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Adsorption Behavior of Methylene Blue Dye Using Carob Powder as Eco-Friendly New Adsorbent For Cleaning Wastewater: Optimization By Response Surface Methodology

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Abctract

The use of cheap, efficient and environmentally friendly adsorbents has served as an alternative source of carob in order to remove dye-stuffs from waste water. This study has researched the potential use of carob powder as alternative adsorbent for the removal of methylene blue from wastewater. Experiment parameters pH, ultrasonic frequency, particle size, contact time, temperature and initial concentration of dissolved methylene blue (MB) dye were investigated. Thereafter, Box-Behnken design experiment was applied the adsorption experiments. The equilibrium time was 267.63min for methelene blue dye. The results showed that physisorption seemed to play a major role in the adsorption process. The adsorption process of methylene blue on carob powder was found to rate of adsorption decreases with increasing temperature and the process exothermic. Regression analysis results demonstrated that is good for the experimental data to the non-linear model with correlation coefficients of (R^2) value of 0.8899 and 0.9830. The maximum adsorption value was determined as 256,4355 mg/g. This result appears to be important when compared with other studies reported in the literature. According to the results of the study was observed carob bean can be used as an alternative adsorbent.

Keywords: Adsorption, Box-Behnken Design, Carob powder, Methylene Blue, Ultrasound –Assisted

Atık Suyunun Temizlenmesi İçin Çevre Dostu Yeni Adsorbent Olarak KeçiboynuzuTozunun Kullanılarak Metilen Mavi Boyasının Adsorpsiyon Davranışı: Tepki Yüzey Metodolojisiyle Optimizasyon

Öz

Ucuz, verimli ve çevre dostu adsorbanların kullanımı, atık sudan boya maddelerini çıkarmak için alternatif bir keçiboynuzu kaynağı olarak hizmet etmiştir. Bu çalışma, atık sudan metilen mavisi çıkarılması için alternatif bir adsorban olarak keçiboynuzu tozunun potansiyel kullanımını araştırmıştır. Deney parametreleri pH, ultrasonik frekans, partikül boyutu, temas süresi, sıcaklık ve çözünmüş metilen mavisi (MB) boyasının başlangıç konsantrasyonu incelenmiştir. Daha sonra, Box-Behnken tasarım deneyi adsorpsiyon deneylerine uygulandı. Denge zamanı, metali mavi boya için 267.63 dk. Sonuçlar, fiziksel adsorpsiyon sürecinde önemli bir rol oynadığını gösterdi. Metilen mavisinin keçiboynuzu tozu üzerindeki adsorpsiyon sürecinin, artan sıcaklık ve ekzotermik proses ile adsorpsiyon oranlarında azalma olduğu bulunmuştur. Regresyon analizi sonuçları, deneysel veriler için doğrusal olmayan modele (R2) 0.8899 ve 0.9830 arasındaki korelasyon katsayıları için iyi olduğunu göstermiştir. Maksimum adsorpsiyon değeri 256.4355 mg/g olarak belirlendi. Bu sonuç literatürde bildirilen diğer çalışmalarla karşılaştırıldığında önemli olduğu görülmüştür. Çalışmanın sonuçlarına göre, keçiboynuzu tozunun alternatif bir adsorban olarak kullanılabileceği gözlenmiştir.

Anahtar Kelimeler: Adsorbsiyon, Box-Behnken tasarım, Keçiboynuzu tozu, Metilen mavisi, Ultrases banyo

1. Introduction

A wide variety of industrial materials such as wood, carpet, rubber, cosmetics, paint, textile, leather, paper, plastics etc. are used in wastewater (Chiou et al., 2003). These industrial wastes are discharged into the surrounding rivers and cause extremely damage to the environment (Aksu et al., 2001). At the same time, the discharge of wastewater brings about problems such as toxicity of waste material and the increase of chemical oxygen demand (Bulut et al., 2006). The organic molecules in the wastes are very difficult to process due to their resistance to

