

L.M. Soldatkina, M.A. Yanar

# ADSORPTION OF CATIONIC DYES ON BARLEY STRAW MODIFIED BY CITRIC ACID: KINETIC, EQUILIBRIUM, AND THERMODYNAMIC STUDIES

*Odesa I. Mechnikov National University**2 Dvoryanska Str., Odesa, 65082, Ukraine, E-mail: soldatkina@onu.edu.ua*

*The adsorption performance of cationic dyes (methylene blue and malachite green) on barley straw modified by citric acid has been studied. Barley straw modified by citric acid is a low-cost and eco-friendly adsorbent, however the effectiveness of the adsorbent towards cationic dyes have not yet been examined. Accordingly, kinetic, equilibrium, and thermodynamic aspects of the cationic dyes adsorption from aqueous solution were studied in order to evaluate the citric acid modified barley straw efficiency. The modified barley straw was characterized versus unmodified matter using Fourier Transform Infrared spectroscopy (FT-IR). FT-IR analysis showed that modification of barley straw using citric acid allowed us to increase the number of carboxyl groups on the straw surface. Adsorption studies were conducted on a batch process, to study the effects of contact time, concentration of cationic dyes, and temperature. The results of kinetic experiments showed that adsorption process attained equilibrium within 120 and 90 min for methylene blue and malachite green, respectively, and equilibrium time for both the cationic dyes was temperature independent. The adsorption kinetics of the cationic dyes was well described by the pseudo-second order model. The equilibrium data are analyzed by the Freundlich, Langmuir, and Temkin isotherms. The experimental data of adsorption indicated more conformity with the Langmuir isotherm model for methylene blue and malachite green adsorption on the modified straw. Furthermore, the thermodynamic parameters calculated at 293–333 K showed that the adsorption of methylene blue and malachite green on the modified straw was endothermic. Negative results of  $\Delta G^\circ$ -values (between  $-32.1$  and  $-24.6$  kJ mol $^{-1}$ ) indicated that the adsorption process was spontaneous at all the tested temperatures. Desorption of methylene blue and malachite green from the exhausted adsorbent was estimated using water and aqueous solutions of hydrochloric and acetic acids. Desorption efficiency follows the order: HCl > CH $_3$ COOH > H $_2$ O. The study has revealed that citric acid modified barley straw is an effective adsorbent and can be used as an alternative for more costly adsorbents used for cationic dyes removal from wastewater.*

**Keywords:** *modified barley straw, citric acid, cationic dyes, adsorption, equilibrium, kinetics, thermodynamics*

## INTRODUCTION

In the last few decades, the issue of synthetic dyes removal from model and real wastewater has been a matter of research in many countries [1–5] because these pollutants get introduced to the environment by activities of various industries, such as the textile, pulp and paper, leather, rubber, plastics, cosmetics, pharmaceutical, and foods. Frequently, wastewater containing synthetic dyes is discharged into the surface water bodies without any prior treatment, and they can cause serious problems to the environment and human health due to their harmfulness and toxicity [4].

To reduce the presence of dyes in wastewater, a variety of technique, including chemical precipitation, coagulation, flocculation, biodegradation, ion-exchange, oxidation, membrane separation, and adsorption on activated carbons, have been used [1, 4, 6]. However, many of these conventional methods

for treating dye wastewater have not been widely applied due to the high cost, time-consuming, low efficiency, use of toxic reagents or secondary pollution possibilities.

Currently, among the treatment methods of wastewater containing dyes, adsorption is more efficient, eco-friendly, easy to operate, and cost effective [2, 7]. Nevertheless, in the adsorption process, development of low-cost adsorbents remains a major challenge for researchers [3]. In this respect, such agricultural wastes as straw of cereal plants have attracted significant attention owing to its abundance, low cost, surface functionality, non-toxicity, and biodegradable properties [1, 5, 6].

As a rule, straw of cereal plants is the stalks of wheat, barley, corn, rice, sesame, oat, rye, and some other crops that remain after the grain is harvested. Straw represents the major fraction of lignocellulosic agricultural wastes generated

worldwide [1]. According to [8], up to 215 million metric tons of harvestable straw are available in Europe (of this, 50 % is from wheat, 25 % from corn, and 25 % from barley) and three countries (France, Germany, and Ukraine) are responsible for 50 % of the recorded straw volumes. Unfortunately, the main way of disposal for the excess straws is still incineration [1], which is not only destruction of the atmospheric environment, but also waste of resources. One of the promising ways to use this precious lignocellulosic material is to produce adsorbents [3, 5].

As a surface phenomenon, adsorption efficiency relies heavily on the surface chemistry of adsorbents. Chemical modification with various chemicals alters the structure and the surface properties of adsorbents, allows one improving their adsorption performance [1, 2]. Generally, native straw of cereal plants as an adsorbent has the low adsorption capacity and its modification using citric acid increases of carboxyl groups in lignocellulosic materials and is efficient, economical, environmentally friendly, and easily produced [9–17].

