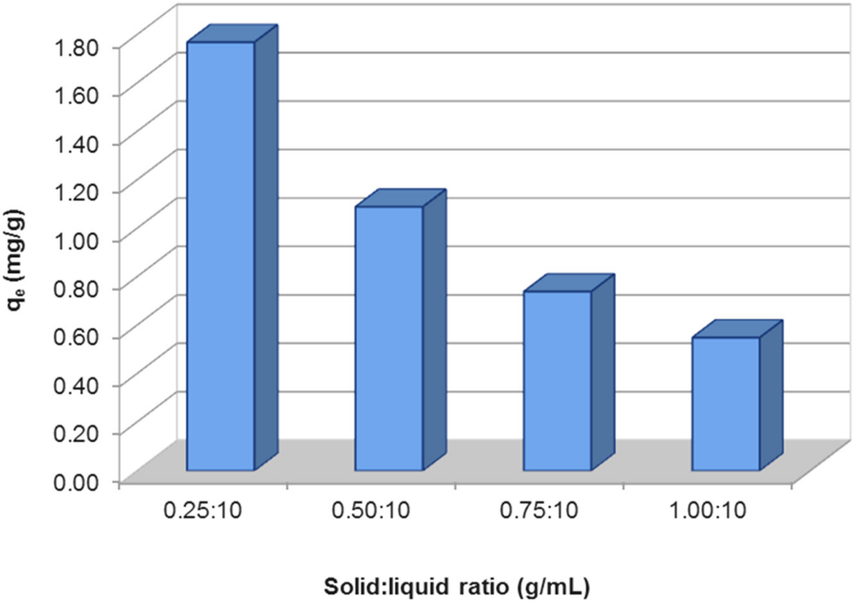

Figure 3. Solid:liquid ratio influence over the adsorption capacity of ZVT in the MG adsorption process (50 mg/L, 25°C, 0.2-0.4 mm grain size, 360 min).

in Figure 4. This evolution might be correlated with diffusional limitations that occur due to the MG molecule size, adsorption taking place mostly on the external surface of the grain. Removal efficiency values followed the same trend with a maximum value of about 98% for 1.25-1.60 mm.

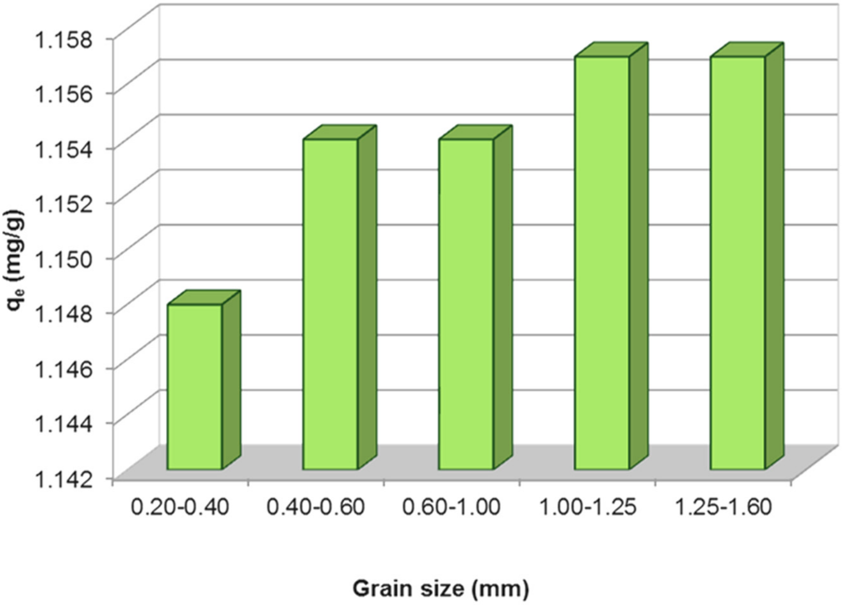

Figure 4. Variation of adsorption capacities obtained for MG adsorption on ZVT at different grain size (50 mg/L, 25°C, 0.50:10 g/mL, 360 min).

Adsorption isotherms

Equilibrium experiments were carried out for different initial concentrations in 10-250 mg/L range at 25°C for 420 min.