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aerobic digestion, heat, and oxidation (Crini, 2006; Ravi Kumar et al., 1998; Sun et al., 2003). Nowadays, the increase in the use of synthetic fine powders is affecting this pollution in a big way. It has been determined that more than 100,000 distinct chemical dyes are produced in the market. It is estimated that the use of paint and dye intermediates in the world is more than 7 × 108 kg / d per year (McMullan et al., 2001; Toh et al., 2003). Transferring directly the waste dyes into water sources affects life and food negatively. These dyes have also been shown to cause mutagenic and skin irritation (Crini, 2006) In aquatic life, as well as diseases such as mutagenic, carcinogenic, and allergic dermatitis. In recent years, the use of methods such as oxidation processes, nanofiltration, chemical precipitation, ion exchange, chemical coagulation/flocculation, ozonation, ozone depletion, ultra-reverse filtration and various physical techniques (Lorenc-Grabowska et al., 2007; Malik et al., 2003; Mittal, 2006) are very expensive with being effective. Therefore, adsorption techniques have gained a great importance in wastewater disposal methods. Nowadays active carbon is very effective and widely used because of its excellent adsorption ability in commercial systems (Crini, 2006; El-Geundi, 1991). In developing countries, low-cost adsorbents started to be used as an alternative to expensive active carbon. There are low price adsorbents in the literature. These include digestive bacteria (Nassar et al., 1991; McKay et al., 1998), corn cobs El-Geundi, 1991), sun flower (Sun et al., 1997), ashes (Gupta et al., 2000), peat shavings (El-Nabarwy et al., 2000), seaweed (Zhao et al., 2003), fungal biomass (Basibuyuk et al., 2003) wasted activated sludge (Annadurai et al., 2003), mud (Weng et al., 2001), red mud (Namasivayam et al., 1997), coconut marrow (Namasivayam et al., 2001), Neem leaf (Bhattacharyya et al., 2003), organic crust waste (Namasivayam et al., 1996), tree fern (Ho et al., 2005). Since agricultural wastes and other wastes are cheaper, different alternative materials have begun to be used as adsorbents. Such inexpensive adsorbents (Bhattacharyya et al., 2005) have provided laboratory-scale investigations for color grades of different grades. In recent years, some research has been conducted to develop cheaper and more effective adsorbents. Numerous non-traditional low-priced adsorbents are proposed from natural materials, biosorbents and waste materials such as industrial and agriculture (Ferrero, 2007).

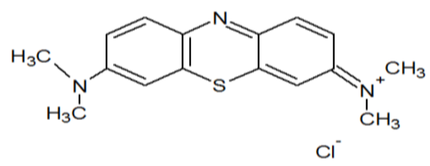

Figure 1. Chemical structure of MBmolecule.

Methylene blue (MB) is one of the best frequently used dyes among cationic dyes (Fig. 1). Although MB is not absolutely dangerous, it has been found to cause some detrimental effects. MB adsorption adsorbents over the aqueous phase are helpful to control the product cost. Carob tree derives from the Greek keras scientific name, "horn" and Latin Jovinus, expressed in the hardness and capsule. Common name is derived from the Hebrew kharuv derived kharoub (arabic) and contains algarrobo (Spanish), carob (English), keration (in Greeek), kebir and harun (Turkish), as well as St.Jean's bread (Tunalıoğlu et al., 2003; Battle et al., 1997). The production of locust concentrates in the Mediterranean (96%) and Izmir (5%) regions in the Aegean (4%) regions (Tunalıoğlu et al., 2003; Battle et al., 1997). In some studies, the use of carob bean for the benzodiazepine receptors has become an easy and inexpensive material (Makris et al., 2004; Avallone et al., 2002). This material is mainly used as an active carbon source in some works to remove Methylene blue. The response surface method (RSM) is used to determine quantitative data for experimental designs. The Box-Behnken design is a globural design model (Evans, 2003), which is a point in the center and centers of the cube edges bounded around the sphere. These may be represented in 3D graphics as response surfaces. Many factors explain the influence of each other. It also forms a mathematical model. Nowadays has not researched the adsorption of some dyes like methylene blue on carob bean yet. In this paper the activation parameters does contain the effect of some parameters such as particle size, temperature, frequency, pH, time and concentration. The most important goals of this study were: (1) to work with an adsorbent which is economically feasible and easy to procure; (2) to adsorption kinetics to remove the methylene blue (MB) from the water by adsorption; (3) to the most suitable method to identify the mechanism and the factors controlling the adsorption rate; (4) to the impacts of initial MB concentration, particle size, temperature, frequency, solution pH, time and concentration on adsorption was evaluated.

