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Optimization of Adsorption Parameters for Removal of Cationic Dyes on Lignocellulosic Agricultural Waste Modified by Citric Acid: Central Composite Design

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Abstract: Barley straw (BS-C) and corn stalks (CS-C) modified by citric acid are hopeful adsorbents for the removal of cationic dyes from aqueous solutions. Optimization of adsorption factors to improve removal of methylene blue (MB) and malachite green (MG) on BC-C and CS-C was carried out by response surface methodology with central composite design. The effect of pH, time, dye concentration, and adsorbent dose on the removal efficiency of cationic dyes was investigated. The experimental data were in good agreement with the predicted data obtained by mathematical models. Accordingly, the maximum MB removal efficiency on BS-C of 97% was achieved with a pH of 6.4, time of 50 min, an adsorbent dose of 11 g L^{-1}, and an initial MB concentration of 26 mg L^{-1}; the maximum MG removal efficiency on BS-C of 95% was achieved with a pH of 7.2, time of 60 min, an adsorbent dose of 14 g L^{-1}, and an initial MG concentration of 24 mg L^{-1}; the maximum MB removal efficiency on CS-C of 97% was achieved with a pH of 6.5, time of 45 min, an adsorbent dose of 11 g L^{-1}, and an initial MB concentration of 20 mg L^{-1}; the maximum MG removal efficiency on CS-C of 94% was achieved with a pH of 6.6, time of 50 min, an adsorbent dose of 12 g L^{-1}, and an initial MG concentration of 24 mg L^{-1}.

Keywords: adsorption; methylene blue; malachite green; citric acid; modified barley straw; modified corn stalks; central composite design

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1. Introduction

Synthetic dyes are substances with coloring capacity used to impart color to materials in textile, paper and printing, leather, pharmaceutical, painting, plastic, cosmetics, etc. [1–3]. Synthetic dyes could be classified into three main groups based on their dissolution in water: anionic, cationic, and nonionic. Among synthetic dyes, cationic dyes have received special attention because they have carcinogenic, allergenic, and mutagenic properties [2,4]. Hence, natural reservoirs pollution due to contamination of cationic dye containing effluents can bring adverse effects to aquatic organisms and human beings [1].

The treatment of cationic dye-bearing effluents is a general problem because traditional treatment methods are not always effective. In recent decades, coagulation, flocculation, chemical oxidation, membrane separations, and adsorption have been applied to remove cationic dyes [1,3]. Among these methods, adsorption is the most efficient and simplest treatment method of the wastewater before discharging into nature reservoirs or their reuse as purified water.

Nowadays, activated carbons are the most widely used as effective adsorbents but they take significant costs to produce and regeneration. Considering Green Chemistry approaches and the importance of waste-free technologies, lignocellulosic agricultural wastes are perspective materials for the obtaining of new low-cost adsorbents. It is known that the lignocellulosic agricultural wastes have numerous advantages: availability, low cost, and easy technical feasibility [4]. However, native lignocellulosic agricultural wastes usually have low adsorption capacities, but their adsorption capacities can be increased by modification. Recently, wheat [5], rye [6], barley [7] and rice [8] straws, Jerusalem artichoke stems [7], peanut husks [9], and corn cobs [10] have been modified using citric acid and studied as adsorbents of cationic dyes. In these studies, the adsorption process was investigated by the traditional method when only one factor was changed, and other process factors were kept constant. Besides, the studies were carried out without considering of the effect of the adsorption factors each other. It should be taken into account that the conventional method of adsorption studying takes a long time and requires a great deal of experiments to determine optimum levels, which are unreliable [11,12].

The use of response surface methodology with central composite design modeling (RSM-CCD modeling) enables us to eliminate the disadvantages of the conventional method. RSM is a combination of mathematical and statistical techniques and CCD is the most widely-used design method to create a second-order response surface model in environmental processes [12]. The optimal values of adsorption factors and effect of the factors on response if factors will be over or below the chosen levels in the selected experimental variation field of each factor find by CCD. Predictions of linear and quadratic interaction effects of adsorption factors are also provided by CCD.

