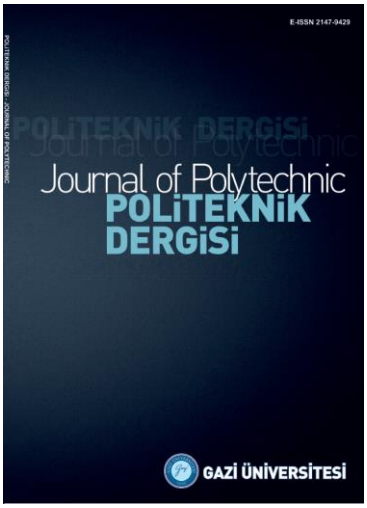

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Fındık kabuğundan biyokömür hazırlanması ve karakterizasyonu ve metilen mavisi boya için adsorpsiyon özellikleri

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Preparation and Characterisation of Biochar from Hazelnut Shell and Its Adsorption Properties for Methylene Blue Dye

Araştırma Makalesi / Research Article

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ABSTRACT

One of the major pollutants in water resources are organic dyes that are widely used by different industries. Methylene blue (MB) is one of them which is quite harmful for aquatic life. This pollutant must be removed with proper methods. Adsorption is one of the most popular methods because of its high purification yield and known as a cost effective process if the sorbent is inexpensive. In this study, biochar which is used as an adsorbent has been produced from hazelnut shells used as the raw material. Chemical, thermal and surface characteristics of raw hazelnut shell were investigated by FT-IR, TG/DTG, SEM and elemental analysis. Biochar characteristics were determined by FT-IR, BET and SEM analysis. The effect of different adsorption parameters such as pH, initial dye concentration, contact time, adsorbent dosage and temperature on the adsorption of MB onto hazelnut shell char were examined in batch experiments. The equilibrium of adsorption was modeled using Langmuir and Freundlich isotherm models. The maximum adsorption yield of MB was found to be 83% at pH 4.0, adsorbent dosage of 4 g/L, contact time of 300 min., initial dye concentration of 15 mg/L and temperature of 45 ^{o}C. In addition, the Freundlich isotherm was found to be the best fitting isotherm model for the adsorption process. The pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data and thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were determined.

Keywords: Adsorption, methylene blue, hazelnut shell, carbonization, biochar.

Fındık Kabuğundan Biyokömür Hazırlanması ve Karakterizasyonu ve Metilen Mavisi Boya İçin Adsorpsiyon Özellikleri

ÖZ

Su kaynaklarındaki en büyük kirleticilerden biri, farklı endüstriler tarafından yaygın olarak kullanılan organik boyalardır. Metilen mavisi bunlardan biri olup, sucul yaşam için oldukça zararlıdır. Bu kirletici uygun yöntemlerle uzaklaştırılmalıdır. Adsorpsiyon, yüksek saflaştırma verimi nedeniyle en popüler yöntemlerden biridir ve sorbent ucuz olduğu takdirde uygun maliyetli bir işlem olarak bilinmektedir. Bu çalışmada, adsorbent olarak kullanılan biyokömür, hammadde olarak kullanılan fındık kabuklarından üretilmiştir. Ham fındık kabuğunun kimyasal, termal ve yüzey özellikleri FT-IR, TG/DTG, SEM ve elementel analiz ile araştırılmıştır. Biyokömürün özellikleri ise FT-IR, BET ve SEM analizi ile belirlenmiştir. Metilen mavisinin fındık kabuğundan üretilen kömür üzerine adsorpsiyonuna pH, başlangıç boya konsantrasyonu, temas süresi, adsorbent miktarı ve sıcaklık gibi farklı adsorpsiyon parametrelerinin etkisini belirlemek için kesikli deneyler gerçekleştirilmiştir. Adsorpsiyon dengesi Langmuir ve Freundlich izoterm modelleri kullanılarak modellenmiştir. Metilen mavisi için maksimum adsorpsiyon verimi; pH 4.0' de, 4 g/L adsorbent miktarında, 300 dakika temas süresinde, 15 mg/L başlangıç boya konsantrasyonunda ve 45 ^{o}C'de %83 olarak bulunmuştur. Buna ek olarak, Freundlich izoterminin adsorpsiyon işlemi için en uygun izoterm modeli olduğu bulunmuştur. Deneysel verilere yalancı birinci derece ve yalancı ikinci derece kinetik modeller uygulanmış ve Gibbs serbest enerjisi, entalpi ve entropi gibi termodinamik parametreler belirlenmiştir.

Anahtar Kelimeler: Adsorpsiyon, metilen mavisi, fındık kabuğu, karbonizasyon, biyokömür.

1. INTRODUCTION

Today, over 100,000 synthetic dyes are used commercially and 700,000 tons of dye is produced annually. These synthetic dyes are widely used in textile, paint, paper, printing, food, plastics and cosmetics industries and cause serious environmental problems because of they contain hazardous organic substances at high levels. When considered the residual amount of dye used in these industries, environmentally importance of coloured wastewater come out [1, 2]. The presence of dyes in water, even at very low concentrations, represents a serious problem due to their negative ecotoxicological effects and bioaccumulation in wildlife [3]. Methylene blue which is the most commonly used substance for dyeing cotton, wood and silk is one of them. It has

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harmful effects on living organisms on short periods of exposure [4].

There are many processes available for the removal of dyes by conventional treatment technologies such as chemical, biological and photocatalytic oxidation, coagulation-flocculation, filtration, adsorption, membrane separation and ion-exchange [5]. Amongst these techniques, adsorption which is an environmentally friendly and cost effective procedure is widely acknowledged as the most efficient method because of its ability to remove toxic pollutants from aquatic systems [6]. Activated carbon is the most commonly used adsorbent for dye removal by adsorption because of its large surface area, microporous structure and high adsorption capacities [7]. Especially it is very effective for the adsorption of cationic dye, mordant and acid dyes [8]. The biggest disadvantages of commercial activated carbon is its relatively high cost. Therefore, many researchers has focused on the inexpensive alternative substitutes to commercial activated carbon.