At the same time, for novel adsorbents' introduction, the adsorption studies of kinetics, isotherms and thermodynamics are essential in supplying the basic information required for the design and operation of adsorption equipment for

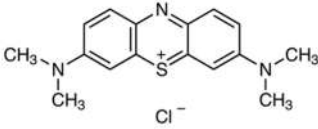
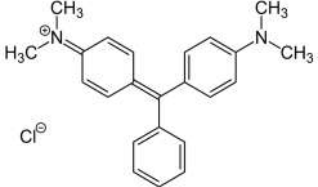
wastewater treatment. Concluding from the literature [9–17], the kinetics, equilibrium, and thermodynamics of cationic dyes adsorption on citric acid modified wheat straw [9, 10], citric acid modified corn straw [11, 12] as well as on citric acid modified rice straw [13–15] is well understood. In this paper, the focus of the study was to investigate kinetic, equilibrium, and thermodynamic aspects in order to evaluation cationic dyes (methylene blue and malachite green) adsorption efficiency on citric acid modified barley straw because these issues have not yet been examined [17].

## EXPERIMENTAL

Chemical reagents  $C_6H_8O_7 \cdot H_2O$ , NaOH, HCl, and  $CH_3COOH$  were of analytical grade and purchased from Cherkasy State Chemical Plant (Cherkasy, Ukraine). Standard buffer solutions (pH = 1.68, 6.86, 9.18) were obtained from Kyiv Plant of Reagents, Indicators and Analytical Products "RIAP" (Kyiv, Ukraine). Cationic dyes (methylene blue (MB) and malachite green (MG)) were purchased from Ukrainian company "Fine organic synthesis plant "Barva AG"" (Yamnytsia, Ukraine).

The cationic dyes characteristics are given in Table 1.

**Table 1.** Physicochemical characteristics of the cationic dyes

Characteristics	Dye	
	Methylene blue	Malachite green
Color Index No.	52015	42000
Structure		
Molecular formula	$C_{16}H_{18}N_3SCl$	$C_{23}H_{25}N_2Cl$
Van der Waals area <sup>1</sup> (nm <sup>2</sup> )	1.01	1.19

<sup>1</sup> Van der Waals areas of the cationic dye molecules were calculated using software package ChemAxon Marvin 5.2 [18]

Dyes stock solutions (1000 mg L<sup>-1</sup>) were prepared by dissolving an accurately weighed amount of the cationic dyes in distilled water and further diluted to the working solutions in the range of 10 to 1000 mg L<sup>-1</sup> at the pH value of 6.0. The solution pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a pH meter

(Universal ionomer EV-74, Gomel, Belarus) calibrated with standard buffer solutions.

All adsorption experiments were carried out at the pH value of 6.0. Our preliminary studies showed that adsorption removal of the cationic dyes on BS-C was maximum at pH = 6–10 (removal efficiency of methylene blue: 94–98 %,

malachite green: 85–92 %), while the adsorption removal of the cationic dyes on BS-C at pH = 2–4 had decreased (removal efficiency of methylene blue: 45–65 %, malachite green: 39–53 %). It was also taken into account that, the color change of the dye in solution can occur due to a chemical reaction between the dye cations and OH-ions in pH range between 8.0 and 11.0 [19].

Raw barley straw was collected from the countryside in the Odesa region, Ukraine. The agricultural waste was dried at room temperature for several days until its moisture was 8 %, and then ground in the electrical universal grinder and sieved to obtain the fraction < 250  $\mu\text{m}$ . This material was further applied for the preparation of surface modified adsorbent.

**Table 2.** Characteristics of BS and BS-C

Adsorbent	Specific Surface Area ( $\text{m}^2 \text{g}^{-1}$ )	pH <sub>pzc</sub>	COOH ( $\text{mmol g}^{-1}$ )
BS	18.8	5.1	0.9
BS-C	43.4	3.5	3.4

FT-IR analysis was used to determine the functional groups in BS and BS-C. The spectra were collected on a Fourier transform infrared (FT-IR) spectrophotometer (Perkin-Elmer Spectrometer, Waltham, MA, USA) and scanned from 800 to 4000  $\text{cm}^{-1}$ . In each case, 1.0 mg of dried sample and 100.0 mg of KBr were homogenized using mortar and pestle and thereafter pressed into a pellet using a press.

Both kinetic and isotherm tests were conducted on a batch process under atmospheric conditions in a rotary shaker (Elpan type 357, Lubawa, Poland), stirred at 150 rpm and a constant temperature (293, 313, and 333 K). The kinetic tests were carried out by varying contact time from 5 to 210 min at 35  $\text{mg L}^{-1}$  of the dye concentration and 5 g of BS-C in 500  $\text{cm}^3$  of the dye solution. The isotherm tests were conducted by contacting 10  $\text{cm}^3$  of dye solutions with different initial concentrations (20–1000  $\text{mg L}^{-1}$ ) and 0.1 g of BS-C in 50  $\text{cm}^3$  conical flasks at equilibrium time (for methylene blue and malachite green 120 and 90 min, respectively).

After adsorption, treated water was drawn and centrifuged at 4000 rpm for 10 min using laboratory centrifuge (OPN-8, Bishkek, Kyrgyzstan). The amount of the dye on the

The sample of citric acid modified barley straw (BS-C) was used from our previously research [20]. The modified barley straw was soaked in distilled water for 1 h, then washed repeatedly with distilled water to remove completely unreacted citric acid. The presence of citric acid in wash waters was tested by adding 0.1 M lead(II) nitrate solution. Washing was terminated when no turbidity from lead(II) citrate was observed. The dried BS-C was kept in plastic container and preserved in a desiccator for further use.

