



Optimization of high surface area activated carbon production from miswak (*Salvadora Persica*) with ZnCl_2 using Taguchi method and its application in methylene blue removal

Serdar Aral¹ · Gamze Güven Kaya¹ · Ayşe Vildan Beşe¹

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Abstract

In the first part of this two-stage study, the optimum conditions for one-step AC production from miswak with zinc chloride were examined using the Taguchi optimization method. Impregnation time (1–3 h), impregnation ratio (1:1–3:1), activation temperature (350–650 °C), and activation time (1–2 h) were selected as experimental parameters, and each parameter was examined at three levels. The AC produced under optimum conditions (impregnation time: 3 h, impregnation ratio: 3/1, activation temperature: 650 °C, and activation time 1 h) has a high surface area of 1702 m²/g. The characterization of AC produced under optimum conditions has been elucidated by advanced analytical methods such as SEM, FTIR, BET, and pH_{pzc} . In the second part, the methylene blue removal performance of OAC was investigated with a series of batch adsorption experiments. The effects of pH (2–10), initial dye concentration (500–1500 mg/L), adsorbent dosage (0.5–3.5 g/L), and temperature (25–55 °C) on the methylene blue removal efficiency were examined. The adsorption data were applied to isotherm (Langmuir, Freundlich, and Temkin) and kinetics models (pseudo-first order, pseudo-second-order, Elovich, and intra-particle diffusion). The isotherm and kinetics models that best represented the adsorption of methylene blue by OAC were the Langmuir isotherm and the pseudo-second-order kinetic model, respectively.

Keywords Activated carbon · Adsorption · Methylene blue · Miswak · Optimization · Taguchi

1 Introduction

Fresh water is the most valuable substance necessary for living things to survive. Although 70% of the planet we live on is water, only 3% of this amount is usable fresh and clean water. In parallel with population growth and industrial development, the demand for usable water is increasing day by day. The distribution of consumption rates of usable water resources is approximately 67% in agriculture, 23% in industry, and 10% in domestic consumption. As a result of agricultural and industrial uses, water resources are polluted by many chemicals such as agricultural chemicals, heavy metals, synthetic dyes, and petroleum products. It is predicted that there will be a serious water crisis in the coming years if the necessary measures are not taken [1].

Dyes are widely used in food, medicine, plastic, paper, leather, cosmetics, and textile industries [2, 3]. According to the World Health Organization (WHO) report, synthetic dyes are among the top ten chemicals in the chemical pollutant class due to their polluting properties [4]. Especially in recent years, increasing demand due to developments in fashion has made the textile industry the area where synthetic dyes are consumed the most. The textile industry uses approximately 10,000 tons of dyes per year and approximately 100 tons of these dyes are disposed of as waste [5]. Biological and phytochemical activities of aquatic living things deteriorate because they prevent the passage of sunlight and oxygen to waters polluted by dyes [6]. Also, these toxic substances transferred to humans and animals through the food chain cause serious health problems [7]. The methylene blue (MB), which is a cationic dye, is widely used to dye silk, cotton, wood, and wool. Exposure to methylene blue can cause mental disorders, vomiting, jaundice, necrosis, and permanent eye damage [8].

In today's world, where it is difficult to get clean water resources, wastewater treatment becomes very important.

✉ Ayşe Vildan Beşe
vbese@atauni.edu.tr

¹ Department of Chemical Engineering, Faculty of Engineering, Ataturk University, Erzurum, Turkey

For the treatment of the dye-containing wastewater, a lot of methods are used such as coagulation [9], membrane separation [10], electrochemical degradation [11], sedimentation [12], ion exchange [13], biological processes (anaerobic and aerobic digestion) [14], oxidation [15], and adsorption [16]. The high cost of many of these processes limits their use. Adsorption is preferred owing to its environmentally friendly, cheap, effective, and easy application properties [17].