2. Material and Method

2.1. *Materials and Analytical measurements*

Carobs are used in this study were provided from the White Sea Region of Turkey. Firstly dried, and sieved to obtain a particle size between 50, 100 and 150 μm (Fig. 2). In the same working conditions, seed size handling, processing and storage play an important role (Masoumi et al., 2003). MB was Merck product. The molecular structure of MB used has shown in Fig. 1. Nitrogen and sulfur atoms were inside of the aromatic moiety of MB. Dimethylamino groups were engaged in it, at the aromatic unit. The molecule is positively charged and the aromatic moiety is planar (Weng et al., 2006).

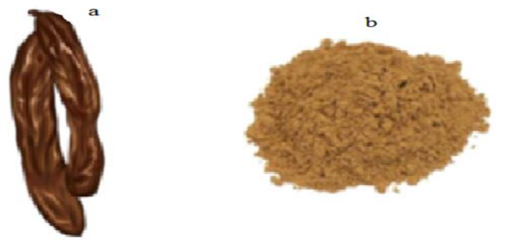

Figure 2. Carobs bean gum (a) pods and (b) powder.

Methylene blue (MB), NaOH and HCl were purchased from Sigma-Aldrich. Deionized water (Milli-Q System) is used at each step of the experiment. Adsorption method was investigated using Perkin Elmer Lambda 25 UV–vis spectrophotometer at 663 nm. Mass experiment program: For each adsorption experiments, 0.5 g of the carob powders having different particles dimension. The first tried concentrations of MB solution were 10, 20 and 30mg L^{-1}. The impact of pH on the quantity of colour 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. The experiments were realized at 25, 35, and 45 °C. Moreover, 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 quantity of absorber paint. Using the calibration curve and the absorbance data, the amount of paint adsorbed was calculated by the following equation:

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

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-Behnken method is effective in establishing statistical properties. These designs are available in 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 repetitive for different groups (Lawson, 2010; Vining et al., 2010). In this study, Box–Behnken design model was used as a statistical program for investigating and validate of adsorption process parameters that are the effect on the removal of MB dye by carob powder. Variable input parameters are 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) . Variable levels are designated in Table 1 and 2.

Table 1. The level of variables used in the RSM.

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

Two different experimental prescriptions were prepared to total of 34 (17+17) experiments were performed. Actual values used in our experiment are shown in Table 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)	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

2.2. Mathematical modeling

According to the results of multiple regression analysis and BBD experiment design, 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).

3. Result and Discussion

3.1. Design model

It was found in the MB removal efficacy experiment with carob powder were significantly effective (Mall et al., 2007). Statistically designed experiments were used to examine the effect of these factors as a whole. The Y (reaction) results of the MB dye on the carob powders are shown at Table 2 and Table 3. In several variant systems, the main effects are affected by their low interaction. For this reason, only two-way interactions are considered in our work. Regression equations were obtained by placing experimental data these models. In this study, (Namasivayam et al., 2001) results are obtained by applying model summary statistics are given in Table 4 and 5.

Table 4. The suitability of the tested model of Table 2.

Source	Sum of squares	df	Mean square	F value	Prob> F	Remark
Mean	9.047E+005	1	9.047E+005			Suggested
Linear	3937.50	3	1312.50	1.75	0.2067	
2FI	1097.93	3	365.98	0.42	0.7412	
Quadratic	7157.92	3	2385.97	11.07	0.0048	Suggested
Cubic	1135.98	3	378.66	4.07	0.1045	Aliased
Residual	372.60	4	93.15			
Total	9.184E+005	17	54021.51			

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 3.