In our previously research [20] the characteristics of BS-C versus with unmodified barley straw (BC) were also obtained, and they are presented in Table 2.

adsorbent ( $q$ ,  $\text{mg/g}$ ), which represents the dye uptake, was calculated according to Equation (1):

$$q = \frac{C_0 - C}{m} \cdot V \quad (1)$$

where  $C_0$  is the initial dye concentration,  $\text{mg L}^{-1}$ ;  $C$  is the dye concentration after adsorption at time  $t$ ,  $\text{mg L}^{-1}$ ;  $m$  is the mass of the adsorbent;  $g$ ;  $V$  is the volume of the dye solution, L.

The concentrations of methylene blue and malachite green in liquid phase before and after adsorption were estimated by monitoring the change in absorbance values at maximum wavelengths of 665 and 617 nm, respectively, using a UV/VIS spectrophotometer (SF-56, Spectral, LOMO, St. Peterburg, Russia).

When time  $t$  is equal to the equilibrium time ( $t_e$ ), the amount of the dye on the adsorbent at equilibrium time ( $q_e$ ) was calculated using Equation (1).

In order to ensure the reproducibility of the results, all the adsorption experiments were performed in triplicate, and the average values were used in data analysis. Relative standard deviations were found to be within  $\pm 3$  %.

Desorption experiments were performed on the BS-C with preadsorbed cationic dyes using

various eluents: H<sub>2</sub>O, 0.1 M HCl, 0.2 M HCl, and 0.1 M CH<sub>3</sub>COOH. Desorption studies were carried out according to [11]. The efficiency of dye desorption removal was calculated by Equation (2):

$$S = \frac{C_d \cdot V_d}{q_e \cdot m} \cdot 100\%, \quad (2)$$

where  $q_e$  is the equilibrium amount of the dye adsorbed on the adsorbent, mg g<sup>-1</sup>;  $C_d$  is the dye concentration in solution after desorption, mg L<sup>-1</sup>;  $V_d$  is the volume of the eluent, L;  $m$  is the mass of the adsorbent, g.

The adsorption kinetics of the cationic dyes on BS-C was investigated the pseudo-first order (Equation (3)), pseudo-second order (Equation (4)), Elovich (Equation (5)), and Weber–Morris (intraparticle diffusion) (Equation (6)) kinetic models:

$$\ln(q_e - q) = \ln q_e - k_1 t, \quad (3)$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (4)$$

$$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t, \quad (5)$$

$$q = k_{id} t^{1/2} + I, \quad (6)$$

where  $q_e$  and  $q$  are the amounts of the dye on the adsorbent at equilibrium and various time  $t$ , respectively, mg g<sup>-1</sup>;  $k_1$  is the adsorption rate constant of pseudo-first order model, min<sup>-1</sup>;  $k_2$  is the adsorption rate constant of pseudo-second order model, g mg<sup>-1</sup> min<sup>-1</sup>;  $\alpha$  is the initial adsorption rate, mg g<sup>-1</sup> min<sup>-1</sup>;  $\beta$  is the desorption constant, g mg<sup>-1</sup>;  $k_{id}$  is the adsorption rate constant of the intraparticle diffusion model, mg g<sup>-1</sup> min<sup>-1/2</sup>;  $I$  is the constant, which gives an idea about the boundary layer thickness, mg g<sup>-1</sup>.

The adsorption isotherms for adsorption removal of the cationic dyes on BS-C were investigated using two-parameter adsorption models, viz., the Freundlich (Equation (7)), Langmuir (Equation (8)), and Temkin (Equation (9)):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}, \quad (7)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (8)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e, \quad (9)$$

where  $C_e$  is the equilibrium dye concentration in solution, mg L<sup>-1</sup>;  $K_F$  is the Freundlich constant related to the adsorption capacity, mg<sup>1-1/n</sup> L<sup>1/n</sup> g<sup>-1</sup>;  $1/n$  is the adsorption intensity;  $q_m$  is the monolayer capacity of the adsorbent, mg g<sup>-1</sup>;  $K_L$  is the Langmuir constant that relates to energy of adsorption, L mg<sup>-1</sup>;  $K_T$  is the Temkin equilibrium constant corresponding to the maximum binding energy, L g<sup>-1</sup>;  $b$  is the heat of adsorption, kJ mol<sup>-1</sup>.

The adsorption thermodynamic parameters (standard Gibbs free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ )) are used in the determination of spontaneity of the adsorption process, the nature of the adsorption process, and the adsorbent applicability [21]. In this study the thermodynamic parameters were calculated by equations (10)–(12):

$$\Delta G^\circ = -RT \ln K^\circ, \quad (10)$$

$$K^\circ = K_L \cdot \gamma \cdot \frac{s_o}{s}, \quad (11)$$

$$\ln K^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}, \quad (12)$$

where  $\Delta G^\circ$  is the standard Gibbs free energy change, J mol<sup>-1</sup>;  $R$  is the universal gas constant ( $R = 8314 \text{ J mol}^{-1} \text{ K}^{-1}$ );  $T$  is the absolute temperature, K;  $K^\circ$  is the dimensionless thermodynamic adsorption constant;  $K_L$  is the Langmuir constant, L mol<sup>-1</sup>;  $\gamma$  is the number of moles of pure water per liter, mol L<sup>-1</sup>;  $s_o$  and  $s$  are the van der Waals areas of water ( $s_o$  (H<sub>2</sub>O) = 0.0959 nm<sup>2</sup>) and dye molecules (the data are presented in Table 1);  $\Delta S^\circ$  is the standard entropy change, J mol<sup>-1</sup> K<sup>-1</sup>;  $\Delta H^\circ$  is the standard enthalpy change, J mol<sup>-1</sup>.

