APPLICATION OF BOX–BEHNKEN DESIGN FOR OPTIMIZATION OF MALACHITE GREEN REMOVAL FROM AQUEOUS SOLUTIONS BY MODIFIED BARLEY STRAW

GHASEMI S.M[1,*], GHADERPOORI M[2, 3, **], MORADI M[4], TAGHAVI M[5], KARIMYAN K[6]

1: Deputy of Health, Babol University of Medical Sciences, Babol, Iran. Email: ghasemimehdi61@gmail.com

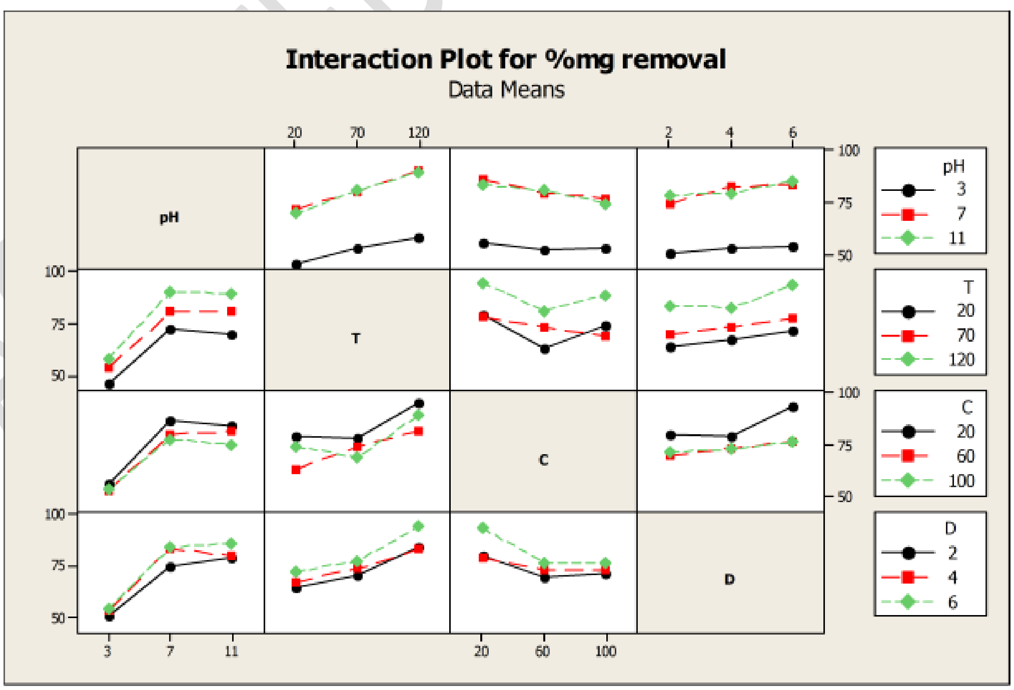
2: Department of Environmental Health Engineering, School of Health and Nutrition, Lorestan University of Medical Sciences, Khorramabad, Iran. 6813833946. Email: mghaderpoori@gmail.com
3: Nutritional Health Research Center, Lorestan University of Medical Sciences, Khorramabad, Iran

4: Master of Science, Department of Health Public, Kermanshah University of Medical Sciences, Kermanshah, Iran. 6719851351. Email: bigard.morady@yahoo.com

5: Department of Environmental Health Engineering, School of Public Health, Social Development & Health Promotion Research Center, Gonabad University of Medical Sciences, Gonabad, Iran
. Email: taghavi66@yahoo.com

6: Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
Email: kamal.karimyan@gmail.com
***Corresponding author:** GHASEMI S.M (ghasemimehdi61@gmail.com), GHADERPOORI M (mghaderpoori@gmail.com)
TEL:+989101052183, postal cod**:**4714934937

GRAPHICAL ABSTRACT



ABSTRACT

Untreated wastewater can have important effects on the environment and human. The work aimed to evaluate the effectiveness of modified barley straw to remove Malachite Green (MG) from industrial wastewater. Studied variables were pH, contact time, initial malachite green concentration, and adsorbent dosage. Box–Behnken design method was used for modelling the process of adsorption. The results of the analysis of variance showed that there is a significance relative among process parameters. The high value of R^2 (0.9753) indicated that there was a high correlation between the predicted and experimental values. The removal efficiency of malachite green increased by increasing of modified barley straw dosage, pH and contact time, and decreasing of color concentration. Remove the color was better in alkaline conditions and the best pH was equal to 9.5. The optimum contact time to remove was 120 min. The findings of this study showed that the Box-Behnken model can efficiently optimize the malachite green adsorption onto modified barley straw from aqueous solutions.

Keywords: Adsorption, barley straw, Box–Behnken design, Malachite Green

1. Introduction

Discharge of color materials to the surrounding environment have harmful effects (Demirbas, 2009). It is estimated that there are more than ten thousands of various chemical dye (Golmohammadi et al., 2016; Kamarehie et al., 2018). Annually, more than 700000 tons of dye produced worldwide (Demirbas 2009; Massoudinejad et al., 2015; Saleh et al., 2018). The results of various studies show that during the manufacturing and processing of dye, almost 10% lost and this amount lost 20 percent goes to the industrial system (Chakraborty et al., 2011). The presence color can be seen in very low concentrations (Even lower than 1 mg L^{-1}) and have adverse effects on water quality (Rafatullahet al., 2010). The harmful effects of Discharge of untreated effluent/wastewater on the environment include toxicity of aquatic lives, reduce light transmission, thus reducing photosynthesis (Gözmen et al., 2009, Ghaderpoori et al., 2016). Health effects on the human being include vomiting, jaundice, shock, quadriplegia, cyanosis, allergy, skin irritation, dermatitis, mutations and tissue necrosis, and finally cancer and death (Noroozi et al., 2007, Belala et al., 2011). Based on the solubility and insolubility, color can be classified. Soluble dyes include acidic, basic, metal, mordant, complex, direct, and reactive. Insoluble dyes include sulfur, azoic, and disperse (Gupta and Suhas, 2009). In one direction, colors are divided into three groups: cationic, anionic, and nonionic (Salleh et al., 2011). Anionic colors have less toxicity than cationic colors (El-Sayed, 2011). N-methylated diamino triphenylmethane dye (also known as Malachite Green, MG) is a cationic color. It has a high solubility in water. Its industrial applications are coloring in cotton, paper, leather, wool and silk (Saha et al., 2010; Banerjee et al., 2016; Jiang et al., 2017). So far, various methods have been used to remove them from the environment. These methods include flocculation and precipitation, ion exchange, membrane filtration, irradiation and ozonation, and electrochemical destruction. However, the methods have disadvantages such as