Table 1 summarizes recent reported adsorption studies of the cationic dyes removal based on CCD. Optimum conditions of adsorption are important information for effective implementation of process in water/wastewater treatment. As can be seen from Table 1, the efficiency of cationic dyes removal from aqueous solution can depend on adsorbent nature and structure and the factors like pH, adsorbent dose, initial dye concentration, time of adsorption, shaking speed and temperature.

Thus, CCD is widely employed as an optimization tool of the adsorption removal of cationic dyes on various adsorbents: activated carbon, ash, unmodified and modified agricultural waste, and clays [11–23]. An examination of the literature revealed that RSM using CCD was never used to maximize the removal of cationic dyes on barley straw and corn stalks modified by citric acid.

This study is aimed to establish mathematical models which describe the adsorption removal efficiency of methylene blue and malachite green from simulated wastewater on citric acid-modified barley straw and corn stalks using RSM based on CCD. To optimize the four operating factors (pH, time, initial dye concentration, and adsorbent dose), a statistical analysis was used to achieve the maximum adsorption removal of cationic dyes.

Table 1. RSM-CCD modeling in the adsorption removal of cationic dyes.

Cationic Dye	**Adsorbent**	**Factors**	**Optimum Conditions**	**Optimum Response Removal Efficiency (%) or Adsorption Capacity (mg g^{-1})**		**References**
				Experimental	**Predicted**	
Methylene blue	Activated carbon prepared from cashew nutshell	pH Adsorbent dose (m) Initial dye concentration (C) Time (t)	pH = 10 m = 2.18 g L^{-1} C = 50 mg L^{-1} t = 63 min	99.97%	100%	[11]
Methylene blue	Orange tree sawdust modified using alkaline	Concentration of NaOH (C$_1$) Adsorbent dose (m) Time (t) Initial dye concentration (C$_2$)	C$_1$ = 0.14 M m = 50 g L^{-1} t = 60 min C$_2$ = 69.5 mg L^{-1}	95.34%	100%	[13]
Crystal violet	Polyphenol-extracted coffee grounds	pH Adsorbent dose (m) Initial dye concentration (C) Time (t$_1$) Time of the adsorbent microwave activation (t$_2$)	pH = 8.53 m = 14.8 g L^{-1} C = 242.38 mg L^{-1} t$_1$ = 7 min t$_2$ = 31.97 s	99.63%	100%	[14]
Methylene blue	Modified oak waste residues	pH Adsorbent dose (m) Initial dye concentrations (C) Time (t)	pH = 6.2 m = 2 g L^{-1} C = 70 mg L^{-1} t = 160 min	85.36%	84.15%	[15]
Methyl violet	Raw date pits	pH Initial dye concentration (C) Temperature (T)	pH = 7.28 C = 60.25 mg L^{-1} T = 37.96 °C	100%	100%	[16]
Basic red 2	Raw date pits	pH Initial dye concentration (C) Temperature (T)	pH = 7.70 C = 59.77mg L^{-1} T = 38.75 °C	96.66%	100%	[16]
Acridine orange	A. esculentus seeds powder	pH Adsorbent dose (m) Initial dye concentrations (C) Time (t)	pH = 8.96 m = 1.89 g L^{-1} C = 867.71 mg L^{-1} t = 32.06 min	312.1 mg g^{-1}	313.4 mg g^{-1}	[17]
Methylene blue	Banana leaves ash	Adsorbent dose (m) Time (t) Shaking speed (s)	m = 0.239 g L^{-1} t = 180 min s = 356 rpm	93.75%	100%	[18]