The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were evaluated from the intercept and slope of the van't Hoff plot of  $\ln K^\circ$  vs.  $1/T$ , respectively [19], assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  are temperature independent from 293 to 333 K.

The applicability of the employed models for the experimental adsorption kinetic and equilibrium data was analyzed on the basis of linear regression coefficient ( $R^2$ ), standard error (SE) and chi-square test ( $\chi^2$ ).

SE and  $\chi^2$  — values were calculated using Equation (13) and Equation (14) respectively:

$$SE = \sqrt{\frac{\sum_{i=1}^N (q_{i,calc} - q_{i,exp})^2}{N-2}}, \quad (13)$$

$$\chi^2 = \sum_{i=1}^N \frac{(q_{i,calc} - q_{i,exp})^2}{q_{i,calc}}, \quad (14)$$

where  $q_{i,calc}$  is the theoretical amount of the adsorbed dye on the adsorbent, which was calculated from one of the isotherm or kinetic model equations,  $\text{mg g}^{-1}$ ;  $q_{i,exp}$  is the experimental amount of the adsorbed dye on the adsorbent,  $\text{mg g}^{-1}$ ;  $N$  is the number of the data points.

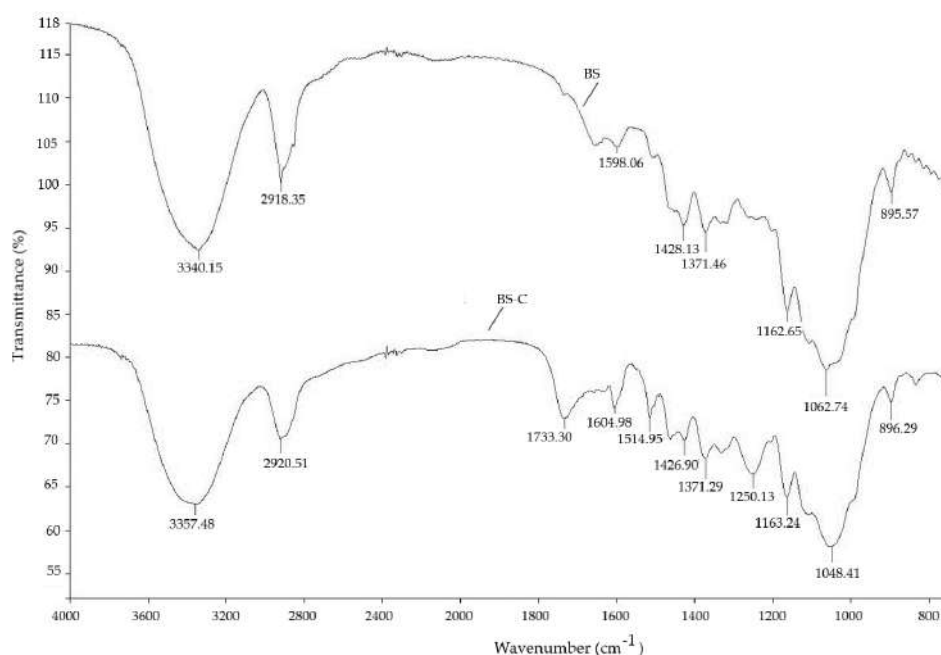
The higher values for  $R^2$  and the smaller values for SE and  $\chi^2$  were taken into account when choosing the most suitable adsorption models.

## RESULTS AND DISCUSSION

**Characterization of adsorbent.** FT-IR spectra of BS and BS-C are shown in Fig. 1. The characteristic broad peaks at 3340 and 3357  $\text{cm}^{-1}$  corresponds to  $-\text{OH}$  stretching vibration of hydroxyl functional groups in the structure of BS and BS-C, respectively [19]. The absorption bands at 2918 and 2920  $\text{cm}^{-1}$  in BS and BS-C, respectively, were assigned to stretching vibration

of  $-\text{CH}$  bond in methyl and methylene groups [7, 22]. The peaks at 1163 and 1162  $\text{cm}^{-1}$  in BS and BS-C, respectively, are related to  $\text{C}-\text{O}-\text{C}$  vibration in cellulose and hemicellulose [22]. The peak at 1371  $\text{cm}^{-1}$  is related to  $-\text{CH}$  stretching vibration of cellulose/hemicellulose and other groups that are bound to methyl radicals, which are common in lignin [22]. The peaks at 1426 and 1428  $\text{cm}^{-1}$  in BS and BS-C, respectively, are related to stretching vibration  $\text{C}-\text{O}$  from carboxyl group [22]. Comparing the IR spectra of BS and BS-C showed a strong characteristic stretching vibration absorption band of carbonyl group at 1733  $\text{cm}^{-1}$  [22] in IR spectrum of BS-C. This result reflected esterification between the citric acid and  $-\text{OH}$  groups of the cellulose in the barley straw.

The similar results indicating increase in carboxyl groups of lignocellulosic materials after their modification by citric acid were also published by Han *et al.* [10] and Gong *et al.* [14].



**Fig. 1.** FTIR spectra for BS and BS-C

**Kinetic studies.** The kinetic curves of methylene blue and malachite green adsorption on BS-C at different temperatures are shown in Fig. 2.