High cost, high sludge production, and production of by-products. Among the used processes, the adsorption is one of the most important processes that can be considered seriously. Advantages of the adsorption process are: the lower cost of operation, the need for simple force, the recovery of used adsorbent. In the adsorption process, various adsorbents can be used. Each adsorbent has advantages and disadvantages. Activated carbon is a suitable absorbent but its initial cost is high. Also, due to economic considerations, it cannot be used on a large scale for treatment of large quantity of effluents. In recent years, the use of cheap and low-cost absorbents has been accelerating (Ahmad, 2009; Akar et al., 2009; Karim et al., 2009; Sharma et al., 2012). One of the materials that can be used as a low-cost absorbent is agriculture waste. The ingredients of this waste are lignin, cellulose (as the main combination), aldehydes, alcohols, carboxylic, ketones, phenolic, and ether groups (as functional groups). The presence of various functional groups in these adsorbents can effectively affect the adsorption of pollutants (Demirbas, 2008). So far, various agriculture waste have been used such as rice husk, wheat straw, sugarcane bagasse, corncob shreds, maize cob, barley husk, almond shell, banana pith, hazelnut shell, apricot stone, orange peel, walnut shell, tree fern, olive pomace, saw dust, and wood shaving(Sharma et al., 2011). Studies have shown that modifying agricultural adsorbents with organic substances such as citric acid increases the Carboxyl group at the adsorbent surface and thereby increases the removal of pollutants (Zhu et al., 2008). So, the purpose of this study was to optimize MG adsorption using citric acid modified barley straw from aqueous solutions. Box–Behnken design (BBD) was used to develop a mathematical correlation among MG adsorption and independent variables.

2. Materials and methods

2.1. Materials and apparatus

Malachite green was obtained from Alvan sabet Company. Its molecular weight is 365 g mol^{-1}. MG chemical formula is $C_{23}H_{25}N_2Cl$. The chemical structure of MG is shown in Fig.1.

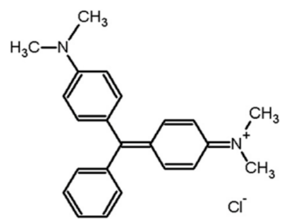


Figure 1. Chemical structure of Malachite Green

2.2. Preparation of adsorbent

At first, ground barley straw mixed with 0.6 mol L^{-1} of citric acid at the ratio of 1:12 (straw/acid, w/v) and stirred for 30 min at 20^{0C}. The acid straw slurries placed in a stainless steel tray and dried at 50^{0C} for 24 h in a forced-air oven. Then, the thermochemical esterification between acid and straw was proceeded by raising the oven temperature to 120^{0C} for 90 min. After cooling at lab temperature, the barley straw was washed with distilled water until reaching natural pH and filtered. After filtration, barley straw was suspended in 0.1 mol L^{-1} of NaOH solution at a suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali. Finally, modified adsorbent dried at 50^{0C} for 24 h and preserved in a desiccator for next (Han et al., 2010). The surface morphology of the adsorbent was characterized with Scanning electron microscope (KYKY,EM3200).

2.3. Adsorption study

All experiments were performed in the batch conditions. The variables such as the initial concentration of MG, pH and modified barley straw dosage were investigated. First, pH was adjusted using HCl (0.1N) and NaOH (0.1N). Then, the modified barley straw was added to the MG solution. The MG solution was stirred at a constant speed of 150 rpm. To separate the absorbent solution, a membrane filter 0.45 μm was used. The final concentration of MG was measured using a spectrophotometer (UV-VIS) at a wavelength of 618 nm (Chowdhury, Mishra et al. 2011, Safronov, Strelov et al. 2012). The removal of dye (%) was calculated using Eq. 1 (Ghasemi et al., 2017):

$$R, \% = (C_0 - C_e)/C_0 \times 100 \quad (1)$$

Where, C_0 and C_e are the initial and final concentrations of MG (mg l^{-1}), respectively.

2.4. Response Surface Methodology and experimental design

RSM is a statistical technique for design of experiments. The software has different methods of modelling. The main advantage of this software is to reduce the number of experiments (Zainal et al., 2013; Massoudinejad et al., 2016). Among different approaches to modelling, usually, three methods central composite design (CCD), Box–Behnken design (BBD), and Doehlert matrix (DM) is most recommended (Zolgharnein et al., 2013). In the current study, Box-Behnken design was used to determine the relationship between independent and dependent variables in MG adsorption. Design of experiments (four variables at three levels) was done using Minitab 16 software. The independent variables of input to the software were: initial MG concentration, adsorbent dosage, pH, and contact time. Table 1 shows the input variables to the model. According to the formula $N=2k(k-1)+C_0$, k is the number of variables and C_0 is the number of center points

(Zolgharnein et al., 2013), the total number of the experiment was 27. The actual experimental design matrix shows in Table 2.

Table 1. Experimental range and levels of independent process variables

Main variables	Range and levels		
	Low level (-1)	Center level (0)	High level (+1)
pH	3	7	11
Contact time (min)	20	70	120
Initial MG concentration (mg L^{-1})	20	60	100
Adsorbent dose (g L^{-1})	2	4	6

For RSM, the most commonly used second-order polynomial equation developed to fit the experimental data and determine the relevant model terms can be written as follow (Eq. 2) (Olmez, 2009):

$$Y,\% = \beta_0 + \Sigma\beta_i X_i + \Sigma\beta_{ii} X_i^2 + \Sigma\beta_{ij} X_i X_j^2 \quad (2)$$

Where, Y is the percentage of adsorbed MG, β_0 is the constant coefficient. β_i, β_{ii}, and β_{ij} are the effect of first-order, second-order, and interaction. X_i and X_j are the independent variables (Olmez 2009). The goodness of fit for this study was calculated using the coefficient of determination (R^2) and the analysis of variance. A p-value of less than 0.05 indicates model terms are significant.

Table 2. Box-Behnken design and experimental and predicted values

Run	Experimental conditions				Final concentration (mg L^{-1})	Predict concentration (mg L^{-1})
	pH	Contact Time (min)	Initial concentration (mg L^{-1})	Adsorbent Dose (g L^{-1})		
1	7	70	60	4	10.20	10.80
2	3	70	60	6	27.60	27.30
3	11	70	100	4	25.00	23.63
4	3	70	20	4	8.80	8.62
5	7	20	60	2	21.60	19.47
6	11	20	60	4	18.00	18.03
7	7	120	20	4	1.00	0.93
8	3	120	60	4	25.20	24.12
9	11	120	60	4	6.00	5.13
10	3	70	60	2	29.40	30.70
11	3	70	100	4	47.00	48.30
12	7	70	60	4	10.80	10.8
13	11	70	20	4	3.20	2.49
14	7	120	60	2	9.60	9.57
15	7	120	100	4	11.00	13.34
16	7	120	60	6	3.60	4.38
17	7	70	20	2	4.00	4.17
18	7	20	100	4	26.00	30.34
19	3	20	60	4	32.40	32.22
20	7	70	20	6	1.40	1.84
21	11	70	60	2	12.60	15.30
22	11	70	60	6	8.40	9.50
23	7	70	60	4	11.40	10.80
24	7	20	20	4	4.20	4.53
25	7	20	60	6	16.80	15.48
26	7	70	100	6	24.00	21.38
27	7	70	100	2	29.00	25.05