Table 1. *Cont.*

Cationic Dye	**Adsorbent**	**Factors**	**Optimum Conditions**	**Optimum Response Removal Efficiency (%) or Adsorption Capacity (mg g^{-1})**		**References**
				Experimental	**Predicted**	
Basic yellow 2	Montmorillonite	Adsorbent dose (m) Initial dye concentration (C) Time (t) Temperature (T)	m = 0.6 g L^{-1} C = 60 mg L^{-1} t = 10 min T = 25 °C	97.32%	100%	[19]
Malachite green	Chrysanthemum indicum flowers	pH Adsorbent dose (m) Time (t) Shaking speed (s)	pH = 11 m = 3 g L^{-1} t = 75 min s = 150 rpm	99.3%	100%	[20]
Malachite green	Sodium alginate/ NaOH treated activated sugarcane bagasse charcoal composite beads	pH Adsorbent dose (m) Time (t)	pH = 8 m = 0.3 g L^{-1} t = 115.43 min	97.78%	100%	[21]
Methylene blue	Fe-modified banana peel	Temperature (T) Initial dye concentration (C) Adsorbent dose (m) Time (t)	T = 45 °C C = 5 mg L^{-1} m = 2.5 g L^{-1} t = 50 min	91.89%	100%	[22]
Malachite Green	Sepiolite clay	Adsorbent dose (m) Initial dye concentration (C) Time (t)	m = 26 g L^{-1} C = 77 mg L^{-1} t = 42 min	99%	100%	[23]

2. Materials and Methods

2.1. Materials

All chemicals were analytical laboratory grade and used without purification. NaOH and HCl were purchased from Cherkassy State Chemical Plant (Chercassy, Ukraine). Methylene blue (MB) and malachite green (MG) were purchased from the Ukrainian company "Fine organic synthesis plant "Barva AG"", section of Fine Organic Synthesis.

Methylene blue is a dye of thiazine type ($C_{16}H_{18}N_3SCl$, C. I. No. 52015, MW = 319.5 g mol^{-1}, λ_{max} = 665 nm). Malachite green (MG) is a dye of diaminotriphenylmethane type ($C_{23}H_{25}N_2Cl$, C.I. No. 42000, MW = 364.5 g mol^{-1}, λ_{max} = 617 nm).

Methylene blue is used for dyeing of silk, leather, plastics, paper, and cotton mordant with tannin, as well as to produce ink and copying paper in the office supplies industry [11]. Malachite green is used as staining solutions in medicine and biology, dyeing cotton, wool, leather, nylon, and silk [24]. Methylene blue and malachite green have the potential to irritate and damage human skin, the gastrointestinal tract, and eyes [25]. Chemical structures of both cationic dyes are shown in Figure 1.

MB MG

Figure 1. Chemical structure of the cationic dyes.

Samples of barley straw and corn stalks modified citric acid were used from our prior research [26]. Some characteristics of the adsorbents have been described earlier [26] and are shown in Table 2.

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

Adsorbent	**Specific Surface Area (m^2 g^{-1})**	**pH_{pzc}**	**COOH (mmol g^{-1})**
BS-C	43.4	3.5	3.4
CS-C	45.3	3.3	3.5

2.2. Methods

2.2.1. Cationic Dyes Solution Preparation

An amount of 1g of the cationic dyes was dissolved in 1000 mL of distilled water and solutions obtained were diluted with distilled water in the desired concentration. The pH of the initial dyes solutions was adjusted by adding of HCl and NaOH solutions using a pH meter (Universal ionomer EV-74, BLR).

2.2.2. Batch Adsorption Procedure

The batch adsorption experiments were carried out at a constant temperature (293 K) in a rotary shaker (Elpan type 357, Lubawa, Poland) with a shaking speed of 150 rpm under specific conditions (Table 3). Adsorption studies were carried out by 100 cm^3 of dye solutions coming in contact with different initial dye concentrations and different doses of adsorbents in 250 cm^3 conical flasks.

After each adsorption test, the adsorbent was separated by centrifugation at 4000 rpm for 10 min. Methylene blue and malachite green concentrations in the pre- and post-adsorption solutions were estimated using a UV/VIS spectrophotometer (SF-56, Spectral, LOMO, St. Peterburg, Russia) at maximum wavelengths of 665 and 617 nm, respectively.

The experimental dye removal efficiency was determined in accordance with Equation (1):

$$\alpha = \frac{C_o - C}{C_o} \cdot 100\% \quad (1)$$

where C_o and C are the concentrations of dye before and after adsorption (mg L^{-1}).

Table 3. Coded and uncoded levels of factors for the CCD.