In order to establish which isotherm model describes better the adsorption of MG on ZVT, Langmuir, Freundlich, Dubinin-Radushkevich and Temkin equations were considered. The parameters obtained from experimental data and the related correlation coefficients are presented in Table 1. All values of correlation coefficient (R^2) were higher than 0.9, but Temkin model yields a better fit, with a 0.9864 value, than Langmuir, Freundlich and Dubinin-Radushkevich models, with 0.9421, 0.9275, and 0.9490, respectively. Previous studies in similar systems showed that the adsorption of dyes (methyl orange and methyl violet) was best described by Temkin model [11].

Table 1. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms parameters for the adsorption of MG onto ZVT (10-250 mg/L, 25°C, 0.50:10 g/mL, 0.60-1.00 mm, 420 min)

Langmuir			**Freundlich**			**Dubinin-Radushkevich**			**Temkin**		
K_L (L/mg)	**q_m (mg/g)**	**R^2**	**n**	**K_F ($mg^{(1-1/n)}L^{1/n}/g$)**	**R^2**	**K_D (mol^2/kJ^2)**	**E_D (kJ/mol)**	**R^2**	**A_T (L/g)**	**B**	**R^2**
0.0504	4.0519	0.9421	1.9952	0.2985	0.9275	4×10^{-9}	11.18	0.9490	2.0326	2×10^{-6}	0.9864

Adsorption kinetics

The rate constants and the adsorption mechanism of MG adsorption onto ZVT were evaluated by using different kinetic models, such as pseudo-first-, pseudo-second-order, intra-particle, and liquid film diffusion. The results obtained for all considered kinetic models are presented in Table 2. Taking into consideration the correlation coefficients obtained for all considered models, the fact that $q_{e,calc}$ for pseudo-first- and pseudo-second-order exhibit considerable difference towards the $q_{e,exp}$ values, and also that the intercept values in case of diffusion models are very close to 0 [12], support the conclusion that intra-particle diffusion might be rate-determining step for this system (concentrations higher than 50 mg/L). Experimental results obtained for various grain sizes of the ZVT (adsorption capacity increases with an increase in grain size) also support this conclusion.

Table 2. Pseudo-first-, pseudo-second-order, intra-particle and liquid film diffusion parameters for the adsorption of MG onto ZVT (10-250 mg/L, 25°C, 0.50:10 g/mL, 0.60-1.00 mm, 420 min)

		Pseudo-first-order			**Pseudo-second-order**			**Intra-particle diffusion**			**Liquid film diffusion**		
C_0	**$q_{e,exp}$ (mg/g)**	**k_1 (1/min)**	**$q_{e,calc}$ (mg/g)**	**R^2**	**k_2 (g/mg·min)**	**$q_{e,calc}$ (mg/g)**	**R^2**	**k_{ip} (mg/g min$^{1/2}$)**	**Intercept**	**R^2**	**k_{fd} (1/min)**	**Intercept**	**R^2**
10	0.2031	0.0124	0.1838	0.9847	0.0781	0.2363	0.9982	0.0095	0.0370	0.8975	0.0123	-0.1170	0.9847
25	0.5562	0.0140	0.8254	0.9641	0.0074	0.8260	0.9726	0.0321	-0.0207	0.9437	0.0140	0.3890	0.9641
50	1.0420	0.0082	1.4299	0.9397	0.0011	2.1354	0.9762	0.0635	-0.1956	0.9949	0.0082	0.2884	0.9398
100	1.8225	0.0074	2.4227	0.9178	0.0005	4.1528	0.9861	0.1090	-0.3459	0.9971	0.0074	0.2500	0.9178
150	2.1840	0.0067	2.7451	0.9563	0.0006	4.2409	0.9550	0.1306	-0.3785	0.9955	0.0067	0.1685	0.9563
200	2.7314	0.0075	3.6888	0.9146	0.0002	6.8871	0.9538	0.1649	-0.5542	0.9963	0.0075	0.2675	0.9146
250	2.8993	0.0068	3.5898	0.9321	0.0008	4.6642	0.9483	0.1651	-0.3983	0.9964	0.0068	0.1679	0.9321

The pore diffusion coefficients determined are presented in Table 3, with the smallest value of 8.69×10^{-10} cm^2/s. Although the values are not in the rate determining range (10^{-11} - 10^{-13} cm^2/s) [13-14] it is reasonable to assume that internal diffusion plays a significant role for the considered system especially in the higher concentration range.