Activated carbon (AC) is a unique adsorbent due to its large surface area, high porosity (micropores, mesopores, macropores) properties and high surface reactivity [18]. Because of these properties, AC plays an important role in many fields of industry such as water treatment, chemical and petroleum industries, catalysis, batteries, fuel cells, pharmaceutical medicine, and hydrometallurgy [19]. Activated carbon (AC) is an amorphous material produced from carbon-rich organic structures such as wood, lignite, and coal. In recent years, it has been preferred to produce AC from agricultural wastes such as fruit peels, seeds, and tropical woods to produce low-cost AC [20]. The physical and chemical activation methods are used to develop the physical properties of AC. While the physical activation process is mostly used in commercial production, the chemical activation process is applied to biomass or biowaste containing cellulosic structure [21]. KOH [22], NaOH [23], H_3PO_4 [24], ZnCl_2 [25], or metal salts [26] are widely used as chemical activators. Among these activation agents, ZnCl_2 is especially preferred when producing AC from lignocellulosic and cellulosic biomass. ZnCl_2 causes an electrolytic effect called swelling in the molecular structure of celluloses, which breaks down the cellulose molecules. As a result, the produced AC has a larger surface area and pore volume [27]. Methylene blue removal from aqueous media using activated carbon produced with ZnCl_2 from many biomass such as coconut shell [28], shaddock peel [29], mango peels and seeds [30], woody lignocellulosic waste [31], and bamboo waste [32] has been successfully applied.

The pore structure and surface properties of AC are closely related to the synthesis conditions such as activator, time, and pyrolysis temperature [21]. For this reason, optimization of process parameters becomes important for effective active carbon synthesis for both adsorption and use

in various applications. However, determining the optimum values of the parameters requires an excessive number of experiments and long periods. Taguchi experiment design (DoE), which uses orthogonal indices to minimize the influence of uncontrollable factors, is an efficient optimization method used to minimize the number of experiments to improve quality. Since its application is easy and systematic, it is preferred in the optimization of different engineering problems [33]. Many studies have been reported in the literature in which the Taguchi method has been successfully applied to produce AC from various biomass [34–37].

Salvadora Persica, also known as arak, miswak, or tooth stick, is a short tree species that grows wild in Asia and South Africa. Miswak sticks have been used as a natural toothbrush for many centuries, and the World Health Organization (WHO) supports its use in oral hygiene. The organic part of miswak consists of lignin, cellulose, and hemicellulose [38]. The literature review has shown that miswak is generally used as a biosorbent in the removal of lead [39], cadmium [40], nickel, chromium, copper [41], and uranium, thorium, barium, strontium, and arsenic [42] from aqueous solutions.

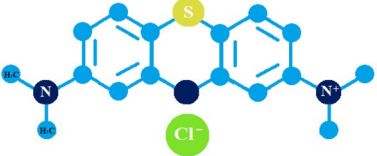
The main objective of this study was to determine the optimum conditions for the production of high surface area activated carbon from miswak with ZnCl_2 using the Taguchi method, to elucidate the characterization of activated carbon produced under optimum conditions (OAC) by analytical techniques and to evaluate the methylene blue removal performance of the AC produced under optimum conditions.

2 Materials and methods

2.1 Materials

Miswak sticks were obtained from a local market in Erzurum. Zinc chloride (ZnCl_2 , purity of %99) was used as the activating agent in the production of activated carbon. An inert atmosphere was provided by using nitrogen gas (N_2 , purity of %99) during the activation process. The methylene blue (MB) dye was chosen for adsorbate use in adsorption experiments. The molecular structure and characteristics of MB are given in Table 1. NaOH and HCl were used to adjust

Table 1 Characteristic properties of MB [43]

The structure of chemical	Molecular formula	M_w (g/mol)	Characteristic
	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 3\text{H}_2\text{O}$	319.85	Cationic $\text{pK}_a=5.80$ $\lambda_{\text{max}}=664\text{nm}$

the pH of the solutions in adsorption studies. All chemicals used in the experiment were obtained from Sigma Aldrich. Deionized water was employed washing of AC and preparation of solutions.

2.2 Synthesis of activated carbon

Miswak sticks were washed several times with deionized water to remove dust and dirt and then dried in an oven at 105 °C. They were first cut to approximately 2 cm in size, then ground in a rotary blade grinder and sieved through a 2-mm size sieve. Particles under 2 mm, which constitute 95% of the total mass, were used in the study. Impregnation time (A), impregnation ratio (B), activation temperature (C), and activation time (D) were selected as process parameters in AC production. The activation temperature range was determined using the TGA analysis of miswak. Literature data was used to determine other parameters and ranges. Parameters and their levels are given in Table 2.

AC synthesis experiments, each parameter examined at three levels, were carried out according to the $L_9(3^4)$ orthogonal array. Fifteen grams of ground miswak sample was used for each experiment. According to the impregnation ratios ((ZnCl_2 (g)/miswak (g)) given in Table 2, ZnCl_2 was dissolved in 100 mL of deionized water and then added to the miswak samples. The samples were kept in a water bath at 80 °C for the determined impregnation time and then dried at 105 °C for 24 h. The impregnated dried sample was placed in a ceramic crucible and placed in an oven with a heating rate of 10 °C/min. Activation processes were carried out at the determined activation temperature and time in a constant N_2 flow atmosphere of 100 mL/min. At the end of the experiment period, the sample was cooled to room temperature in a nitrogen atmosphere. The synthesized samples were washed with distilled water until the pH became 7. After washing, the ACs were dried in a 105 °C oven.