Factors	Unit	Symbols	Coded Levels				
			−2 (−α)	**−1**	**0**	**+1**	**+2 (+α)**
			Original Levels				
pH	-	x_1	4	5	6	7	8
Time (t)	min	x_2	20	30	40	50	60
Dye concentration (C)	mg L^{-1}	x_3	5	15	25	35	45
Adsorbent dose (m)	g L^{-1}	x_4	6	8	10	12	14

2.3. Experimental Design

RSM is a collection of mathematical and statistical techniques that make it possible to get a polynomial equation in order to make statistical predictions [27]. The aim of the method is to simultaneously optimize independent variables of the process and achieve the desired response depending on the defined specification.

In this paper, four factors such as pH, time, initial dye concentration, and adsorbent dose were selected as the independent variables and the removal efficiency of dyes was selected as the dependent output response variable. Stirring rate and temperature were fixed. The levels and diapasons of independent variables (factors) can be found in Table 3.

The number of experiments (N) required for CCD was obtained in accordance with the Equation (2):

$$N = 2^k + 2k + n_o \quad (2)$$

where k is the number of independent variables (k = 4) and n_o is the number of central points (n_o = 7).

The center points were chosen to verify any change in the estimation procedure, as a measure of precision property [11].

For statistical calculations, the experimental variables X_i were coded as x_i (dimensionless values) by Equation (3):

$$x_i = \frac{X_i - X_o}{\Delta X_i} \quad (3)$$

where X_i is the independent variable; Xo is the value of X_i at the central point; and ΔX_i is the step change of value of variable X_i.

In this study a total of 31 numbers of experiments were conducted with 16 factorial points, 8 axial points, and 7 center points (Table 4). Each experiment was performed in duplicates to minimize the experimental error and to check the variation in the outcomes.

Basically, the optimization process involves three major steps [28]: (i) performing the statistically designed experiments, (ii) estimating the coefficients in a mathematical model, and (iii) predicting the response and checking the adequacy of the model. The empirical relationship between the four selected independent variables was derived from the quadratic polynomial equation described below:

$$y = b_o + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j \quad (4)$$

where y is the output response variable; x_i, x_j are the coded independent variables (factors) of adsorption process; and b_o, b_{ii}, b_{ij} are the model (regression) coefficients (i, j = 1, 2, 3, 4).

Table 4. Experimental and predicted results of the CCD model for the cationic dyes adsorption on BS-C and CS-C.

Run	**Coded Factors**				**BS-C**		**CS-C**		**BS-C**		**CS-C**	
	x_1 **(pH)**	x_2 **(t)**	x_3 **(C)**	x_4 **(m)**	**MB**				**MG**			
					α, %							
					Exp.	**Pred.**	**Exp.**	**Pred.**	**Exp.**	**Pred.**	**Exp.**	**Pred.**
1	−1	−1	−1	−1	67	69	70	71	57	55	60	59
2	+1	−1	−1	−1	78	79	82	82	65	64	66	66
3	−1	+1	−1	−1	68	66	71	70	50	56	55	51
4	+1	+1	−1	−1	81	83	85	87	76	75	76	78
5	−1	−1	+1	−1	65	64	69	67	55	53	60	57
6	+1	−1	+1	−1	78	78	81	82	62	61	65	63
7	−1	+1	+1	−1	62	63	66	67	42	44	48	49
8	+1	+1	+1	−1	85	85	89	88	71	73	73	75
9	−1	−1	−1	+1	78	78	82	83	64	66	65	69
10	+1	−1	−1	+1	88	87	91	90	76	75	78	85
11	−1	+1	−1	+1	75	75	83	81	60	63	63	71
12	+1	+1	−1	+1	90	91	93	95	86	87	88	88
13	−1	−1	+1	+1	78	76	82	80	63	64	65	66
14	+1	−1	+1	+1	87	89	91	91	77	81	76	83
15	−1	+1	+1	+1	75	75	79	79	60	60	63	69
16	+1	+1	+1	+1	96	95	99	97	85	84	86	85
17	−2	0	0	0	57	58	60	62	37	34	43	48
18	+2	0	0	0	85	83	89	86	71	73	74	76
19	0	−2	0	0	88	88	91	91	76	74	77	75
20	0	+2	0	0	92	91	95	94	80	81	81	78
21	0	0	−2	0	80	78	84	82	68	71	75	74
22	0	0	+2	0	75	77	78	80	63	68	68	70
23	0	0	0	−2	84	82	88	85	71	70	74	74
24	0	0	0	+2	98	99	99	100	90	89	89	90
25	0	0	0	0	92	91	95	94	81	80	81	82
26	0	0	0	0	91	91	94	94	80	81	80	82
27	0	0	0	0	92	91	95	94	81	81	81	82
28	0	0	0	0	90	91	93	94	77	81	81	82
29	0	0	0	0	92	91	95	94	78	81	80	82
30	0	0	0	0	92	91	94	94	80	81	80	82
31	0	0	0	0	90	91	95	94	78	81	83	82