As can be seen from Fig. 2, the cationic dyes adsorption was rapid initially due to abundantly available active sites on the adsorbent surface that

got occupied with time and finally reached equilibrium. The time taken to reach equilibrium was found to be 120 and 90 min for methylene blue and malachite green, respectively, and temperature independent. The similar result indicating temperature independence of equilibrium time (100 min) of methylene blue

adsorption on citric acid modified wheat straw was also published by Zhang *et al.* [3].

The kinetic studies are useful for the prediction of adsorption rate and give important information for the adsorption process designing and modeling. For better understanding the

adsorption process, kinetic curves were fitted with four kinetic adsorption models (pseudo-first order, pseudo-second order, Elovich, and Weber–Morris). Parameters of the kinetic models obtained from linearized form of equations are summarized in Table 3.

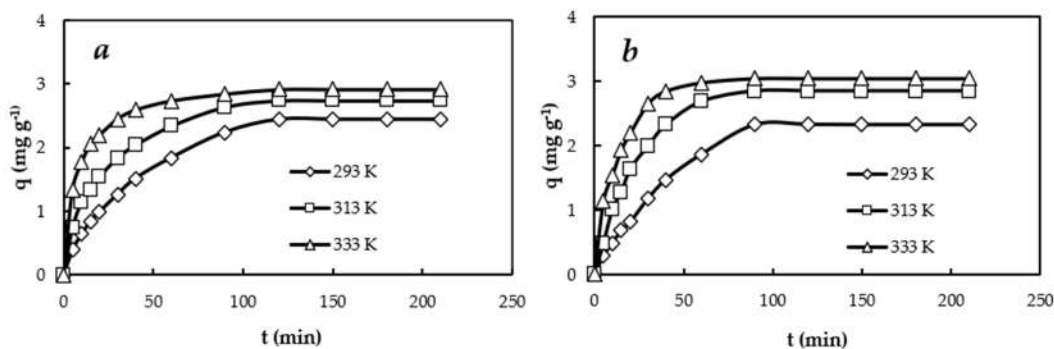


Fig. 2. Kinetic adsorption curves of MB (a) and MG (b) on BS-C at different temperatures

Table 3. Comparison of the kinetic models

Kinetic model	Parameter	MB			MG		
		293 K	313 K	333 K	293 K	313 K	333 K
Experimental data	$t_e$ (min)	120	120	120	90	90	90
	$q_e^{exp}$ (mg g <sup>-1</sup> )	2.44	2.74	2.91	2.33	2.85	3.05
Pseudo-first order	$q_e^{calc}$ (mg g <sup>-1</sup> )	2.26	2.17	1.50	2.47	3.16	2.77
	$k_1 \cdot 10^2$ (min <sup>-1</sup> )	2.21	2.85	3.93	2.71	4.75	6.33
	$R^2$	0.9995	0.9968	0.9511	0.9926	0.991	0.9964
	SE	0.23	0.64	1.50	0.14	0.33	0.31
	$\chi^2$	0.51	3.58	24.62	0.16	0.46	0.54
Pseudo-second order	$q_e^{calc}$ (mg g <sup>-1</sup> )	2.95	3.02	3.03	2.96	3.19	3.20
	$k_2 \cdot 10^2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.95	1.94	4.95	0.77	1.67	4.15
	$R^2$	0.9946	0.9985	0.9998	0.9826	0.9945	0.9989
	SE	0.08	0.07	0.04	0.21	0.15	0.15
	$\chi^2$	0.04	0.03	0.01	0.15	0.14	0.11
Elovich	$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	0.18	0.37	1.54	0.06	0.29	0.71
	$\beta$ (g mg <sup>-1</sup> )	1.55	1.51	1.88	1.38	1.15	1.37
	$R^2$	0.9666	0.9948	0.9812	0.9415	0.9915	0.9625
	SE	0.11	0.04	0.09	0.65	0.13	0.18
	$\chi^2$	0.20	0.01	0.03	0.06	0.13	0.10
Weber and Morris	$k_{id}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	0.20	0.26	0.20	0.02	0.25	0.27
	$I$ (mg g <sup>-1</sup> )	0.13	0.32	1.19	0.46	0.22	0.83
	$R^2$	0.9917	0.9768	0.8824	0.9057	0.9591	0.8667
	SE	0.26	0.08	0.15	0.76	0.10	0.22
	$\chi^2$	0.08	0.05	0.10	9.27	0.07	0.21

The data given in Table 3 showed that the predicted  $q_e$  values estimated from the pseudo-first order kinetic models in general differed from the experimental values for both cationic dyes. In

case of the pseudo-second order kinetic model, the  $q_e$  values calculated are close to the experimental values  $q_e$ . One suggestion for the differences in experimental and theoretical  $q_e$

values is that there is a time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the adsorption [23]. It can be also seen that the  $R^2$  values for the pseudo-second order model are very high and the SE and  $\chi^2$ -values are very small as compared to the pseudo-first order model. It implies that experiment results of adsorption kinetics support the assumption in the pseudo-second order model that the rate limiting step in adsorption of dyes is chemisorption [16, 23, 24]. The citric acid was used as a modifier of barley straw. It contains three carboxylic acid groups, the ester formation at modification of straw provided covalent attachment of free carboxyl groups, and these groups are very effective in capturing dye cations from aqueous solution.