Table 3. Pore diffusion coefficients

C_0 (mg/L)	**D (cm^2/s)**	**C_0 (mg/L)**	**D (cm^2/s)**
10	5.90×10^{-9}	150	8.69×10^{-10}
25	1.95×10^{-9}	200	5.44×10^{-10}
50	7.40×10^{-10}	250	1.23×10^{-9}
100	6.41×10^{-10}		

Adsorption thermodynamics

The adsorption of MG dye onto ZVT was studied at temperatures in 298-328 K interval. In order to estimate the effect of temperature for the considered adsorption system, Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined. The values obtained are listed in Table 4. ΔH^0 positive value, also less than 84 kJ/mol indicates the endothermic nature and that the process is physical in nature [4]. The small positive value of ΔS^0 confirmed the increased randomness at the solid-solution interface during adsorption [3]. ΔG^0 values for all temperatures are positive, and the value decrease with increase of temperature, which indicates the fact that the considered adsorption process will be promoted by specific temperature conditions, leading to increased adsorption capacities [15].

Table 4. Thermodynamic parameters for the adsorption of MG onto ZVT (50 mg/L, 25-55°C, 0.50:10 g/mL, 0.60-1.00 mm, 420 min)

T (K)	**ΔS° (kJ/K·mol)**	**ΔH° (kJ/mol)**	**ΔG° (kJ/mol)**
298	0.11	39.17	6.73
308			5.64
318			4.55
328			3.46

CONCLUSIONS

This work presents the results obtained for malachite green removal from aqueous solution using a zeolitic volcanic tuff from Măcicaş deposit, Cluj County, as adsorbent. The study of various parameters showed that the ZVT sample has a high capacity to remove MG dye from aqueous solution with removal efficiencies up to 99%. Also as the initial concentration of dye increases, adsorption capacity of the ZVT increases suggesting its increased ability to efficiently remove MG even at high concentrations. The kinetic study showed that intra-particle diffusion might be the rate determining step for this particular system. Thermodynamic analysis showed that MG adsorption onto ZVT is an endothermic, non-spontaneous process. According to the obtained results it can be concluded that the zeolitic volcanic tuff from Măcicaş could be used as an efficient adsorbent for MG dye removal from aqueous solutions.

EXPERIMENTAL SECTION

Materials

In this work, a representative sample of zeolitic volcanic tuff (ZVT) collected from Măcicaş deposit (Cluj County, Transylvania, Romania) was used. Raw ZVT was subjected to a grinding process, followed by size separation in order to obtain the 0.2-0.4, 0.4-0.6, 0.6-1.0, 1.0-1.25 and 1.25-1.6 mm fractions, which were further used throughout the experiments. Raw ZVT was then washed few times with distilled water in order to remove fine particles and dried at 105°C for 24 h.

All reagents were of analytical purity and used as received. Distilled water was used throughout this work.

Adsorption experiments

Malachite green (MG) adsorption process was conducted in batch conditions, in a thermostated batch reactor using a three-dimensional shaker (50 rpm), for 420 min. various parameters that could influence the adsorption process were considered. Thus the experiments were carried out using different contact times (10-420 min), temperatures (25-55°C), MG initial concentrations (10-250 mg/L), solid:liquid ratios (0.25:10-1.00:10 g/mL) and different ZVT grain sizes (0.2-0.4, 0.4-0.6, 0.6-1.0, 1.0-1.25 and 1.25-1.6 mm).

MG concentration in solution was determined using a UV/VIS T70+ spectrophotometer (λ_{MG} = 618 nm). All the experiments were realized in triplicate, the presented values are averaged values.