Minitab 21 statistical software (Minitab, Inc., State College, PA, USA) was used to analyze and interpret the results of the experimental design. The software helps to determine the coefficients in regression equations, evaluate the adequacy of the obtained mathematical models, study the effects of experimental variables on dyes removal, optimize the adsorption process factors, and visualize regression equations.

3. Results and Discussion

RSM-CCD modeling was applied to optimize the adsorption conditions for methylene blue and malachite green removal using BS-C and CS-C as adsorbents. The complete design matrix with combinations of four independent variables and the experimental and predicted values of adsorption efficiencies of the cationic dyes is shown in Table 4. The values of experimental adsorption efficiencies changed from 62 to 98% for methylene blue on BS-C, from 66 to 99% methylene blue on CS-C, from 42 to 90% for malachite green on BS-C, and from 43 to 89% malachite green on CS-C. Thus, values of efficiency adsorption removal of the cationic dyes were dependent to the studied factors.

3.1. Statistical Analysis

Regression coefficients, standard errors (SE), Student's test (t values), and probabilities of significance (*p* values) for the various factors were presented in Table 5. In general, the larger the magnitude of the t value and the smaller the *p* value, the more significant the corresponding coefficient term [11]. In this study, the level of confidence was chosen as 95% ($p < 0.05$).

Table 5. Estimated regression coefficients.

Term	Coefficient	SE	t	*p*	Coefficient	SE	t	*p*
	MB on BS-C				**MG on BS-C**			
Constant	91.29	1.14	80.09	0.000	79.29	1.06	74.90	0.000
pH	7.125	0.616	11.57	0.000	8.958	0.572	15.67	0.000
t	0.875	0.616	1.42	0.174	0.792	0.572	1.38	0.185
C	−0.375	0.616	−0.61	0.551	−1.208	0.572	−2.11	0.051
m	4.625	0.616	7.51	0.000	5.375	0.572	9.40	0.000
pH^2	−5.769	0.564	−10.23	0.000	−6.957	0.524	−13.28	0.000
t^2	−1.019	0.564	−1.81	0.090	−0.957	0.524	−1.83	0.086
C^2	−4.144	0.564	−7.35	0.000	−4.082	0.524	−7.79	0.000
m^2	−0.769	0.564	−1.36	0.191	−0.457	0.524	−0.87	0.396
pH·t	1.813	0.754	2.40	0.029	4.062	0.700	5.80	0.000
pH·C	1.062	0.754	1.41	0.178	0.187	0.700	0.27	0.792
pH·m	−0.312	0.754	−0.41	0.684	0.437	0.700	0.62	0.541
t·C	0.437	0.754	0.58	0.570	−0.562	0.700	−0.80	0.434
t·m	−0.187	0.754	−0.25	0.807	0.688	0.700	0.98	0.341
C·m	0.562	0.754	0.75	0.466	1.063	0.700	1.52	0.149
	MB on CS-C				**MG on CS-C**			
Constant	94.43	1.11	85.08	0.000	80.86	1.09	73.85	0.000
pH	6.958	0.599	11.61	0.000	7.875	0.591	13.32	0.000
t	1.042	0.599	1.74	0.101	1.042	0.591	1.76	0.097
C	−0.542	0.599	−0.90	0.380	−1.125	0.591	−1.90	0.075
m	4.625	0.599	7.72	0.000	4.708	0.591	7.96	0.000
pH^2	−5.576	0.549	−10.15	0.000	−6.433	0.542	−11.87	0.000
t^2	−0.951	0.549	−1.73	0.103	−1.183	0.542	−2.18	0.044
C^2	−3.951	0.549	−7.19	0.000	−3.183	0.542	−5.88	0.000
m^2	−0.701	0.549	−1.28	0.220	−0.683	0.542	−1.26	0.225
pH·t	1.562	0.734	2.13	0.049	3.688	0.724	5.09	0.000
pH·C	1.187	0.734	1.62	0.125	−0.062	0.724	−0.09	0.932
pH·m	−0.813	0.734	−1.11	0.285	0.937	0.724	1.29	0.214
t·C	0.187	0.734	0.26	0.802	−0.562	0.724	−0.78	0.449
t·m	−0.062	0.734	−0.09	0.933	0.938	0.724	1.29	0.214
C·m	0.312	0.734	0.43	0.676	0.438	0.724	0.60	0.554