The Elovich equation could also be used to describe adsorption of cationic dyes on BS-C since the  $R^2$  values are between 0.9415 and 0.9948, and the SE and  $\chi^2$  – values are more than in the pseudo-second order model but less than those in the other studied kinetic models (Table 3). It was found that the values of the initial adsorption rate and desorption constant varied as a function of temperature. The initial adsorption rate increased in 8.6 and 11.8 times for methylene blue and malachite green, respectively, as the temperature increased from 293 to 333 K. The desorption constant fluctuated with change of

temperature for both cationic dyes:  $\beta$  values decreasing when the temperature increased from 293 to 313 K and then increasing at 333 K.

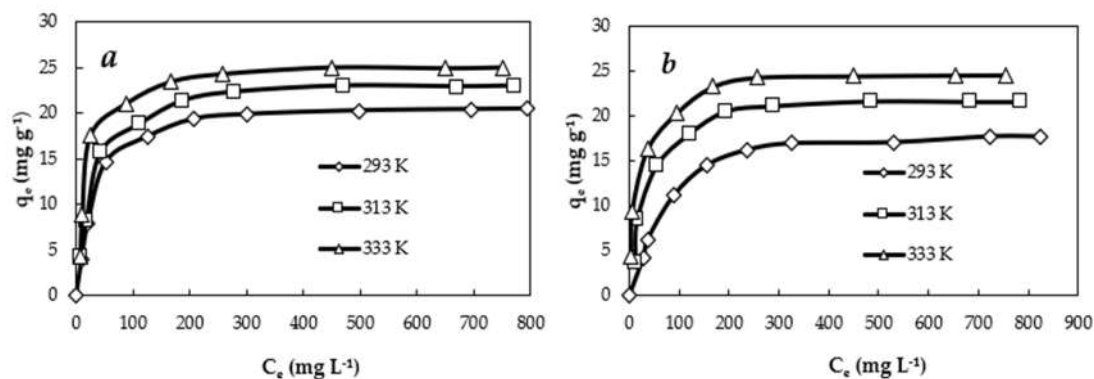
As it is listed in Table 3, in the case of the Weber–Morris kinetic model the linear plots  $q_t$  vs  $t^{1/2}$  did not have zero intercepts, it can be inferred that the cationic dyes removal on BS-C is governed by both film diffusion and intraparticle that diffusion together [23]. It was found (Table 3), in most cases the calculated values of  $k_{id}$  and  $I$  are close, which can be explained by the almost equal contribution of diffusion in the pores and surface diffusion.

**Equilibrium studies.** Equilibrium adsorption isotherms play a major role in determining the interactive behaviors between the adsorbates and adsorbents [3] and allow calculating maximum capacities of adsorbents. The adsorption isotherms of methylene blue and malachite green on BS-C at different temperatures are obtained by plotting  $q_e$  in terms of  $C_e$  and presented in Fig. 3. As can be seen from Fig. 3 the isotherms obtained are of type L according to the classification of Giles [25] which shows that the process of adsorption of the cationic dyes on BS-C could occur in monolayers.

According to Fig. 3 and Table 4, the adsorption capacity for both cationic dyes on BS-C increased as the temperature increased from 293 to 333 K, indicating that the adsorption was an endothermic process.

**Table 4.** Comparison of the isotherm models

Isotherm model	Parameter	MB			MG		
		293 K	313 K	333 K	293 K	313 K	333 K
Langmuir	$q_m$ (mg g <sup>-1</sup> )	23.15	24.81	26.60	19.46	22.73	25.13
	$K_L \cdot 10^2$ (L mg <sup>-1</sup> )	3.33	3.88	5.36	1.47	3.12	6.76
	$R^2$	0.9994	0.9997	0.9996	0.9966	0.9983	0.9998
	SE	0.79	0.70	1.44	0.89	1.11	1.20
	$\chi^2$	0.54	0.30	1.40	0.62	1.16	0.96
Freundlich	$I/n$	0.33	0.32	0.30	0.39	0.34	0.28
	$K_F$ (mg <sup>1-1/n</sup> L <sup>1/n</sup> g <sup>-1</sup> )	2.80	3.36	4.31	1.59	2.80	4.83
	$R^2$	0.8233	0.8571	0.7705	0.8519	0.7939	0.8712
	SE	3.55	3.75	4.74	2.80	3.83	4.13
	$\chi^2$	5.81	5.82	9.24	3.85	6.45	6.34
Temkin	$K_T$ (L g <sup>-1</sup> )	1.27	1.22	4.03	0.25	1.34	4.35
	$b$ (kJ mol <sup>-1</sup> )	0.767	0.721	0.829	0.682	0.778	0.855
	$R^2$	0.8979	0.9154	0.9419	0.8979	0.9154	0.9419
	SE	2.19	2.07	3.16	2.94	3.76	3.39
	$\chi^2$	3.26	2.61	5.62	7.92	10.03	8.84



**Fig. 3.** Adsorption isotherms of MB (a) and MG (b) on BS-C at different temperatures

The maximum Langmuir adsorption capacity for methylene blue increased from 23.15 mg/g at 293 K to 26.60 mg/g at 333 K, and for malachite green, it increased from 19.41 mg/g at 293 K to 25.13 mg/g at 333 K (Table 3). The positive influence of temperature on the adsorption of the cationic dyes on BS-C can be related to the enhancement of the diffusion rate of the dye cations through the boundary layer due to decrease of solution viscosity as well as increasing of mobility of the dye cations in internal pores of BS-C. The positive influence of temperature on adsorption of methylene blue and crystal violet has been also observed on citric acid-modified wheat straw [9, 10] and citric acid-modified sesame straw [16].