2.4 Adsorption kinetics and isotherms

Common isotherms and kinetic models were studied to assign the behavior of MG adsorption onto modified barley straw. The model of adsorption isotherms are studied such as Langmuir (Eq. 3), Fraundlich (Eq. 4), and Temkin (Eq. 5) in order to assign the relationship between equilibrium concentration and equilibrium capacity(Kamarehie et al., 2018). Adsorption kinetics were investigated to forecast the reaction rate of MG adsorption and adsorption mechanisms on the new adsorbent. In present work, kinetic models of pseudo-first-order (Eq. 6), pseudo-second-order (Eq. 7), Intra particle diffusion model (Eq. 8) and Elovich (Eq. 9), were studied to define the kinetics of MG adsorption onto the modified barley straw (Ghasemi et al. 2016; Mohsenibandpei et al., 2016).

$$C_e/q_e=[1/(k_L \,.\, q_m)]+[(1/q_m) \,.\, C_e)] \quad (3)$$

$$\text{Log } q_e=1/n \,.\, \log C_e+\log K_F \quad (4)$$

$$q_e = B1 \ln (k_t)+B1 \ln (C_e) \quad (5)$$

$$\log(q_e–q_t)=\log q_e–(k_1 \,.\, t/2.303) \quad (6)$$

$$t/q_t=1/(k_2.\, q_e^2)+[(1/q_e).\, t] \quad (7)$$

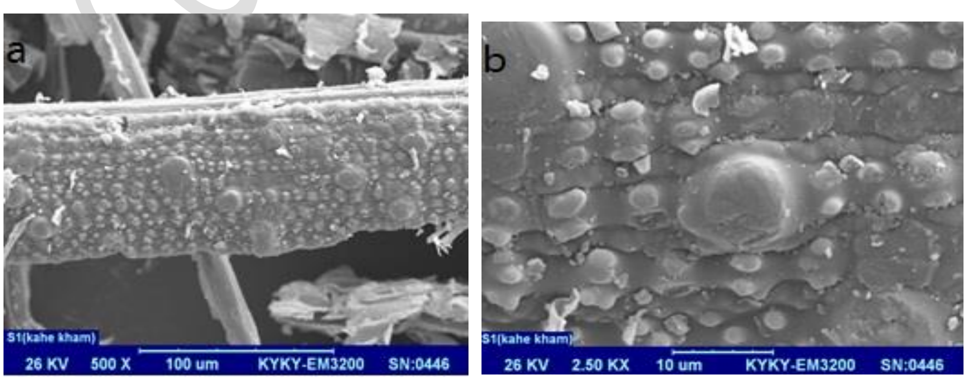
$$q_t = k_i \,.\, t^{0.5}+c \quad (8)$$

$$q_t =1/\beta \ln (\alpha\beta) +1/\beta \ln t \quad (9)$$

3. Results and discussion

3.1 Characterization of adsorbent

Scanning electron microscope (SEM) was used to analyze the surface morphology of crude and modified barley straw. As can be seen in Fig. 2, before the acid modification, the straw surface was smooth with fewer holes.



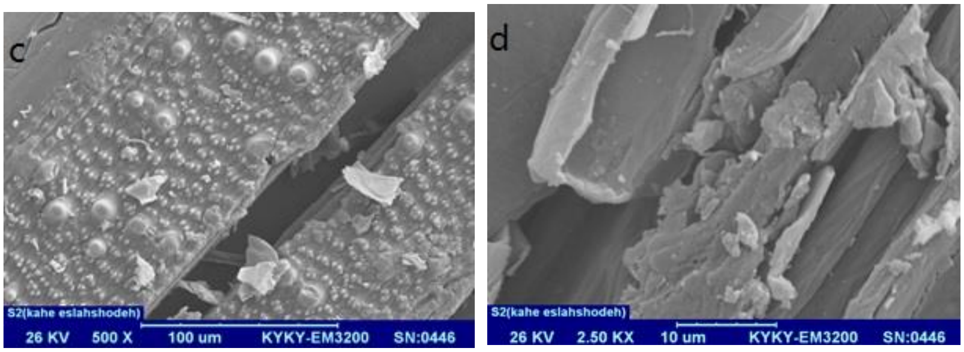


Figure 2. SEM images of the samples (a and b) crude barley straw; (c and d) modified barley straw

3.2. The validation of the response surface model

Data analysis was done using the Minitab 16 Software. For proper analysis, these assumptions should be considered: (a) The residuals have a normal distribution with zero means, (b) there is constant variance, and (c) the residuals are independent. The results of this part shown in Fig. 3. Fig. 3-a show normal-probability plots of the residuals from the least-squares fitting. These points are a straight line that confirms the error is close to zero. Fig. 3-b show random-scatter plots of the residuals versus the fitted values. This chart shows that do not have any obvious pattern. The predicted results were revealed to be randomly scattered around the zero lines (above and below the X-axis), which supports the adequacy of the proposed model. Figure 3-c show the frequencies of the residuals, and it confirmed that there are no outliers in the data. Finally, Fig. 3-d show the ordered residuals oscillate in a random pattern around the zero lines. The residuals appear to be randomly scattered along the zero lines that indicate the error terms do not correlate with each other. Tables 3 and 4 show the results of ANOVA and regression coefficients, respectively. According to Joglekar and May study proposal, square R (or R^2) should be at least 0.8 to the goodness of fit of the model (Joglekar and May, 1987). The square R for data obtained 0.97 that was higher than 0.8. According to the software instructions, the difference in adjusted R^2 and predicted R^2 should not be greater than 0.2. In this study, adjusted R^2 and predicted R^2 were 0.95 and 086 respectively. The lack-of-fit test was designed to determine whether the model is adequate to describe the observed data or whether a more complicated model should be used. Since the P-value for lack of fit in the ANOVA is greater or equal to 0.05, the model appears to be adequate for the observed data at the 95% confidence level (Simsek, Özdemir et al. 2013). Besides, the F value for lack-of-fit is insignificant (p_{value}=0.07>0.05) thereby confirming the validity of the model. Hence, the response surface model developed in this study for predicting MG removal efficiency was considered to be satisfactory. By ignoring the insignificant terms (p_{value}>0.05) in Table 3, the model equation (Eq. 10) can be written as:

$$Y=82+13.83pH+8.75T-4.08C+3.83D-14.62(pH)^2 \quad \text{(coded units)} \quad (10)$$