Source	Sum of squares	df	Mean square	F value	Prob> F	Remark
Mean	5.188E+005	1	5.188E+005			Suggested
Linear	19175.60	3	6391.87	55.89	< 0.0001	
2FI	291.77	3	97.26	0.81	0.5149	
Quadratic	843.92	3	281.31	5.61	0.0281	Suggested
Cubic	345.35	3	115.12	81.32	0.0005	Aliased
Residual	5.66	4	1.42			
Total	5.395E+005	17	31735.11			

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

As a result of the study, the quadratic model has the maximum value according to the values of "Corrected R-Square" and "Predicted R-Square" in statistical summaries. Therefore, a second-order model is applied for further analysis.

3.2. 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. The final equation from the real factors is given below:

$$Y_1(q_e) = -347.319 + 36.923X_1 + 17.985X_2 + 2.631X_3 + 0.056X_1X_2 + 0.014X_1X_3 - 0.032X_2X_3 - 3.502X_1^2 - 0.189X_2^2 - 5.544E-003X_3^2 \quad (3)$$

$$Y_2(q_e) = +390.362 - 10.101X_4 - 3.140X_5 + 0.456X_6 + 0.019X_4X_5 - 6.341E - 003X_4X_6 + 2.812E - 003X_5X_6 + 0.093X_4^2 + 0.076X_5^2 - 5.430 - 004X_6^2 \quad (4)$$

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) ANOVA analysis for the second-order equations is shown at Table 6 and 7. In the ANOVA analysis, the relationship between the response of the equation and the significant variables was adequately represented. According to ANOVA (Table 6-7), the F values of all regressions are very high. The associated p-value is used to determine whether F is statistically important. The fact that each p-value is lower than 0.05 indicates that the applied model is statistically important (Segurola et al., 1999). MB shows an F-value ANOVA of 45.01 for the dye carob powder system; this indicates that the terms used in the model have a considerable influence on the dye removal. MB shows an F-value ANOVA of 45.01 for the dye-carob powder system; this indicates that the terms used in the model have a considerable influence on the dye removal. The model provided a correction R2 value of 0.8899 – 0.9830 and an adjusted R2 value of 0.7483 – 0.9612. The possibility p(<0.05) is less than 0.05.

Table 6. ANOVA analysis for of Table 2.

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				

Table 7. ANOVA analysis for of Table 3.

Source	Coefficient estimate	Sum of squares	df	Mean square	F value	Prob> F	Remark
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				

The selected model in the analysis used indicated that the relationship between the factors and the response was sufficient to determine the power (Kim et al., 2003). "Adeq Precision" measures the signal/noise ratio. For this reason a rate greater than 4 is required. In this study, the ratio of signal to noise is found to be 6.608 and 22.921, which indicates an adequate signal. For this reason, a second-order model can be used to navigate the design area. In Fig. 3, the developed model was found to be sufficient. Because most of the reactions predict less than 10% of residuals and show that the residues are close to true.

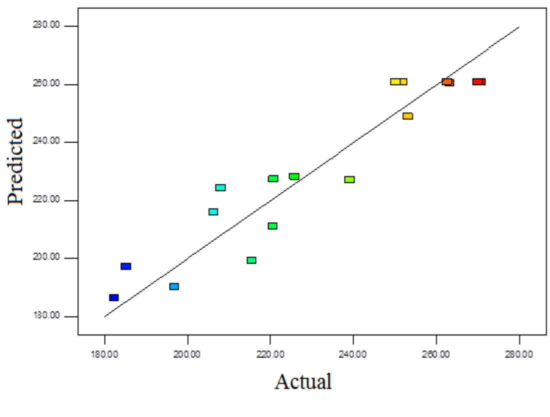

Figure 3. Dispersion diagram for the real answer to the dye - carob powder adsorption system.