As seen in Table 5, for both cationic dyes the most significant factors were pH (x_1) and adsorbent dose (x_4) because their t values were more than the tabulated t value (2.12) and the *p* values were less than 0.05. The quadratic terms of pH (x_1^2) and the dye concentration (x_3^2) were also important for both cationic dyes. It was found that the quadratic effects of pH (x_1^2) were less significant than their respective linear effects for all systems examined. At the same time, the first-order main effect of the initial dye concentration (x_3) was less significant than its quadratic effect which showed the no-linear influence of the initial dye concentration on methylene blue and malachite green adsorption. The quadratic effect of time (x_2^2) for malachite green adsorption on CS-C was found to be more significant than its respective linear effect. The two-way interaction pH·t for all studied systems was also significant. All other two-way interactions had smaller effects and were statistically insignificant.

Thus, pH, adsorbent dose, quadratic effect of pH, and quadratic effect of initial dye concentration are the important terms and must be taken into account when predicting the removal efficiency of cationic dyes.

The regression model equations relating the removal efficiency of the cationic dyes with significant regression coefficients are given in Equations (5)–(8):

MB on BS-C

$$y = 91.29 + 7.125x_1 + 4.625x_4 - 5.769x_1^2 - 4.144x_3^2 + 1.813x_1x_2 \tag{5}$$

MG on BS-C

$$y = 79.29 + 8.958x_1 + 5.375x_4 - 6.957x_1^2 - 4.082x_3^2 + 4.062x_1x_2 \tag{6}$$

MB on CS-C

$$y = 94.43 + 6.958x_1 + 4.625x_4 - 5.576x_1^2 - 3.951x_3^2 + 1.562x_1x_2 \tag{7}$$

MG on CS-C

$$y = 80.86 + 7.875x_1 + 4.708x_4 - 6.433x_1^2 - 1.183x_2^2 - 3.183x_3^2 + 3.688x_1x_2 \tag{8}$$

The regression equations of the relationship between the independent variables (Equations (5)–(8)) and dependent response are presented in terms of the coded factors. Various signs of the coefficients in the regression equations indicate synergistic and antagonistic effects of the studied variables.

As seen in Equations (5)–(8), the pH and adsorbent dose have a strong positive effect upon efficiency removal of cationic dyes, but the pH has a more positive influence upon removal efficiency of cationic dyes than the adsorbent dose. The increasing of the pH and the adsorbent dose increases the adsorption of cationic dyes. The pH and the dye concentration have quadratic effects on dye removal efficiency, while adsorbent dose only has a linear effect. The quadratic effects of the pH and the initial dye concentration have a very strong negative effect upon responses.

The synergistic effects of the pH, antagonistic effects of the initial dye concentration of cationic dyes (basic red 2 and methyl violet) for their removal efficiency on raw date pits were found [16]. When nanoclay was used as adsorbent of basic yellow 2, the adsorbent initial dye concentration had an antagonistic effect and the adsorbent dose had synergistic effect [19]. According to [16,19], temperature and time were nonsignificant in the prediction of the adsorption removal of the cationic dyes.

3.2. ANOVA

Assessing the suitability of mathematical models was done using a variance analysis (ANOVA). To verify the statistical significance of each variable, we compared the distribution of variance (F) with the probability of the variables studied. The high values of Fischer's test coefficients (F values) with low values of probability (p values) define the significance of the regression model [13]. The higher value of the calculated F value compared with the tabulated F value in a specific number of degrees of freedom reveals the significance and high capability of the model to find the experimental results [15].