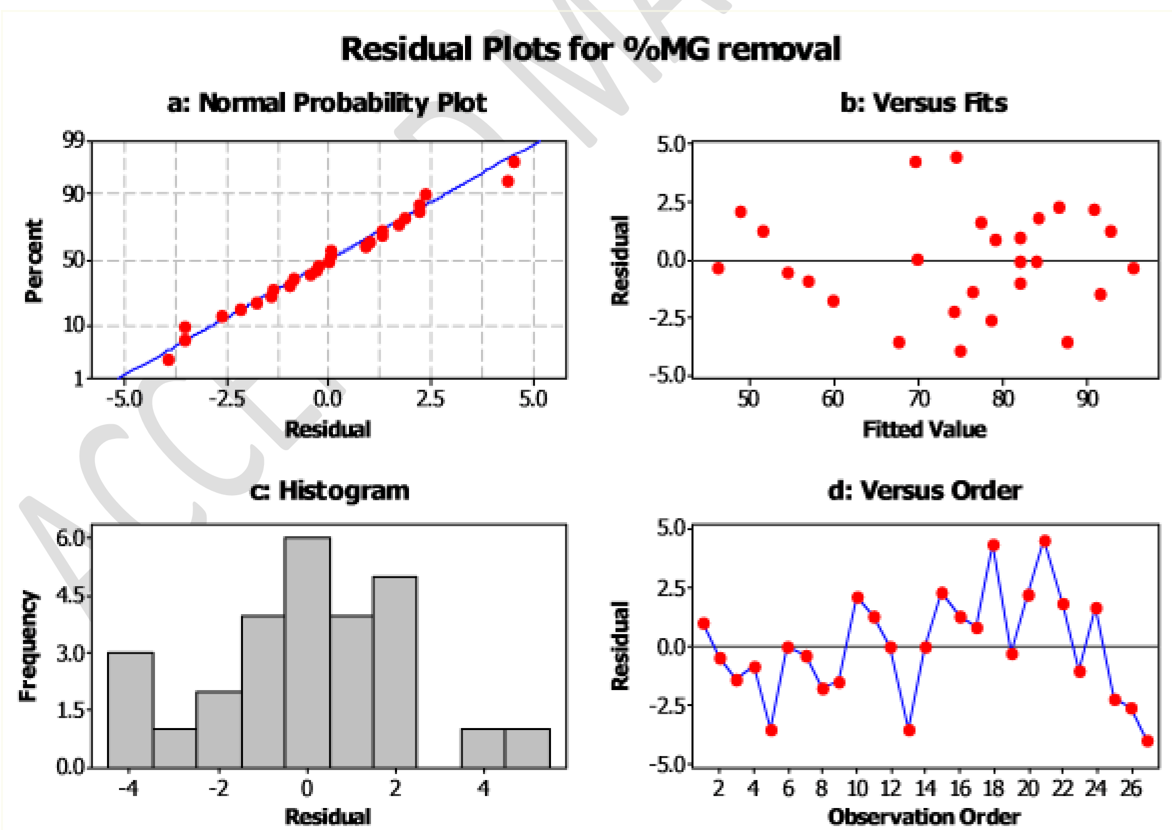


Figure 3. Residual plots for MG adsorption on the modified barley straw

Table 3. Estimated regression coefficients for MG adsorption onto modified barley straw

term	Coef.	SE Coef.	T	P_{value}
Constant	82	1.88	43.61	0.000
pH	13.83	0.94	14.72	0.000
T	8.750	0.94	9.31	0.000
C	-4.08	0.94	-4.34	0.001
D	3.83	0.94	4.08	0.002
pH*pH	-14.62	1.41	-10.37	0.000
T*T	-0.50	1.41	-0.35	0.729
C*C	0.75	1.41	0.53	0.605
D*D	-1.8750	1.4101	-1.330	0.208
pH*T	2.0000	1.6282	1.228	0.243
pH*C	-1.5000	1.6282	-0.921	0.375
pH*D	1.0000	1.6282	0.614	0.551
T*C	-0.2500	1.6282	-0.154	0.881
T*D	0.5000	1.6282	0.307	0.764
C*D	-2.0000	1.6282	-1.228	0.243

R^2 = 97.53% R^2(Adj.)=94.66% R^2(Pred.) = 85.93%

Table 4. ANOVA table for MG adsorption in the Box–Behnken design

Source	DF	Seq SS	Adj SS	Adj MS	F value	P-value
Regression	14	5031.42	5031.42	359.39	33.89	0.000
Linear	4	3591.50	3591.50	897.88	84.67	0.000
pH	1	2296.33	2296.33	2296.33	216.55	0.000
T	1	918.75	918.75	918.75	86.64	0.000
C	1	200.08	200.08	200.08	18.87	0.001
D	1	176.33	176.33	176.33	16.63	0.002
Square	4	1393.67	1393.67	348.42	32.86	0.000
pH*pH	1	1363.27	1140.75	1140.75	107.58	0.000
T*T	1	0.31	1.33	1.33	0.13	0.729
C*C	1	11.34	3	3	0.28	0.605
D*D	1	18.75	18.75	18.75	1.77	0.208
Interaction	6	46.25	46.25	7.71	0.73	0.637

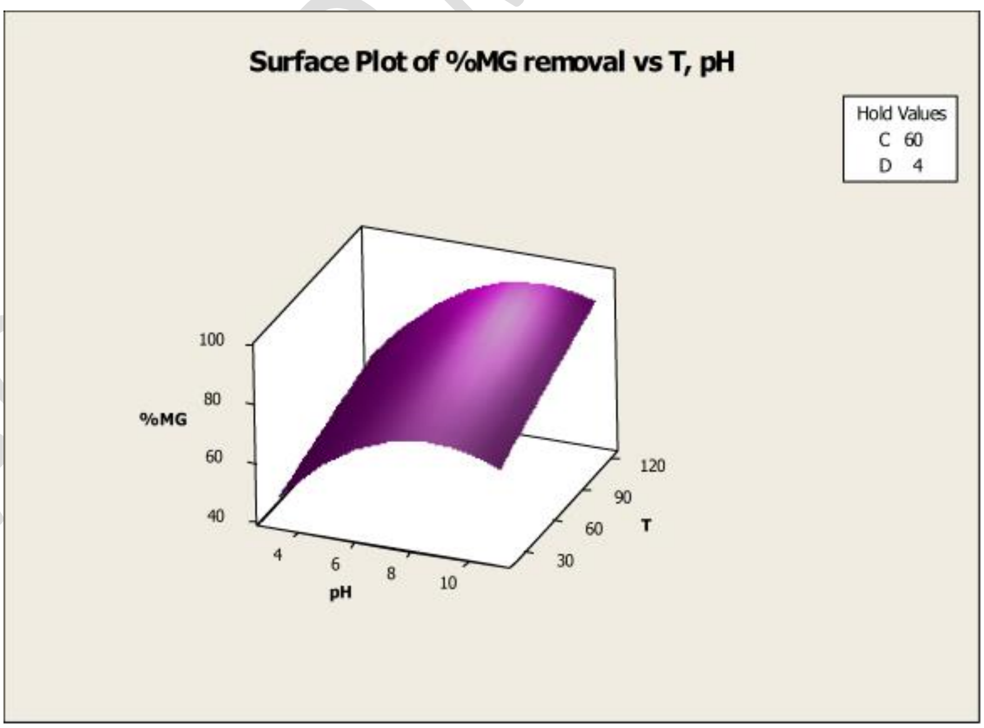
pH*T	1	16	16	16	1.51	0.243
pH*C	1	9	9	9	0.85	0.375
pH*D	1	4	4	4	0.38	0.551
T*C	1	0.25	0.25	0	0.02	0.881
T*D	1	1	1.	1	0.09	0.764
C*D	1	16	16	16	1.51	0.243
Residual error	12	127.25	127.25	10.6		
Lack-of-Fit	10	125.25	125.25	12.53	12.53	0.076
Pure Error	2	2	2	1		
Total	26	5158.67				