3.3. Characterization of carob powder

SEM images of carob powder samples prepared by ultrasound were used to investigate pore structures at different magnification ratios (Fig. 4a-4b). When there was not a 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. The importance of adsorption is that the porous structure is 1µm in size (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 can be seen.

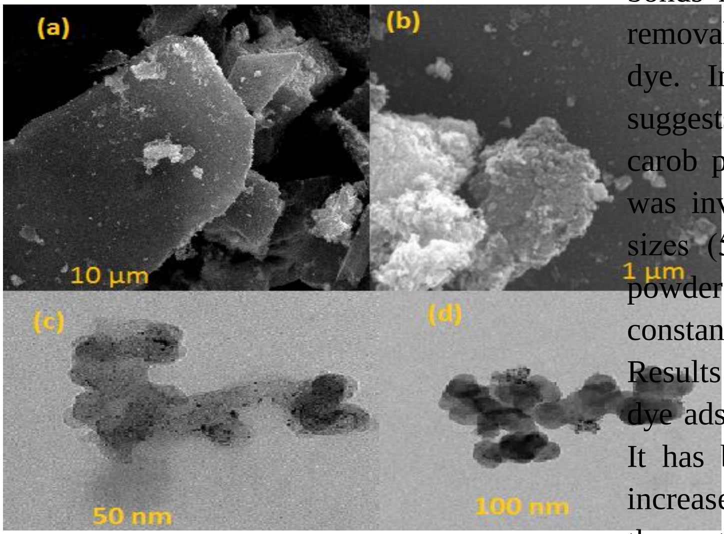

Figure 4. SEM images (a) and (b), TEM images (c) and (d) of treated carob powder different magnifications

Fig. 4 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.

3.4. Effect of the reaction system

Impact of two parameters on MB of carob powder: Fig. 5a shows the 3D plots of pH and frequency. The impact of paint adsorbed at different pH ranges was examined under different fixed pH parameters (Fig. 5). There was an increase in the pH change of the dye solution from 2 to 8 due to removal of MB with carob powder. There was an increase in the adsorption rate of MB on the carob bean according to the increase of pH value. In various studies, it was generally expressed that MB attraction increases with increasing pH (Gupta et al., 2014; Singh et al., 2003). It is likely that the electrostatic attraction between the dye composition and the carob surface increases with increasing pH. Thus, at high pH values, the electrostatic repulsion between the negatively charged surface of the adsorbent and the MB dye ions begins. It is striking that carob powder has an isoelectric point at pH 5.85. In addition, the inability to form pi-bonds results in a marked reduction in the removal of the aqueous solution from the dye. In this study, chemical absorption suggests that MB is effective in adsorbing carob powder. The MB dye adsorption rate was investigated for three different particle sizes (50, 100 and 150 μm) of the carob powder while keeping the other parameters constant at each step of the experiment. Results of these particle sizes that affect the dye adsorption rate are shown in Fig. 5b-5c. It has been examined that there is sharply increase in dye adsorption rate according to the particle size decline. Most of the particle interior surface cannot be used for adsorption. Thus, the amount of adsorbed paint is reduced (Annadurai et al., 2002). The increase in temperature affect the reaction of the adsorption studied. The impact of MB on the carob bean adsorption rate was researched at temperatures of 25, 35 and 45 °C. The temperature has two important effects on the adsorption process. Because of the decrease in viscosity of the solution by increasing the temperature, it has been found that the adsorbate molecules increase the spreading rate along the outer boundary layer and in the inner pores of the adsorbent particle. In addition, changing the temperature will cause a change in the equilibrium capacity of the adsorbent for a given adsorbate (Dogan et al., 2006). It is known that the adsorbent molecules raise the diffusion rate along the inner pore of the outer boundary layer. It can be seen in Fig. 5d-5e, a rise can be seen in the biosorption capacity of the locust powder. (Doğan et al., 2007). The equilibrium adsorption capacity of MB on carob powder was found to decrease with increasing temperature, increasing from 242.12 mg/g at 25°C, 198.14 mg/g at 35°C and 147.03 mg/g at 45°C. The dye adsorption on the adsorbent was unfavorable at higher temperatures. This effect proposes that the adsorption mechanism associated with the removal of

