International Journal of Agriculture, Forestry and Life Science, 2 (1) 2018, 1-14

IJAFLS

ORIGINAL PAPER

e-ISSN: 2602-4381 Received: 21.01.2018 Accepted: 14.05.2018 Published: 15.06.2018

ADSORPTION CAPACITY FOR THE REMOVAL OF ORGANIC DYE POLLUTANTS FROM WASTEWATER USING CAROB POWDER

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Abstract

In this study, Carob powder was used as the adsorbent to remove the aqueous solvent paint. The as-prepared carob powder was structurally characterized by scanning electron microscopy(SEM), transmission electron microscopy (TEM). In the experiments, six inputs pH (2-8), ultrasound frequency (50-150 hz), particle size (50-150 µm), adsorption temperature (25-40 °C), solution concentration (10-30 mg/L) and adsorption time (120-360 min) were examined using the statistical Box-Behnken design with parameters. The quadratic model was selected with the coefficient (R^2) found 0.8899 and 0.9830 in the experimental data. Under the optimum conditions (pH= 5.85, ultrasound frequency= 36.40 Hz, particle size= 137.63 µm, adsorption temperature= 25.38℃, solution concentration= 29.30 mg/L and adsorption time= 267.63 min) 6 different experimental setups were prepared. The average amount of dye recovery obtained from the test results was found to be 256,4355 mg/g. As a result of the present work, it was seen that carob powder could be a strong alternative adsorbent for methylene blue removal.

Keywords: Methylene blue, adsorption, Ultrasound-assisted, response surface methodology, Box-Behnken design

INTRODUCTION

Wastewater, food, carpet, rubber, cosmetics, paint, textile, leather, paper, plastic and so on. a wide variety of industrial materials are used (Chiou and Li, 2003). The wastes in these industries are discharged into the surrounding rivers, which causes serious damage to the environment (Aksu and Tezer, 2001). In addition, problems such as discharging wastewater, increasing the toxicity of the waste material and increasing the chemical oxygen demand also arise (Bulut and Aydın, 2006). Waste products are a major problem that damage the environment (Lorenc-Grabowska and Gryglewicz, 2007). Wastewaters containing paint materials are very difficult to treat because they are resistant to aerobic digestion and are resistant to light, heat, and oxidation because of the presence of dyestuffs, stubborn organic molecules (Crini, 2006; Ravi et al., 1998, Sun and Tang, 2003). Today, the increase in the use of synthetic fines greatly affects pollution. More than 100,000 different chemical paints were produced in the market. It is estimated that the production of dye and dye intermediates in the world is 7 × 108 kg / d for each year (McMullan et al., 2001, Toh et al., 2003). Emptying waste paint into water sources affects life and food in a negative way. These stains have been shown to cause mutagenic and skin irritation (Lorenc-Grabowska and Gryglewicz, 2007) in water life as well as diseases such as mutagenic, carcinogenic and allergic dermatitis. There is an increasing interest in the inclusion of healthy organic productions, especially fruits in the human diet mainly for the health benefits associated with their consumption (Okatan et al., 2015; Okatan et al., 2017).

In recent years, removal of dyes has been effective in the by osmosis, filtration (Lorenc-Grabowska and Gryglewicz, 2007; Malik and Saha, 2003; Mittal, 2006), oxidation processes, nanofiltration, chemical precipitation, ion exchange and chemical coagulation/flocculation.

Biological processes are not enough to remove water from the water. In recent years, adsorption techniques have begun to gain considerable importance in the treatment of sewage treatment methods. Active carbon production is very effective and widely used due to its excellent adsorption ability (Crini, 2006; El-Geundi, 1991). A low-cost alternative to an adsorbent was born as an alternative to activated carbon at high cost during work. These include digestive bacteria (Nassar and El-Geundi, 1991; Mckay et al., 1998), corn cobs (El-Geundi, 1991), sunlight (Sun and Xu, 1997), ashes (Gupta et al., 2000) gets. (Annadurai et al., 2003), mud (Weng et al., 2003), fungal biomass (Basibuyuk and Forster, 2003) (Namasivayam et al., 1996), red mud (Namasivayam and Arasi, 1997), coconut shell (Namasivayam et al., 2001), Neem leaf (Bhattacharyya and Sarma, Ho et al., 2005).