3.3. The effect of modified absorbent on MG adsorption

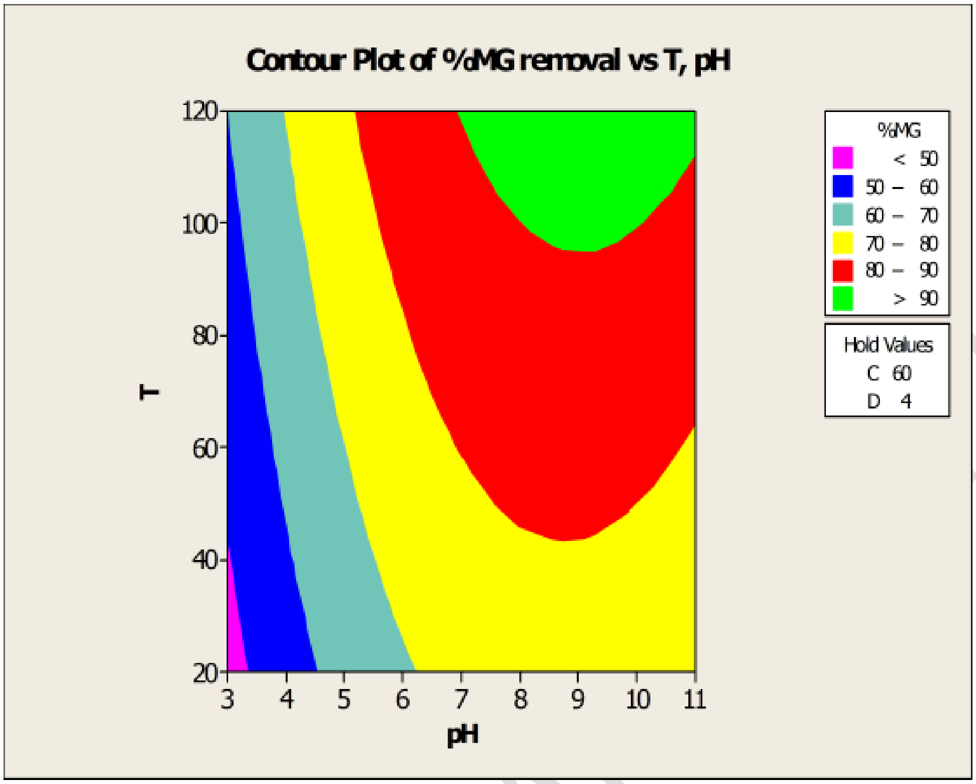
So far, many adsorbents have been modified with agents such as mineral and organic acid solutions (e.g. hydrochloric acid, phosphoric acid, tartaric acid, citric acid, thioglycolic acid), basic solutions (e.g. NaOH), etc (Han et al., 2010). Wong et al used modified adsorbent by carboxylic acids like salicylic acid, oxalic acid, tartaric acid, mandelic acid, malic, and nitrilotriacetic acid to remove Cu (II) and Pb (II). The findings showed that the adsorption capacity of modified adsorbent for these pollutants has increased (Wong et al., 2003). Zhu et al used tartaric acid modified maize hull (modified by free carboxyl groups) to remove Cu from aquatic solutions. The final results showed that the adsorption capacity of modified adsorbent for Cu(II) enhanced (Zhu et al., 2008). In another study, Yang et al used modified pine sawdust by CA to remove Ni (II), Cu (II), Cd (II), Pb (II), and Zn (II). The results showed that modified adsorbent enhanced the adsorption of these elements (Yang et al., 2010). In the present study, barley straw adsorbent was modified by citric acid. The modified adsorbent is new and biodegradable. Modification by acid also breaks the covalent bonds among lignocelluloses, hydrolyzing hemicelluloses, and depolymerizing lignin thereby increasing the exposure of cellulose which further enhances the adsorption properties of barley straw (Chakraborty et al., 2013). Modification with CA also can enhance the contact surface between adsorbent and pollutants (Han et al., 2010).

3.4. Effect of pH and contact time on MG removal

The interaction effects of pH and contact time of MG show in Fig. 4 and Fig. 6. The findings showed that with decreasing pH and contact time, MG adsorption decreased. The pH_{zpc} of modified barley straw is 5.6, thus it is negatively charged at $pH>pH_{zpc}$ and is positively charged at $pH<pH_{zpc}$. On the other hand, MG can show a different cationic ($pH>pK_a$) or anionic ($pH<pK_a$) structure due to pK_a value (pK_a=6.9). Thus, by increasing pH(alkaline conditions), the electrostatic attraction force between the negative surface of the adsorbent and the cationic dye increases the removal efficiency (Güler et al., 2019). At acidic conditions, carboxyl group becomes a non-ionic form group ($-CO_2H$) that this form is not suitable for adsorption (Gong et al., 2009). The results showed when the contact time increases, MG adsorption improved. According to Rastogi et al findings, the cause of this increase can be the presence of vacant sites of adsorption onto the modified adsorbent surface (Singh et al., 2005).



a

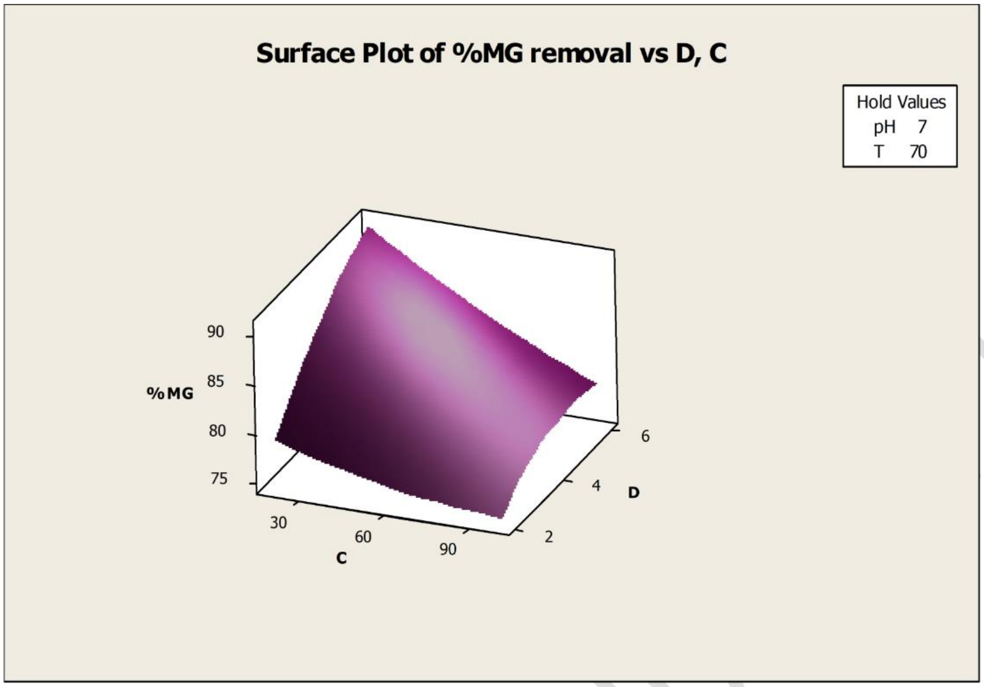


b

Figure 4. Response (a) surface plot and (b) contour plot of the MG removal efficiency (%) as a function of contact time and pH