Based on ANOVA analyses (Table 6), the regression equations obtained had F value higher (24.72 and 42.66 for MB and MG on BS-C, 24.85 and 31.48 for MB and MG on CS-C, respectively) than the tabulated F value ($F_{0.05,14,18} = 2.37$) and a very low probability value ($p = 0.000$). It confirms that the proposed mathematical models were adequate.

Table 6. ANOVA of cationic dye removal efficiency.

Term	DF	Adj SS	Adj MS	F	*p*	DF	Adj SS	Adj MS	F	*p*
			MB on BS-C					**MG on BS-C**		
Model	14	3147.91	224.85	24.72	0.000	14	4685.58	334.68	42.66	0.000
Linear	4	1753.50	438.38	48.20	0.000	4	2669.50	667.37	85.08	0.000
Square	4	1313.53	328.38	36.11	0.000	4	1717.71	429.43	54.74	0.000
Two-Way Interaction	6	80.87	13.48	1.48	0.246	6	298.37	49.73	6.34	0.001
Error	16	145.51	9.09			16	125.51	7.84		
Lack-of-Fit	10	140.08	14.01	15.48	0.002	10	110.08	11.01	4.28	0.044
Pure Error	6	5.43	0.90			6	15.43	2.57		
Total	30	3293.42				30	4811.10			
			R-Sq = 95.58% R-Sq(adj) = 91.72%					R-Sq = 97.39% R-Sq(adj) = 95.11%		
			MB on CS-C					**MG on CS-C**		
Model	14	2999.46	214.25	24.85	0.000	14	3698.69	264.19	31.48	0.000
Linear	4	1708.50	427.13	49.53	0.000	4	2076.83	519.21	61.87	0.000
Square	4	1216.58	304.15	35.27	0.000	4	1367.99	342.00	40.75	0.000
Two-Way Interaction	6	74.37	12.40	1.44	0.261	6	253.87	42.31	5.04	0.004
Error	16	137.96	8.62			16	134.27	8.39		
Lack-of-Fit	10	134.25	13.43	21.69	0.001	10	127.42	12.74	11.15	0.004
Pure Error	6	3.71	0.62			6	6.86	1.14		
Total	30	3137.42				30	3832.97			
			R^2 = 95.60% R^2 (adj) = 91.75%					R^2 = 96.50% R^2 (adj) = 93.43%		

In this study, the regression models obtained were able to explain the experimental results on cationic dyes removal efficiency with $p = 0.000$. The regression model, linear model, and square model all fitted well with a 100% confidential level. Effects of the two-way interactions were not very significant in comparison to the interactive effects. Only the two-way interactions between time and pH were found to be significant for all studied systems. Therefore, the significance of two-way interactions pH with time would not be considered if the adsorption experiments were carried out as one-factor experiments.

The results obtained showed high values of the determination coefficients R^2 and R^2(adj) indicating a high significance of the models obtained for prediction (Table 5). For example, in case of adsorption of malachite green on BS-C coefficient R^2 = 97.39% indicates that the obtained mathematical model does not explain only 2.61% of the variations. The value of R^2(adj) = 95.11 for the regression equation that describes malachite green removal on BS-C less than R^2 value and corrects the value of R^2 based on sample size and the number of factors. Experimental and predicted adsorption data presented in Table 4 indicate about a good fit between the observed and the theoretical values.

The contour plots allow us to visualize the regression equations and represent optimum levels for factors and their diapasons where a response has the same magnitude. The two-dimensional contour plots describe the effect of pH and adsorption dose on the cationic dyes adsorption efficiency removal and are presented in Figure 2.

As shown in Figure 2, the increase of efficiency removal of the cationic dyes on CS-C and BS-C is observed at the pH above 6–6.5 and at an adsorbent dose above 11 g L^{-1}. The decrease of efficiency removal of the cationic dyes on CS-C and BS-C is observed with the decrease in their values.