From the Langmuir model only one dye molecule is adsorbed on each adsorption active site to form a monolayer. The Freundlich model describes adsorption on heterogeneous surfaces following a multilayer adsorption mechanism. The Temkin isotherm considers the effect of the adsorbate interaction on the adsorbent based on the uniformly distributed binding energies. It also assumes that the heat of sorption of all the molecules in the layer decreases linearly with coverage due to adsorbate/adsorbent interactions [26].

According to Table 4, for all the temperatures,  $R^2$  values being higher for the Langmuir model than for the Temkin and Freundlich models (Langmuir > Temkin > Freundlich). In addition, this result for the Langmuir model also compliments to the error function analysis where the calculated value of SE and  $\chi^2$  are the lowest among the three isotherm models. Feng *et al.* [16] used citric acid modified sesame straw for the removal of methylene blue from the solution and

obtained that the Langmuir model gave better fit for the isotherm data than the Freundlich model. The applicability of the Langmuir model indicates as a result the use of monolayer coverage of methylene blue and malachite green on the surface of BS-S.

Temkin revealed that in physical adsorption the adsorbate is absorbed by the electrostatic force of interaction [27]. Moreover, in agreement with the cationic dyes adsorption change with temperature (Fig. 3), the adsorption process is endothermic since  $b$  values from Temkin isotherms are positive [26].

**Thermodynamic studies.** The thermodynamic parameters of adsorption ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) of methylene blue and malachite green on BS-C are shown in Table 5.

The analysis of these thermodynamic parameters reveals that the negative value of standard free energy change indicates that the adsorption of both cationic dyes on BS-C was spontaneous and thermodynamically favored. The decrease of the  $\Delta G^\circ$  values with increasing temperature from 293 to 333 K shows that adsorption is more favorable at high temperature. The  $\Delta H^\circ$ -values were positive for both cationic dyes, which indicates the adsorption was an endothermic reaction. The  $\Delta S^\circ$  - values are positive, which means that the cations of the dyes in the aqueous phase are more organized than those in the solid-liquid interface.

In addition, when  $\Delta H^\circ < 20 \text{ kJ mol}^{-1}$ , the physical adsorption is affected by van der Waals interactions [28]. Generally, a value of  $\Delta G^\circ$  in between 0 and  $-20 \text{ kJ/mol}$  is consistent with electrostatic interaction between adsorption sites and the adsorbing ion (physical adsorption) while a more negative  $\Delta G^\circ$  value ranging from  $-80$  to

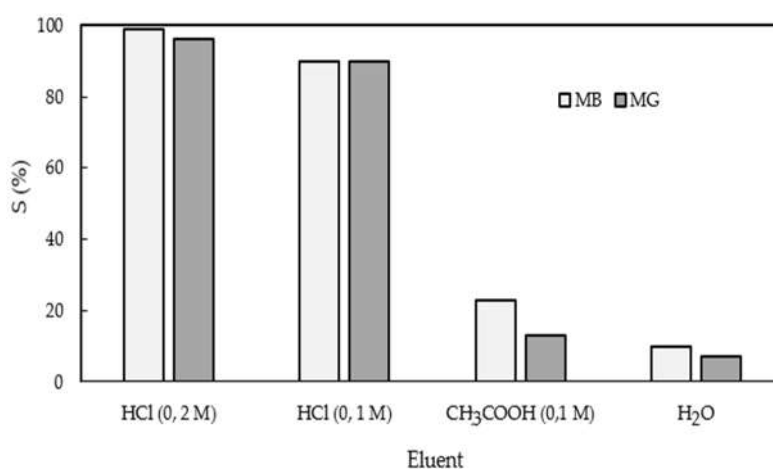


-400 kJ/mol indicates that the adsorption involves charge sharing or transferring from the adsorbent surface to the adsorbing ion to form a coordinate bond (chemisorption) [29]. The

calculated value presented in Table 5 suggests the cationic dyes adsorption on BS-C based on physisorption and enhanced by a small chemical effect [30].

**Table 5.** Thermodynamic parameters of adsorption of the cationic dyes on BS-C

Dye	T (K)	$K^{\circ} \cdot 10^{-4}$	$-\Delta G^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta H^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\circ}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
MB	293	5.6	26.6	9.6	123
	313	6.5	28.9		
	333	9.0	31.6		
MG	293	2.3	24.6	30.9	189
	313	5.1	28.2		
	333	1.1	32.1		



**Fig. 4.** Desorption of the cationic dyes from dye-loaded BS-C by different eluents

**Desorption studies.** In general, desorption studies of dyes are important to understand adsorption nature and their results can help to reuse an adsorbent in practical applications for dye removal from wastewaters [31]. Reversibility of adsorption depends on the strong (covalent and ionic bindings) and weak (van der Waals' forces and a dipole-dipole interaction) binding forces that formed between the adsorbent surface and dye ions.

In desorption studies, it is selected a certain type of eluent, an exhausted adsorbent is treated with this eluent, and it is studied the bond broke between adsorbent and adsorbate. Selection of eluent for desorption is based upon type of adsorbate-adsorbent system [10]. Desorption of methylene blue and malachite green from exhausted BS-C was estimated using 0.1 and 0.2 M hydrochloric acid, 0.1 M acetic acid, and H<sub>2</sub>O. Fig. 4 shows the desorption efficiency of these eluents. Hydrochloric acid (0.2 M) was

found as being the best eluent with efficiency of about 99 % for methylene blue and 96 % for malachite green. According to [6], acid is an effective eluent for desorption of cationic adsorbates. In this case, ion exchange process between adsorbent-adsorbate system and eluent is involved in desorption.