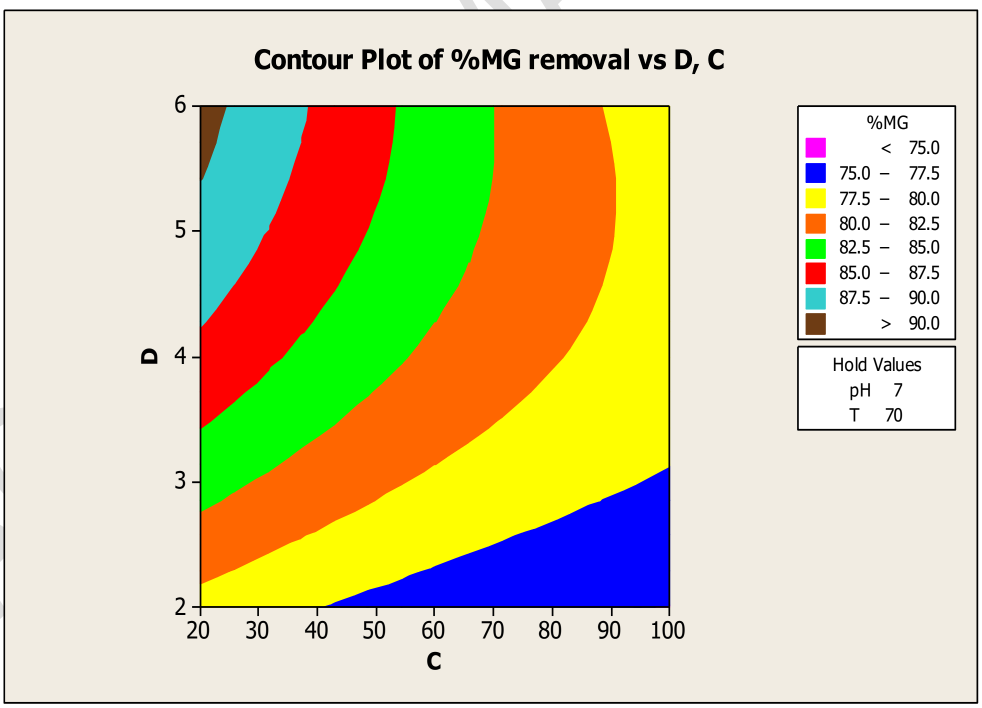
3.5. Interaction Effects of modified barley straw dosage and MG concentration onto MG adsorption

The interaction effects of adsorbent dosage and initial concentration of MG show in Fig. 5 and Fig. 6. The best adsorption of MG is in an adsorbent dose of 6 g L^{-1}. One of the reasons for increasing MG adsorption by increasing the adsorbent dose can be because of the increase in the number of adsorption sites. Various studies confirm this issue (Tilaki et al., 2014). By increasing the MG concentration, removal efficiency decreased. This reduction in removal efficiency can be due to the saturation of sorption sites onto modified barley straw (Deniz and Karaman, 2011).



Surface Plot of %MG removal vs D, C
Hold Values
pH 7
T 70
%MG
90
85
80
75
30
60
90
C
2
4
6
D

a



Contour Plot of %MG removal vs D, C
%MG
< 75.0
75.0 – 77.5
77.5 – 80.0
80.0 – 82.5
82.5 – 85.0
85.0 – 87.5
87.5 – 90.0
> 90.0
Hold Values
pH 7
T 70
D
2
3
4
5
6
20
30
40
50
60
70
80
90
100
C

b

Figure. 5. Response (a) surface plot and (b) contour plot of the MG removal efficiency (%) as a function of adsorbent dosage and MG concentration

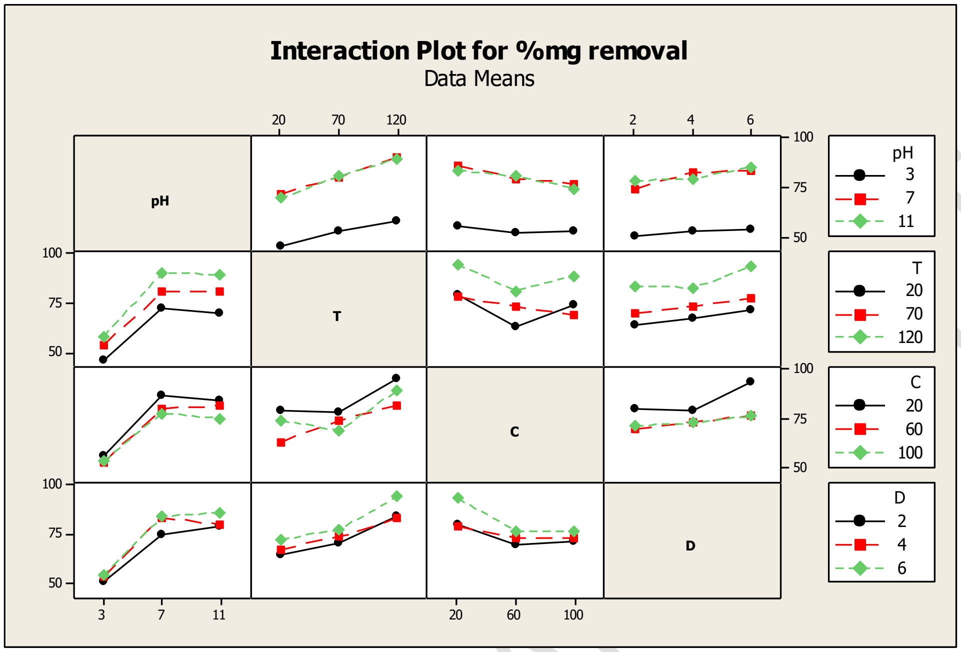


Figure. 6. The interaction effects of the main factors affecting MG adsorption

3.6. Optimization and model validation

The main aim of optimization is to determine the optimum values of independent variables. In this software, the optimization of independent variables is done in three methods: graphical, numerical, and point prediction. In this research, the numerical optimization method was used. To optimize, the dosage of modified barley straw at the minimum level, MG concentration at the maximum level, pH in the range, and for contact time in the range were set for maximum desirability. Optimized variables are shown in Figure 7. The best local maximum was found to be at the pH 9.54, initial MG concentration of 20 mg L^{-1}, modified barley straw dosage of 6 g L^{-1}, and contact time of 120 min. For comparison, MG removal efficiency using several other adsorbents are presented in Table 5. As can be seen, MG removal efficiency by modified barley Straw is almost higher than other studies.