Lignocellulosic materials such as almond, coconut, walnut and hazelnut shells, apricot, olive and cherry stones, rice husk, sawdust are very good precursors because of their availability, cheapness and physico-chemical characteristics for the production of carbon adsorbents based on agricultural wastes [4, 9-11]. The choice of a precursor for the production of effective biochar by pyrolysis or carbonization of raw material is based on low cost, high carbon and low inorganic content because of during carbonization process organics contained in raw material are changed into primary carbon, tar and ash [10, 12].

In this study, hazelnut shell which is the one of low cost agricultural waste by-products was utilized as the raw material for the production of biochar by carbonization process and its adsorption capacity for removal of methylene blue from aqueous solution was evaluated. Contact time (up to 550 min), temperature (25-45 ºC), pH of solution (2-10), adsorbent dosage (1-4 g/L) and initial concentration of dye solution (15-45 mg/L) were considered as variables for the adsorption experiment. The equilibrium of adsorption was modeled using Langmuir and Freundlich isotherm models.

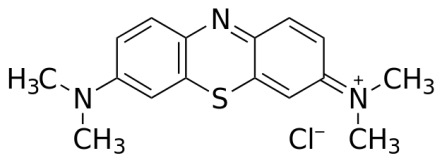
2. MATERIAL AND METHOD

2.1. Materials

Hazelnut shell used as the raw material is one of the highly available cellulosic agricultural wastes in Turkey. In this study, the sample of hazelnut shell (HS) was obtained from the province of Ordu which is located in the north of Turkey. HS was composed of lignin (43%), hemicellulose (30%), cellulose (26%) and extractive substance (1%). The sample was dried by standing for 12 hours at a temperature of 70 °C (UNITERM, mst 55). The dried sample was reduced in size by passing it through a stainless steel blade mill (Waring, USA). Those with dimensions less than 250 μm were used in experiments.

Methylene Blue (MB) dye used in this study was purchased from Merck which was of analytical grade and it was used without further purification. The detailed information of MB is given in Table 1.

Table 1. Details of the dye used

Dyestuff	Basic Blue 9 (BB 9)
IUPAC Name	Methylthioninium chloride, 3,7-Bis(dimethylamino)phenothiazinium chloride, Tetramethylthionine chloride
Commercial Name	Methylene Blue (MB)
C.I. Number	52015
Appearance	Dark green crystalline powder
Empirical Formula	$C_{16}H_{18}ClN_3S$
Molecular Weight	319.86 g/mol
Molecular Structure	
λ_{max}	663 nm

2.1.1. Characterization of raw material

Proximate analysis of the sample was carried out using an ash furnace (E871, D1102-84). For the determination of the volatile matter of the hazelnut shell, the sample was placed in a preheated ash furnace at 950±5 °C for 8-10 minutes and analysis was performed. Ultimate analysis of raw hazelnut shell was performed on the LECO brand CHNS-932 model analyzer. Quantities C, N, H and S were measured simultaneously. The ash content of the hazelnut shell was analyzed at 250 °C for 3 hours and 550 °C for 3 hours. An oxygen bomb calorimeter (e2k) was used when the upper thermal value was determined.

FT-IR spectra of raw hazelnut shell was recorded by Perkin Elmer USA FT-IR spectrometer between 400 cm^{-1} and 4000 cm^{-1}.

Thermal behaviors of crude hazelnut shell sample was examined by TG, DTG analyzes TA brand and DMAQ800 model thermal analyzer. TG and DTG curves were recorded under the specified conditions (Heating rate: 10 °C/min, Heating range: 30-800 °C).

Scanning electron microscopy (SEM) analysis of the hazelnut shell was carried out to examine its surface morphology by using FEI/Quanta 450 FEG.

2.2. Preparation of Hazelnut Shell Char (Pyrolysis Experiment)

10 g of sample was placed in the chamber and the pyrolysis of the hazelnut shell was carried out in an electric heated pyrolysis reactor with a volume of 600 cm^3. Pyrolysis experiments were conducted by passing inert nitrogen gas at a heating rate of 10 °C/min at a flow rate of 100 mL/min at temperatures of 400, 500 and 600

°C. The reactor temperature was supplied by the heat-couple placed inside the reactor from the top of the furnace. After the pyrolysis temperature reached the desired values, it was held at the desired temperature for 60 minutes so that the pyrolysis process could be completed and then the experiment was terminated. Pyrolysis experiments were performed in two times to examine the reusability. The value of mean standard deviation (SD) was 0.15 for reproducibility of carbonisation experimental data. This value indicated that all results exhibited the advantages of high reproducibility and good reusability.

2.3. Characterization of Hazelnut Shell Char

The BET surface area was obtained from nitrogen adsorption isotherms at 77 K by using Quantachrome/IQ-Chemi Surface Area Analyzer. Prior to gas adsorption measurement, the sample was degassed at 200 ^{o}C under vacuum for 12 h. The adsorption datas were obtained in a relative pressure. The BET surface area was calculated from N_2 adsorption isotherms by using Brunauer-Emmett-Teller (BET) equation.

Scanning electron microscopy (SEM) analysis of the hazelnut shell char was carried out to examine its surface morphology and porosity by using FEI/Quanta 450 FEG. For the observation of surface microporous structure, prior to scanning the samples were coated with a thin layer of gold to make it conductive.

FT-IR spectra of hazelnut shell char was recorded by Perkin Elmer USA FT-IR spectrometer between 400 cm^{-1} and 4000 cm^{-1}.

2.4. Batch Adsorption Experiments

To determine the applicability of produced hazelnut shell char as an adsorbent for water treatment, the batch adsorption experiments were performed using MB dye as the adsorbate. The dye stock solution (250 mg/L) was prepared by dissolving accurately weighed quantity of the dye in distilled water and all working solutions for the dye sorption experiments were obtained by diluting the stock solution with distilled water to the desired concentration. Batch equilibrium adsorption studies were performed using 250 mL of dye solutions. Parameters affecting the adsorption process such as pH (2-10), adsorbent dosage (1-4 g/L), initial dye concentration (15-45 mg/L), contact time (up to 550 min) and temperature (25-45 ^{o}C) were studied in a batch system. pH of the solutions was adjusted by 0.1M HCl and 0.1M NaOH solutions. In each adsorption experiment, the mixtures were agitated in a water bath shaker at 150 rpm. The samples were collected at predetermined time intervals and adsorbent separated from the samples by filtering. The filtrate was analyzed by a UV-visible spectrophotometer (Thermo, Genesys 10S) at λ_{max} to determine the residual dye concentration. Based on the acquired values, the amount of dye adsorbed per unit mass of the adsorbent (q_e) was calculated according to the following Equation (1) and the adsorption yield was calculated by using the Equation (2) [13, 14].

$$q_e = (C_o\text{-}C) \times \frac{V}{m} \quad (1)$$

$$\text{Dye Removal (\%)} = \frac{(C_0 - C)}{C_0} x100 \quad (2)$$

where q_e is the amount of adsorbed dye per gram of adsorbent (mg/g), C_o and C are the initial and final dye concentration in solution phase, respectively (mg/L), V is the volume of dye solution (L) and m is the weight of adsorbent (g).