In recent years, discoveries have been made to develop cheaper and more effective adsorbents. As agriculture and other wastes are cheaper, the trend towards different alternative materials for adsorbents has increased (Bhattacharyya and Sarma, 2005). Also clay materials such as bentonite, kaolinite, perlite, zeolites; Agricultural waste such as pulp, corn cob, rice husk, coconut shell; industrial wastes such as waste carbon mud, metal hydroxide mud; chitosan, peat; adsorbents such as starch, cyclodextrin, cotton (Crini, 2006) are used (Ferrero, 2007). Methylene blue (MB) is one of the best frequently used dyes for cationic dyes (Fig. 1). Carob tree Turkey's Aydin, Mersin, Antalya, Mugla and is grown in the provinces of Burdur (Tunalıoğlu and Özkaya, 2003; war and others, 1997). In some studies, it has been reported that carob bean is an easy and inexpensive material for benzodiazepine receptors (Makris and Kefalas, 2004; Avallone et al., 2002).

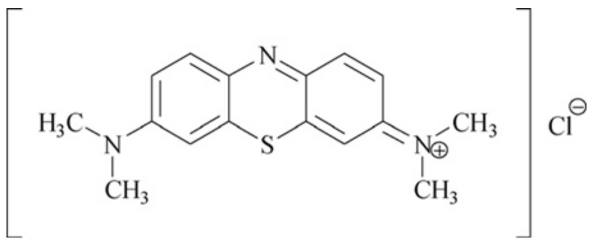

Figure 1. Chemical structure of MB molecule

The response surface method (RSM) is used to determine quantitative data for experimental designs (Evans, 2003). These may be represented in 3D graphics as response surfaces. Many factors explain the influence of each other. It also forms a mathematical model.

In the literature studies, no research has been found on methylene blue dye adsorption using carob. The most important goal of this study was to make an economically cheap and easy-to-obtain adsorbent. In the study, the effects of particle size, temperature, frequency, pH, time and concentration parameters affecting MB adsorption were investigated. Statistical ANOVA analysis was performed.

MATERIALS AND METHODS

Materials

Carob was obtained from the White Sea coast of Turkey. The locust seeds were ground in the mill. In the motorized sieving system, 50, 100 and 150 partm sizes were allocated (Figure 2). Grain size plays an important role in working conditions (Masoumi and Tabil, 2003). MB paint was purchased from Merck. The molecular structure of methylene blue (MB) is reported in FIG. In the study, MB with a molecular length of 16.9, a width of 7.4 and a thickness of 3.8 was used (Weng and Pan, 2006).

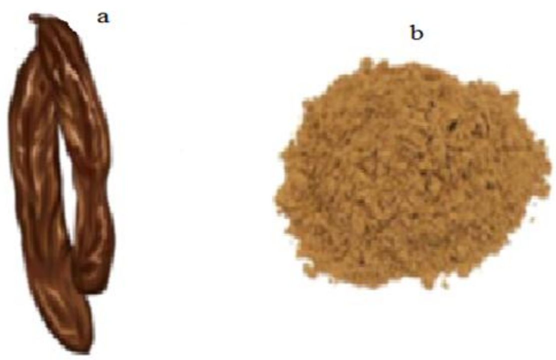

Figure 2. Carobs bean gum (a) pods and (b) powder

Analytical measurements

MB dye in the aqueous solution was analyzed using Perkin Elmer Lambda 25 UV–vis spectrophotometer at 663 nm. MB was chosen as the target compound because it has a net positive charge which would be favorably adsorbed by electrostatic force onto a negatively charged absorbent surface.