Adsorption capacity and MG uptake, q_e and q_t (mg/g), respectively, and removal efficiency, E (%) were calculated in order to establish the effectiveness of the considered sample in the dye removal process.

$$q_{e(t)} = \frac{\left(C_0 - C_{e(t)}\right) \cdot V}{m}$$

$$E = \frac{C_0 - C_e}{C_0} \times 100$$

where: C_0, C_e, and C_t are the initial, equilibrium, and time t MG concentrations in solution, in mg/L, V is the sample volume, in L and m is the adsorbent quantity, in g.

Adsorption isotherms, kinetics and thermodynamics

The equilibrium analysis of the adsorption process of MG on ZVT was carried out using the Langmuir, Freundlich, Temkin and Dubinin-Raduschevich models. For all considered models the equations in the linear form are given in Table 5.

Pseudo-first-, pseudo-second-order, intra-particle diffusion and liquid film diffusion kinetic models were used in order to explain the adsorption mechanism. The pore diffusion coefficient, D (cm^2/s) for the removal of MG by ZVT was also calculated (assuming a spherical geometry of the adsorbents – average size 0.8 mm). The equations used in order to determine the kinetics parameters and pore diffusion coefficient are given in Table 5.

The thermodynamic parameters, Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), for the removal of MG by ZVT were determine using the equations presented in Table 5.

Table 5. Isotherms, kinetics and thermodynamics models.

		Equation	Reference
ISOTHERM	Langmuir	$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m}$	[16,17]
	Freundlich	$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e$	[3,18]

		Equation	**Reference**
	Dubinin-Radushkevich	$\ln q_e = \ln q_s - K_D\varepsilon^2$ $\varepsilon = RT\ln(1+\frac{1}{C_e})$ $E_D = \frac{1}{\sqrt{2K_D}}$	[16,19]
	Temkin	$q_e = B\ln A_T + B\ln C_e$ $B = \frac{RT}{b_T}$	[3,20]
KINETIC	Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	[21,25]
	Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	[22,25]
	Intra-particle diffusion	$q_t = k_{ip} t^{1/2}$	[23,25]
	Liquid film diffusion	$\ln(1-F) = -k_{fd} t$	[24,25]
	Pore diffusion coefficient	$D = 0.003 \cdot \frac{r_0^2}{t_{0.5}}$ $t_{0.5} = \frac{1}{k_2 q_e}$	[25]
TERMODYNAMIC	Gibbs free energy	$\Delta G^\circ = -RT\ln K_d$	[3,26]
	Enthalpy and entropy	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	

Where,

A_T – Temkin isotherm equilibrium binding constant (L/g)
B – constant related to heat of adsorption
b_T – Temkin isotherm constant (J/mol)
C_e – equilibrium MG concentration (mg/L)
D – pore diffusion coefficient (cm^2/s)
E_D – free energy per molecule of adsorbate (kJ/mol)
F – fraction attainment at equilibrium ($=q_t/q_e$)
K_D – Dubinin-Radushkevich isotherm constant (mol^2/kJ^2)
K_d – thermodynamic equilibrium constant (L/g)
K_F – Freundlich isotherm constant ($mg^{(1-1/n)}L^{1/n}/g$)
k_{fd} – liquid film diffusion rate constant (1/min)
k_{ip} – intra-particle diffusion rate constant ($mg/g\ min^{½}$)

K_L – Langmuir adsorption constant (L/mg)
k_1 – pseudo-first-order rate constant (1/min)
k_2 – pseudo-second-order rate constant (g/mg·min)
n – constant related to intensity of adsorption (Freundlich)
q_e – adsorption capacity (mg/g)
$q_{e,exp}$ – experimental amount of dye adsorbed at equilibrium (mg/g)
$q_{e,calc}$ – calculated amount of dye adsorbed at equilibrium (mg/g)
q_t – amount of dye adsorbed at time t (mg/g)
q_m – monolayer capacity of the adsorbent (mg/g)
q_s – theoretical isotherm saturation capacity (mg/g)
r_0 – average ZVT grain diameter (cm)
R – universal gas constant (8.314 J/mol K)
R^2 – correlation coefficient
t – time (min)
$t_{0.5}$ – time for half adsorption (s)
T – absolute temperature (K)
ΔG° – Gibbs free energy (kJ/mol)
ΔH° – enthalpy (kJ/mol)
ΔS° – entropy (kJ/K·mol)

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