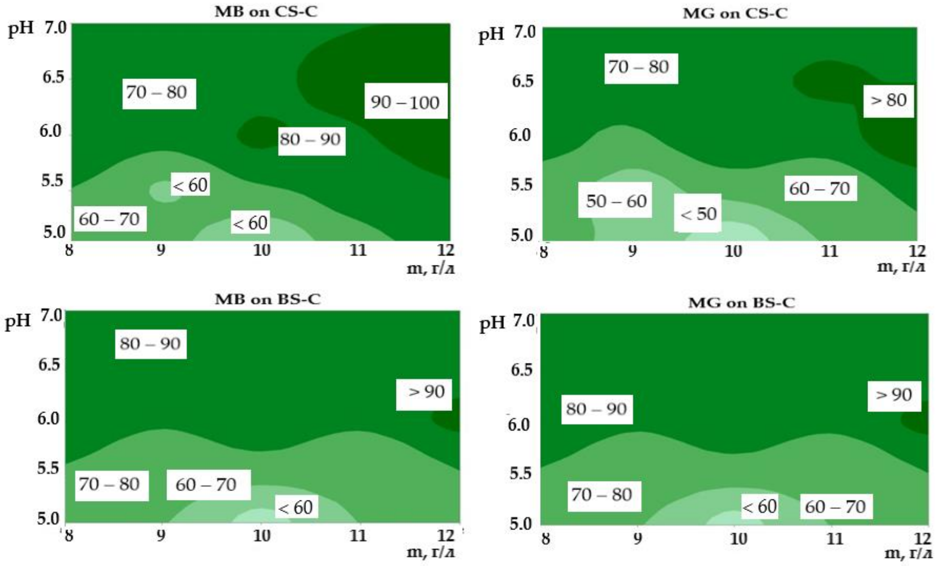

Figure 2. Contour plots showing the effects of pH and adsorption dose on efficiency removal (the corresponding numbers in % were superimposed on the colors) of the cationic dyes (values of other factors in their center point).

3.3. Optimization of the Proposed Mathematical Models

Maximum removal efficiency of the cationic dyes adsorbed on BS-C, CS-C, and the optimal adsorption conditions were predicted by the optimization algorithm in Minitab. Considering of the numerical optimization approach, the value of each independent variable studied (pH, initial dye concentration, time, and adsorbent dose) is selected from the studied range [17].

The predicted optimal adsorption conditions were re-checked in two experimental scenarios. As seen in Table 7, the experimental values differ by about 1–3% from the predicted one and fall within the 95% confidence interval, further supporting the reliability of the developed mathematical models.

Table 7. Optimum values of the adsorption parameter for maximum removal efficiency of the cationic dyes.

Adsorption Scenarios	Factors	BS-C		CS-C	
		MB	MG	MB	MG
Scenario 1	pH	6.5	7.2	6.5	6.6
	t, min	50	60	45	50
	m, g L^{-1}	12	14	11	12
	C, mg L^{-1}	25	24	20	24
	α_{exp}, %	97	95	97	94
	α_{pred}, %	100	98	98	96
Scenario 2	pH	6.0	6.0	6.5	6.0
	t, min	50	40	45	40
	m, g L^{-1}	10	14	11	12
	C, mg L^{-1}	25	25	30	45
	α_{exp}, %	97	89	96	88
	α_{pred}, %	99	90	97	90

4. Conclusions

The research aimed at establishing mathematical models for predicting and optimizing conditions of the adsorption removal of cationic dyes (methylene blue and malachite green) on barley straw and corn stalks modified by citric acid. Four adsorption parameters (pH, dye concentration, adsorbent dose, and time) for the removal of cationic dyes on modified barley straw and corn stalks were selected as independent variables. The regression equations were designed using response surface methodology with central composite design. Minitab software served to obtain and analyze regression equations. The R^2 and R^2(adj) values verified the linearity between the model results and the experimental adsorption data for removal efficiency of the cationic dyes. It was shown that only pH, adsorbent dose, and two-way interaction pH with time were found as the significant factors. The results indicated that the central composite design is an appropriate method to optimize the adsorption removal of the cationic dyes on barley straw and corn stalks modified by citric acid. Further research should focus on the optimization parameters for the adsorption of cationic dyes on barley straw and corn stalks modified by citric acid from real wastewater.

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