Adsorption experiment

For each adsorption experiment, 0.5 g of carob powder having a different particle size was used. The first tried concentrations of MB solution were 10, 20 and 30mg L^{-1}. The impact of pH on the quantity of color removal was investigated in the pH range from 2, 5 and 8. The pH was detected using 0.1M NaOH and 0.1M HCl solutions and measured by an H12211 pH-meter with a combined pH electrode. The experiments were executed at 25, 35, and 45 ℃ in a constant temperature bath. Furthermore, each of samples kept ultrasound-assisted for 120, 240 and 360 minutes time, at 30, 40 and 50 kHz ultrasound-assisted frequency, and at 50, 100 and 150 μm dimension of particles. Subsequently, each of the samples was subjected to centrifugation at 4000 rpm for 15 minutes, and the results of the analysis were determined by monitoring the absorbance values for the most absorbance (664 nm) wavelength using a UV-vis spectrophotometer to the left in the supernatant solution. Experiments in the preliminary stage revealed the influence of the separation time on the amount of absorber paint. Using the calibration curve and the absorbance data, the amount of paint adsorbed by the following equation was calculated:

$$qe = (Co - Ce)\, V / m \qquad (1)$$

In the Eq.1, qe, Co, Ce, V, and m represent the concentration of dye adsorbed (mg/g), initial concentration of dye (mg/L), equilibrium concentration of dye (mg/L), mass of the carob powders (g), and volume of solution (L), respectively (Chiou et al., 2004; Xie et al., 2012).

Box-Behnken Experimental Design

In the Box-Behnken design model, only three levels were coded -1 (low), 0 (central point or middle) and +1 (high) (Evans, 2003). Box and Behnken composed this design by combining two-level factorial designs with uncompleted block designs. This method is effective in establishing statistical properties. These designs are available with limited options, out of three-factor versions. In this design, two of the factors are fixed at 0 level, the remaining factors are between +1 and -1 levels. This process is repeated for different groups (Lawson, 2010; Vining and Kowalski, 2010).

In this study, the Box-Behnken experimental design was implemented investigate and validate adsorption process parameters affecting the removal of MB dye by carob powder. pH (2-8), ultrasound frequency (50-150 hz), particle size (50-150 μm), adsorption temperature (25-40 °C), solution concentration (10-30 mg/L) and adsorption time (120-360 min) are variable input parameters. The variables and levels of the Box–Behnken design model are designated in Table 1.

Table 1.Experimental design levels of chosen variables

Type of variable, Unit	**Factor X**	**Level**		
		Low (-1)	**Middle (0)**	**High (+1)**
pH	X_1	2	5	8
Frequency, Hz	X_2	30	40	50
Particle size, μm	X_3	50	100	150
Temperature, °C	X_4	25	35	45
Solution concentration, mg/L	X_5	10	20	30
Time, min	X_6	120	240	360

In this study, two different test prescriptions were prepared to evaluate the effects on MB adsorption. A total of 34 (17 + 17) experiments were performed. The parameters used in the experiment are given in Tables 2 and 3.

Table 2. Experimental real values of dye adsorbed for MB adsorption onto carob powder

Std. order	**pH (X_1)**	**Ultrasound frequency (Hz) (X_2)**	**Particle size (μm) (X_3)**	**Dye adsorbed q_e (mg/g) (Y_1)**
1	2.00	30.00	100.00	185.17
2	8.00	30.00	100.00	220.73
3	2.00	50.00	100.00	196.81
4	8.00	50.00	100.00	239.18
5	2.00	40.00	50.00	182.36
6	8.00	40.00	50.00	206.35
7	2.00	40.00	150.00	220.54
8	8.00	40.00	150.00	253.12

9	5.00	30.00	50.00	215.503
10	5.00	50.00	50.00	225.80
11	5.00	30.00	150.00	263.14
12	5.00	50.00	150.00	208.08
13	5.00	40.00	100.00	270.58
14	5.00	40.00	100.00	250.18
15	5.00	40.00	100.00	262.49
16	5.00	40.00	100.00	269.79
17	5.00	40.00	100.00	251.82

Table 3. Experimental real values of dye adsorbed for MB adsorption onto carob powder

Std. order	**Adsorption temperature (°C)** (X_4)	**İnitial concentration (L)** (X_5)	**Contact time (min)** (X_6)	**dye adsorbed q_e (mg/g)** (Y_2)
1	25.00	10.00	240.00	231.48
2	45.00	10.00	240.00	128.76
3	25.00	30.00	240.00	242.12
4	45.00	30.00	240.00	147.03
5	25.00	20.00	120.00	208.84
6	45.00	20.00	120.00	134.18
7	25.00	20.00	360.00	224.85
8	45.00	20.00	360.00	119.75
9	35.00	10.00	120.00	149.03
10	35.00	30.00	120.00	177.90
11	35.00	10.00	360.00	155.77
12	35.00	30.00	360.00	198.14
13	35.00	20.00	240.00	171.53
14	35.00	20.00	240.00	168.58
15	35.00	20.00	240.00	170.18
16	35.00	20.00	240.00	171.41
17	35.00	20.00	240.00	170.33