MB on carob powder requires a physical process. The increase in the number of molecules can also gain energy to interact with the active region on the surface underground. The dependence of the amount of adsorbed paint on the temperature indicates that the paint penetrates into the carob powder due to the larger diffusion coefficient. Therefore, it is possible to say that the adsorption process is endothermic (Doğan et al., 2006). The concentration of the solution is an important parameter (Ho et al., 2005; Doğan et al., 2006). Adsorption of carob powder adsorbate was evaluated at different time intervals. Fig. 6f shows the impact the carob bean at different starting MB concentrations. There was an increase in adsorption amount depending on the initial MB concentration raised. It was found that the removal of paint by adsorption on carob powder was fast at the beginning of the contact period. Then, depending on the length of contact, it began to slow down. The better adsorption depending on the higher the concentration of solvent (Bulut et al., 2006). The adsorption of MB of ultrasound-assisted was investigated using the frequency 30, 40 and 50 kHz. It was determined that ultrasound-assisted frequency has significant effect on the adsorption of MB (Fig. 5a-5c). In this process, the ultrasonic bath power has significant effects on the samples in the adsorption process (Hoseinzadeh Hesas et al., 2013). Ultrasonic bath strength residual pore volume will gradually increase with time due to formation of new pores. Carob powder surface area will increase at high ultrasonic bath strength due to the carbon-CO2 reaction and further release of volatile substances (Guo et al., 2000). The adsorption capacity will widely increase with increasing the impregnation ratio. It has a very positive effect on the response time of the study parameters. The MB elimination efficiency respectively increases during the study period. In Fig. 5e-5f, we can be seen that as the contact time increases, the amount of adsorbed paint on the surface of the active carbon increases. Time has a important effect on the total pore as well as the surface area. It has been reported that as the time increases, the micropores may grow and thus the total pore volume will increase, although the number of micropores decreases (Liu et al., 2010). Through a complex mechanism involved in the adsorption of the pigments found in the macro and micropores of the active carbon, the process continues until the equilibrium is reached. Physically, it has been observed that both of the carbons have the expected capacity at very short time intervals.

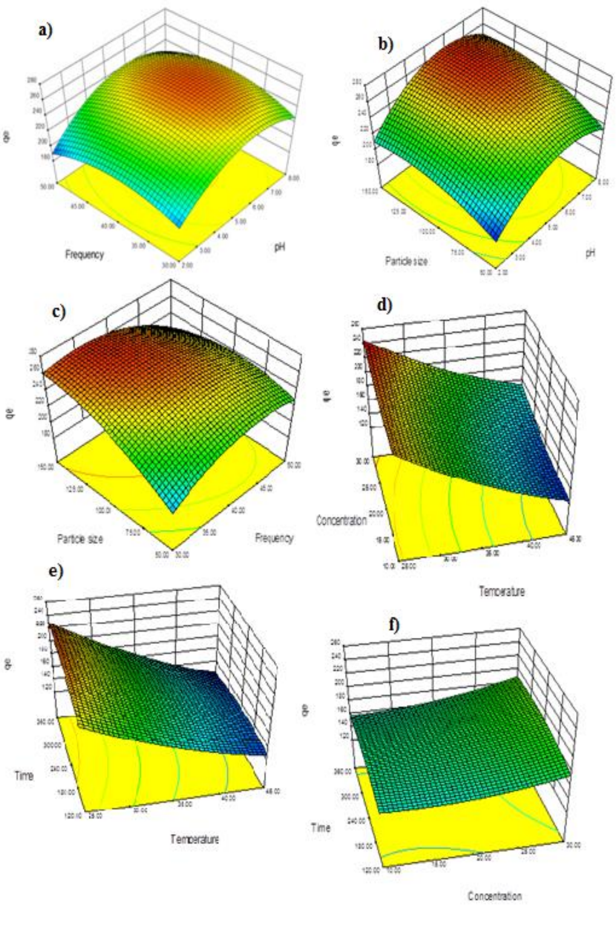

Figure 5. 3D response surface areas on the impact the of variables independent for MB dye carob powder adsorption system.