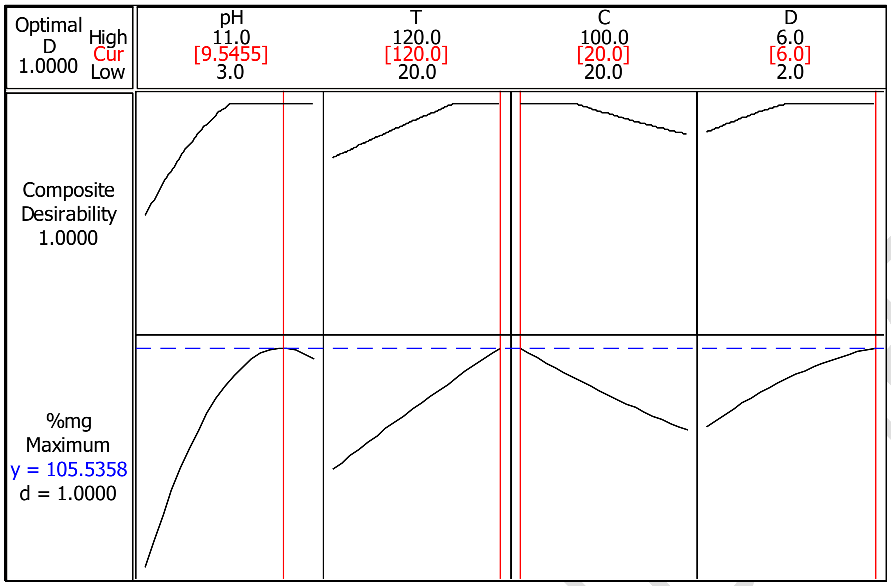


Figure 7. Optimized variables for MG adsorption onto modified barley straw

Table 5. Comparison of the removal efficiency of MG by RSM

Adsorbent	Methods of response surface methodology	Removal efficiency (%)	Reference
magnetic litchi pericarps	BBD	99.5	(Zheng et al., 2015)
lime-peel activated carbon	CCD	94.6	(Ahmad et al., 2017)
Yarrowia lipolytica ISF7	CCD	99.8	(Asfaram et al., 2016)
Chlorella vulgaris	BBD	91.6	(Kousha et al., 2013)
Scenedesmus quadricauda	BBD	73.4	(Kousha et al., 2013)
Oak wood activated carbon	CCD	99.9	(Hajati et al., 2015)
tamarind seed	CCD	99.3	(Rajeshkannan et al., 2011)
sepiolite	CCD	99	(Coruh and Elevli, 2014)
immobilized dead yeast cells	BBD	96.2	(Singh et al., 2012)

Cinnamon bark	CCD	98.2	(Güler et al., 2019)
Barley Straw	BBD	94(Experimental) 100(0ptimized)	present study

3.7. Adsorption isotherms and kinetics

The evaluation of reaction kinetics is essential in order to determine the factors affecting the reaction rate. To better understand the MG adsorption mechanism on Modified Barley Straw, kinetics models were calculated. The study of the different kinetics to forecast the adsorption rate is beneficial for design and modelling a process (Zhao et al., 2014). To compute the reaction kinetics of malachite green (MG) adsorption, pseudo-first order, pseudo-second-order, intraparticle diffusion, and Elovich were used. Fig. 8 presents the kinetics's models of pseudo-first-order (a), pseudo-second-order (b), intraparticle diffusion (c), and Elovich (d). Table 6 presents the calculated kinetic models and kinetic constants for malachite green adsorption. As can be showed in Table 6, the coefficient of determination (R^2) for the pseudo-second-order was greater than the others (R^2=0.9926). As a result, the MG adsorption on Modified Barley Straw could be well represented by the kinetic model of pseudo-second-order. In this model assumes which or chemisorption or chemical adsorption may be the controlling phase of the reaction rate in the adsorption process (Salleh et al., 2011).

The adsorption isotherms were investigated in order to predict the adsorption capacity of Modified Barley Straw to MG as well as its adsorption mechanisms. The MG adsorption isotherms on Modified Barley Straw were studied by changing the initial MG concentration in the range of 1-100 mg L^{-1}. To study the experimental data of MG adsorption, the isotherms models Langmuir, Freundlich, and Temkin were investigated. Fig. 9 presents isotherm models Langmuir (a), Freundlich (b), and Temkin (c). Table 7 presents the calculated isotherms models and kinetic constants for MG adsorption. As can be showed in Table 7, the coefficient of determination (R squared or R^2) for the Langmuir was greater than Freundlich and Temkin (R^2=0.9975). As a result, the MG adsorption on Modified Barley Straw could be well represented by the isotherm model of Langmuir. The model (Langmuir isotherm) define monolayer adsorption of a pollutant onto an absorbent (Ghasemi et al.,2015). Based on the Langmuir isotherm model, the maximum capacity of MG adsorption onto Modified Barley Straw was 6.66 mg g^{-1}.