According to the results of multiple regression analysis, the experiment each parameter could only come in three levels and the most suitable experimental model is the quadratic equation (Eq. (1)):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon \quad (2)$$

Where β_0 is the offset term, β_i is the slope or linear effect of the input factor X_i, β_{ii} is the quadratic effect of input factor xi and β_{ij} is the linear by linear interaction effect between the input factor X_i - X_j and allows random error discrepancies, or reveal uncertainties between the predicted and measured values (Benyounis et al., 2005).

RESULTS AND DISCUSSION

Box-Behnken analysis

Statistically designed experiments were used to examine the overall effect of the parameters. Separate experiments were also performed for different combinations of physical parameters (Mall et al., 2007). MB-colored Y (reaction) results on carob powder were measured according to the design matrix (Table 2 and Table 3). PH, ultrasound frequency, particle size, adsorption temperature, concentration and contact duration parameters were significantly influenced by the carob powder used in the MB extraction experiment (Mall et al., 2007).

In many variance systems, the main effects are affected by their low interaction. For this reason, only two-way interactions are considered in our studies. Regression equations were obtained by placing experimental data in linear, interactive, quadratic and cubic models. In this study (Namasivayam et al., 2001), the results obtained by applying different tests such as square sum and model summary statistics are given in Tables 4 and 5.

Table 4. The suitability of the tested model of table 3

Source	Sum of squares	df	Mean square	F value	Prob> F	Remark
Source	**Std. Dev.**	**R-squared**	**Adjusted R-squared**	**Predicted R-squared**	**PRESS**	**Remark**
Linear	27.41	0.2874	0.1229	-0.1427	15657.10	
2FI	29.44	0.3675	-0.0120	-0.7987	24645.99	
Quadratic	14.68	0.8899	0.7483	-0.3690	18757.89	Suggested
Cubic	9.65	0.9728	0.8912			Aliased

Table 5. The suitability of the tested model of table 4

Source	Sum of squares	df	Mean square	F value	Prob> F	Remark
Source	**Std. Dev.**	**R-squared**	**Adjusted R-squared**	**Predicted R-squared**	**PRESS**	**Remark**
Linear	10.69	0.9280	0.9114	0.8540	3017.71	
2FI	10.93	0.9422	0.9075	0.7219	5747.20	
Quadratic	7.08	0.9830	0.9612	0.7321	5534.43	Suggested
Cubic	1.19	0.9997	0.9989			Aliased

Application of statistical analysis

The values of the variables were entered into the Box-Behnken experimental design model. It has been determined that there is an empirical relationship between the obtained experimental results and the second order polynomial equation. ANOVA is a statistical method that reveals the power of the relationship with the sources of variation determined to test hypotheses on the total variance of the data used in the experiment on the parameters of the applied model (Huiping et al., 2007). Statistical significance of the mean square change rate was tested using ANOVA (Table 6), depending on the regression. In the ANOVA analysis, the relationship between the response of the equation and the meaningful variables was adequately represented. According to ANOVA (Table 6), the F values of all regressions are very high. The associated p-value is used to determine whether F is statistically significant. The smaller value of 0.05 for each p-value indicates that the applied model is statistically significant (Segurola et al., 1999). This shows that the parameters used in the model have a significant effect on paint removal. A correction of 0.8899 - 0.9830 in the model provided a high correlation between the R2 value and the observed value and the predicted value.

Table 6. ANOVA for Response Surface Quadratic Model.