3.5. Use of surface response diagrams to determine optimum conditions

Using the Response Surface Methodology, which is the statistical method, the appropriate conditions of the parameters used in the experiment were determined (Table 8). After, six experiments were conducted under these optimum conditions. The average maximum dye removal was obtained from the results.

The adsorption capacity of the carob bean for MB removal showed a minor decrease for each adsorption-desorption cycle, they still had 87.6 % of the first efficiency after 6 cycles. Hence, our results showed that the regenerated carob bean can be used repeatedly and efficiently adsorbents for MB removal.

Table 8. 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	86.72

3.6. *Adsorption kinetics*

To design an adsorption treatment plant it is important to be able to estimate the removal rate of contamination from aqueous solutions (Gocek et al., 2005). The understanding of adsorption kinetics can determine the duration of effective adsorbed material-adsorbent contact, and there are several kinetic models to study the order in which the rate of adsorption is determined by the order of adsorption. The agreement between the experimental data and the model predicted values is expressed by the correlation coefficients. In the study conducted, the adsorption data were examined using pseudo-first-order and pseudo-second-order kinetic models. Lagrangian expressed the duration of adsorption as a simple kinetic model, pseudo first order kinetic model (Langergren and Svenska, 1898):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (5)$$

Where k1 (min-1) is the first-order rate constant of adsorption; qe is the amount of adsorbed material at equilibrium and qt is the amount of adsorbed material at the end of t. The equation developed by Ho and Mckay (Ho et al., 2000) for the adsorption process is as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

Where k2 (g mg-1 h-1) is the pseudo-second-order adsorption rate constant; qe is the amount of adsorbed material in equilibrium and qt, t is the amount of adsorbed material at the end of time. (6) is rearranged and q0 = 0 at time t = 0 and q = qt at time t = t, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (7)$$

The first k2qe2 in the equation shows the adsorption rate.

In Tables 4 and 5, the correlation coefficients, R2, are very high and the amount of dye under equilibrium for MB can not be ignored. The qe values calculated from the first order kinetic model are very high when compared with the experimental qe values. This finding suggests that the absorption of MB on the locust dust is diffusion controlled and that the process follows Lagergren's expression of the pseudo-first-order adsorption rate. Tables 2 and 3 show the feasibility of applying the equation at the pseudo-second -order. The pseudo-first-order reaction rate is determined by the amount of solute adsorbed on the adsorbent surface and the adsorbed amount under equilibrium. It shows that for all the adsorption system made on the carob powder, it is a fake second order model with very high correlation coefficients for the pseudo-second order kinetic model (Tables 6 and 7). The calculated qe values are also well understood in the case of pseudo-second-order kinetics with experimental data. Similar kinetic results were found for a different dye-adsorbent system, as shown in Table 9.

Table 9. Adsorption of MB dye on various adsorbents.

Adsorbents	Dyes	Referens
Fly ash	Methylene blue	(Kumar et al., 2005)
Biosorbent	Methylene blue	(Rubin et al., 2005)
Actived carbon	Methylene blue	(Kannan, 2001)
Perlite	Methylene blue	(Dogan, 2004)
Sepiolite	Methylene blue	(Dogan, 2007)

4. Conclusion

Our purpose of study, the adsorption of MB dye onto carob powder is investigated. Experimental parameters were; function of 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). The Box-Behnken model and the response surface method were used to investigate the role of six factors on MB extraction. The equilibrium between the adsorbate on the solute and the adsorbent surface was approximately 4 hours. MB was found to be endothermic in nature of carob powder adsorption. This work demonstrates that the response Surface methodology is suitable for optimizing adsorption dyeing experiments. The optimal conditions the greatest were obtained to be at 5.85 for pH, 36.40 Hz for Ultrasound frequency, 137.63 µm Particle size, 25.38 °C for Temperature, 29.30mg/L Solution concentration and 267.63 min Contact time (Table 9).

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