The number of positively charged sites on BS-C increases under acidic conditions. It can increase the desorption efficiency of the cationic dyes due: i) to the electrostatic repulsion between positively surface of BS-C and cations of the dyes; ii) to the abundance of hydrogen ions in the acidic solution and its exchange with the dye cations. Thus, the desorbing agents that can generate more cations in the solution especially hydrogen ions are more effective eluents for the cationic dyes' adsorption from the adsorbent surface [32].

Desorption efficiency of the cationic dyes from exhausted BS-C using distilled water and a

solution of  $\text{CH}_3\text{COOH}$  was obtained as follows: 10 and 23 % of methylene blue; 7 and 13 % of malachite green, respectively.

### CONCLUSIONS

In this paper, kinetic, equilibrium, and thermodynamic studies of cationic dyes adsorption (methylene blue and malachite green) on barley straw modified by citric acid were carried out. The evaluation of the kinetic studies revealed that among the kinetic models tested (pseudo-first order, pseudo-second order, Elovich, and Weber–Morris models) the pseudo-second order model better describes the adsorption kinetics for the cationic dyes on modified barley straw. The Langmuir isotherm model best fitted the data both for methylene blue and malachite green adsorption on modified

barley straw than the Temkin and Freundlich isotherm models. It was found that the maximum adsorption capacity of modified barley straw was noticed to increase with increasing of temperature from 293 to 333 K. The positive values of  $\Delta H^\circ$  confirmed the endothermic adsorption nature of the cationic dyes on modified barley straw. The negative values of  $\Delta G^\circ$  approved the favorability and spontaneity of the adsorption process. The positive values of  $\Delta S^\circ$  pointed out that the dye cations in the aqueous phase are more organized than those in the solid-liquid interface. Desorption efficiency follows the order  $\text{HCl} > \text{CH}_3\text{COOH} > \text{H}_2\text{O}$ . The results obtained from this study showed that citric acid modified barley straw in batch mode was an effective adsorbent for removing both methylene blue and malachite green from aqueous solutions.

## Адсорбція катіонних барвників на соломі ячменю, модифікованій лимонною кислотою: кінетичні, рівноважні та термодинамічні дослідження

Л.М. Солдаткіна, М.А. Янар

Одеський національний університет імені І.І. Мечникова  
вул. Дворянська, 2, 65082, Одеса, Україна, soldatkina@onu.edu.ua

У роботі досліджені адсорбційні властивості катіонних барвників (метиленового блакитного та малахітового зеленого) на соломі ячменю, модифікованій лимонною кислотою. Солома ячменю, модифікована лимонною кислотою, є дешевим та екологічно чистим адсорбентом, однак ефективність цього адсорбента щодо вилучення катіонних барвників ще не вивчена. Для визначення ефективності модифікованої лимонною кислотою соломи ячменю були досліджені кінетичні, рівноважні та термодинамічні аспекти адсорбції катіонних барвників. За допомогою інфрачервоної спектроскопії з перетворенням Фур'є (FT-IR) охарактеризували модифіковану солому у порівнянні з немодифікованою. FT-IR аналіз показав, що модифікація соломи ячменю лимонною кислотою дозволила збільшити кількість карбоксильних груп на поверхні соломи. Досліджено вплив часу контакту, концентрації катіонних барвників та температури на адсорбційне вилучення катіонних барвників. Кінетичні дослідження показали, що процес адсорбції досягає рівноваги протягом 120 та 90 хв для метиленового блакитного і малахітового зеленого відповідно, а час встановлення рівноваги для обох катіонних барвників не залежить від температури. Кінетика адсорбції катіонних барвників добре описувалася моделлю псевдодругого порядку. Рівноважні дані проаналізували за допомогою ізотерм Фрейндліха, Ленгмюра та Тьомкіна. Експериментальні ізотерми адсорбції метиленового блакитного та малахітового зеленого на модифікованій соломі ячменю найкраще описуються ізотермою Ленгмюра. Крім того, термодинамічні параметри, розраховані при 293–333 K, показали, що адсорбція метиленового блакитного і малахітового зеленого на модифікованій соломі ячменю була ендотермічною. Негативні результати величин  $\Delta G^\circ$  (від  $-32.1$  до  $-24.6$  кДж моль $^{-1}$ ) підтверджують, що процес адсорбції є спонтанний при всіх досліджених температурах. Десорбцію метиленового блакитного і малахітового зеленого з відпрацьованого адсорбента оцінювали за допомогою води та водних розчинів соляної та оцтової кислот. Ефективність різних елюентів при десорбції катіонних барвників можна описати за допомогою такого ряду:  $\text{HCl} > \text{CH}_3\text{COOH} > \text{H}_2\text{O}$ . Проведені дослідження показали, що ячмінна солома, модифікована лимонною кислотою, може бути альтернативою більш дорогим адсорбентам, які використовуються для вилучення катіонних барвників зі стічних вод.

**Ключові слова:** модифікована солома ячменю, лимонна кислота, адсорбція, рівновага, кінетика, термодинаміка

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