Source	**Coefficient estimate**	**Sum of squares**	**df**	**Mean square**	**F value**	**Prob> F**	**Remark**
Model		12,193.35	9	1354.82	6.29	< 0.0121	significant
Intercept	260.97						
X_1	16.81	2261.28	1	2261.28	10.49	0.0143	
X_2	-1.83	26.91	1	26.91	0.12	0.7342	
X_3	14.36	1649.30	1	1649.30	7.65	0.00278	
X_1^2	-31.52	4182.90	1	4182.90	19.41	0.0031	
X_2^2	-18.98	1516.90	1	1516.90	7.04	0.0328	
X_3^2	-13.86	808.91	1	808.91	3.75	0.0939	
X_1X_2	1.70	11.59	1	11.59	0.054	0.8232	
X_1X_3	2.15	18.45	1	18.45	0.086	0.7783	
X_2X_3	-16.34	1067.88	1	1067.88	4.96	0.0613	
Residual		1508.58	7	215.51			
Lack of fit		1135.98	3	378.66	4.07	0.1045	not significant
Pure error		372.60	4	93.15			
Cor total		13,701.93	16				
Model		20,311.28	9	2256.81	45.01	< 0.0001	significant
Intercept	170.41						
X_4	-47.20	17,819.89	1	17,819.89	355.37	< 0.0001	
X_5	12.52	1253.75	1	1253.75	25.00	0.0016	
X_6	3.57	101.96	1	101.96	2.03	0.1969	
X_4^2	9.32	365.60	1	365.60	7.29	0.0306	
X_5^2	7.62	244.69	1	244.69	4.88	0.0629	
X_6^2	-7.82	257.43	1	257.43	5.13	0.0578	
X_4X_5	1.91	14.55	1	14.55	0.29	0.6068	
X_4X_6	-7.61	231.65	1	231.65	4.62	0.0687	
X_5X_6	3.37	45.56	1	45.56	0.91	0.3722	
Residual		351.01	7	50.14			
Lack of fit		345.35	3	115.12	81.32	0.0005	significant

Pure error	5.66	4	1.42
Cor total	20,662.29	16	

In the analysis used, the selected model was found to be sufficient in determining the power of the relationship between the factor and the response (Kim et al., 2003). The relationship between the values presents and predicted for the adsorption of the MB dye to the carob powder is shown in Fig 3.

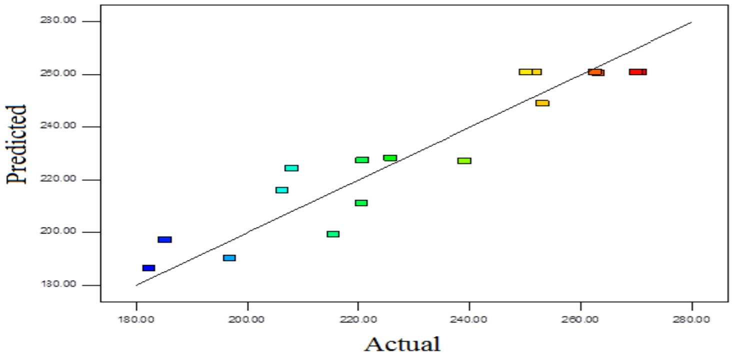

Figure 3. Dispersion diagram for the real answer to the dye - carob powder adsorption system

Morphology of carob powder

SEM images of carob powder samples prepared by ultrasound were used to investigate pore structures at different magnification ratios (Fig. 4). When there is no significant porosity on the surfaces of the samples, the presence of pores is determined when internal structures are examined. The resulting structure shows the presence of meso and micropores, rather than macropores. Important porosity is observed at a scale of 1µm. These pores are proposed to be responsible for the adsorption (Gleisy et al., 2008). The surface of treated carob powder has a polished, smooth and glossy appearance. But if you look at the broken part, marine, fibrous structure is seen. Fig. 5 shows a representative TEM image of carob powder. It can be finalized by the TEM image that the MB was well dispersed over carob powder by preserving their initial morphology and particle size.