In order to ensure the reproducibility of the results, all the adsorption experiments were performed in triplicate and the average values were used in data analysis. Relative standard deviations were found to be within ± 2%.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hazelnut Shell

The proximate and ultimate analysis and higher heating value of hazelnut shell are shown in Table 2, taken after drying the samples at 70 °C.

As seen in Table 2, HS has a high content of volatile matter (84.22%) which can be regarded as suitable for pyrolysis processes [15]. Another important property, ash content, is small in HS (1.32%). High ash content is a disadvantage because it causes the sample not to burn well enough to accumulate [15-17]. The S and N contents of the raw material in the literature varied between 0-4.1 and 0.1-12.2, respectively [17]. According to ultimate analysis results of N (1.09%) and S (1.67%) contents are low. Low N and S contents are important because higher N and S contents can cause toxic NO_x and SO_x emissions during disposal [15, 17]. Because of with high volatile matter and low ash content, hazelnut shell may be considered as a suitable precursor for preparing biochar. The thermal value of HS was calculated to be 18.79 MJ kg^{-1}.

Table 2. Proximate and ultimate analysis of hazelnut shell (dry, ash-free basis)

Proximate analysis (w/w%)	**Hazelnut shell**
Moisture	2.83
Ash	1.32
Volatile matter	84.22
Fixed carbon*	14.46
Ultimate analysis (w/w%)	
C	47.77
H	5.82
N	1.09
S	1.67
O*	43.65
Higher heating value MJ kg^{-1}	18.79

*By difference

FT-IR spectra of HS are shown in Figure 1. When the FT-IR spectra of the raw hazelnut shells are examined, the broad vibration at 3,341 cm^{-1} is the O-H stretching vibration of the water. The peaks observed between 2,933-2,862 cm^{-1} are C-H tensile vibrations of aliphatic hydrocarbons. In the spectrum, the strong peak of the C=O asymmetric stretching vibration is observed at about 1,618 cm^{-1}. This peak shows that the compounds are of aldehyde, ketone and acid groups. The peaks observed between 1,410-1,315 cm^{-1} indicate the C-H bending vibration of the aliphatic hydrocarbons [18-20].

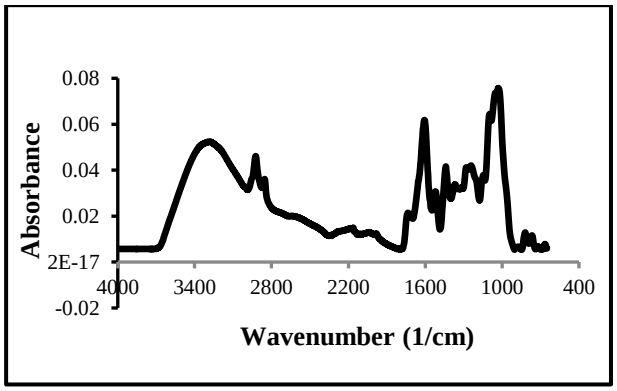


Figure 1. FT-IR spectrum of raw hazelnut Shell

Thermogravimetry (TG) and differential thermogravimetry (DTG) curves of hazelnut shell thermal decomposition at 10 °C min^{-1} heating rate under an inert nitrogen atmosphere are shown in Figures 2a and 2b, respectively. As can be seen from the TG curve given in Figure 2a, moisture and the low molecular weight substances on the surface were removed from the sample up to about 210 °C and the stable structure was not decomposed. Between 210 °C and 400 °C temperatures, most of the sample was separated from the structure and a mass loss of about 63% occurred. The ratio of the sample resulting from the pyrolysis process was determined to be approximately 21%. The differential thermogravimetry curves (DTG) given in Figure 2b were used to determine the mass loss steps of the hazelnut shell in the pyrolysis process. In general, biomass pyrolysis consists of three steps. Dehydration occurs at temperatures of 120 °C. Decomposition of hemicellulose and cellulose, the main components of the biomass, occurs between 120-350 ºC. Decomposition of the lignin takes place at temperatures above 350 °C [21]. When the DTG curve of the hazelnut shell shown in Figure 2b was examined, a mass loss of about 65 °C was observed and the moisture was removed from the sample. The first peak, observed at temperatures of 210 °C to 310 °C, is due to hemicellulose decomposition. The second peak observed at high temperatures is related to the decomposition of cellulose, which is more stable than hemicellulose. The molecular weight of cellulose is higher than that of hemicellulosic, and therefore the decomposition of cellulose occurs at a higher temperature than hemicellulosic (322-398 °C). Although lignin decomposition occurs at higher temperatures than other components, the decomposition reactions of these components proceed at the same time. However, it shows that the most resistant component of wide peak lignocellulosic biomass observed is lignin decomposition. The results are consistent with the decomposition curves of lignocellulosic biomasses such as sugarcane bagasse, corn cobs, pine wood, rice husks, etc., which have previously been reported in the literatüre [22-24].