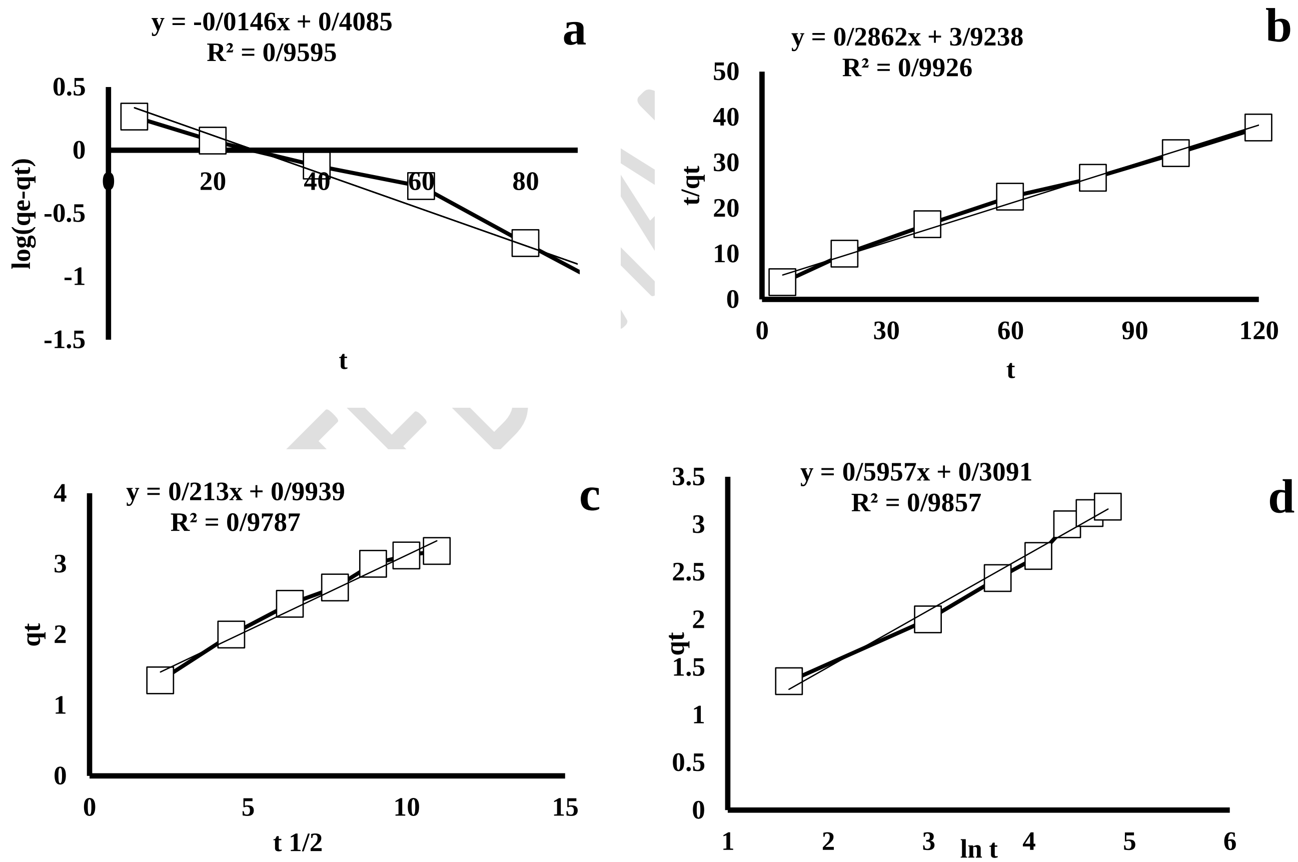


Figure 8. The kinetics's models (a: pseudo-first-order b: pseudo-second-order c: Intra particle diffusion d: Elovich)

Table 6. The adsorption kinetics constants for MG removal

	R^2	q_e	k_1	k_2	k_i	α	β
Pseudo First Order	0.9594	2.56	0.032	-	-	-	-
Pseudo Second Order	0.9926	3.49	-	0.0209	-	-	-
Intra Particle Diffusion	0.9787	-	-	-	0.99	-	-
Elovich	0.9857	-	-	-	-	0.845	2.87

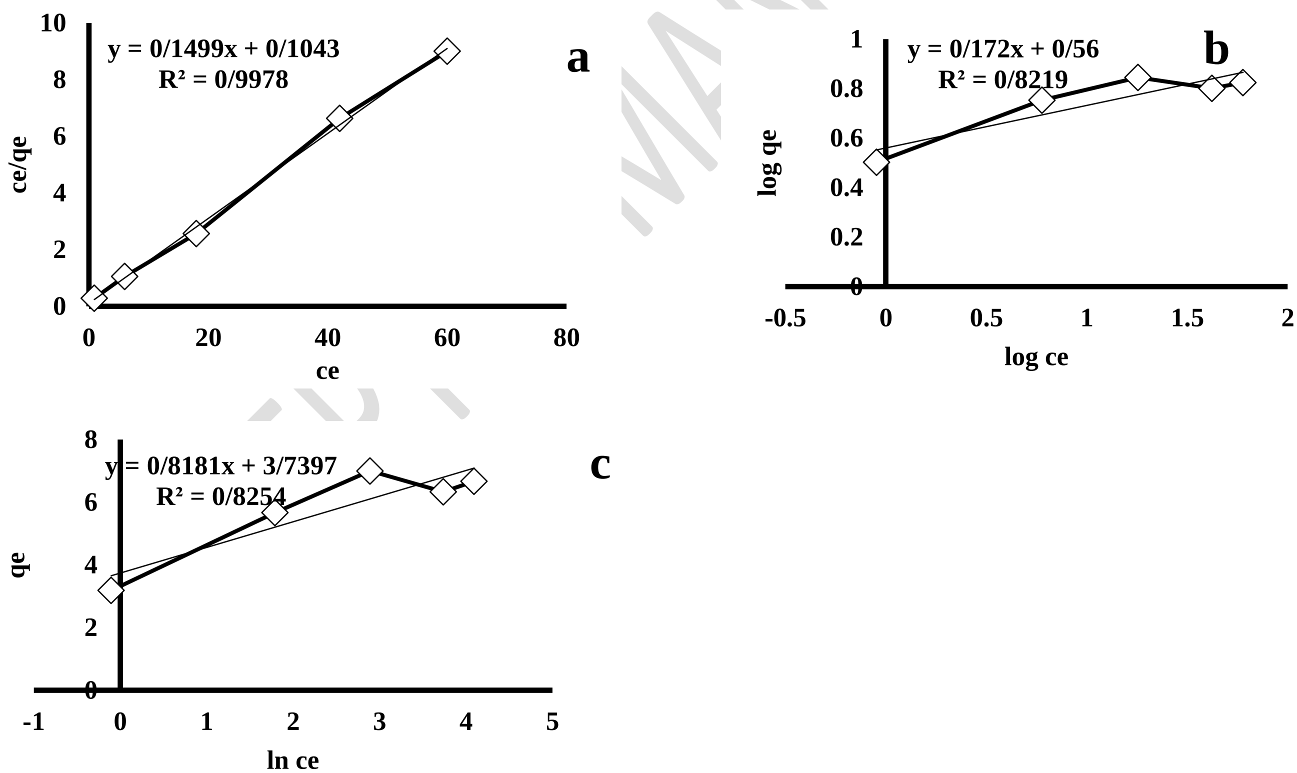


Figure 9. Isotherm models: a) Langmuir, b) Freundlich, and c) Temkin

Table 7. The adsorption isotherms constants for MG removal

	R^2	q_m	K_l	k_f	k_t	n	B_1
Langmuir	0.9975	6.66	0.75	-	-	-	-
Freundlich	0.8219	-	-	3.63	-	5.81	-
Temkin	0.8254	-	-	-	99.97	-	0.81

4. Conclusion

In this research, straw was modified with citric acid according to previous studies. The Box–Behnken design was applied for the modelling and the optimization of MG adsorption. The development of mathematical model and optimization for removal of MG using statistical design of experiments appears to be a useful tool for prediction and understanding of interaction effects between process variables using BBD. The optimization modelling suggested the optimum values of the selected four independent process variables as the initial MG concentration 20 mg l^{-1}, contact time 120 min, initial solution pH 9.54, and the adsorbent dose 6 g l^{-1}, to achieve the maximum reduction of the MG. So, the experimental results showed that under optimized conditions, modified barley straw can be used as an adsorbent for the adsorption of MG in aqueous solutions.

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