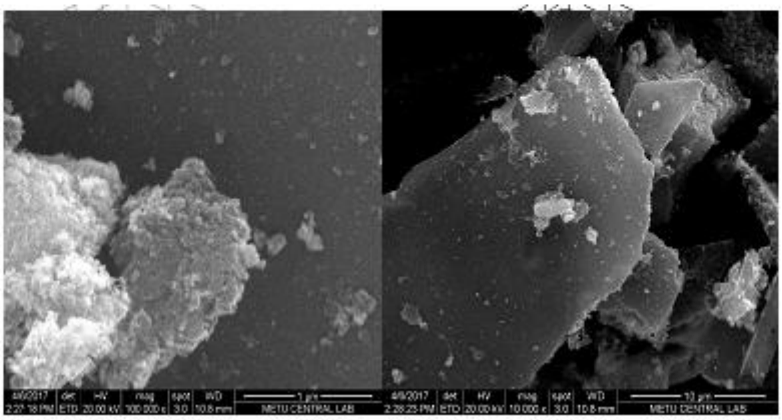

Figure 4. SEM images of treated carob powder

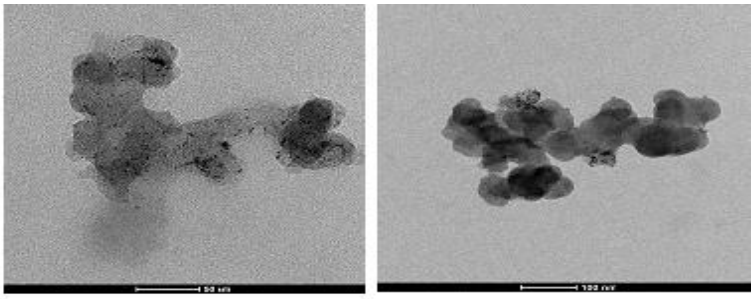

Figure 5. TEM images of treated carob powder different magnifications

Impact of two parameters on MB of carob powders

Impact of solution pH

The effect of dye solubility on the amount of dye adsorbed at different pH ranges was investigated (Figure 6a). With increasing pH value, the carob powder was found to increase the MB adsorption rate. This can be explained by the electrostatic interaction of the cationic MB dye. At high pH values, electrostatic repulsion begins between the negatively charged surface of the MB dye ions and the adsorbent. It has been reported that MB withdrawal in various studies usually increases with increasing pH (Gupta et al., 2004; Singh et al., 2003).

Impact of particle size

MB dye adsorption was investigated for three different particle sizes (50, 100 and 150 μm) of carob powder. The effect of these particle sizes on the dye adsorption rate is shown in Figures 6b-6c. A significant increase in dye adsorption rate was observed due to the low particle size. Diffusion resistance to mass transfer is higher for larger particles and most of the particle inner surface can not be used for adsorption. Thus, the amount of adsorbed paint is reduced (Annadurai et al., 2002).

Impact of temperature

The effect of MB on the carob bean adsorption rate was investigated at 25, 35 and 45 ° C. It is known that the adsorbent molecules increase the diffusion ratio due to the decreased viscosity of the porous particles at the inner boundary of the outer boundary layer (Fig 6d-6e) (Doğan et al., 2007).

Impact of initial MB concentration

The concentration of solution provides an important impetus for the mass transfer resistance of all molecules between aqueous and solid phases (Ho et al., 2005, Dogan et al., 2006). Figure 6f shows the effect of contact time on the amount of MB adsorbed by the carob bean at different starting MB concentrations. As the MB concentration increased, an increase in the amount of adsorption was observed. It has been found that the removal of the paint by adsorption is rapid at the beginning of the contact period. The increase in loading capacity of adsorbents associated with dye ions is due to the high repulsive forces for mass transfer (Bulut and Aydın, 2006).

Impact of ultrasound-assisted frequency

Variation as an ultrasonic-assisted function in the adsorption of MB was investigated using frequencies of 30, 40 and 50 kHz (Figures 6a-6c). In this process, the ultrasonic bath power has significant effects on the samples during the adsorption process (Hoseinzadeh et al., 2013). Due to the formation of pore volume and the formation of new pores, the ultrasonic bath resistance will increase over time (Guo and Lua, 2000).

Impact of time

In Figures 6e-6f, as time increases, the amount of adsorbed dye on the surface of active carbon is observed to increase. The runtime has a significant effect on total pore volume and surface area. As the time increases, it is reported that the micropore can grow and thus the total pore volume will increase but the micropore number decreases (Liu et al., 2010). It has been found that it has the expected capacity in short time intervals. The maximum amount of dye is removed with the lowest possible adsorbent (Table 7). Six experiments were carried out under these optimum conditions. The adsorption capacity of the locust kernel for the removal of MB showed a small decrease for each adsorption-desorption cycle. After 6 cycles, there was still 87.6% of the starting efficiency. For this reason, the regenerated locust bean can be used repeatedly and efficiently as an adsorbent to remove the MB.