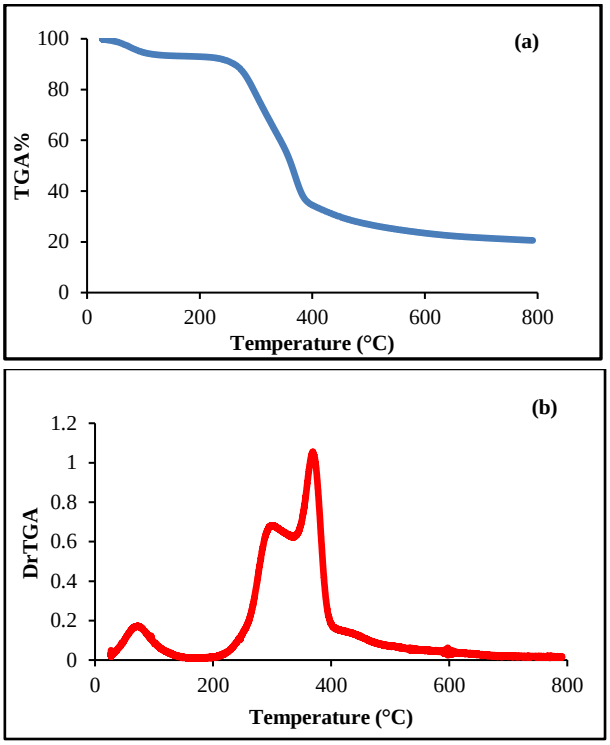


Figure 2. The raw hazelnut shell (a) TGA and (b) DTG curves (10°C/min)

3.2. Characterization of Hazelnut Shell Char

The quality and physicochemical characteristics of hazelnut shell char depend on the physical and chemical properties of raw material used and also the carbonization conditions [12]. Especially carbonization temperature is one of the most important parameters because of it changes the surface area of biochar and also its adsorption capacities. In this study, the pyrolysis process was occurred separately at carbonization temperatures between 400-600 °C under the nitrogen flow of 100 mL/min. Specific surface areas of activated carbons obtained by carbonization of hazelnut shells at different temperatures were determined by Brunauer-Emmett-Teller (BET) method. The effect of carbonization temperature on the BET surface area and hazelnut shell char yield are given in Figure 3.

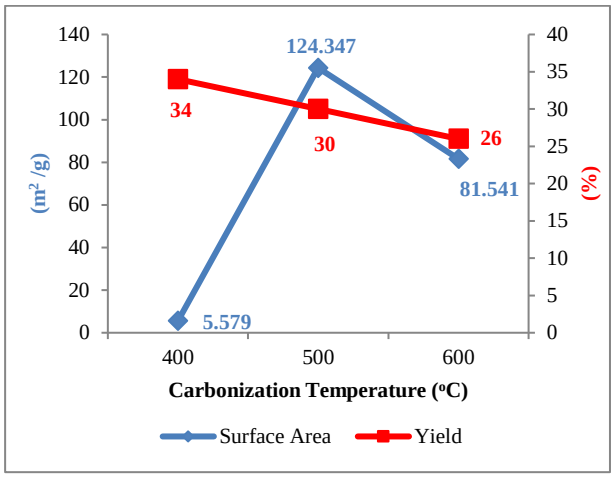


Figure 3. Effect of the carbonization temperature on the surface area and hazelnut shell char yield

As can be seen from Figure 3, with an increase in the carbonization temperature from 400 to 500 °C, the surface area of the hazelnut shell char increased from 5.579 to 124.347 m^2/g and then decreased to 81.541 m^2/g at 600 °C. To occuring some compounds produced from the cross-linking reactions was resulted in increase surface area with temperature up to 500 ºC. The decrease above this temperature was attributed to the collapse of the resultant carbon samples. As a result high temperature has an unfavorable effect on the surface area. Therefore the BET surface area of the hazelnut shell char reach its maximum values at a temperature of 500 °C. In this condition, total pore volume of the biochar was 0.146 cm^3/g. Additionally Figure 3 shows the effects of the carbonization temperature on the yield of hazelnut shell char. The yield was calculated from the weight of resultant biochar divided by the weight of hazelnut shell. According with carbonization temperature increased, the yield of hazelnut shell char decrease. This result can be explained as the weight loss rate is higher primarily due to the initial large amount of volatiles that can be easily released with higher temperature [7].

To determine the surface morphology of the raw hazelnut shell and hazelnut shell char, SEM analysis was used. When compared to raw hazelnut shell's images, the most porous surface structure was clearly observed in the SEM images for bioadsorbent shown in Figure 4b. From these figures, it is clear, there is a good possibility for dye molecules to adsorbed into these pores. Further, the pores on the surface of the adsorbent had highly heterogeneous structure which was provided a large surface area for the adsorption of MB.

The FT-IR spectra was obtained to evaluate qualitatively the chemical structures of hazelnut shell char and is shown in Figure 5. The spectrum displayed the following bands which indicated various surface functional groups. O-H stretching at around 3,500 cm^{-1} was typically attributed to hydroxyl groups. The region of the spectrum of 1,560 cm^{-1} was attributed to carbonyl groups (C=O). C-O stretching was observed at around 1,400 cm^{-1}. This compounds is an evidence of the lignocellulosic structure of hazelnut shell [25].

3.3. Determination of Adsorption Capacity of Hazelnut Shell Char

A biochar which is used in adsorption process as an adsorbent should possess high surface area. Therefore the removal of methylene blue (MB) from aqueous

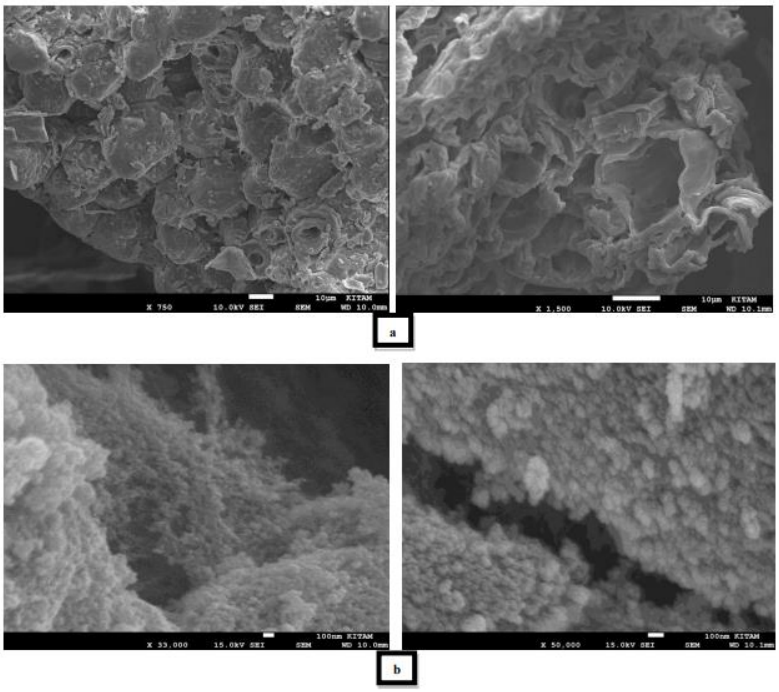


Figure 4. SEM images at different magnification ratio a) raw hazelnut shell b) hazelnut shell char which was carbonized at 500 ºC

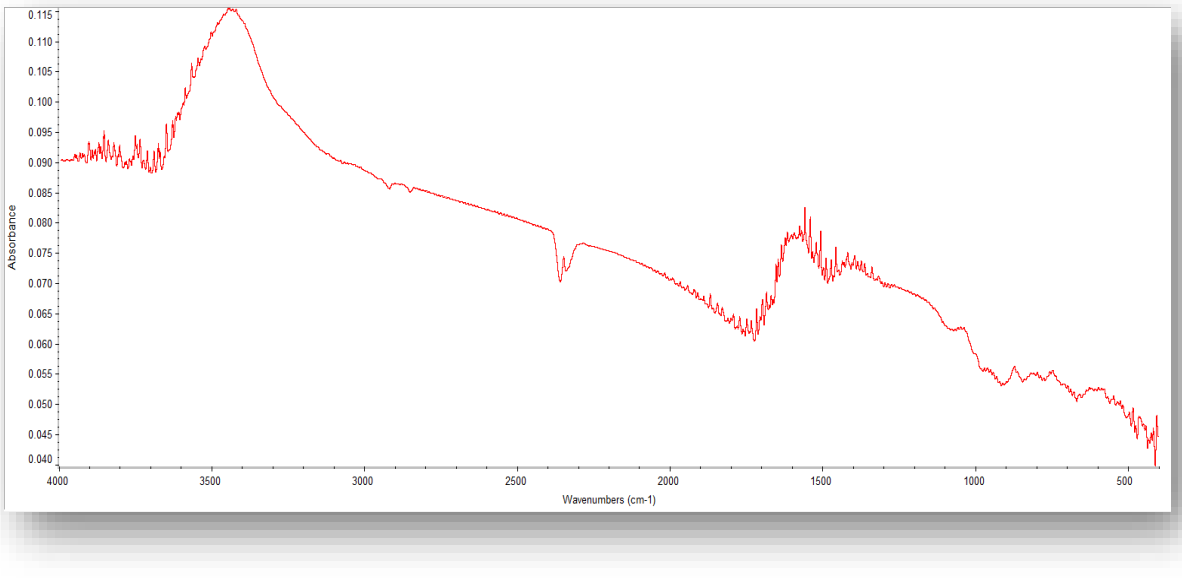


Figure 5. FT-IR spectrum of hazelnut shell char

solution was investigated using hazelnut shell char with the highest surface area (124.35 m^2/g) carbonized at 500 °C.

In adsorption, comparable consequences of various parameters influencing the dye removal process from aqueous solution is an important need. Therefore batch experiments were carried out to determine the effect of pH, initial dye concentration, contact time, adsorbent dosage and temperature in this study.

3.3.1. Effect of contact time and temperature

To evaluate the adsorption characteristics of the produced hazelnut shell char for MB, the change of adsorption rate with time and temperature has been investigated and presented in Figure 6. Experimental results showed that the contact time necessary for maximum adsorption was 300 minute approximately. In addition, MB showed a fast rate of adsorption during the first 180 min of the dye-sorbent contact. This result can be explained due to the large amount of initial surface area and high active binding sites for adsorption of the dye molecules. At higher contact time the rate of adsorption decreased due to decrease in total surface area and reached the equilibrium in 300 minute approximately. After the equilibrium, the amount of dye adsorbed did not change with contact time [3, 26].
Figure 6 indicates that the adsorption of MB as a function of temperature. As depicted in Figure 7, the percentage removal of MB dye increases with increasing temperature. This may be attributed to the increase of diffusion rate of the dye molecules in the solution with

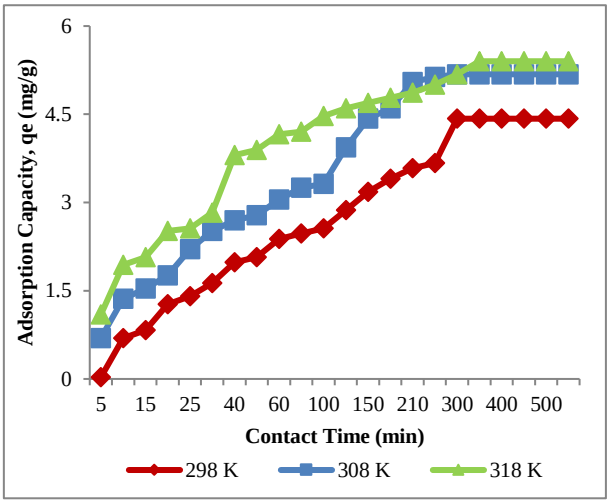


Figure 6. Effect of contact time on adsorption of MB at different temperatures (pH= 4, Adsorbent Dosage= 2 g/L, C_o= 15 mg/L)

temperature. Because the adsorption controlled by the diffusion process from the bulk to the surface. And also strengthening of the bonds between the dye molecules and the binding sites which are activated at higher temperatures of the sorbent might be enhanced the adsorptive interactions. This increasing trend in dye removal capacity with increasing temperature confirmed the endothermic nature of the ongoing process [27].