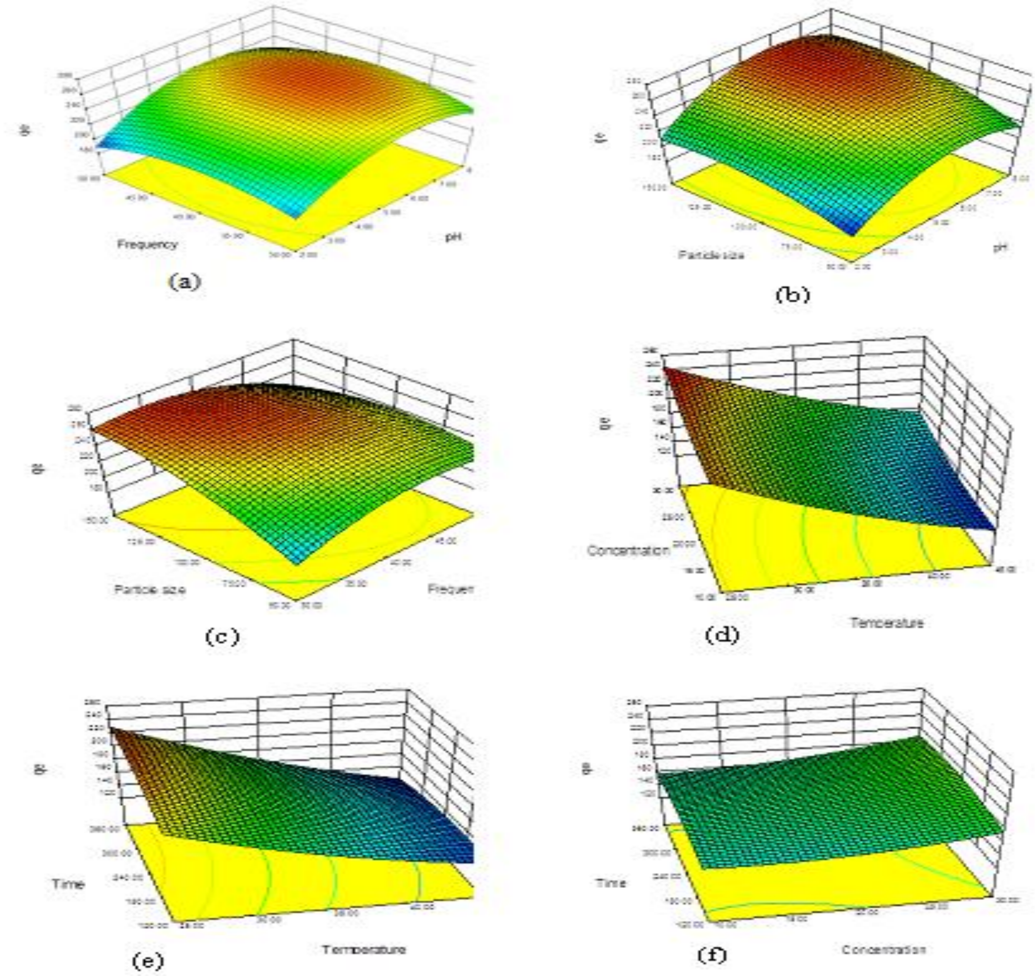

Figure 6. 3D response surface areas on the impact the of variables independent for MB dye carob powder adsorption system

Table 7. Optimum values of different parameters

pH	Ultrasound frequency (Hz)	Particle size (µm)	Temperature (°C)	Solution concentration (mg/L)	Contact time (min)	Dye removal (mg/g)
5.85	36.40	137.63	25.38	29.30	267.63	256.44

CONCLUSION

In our work, adsorption experiments were carried out on the carob powder of the MB dye. In MB extraction, the role of pH, ultrasound frequency, particle size, adsorption temperature, solution concentration and adsorption time factors was investigated. Box-Behnken model was used for ANOVA analysis. Optimum conditions, pH 5.85, Ultrasonic frequency 36.40 Hz, 137.63 Partm Particle size, Temperature 25.38 ° C, 29.30 mg / L Solution concentration and 267.63 min. Contact time (Table 7) was obtained. As a result, carob bean can be used as a cheap adsorbent that does not damage the environment.

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