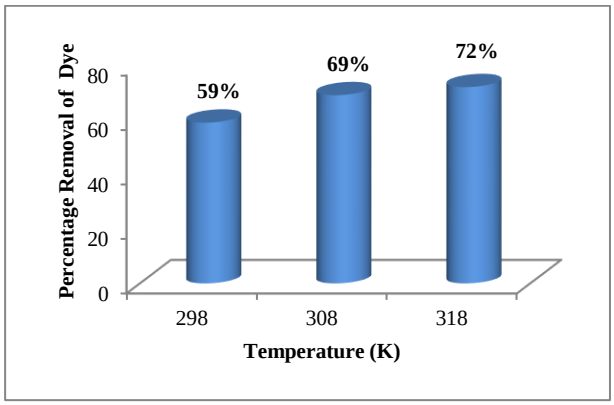


Figure 7. Effect of temperature on percentage removal of MB (pH= 4, Adsorbent Dosage = 2 g/L, C_o= 15 mg/L, Contact Time = 400 min)

3.3.2. Effect of initial dye concentration

Initial concentration of the adsorbate is an important factor to be considered for effective adsorption process. The effect of different initial dye concentration on percentage removal of MB and adsorption capacity are presented in Figure 8. It was seen that percentage removal of dye decreased with increase in initial dye concentration. At higher concentrations, all dye molecules in the solution do not interact with the binding sites of the adsorbent due to adsorbent has a limited number of active binding sites, which become saturated at a certain concentration [13]. However, the adsorption capacity at equilibrium increased with increase in initial dye concentration. This was so because the initial dye concentration provides an important driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase [28].

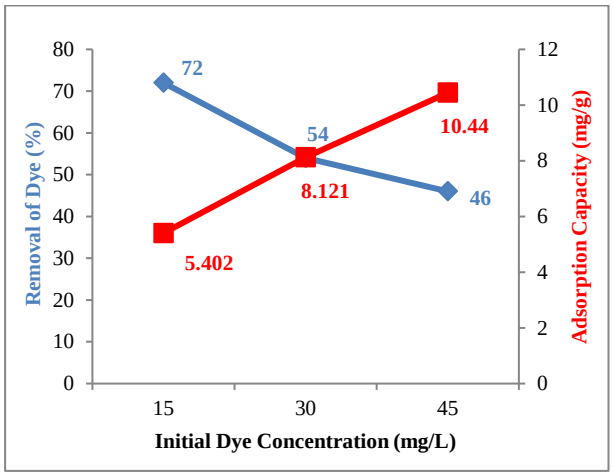


Figure 8. Effect of initial dye concentration on percentage removal of MB (pH= 4, Adsorbent Dosage = 2 g/L, T = 45 ºC, Contact Time = 400 min)

3.3.3. Effect of initial solution pH

pH of solution is an important parameter for adsorption because of affecting the surface charge and/or surface characteristics of adsorbent [29]. In this study, effect of initial pH of solution was investigated at various pH values which are changed between 2-10. As seen from Figure 9, there are no excessive variation in adsorption capacity at each pH studied. As the pH increases, it is usually expected that the adsorption of MB which is a cationic dye increases due to decreasing the number of positively charged sites. However, the high adsorption of MB are favourable at alkaline medium because of electrostatic attraction [4, 30]. But in the experiments, the MB adsorption was not clearly changed with increasing pH of solution [31]. Highest percentage of dye removal (69.07%) was observed at pH 4.0.

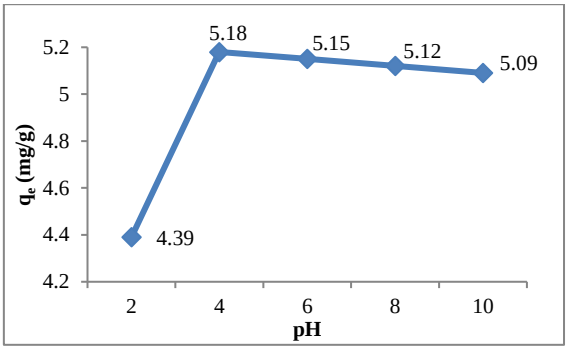


Figure 9. Effect of initial pH of solution on adsorption capacity (C_o= 15 mg/L, Adsorbent Dosage = 2 g/L, T = 35 ºC, Contact Time = 400 min)

3.3.4. Effect of adsorbent dosage

Adsorbent dosage strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. Therefore the influence of adsorbent dosage on MB adsorption by hazelnut shell char was investigated in the range of 1-4 g/L. Results are shown in Figure 10. The adsorption efficiency increased from 36% to 83% as the adsorbent dosage increased from 1 to 4 g/L. This increase could be attributed to an increase in the adsorbent surface area and number of active sites available for adsorption [3, 28].

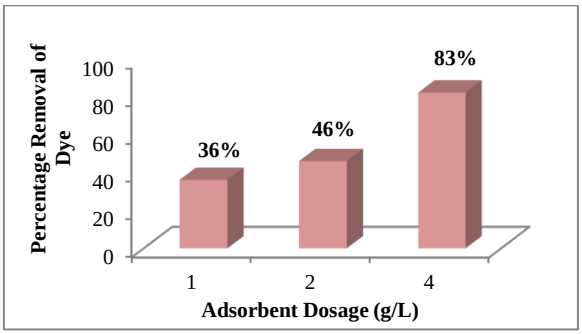


Figure 10. Effect of adsorbent dosage on percentage removal of MB (C_o= 15 mg/L, pH= 4, Contact Time = 400 min, T = 45 ºC)

3.3.5. Adsorption isotherm models

The adsorption isotherm is an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. There are several models for predicting the equilibrium distribution. However, the two models which are Langmuir and Freundlich models are most commonly used for water and wastewater treatment. The Langmuir adsorption isotherm is based on monolayer, uniform, and finite adsorption site assumptions. However, Freundlich isotherm is an empirical equation for multilayer, heterogeneous adsorption sites [32]. The linear form of the Langmuir (Equation 3) and Freundlich (Equation 4) equations are commonly given by:

$$1/q_e = (1/K_L q_m C_e) + (1/q_m) \quad (3)$$

$$\log q_e = \log K_f + n^{-1} \log C_e \quad (4)$$

where C_e is the equilibrium concentration of solute in the bulk solution (mg/L), q_e is the amount of solute (dye) adsorbed per unit mass of adsorbent (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the constant related to the free energy of adsorption (L/mg), K_f is a Freundlich constant indicative of the relative adsorption capacity of the adsorbent [mg/g (L/mg)1/n] and 1/n is the heterogeneity factor which is the constant characteristics of the system [33].

In this study, to quantify the adsorption capacity of hazelnut shell char for the removal of MB from aqueous solution, the Langmuir and Freundlich isotherm models were used to define the equilibrium datas. Linear plots obtained for $1/q_e$ versus $1/C_e$ and log q_e versus log C_e at each temperature for adsorption of MB onto hazelnut shell char are shown in Figure 11. It was observed that

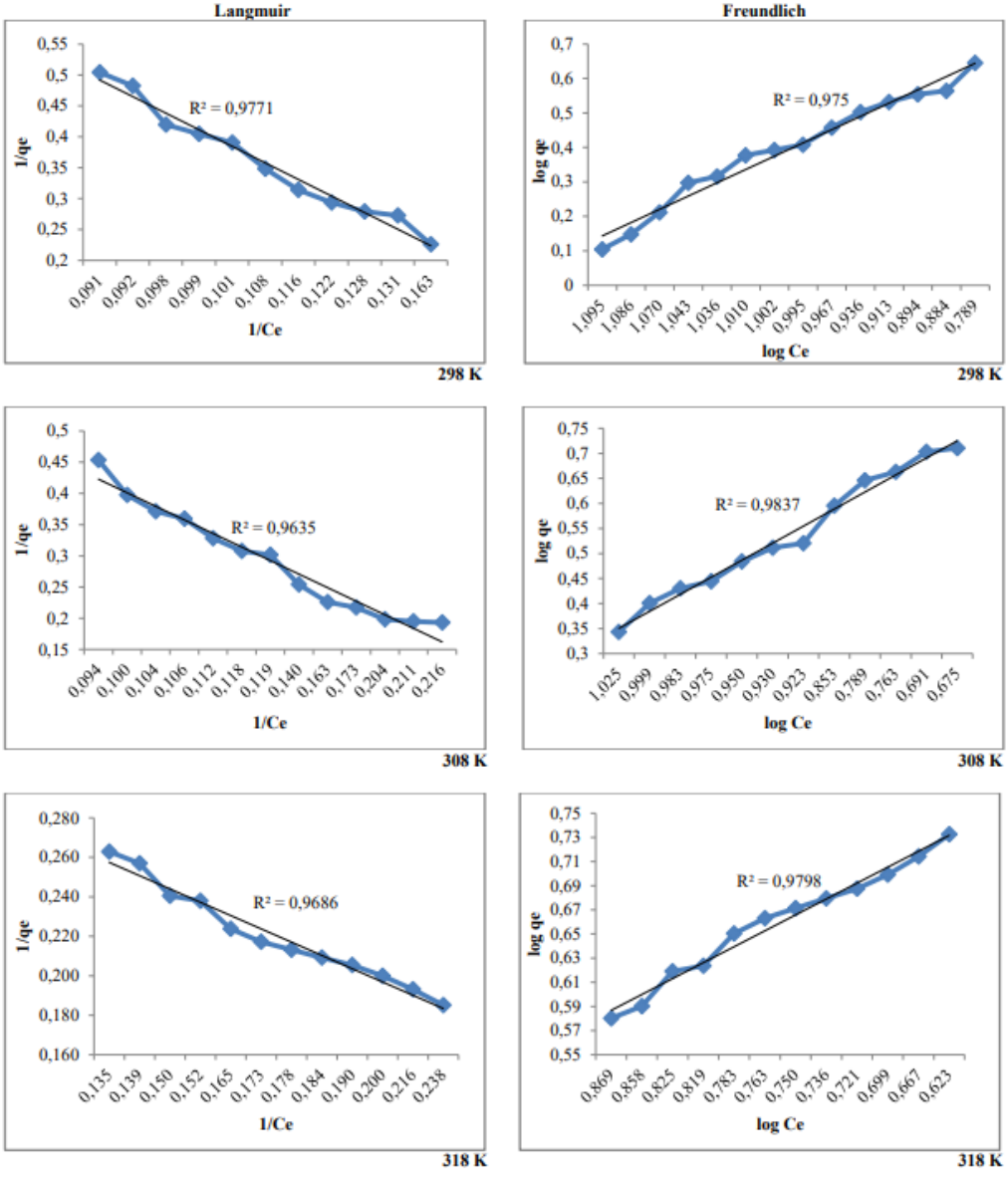


Figure 11. Adsorption isotherms for MB removal using hazelnut shell char

Table 3. The Langmuir and Freundlich isotherm constants for MB adsorption

		Temperature (K)		
Isotherm Model	**Parameters**	**298**	**308**	**318**
Langmuir	q_m (mg/g)	1.927	2.249	3.785
	K_L (L/mg)	0.0194	0.0205	0.0394
	R^2	0.9771	0.9635	0.9686
Freundlich	K_f [mg/g (L/mg)$^{1/n}$]	12.73	20.72	37.45
	n (g/L)	2.597	2.933	7.576
	R^2	0.975	0.9837	0.9798

the Freundlich isotherm model fitted better than the Langmuir isotherm model at all studied temperatures.

The Langmuir and Freundlich isotherm constants for MB adsorption are given in Table 3. The results showed that the values of n lie between 1 and 10 at all studied temperatures, which indicated that the MB dye was favorably adsorbed by hazelnut shell char. In addition, the values of K_F, q_m and n increased with the increase in temperature for MB. So these adsorption isotherms provided some insight into the adsorption mechanism and the surface characteristics of adsorbent [34]

3.3.6. Adsorption kinetics modeling

In order to examine the mechanism of adsorption process, the pseudo first order and the pseudo second order adsorption models were used to adjust kinetic experimental data. The linear form of pseudo first order and pseudo second order rate equations were presented in Equation 5 and 6, respectively.

$$\log \frac{(qe-qt)}{qe} = -\frac{K_1}{2.303} t \quad (5)$$

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \quad (6)$$

where, q_t and q_e denote the sorption capacity (mg/g) at a given time and at equilibrium, respectively, K_1 is the pseudo first order rate constant (min^{-1}), K_2 is the pseudo second order rate constant (g $mg^{-1}min^{-1}$) and t is the time (min) [5]. The linear graphs of $\log(q_e-q_t)$ versus t and t/q_t versus t are shown in Figure 12. The values of kinetic parameters (the rate constants of the two models with the correlation coefficients) of linear form of both rate equations are presented in Table 4.

As can be seen from Table 4, the R^2 values of the pseudo first order model are closer to 1.0 and higher than those of the pseudo second order kinetics. These results shown that the adsorption of MB dye in aqueous solutions using the hazelnut shell char can be described by pseudo first order kinetic model.

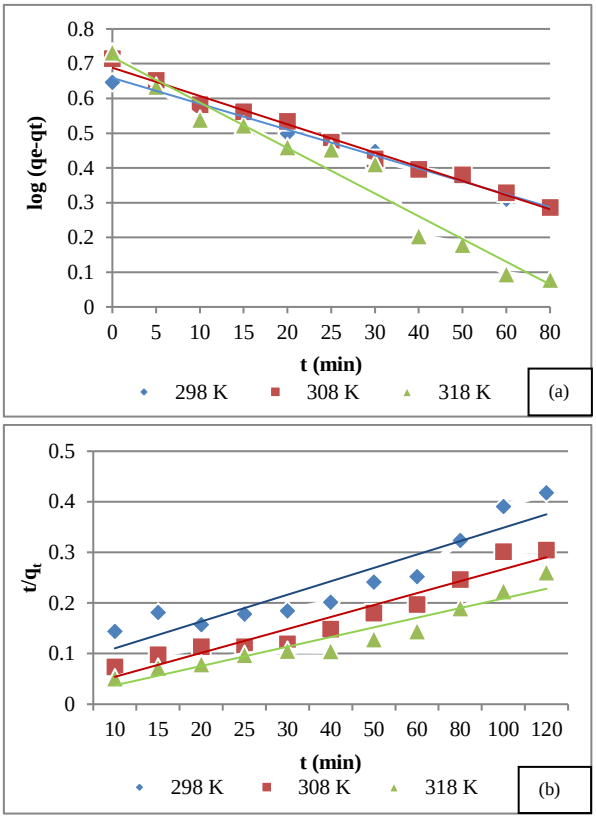


Figure 12. Linear plots of a) pseudo first order and b) pseudo second order model for the adsorption of MB onto hazelnut shell char

Table 4. Rate constants of pseudo first order and pseudo second order models with correlation coefficients

	Pseudo First Order		Pseudo Second Order	
Temperature (K)	K_1 (min^{-1})	R^2	K_2 (g/mg.min)	R^2
298	0.086	0.99	0.0084	0.86
308	0.094	0.99	0.0183	0.93
318	0.151	0.97	0.0200	0.91

3.3.7. Thermodynamic study

Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o for the adsorption system were calculated using the following equations (7-9):

$$K_c = \frac{C_{ads}}{C_e} \quad (7)$$

$$\Delta G = -RT\ln K_c \quad (8)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute solution temperature. The values of ΔH^o and ΔS^o were determined from the slope and intercept of the Van't Hoff plot of $\ln K_c$ versus 1/T which are shown in Figure 13 [35]. The calculated thermodynamics parameters are given in Table 5.

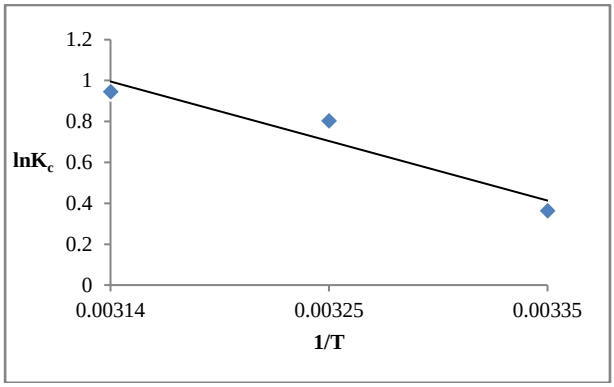


Figure 13. Van't Hoff plot for the adsorption of MB onto hazelnut shell char

Table 5. Thermodynamic parameters of MB adsorption on hazelnut shell char at different temperatures

Temperature (K)	K_c	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol.K)
298	1.439	-0.902	2.42	10.69
308	2.233	-2.057		
318	2.575	-2.501		

As can be seen from Table 5, K_c (equilibrium constant) values increased with an increase in temperature. The positive value of ΔH^o showed the endothermic nature of the process. The positive value of ΔS^o indicated an increase in the randomness at the solid/solution interface during the adsorption of the MB dye on hazelnut shell char. When temperature increased with considered positive values of ΔH^o and ΔS^o, ΔG^o was going to get a negative value and the process are spontaneous. The decrease in $\Delta G°$ values showed the feasibility of adsorption as the temperature increased.

4. CONCLUSIONS

This study aimed to determine the effectiveness of non-commercial activated carbon which is produced from hazelnut shell for the removal of MB dye. Using this material as an adsorbent instead of high cost commercial activated carbon is very important to contribute to industrial ecology at local level because of an alternative green approach for removal of MB is developed. The following conclusions could be made based on the analysis of the results obtained in this work. Experimental results showed that the contact time necessary for maximum adsorption was 300 minute approximately. Highest percentage of dye removal was observed at pH 4.0. It was found that the percentage removal of methylene blue was dependent on the dose of adsorbent. The percent removal of dye increased rapidly with increase in the dose of the adsorbent due to the greater availability of surface area.The kinetics of adsorption process showed that an increase in adsorption capacity with the increasing temperature. This result confirmed the endothermic nature of the ongoing process. It was observed that the adsorption of methylene blue decreased with increasing of the initial dye concentration. The Freundlich equation was found to have the higher applicability (best fit) to the experimental data obtained in this work. The kinetic behaviors of the adsorption of MB dye followed the pseudo first order model and also the adsorption process of MB was spontaneous. As a result, biochar produced from hazelnut shell had sufficient binding capacity to remove methylene blue from water.

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NOMENCLATURE

C_o: Initial dye concentration in solution phase, (mg/L)
C: Final dye concentration in solution phase, (mg/L)
C_e: Concentration of the dye solution at equilibrium, (mg/L)
K_f:Freundlich constant indicative of the relative adsorption capacity of the adsorbent, [mg/g(L/mg)1/n]
K_L: Constant related to the free energy of adsorption, (L/mg)
K_1 : Pseudo first order rate constant, (min^{-1})
K_2 : Pseudo second order rate constant, (g mg^{-1} min^{-1})
m: Weight of adsorbent, (g)
1/n: Heterogeneity factor
q_e: Amount of dye adsorbed per unit mass of adsorbent at equilibrium, (mg/g)
q_m: Maximum adsorption capacity, (mg/g)
q_t : Sorption capacity at a given time, (mg/g)
R^2: Correlation coefficient
t: Contact time, (min)
T: Temperature, (K)
V: Volume of dye solution, (L)

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