2.3 Statistical analysis

Taguchi-based design of experiments (DoE) method was used to determine the optimum conditions for the production of activated carbon. The goal of Taguchi's philosophy is to reduce the number of experiments while preserving process reliability and accuracy. The Taguchi method, a factorial

technique, uses an orthogonal array to determine the effect of diverse process variability on a response change. The method uses the signal to noise ratio (S/N) as the optimization criterion, which is categorized into three classes: bigger better, nominal best, and smaller better [44].

To determine the removal efficiency of the synthesized activated carbons, 50 mL of methylene blue solution (pH = 6, concentration of 500 mg/L) was placed in 150-mL stoppered flasks, and 0.1 g of activated carbons produced under different conditions was added to the flasks. Flasks were placed into a shaking water bath (Mettler, Germany) and kept at 25 °C, at a shaking speed of 250 rpm for 24 h. After dye solutions that reached equilibrium were centrifuged for 5 min at 3000 rpm, the remaining MB concentration in the solution was determined at 664 nm by UV–vis spectrophotometer (Thermo Scientific, ABD). Removal efficiency (R , %) was calculated by Eq. 1.

$$R(\%) = \frac{(C_o - C_e)}{C_o} 100 \quad (1)$$

where C_o and C_e represent the initial dye concentration and the equilibrium concentration.

MINITAB 18 program was used to perform statistical analyses. The data were evaluated using the bigger-is-better results statistics in Eq. 2. The larger the better:

$$SN_L = -10 \log_{10} \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{Y_i^2} \right) \quad (2)$$

2.4 The raw material and OAC characterization

A CHNS analyzer (Flash 2000, Thermo Scientific) was used for elemental compositions (C, H, N, S) of raw miswak and OAC. The amount of oxygen was calculated by subtracting the sum of these four values from 100%. The thermal decomposition behavior of miswak was examined with a thermogravimetric analyzer (TGA, NETZSCH STA 409 Luxx) in a N_2 atmosphere at a heating speed of 20 °C/min, between the room temperature (~20 °C) and 1000 °C. Fourier infrared transformation spectroscopy (FT-IR, Bruker) was used to determine the functional groups of the raw sample and OAC. FT-IR analysis was performed between wavelengths of 650 and 4000 cm^{-1} . The pore properties of OAC, specific surface area, pore distribution, and volume were determined from the adsorption–desorption data of liquid nitrogen at 77 K with a Brunauer–Emmett–Teller (BET) surface analyzer (Micromeritics TriStar II 3030 Plus). The surface morphologies of the synthesized OAC were obtained by scanning electron microscopy (SEM, Nova NanoSEM450).

To determine the pH_{zpc} of OAC, 50 mL of 0.1 M NaCl solution was placed in 150-mL conical flasks, and pH values were

Table 2 Parameters and levels used in the experiment

Parameters			Levels		
A	Impregnation time	(h)	1	2	3
B	Impregnation ratio	(g/g)	1:1	2:1	3:1
C	Activation temperature	(°C)	350	500	650
D	Activation time	(h)	1	1.5	2

adjusted to five different pH (pH_i) values in the pH range of 2–10 with 0.1 M NaOH or 0.1 M HCl solutions. Then, 0.1 g of OAC was added to the solutions and placed in a shaking water bath at 25 °C for 24 h. At the end of the period, the final pH (pH_f) values of the supernate were measured, and the pH_{zpc} value was determined by graphing pH_i versus pH_f [45].

2.5 Batch adsorption experiments

The methylene blue removal performance of AC produced under optimum conditions (OAC) from aqueous solutions was examined according to the batch adsorption method. Experiments were carried out in a temperature-controlled shaker at a constant stirring speed of 250 rpm (Mettler, Germany). Initial pH (2–10), time (0–120 min.), initial MB concentration (500–1500 mg/L), adsorbent amount (0.5–3.5 g/L), and temperature (25–55 °C) were selected as parameters. One hundred milliliters of dye solution at the specified concentration was adjusted to the pH value to be studied by using 0.1 M NaOH and HCl. The pH solution was controlled with a pH meter (Thermo Orion 3). The determined amount of OAC was added to the solution that reached thermal equilibrium at the desired temperature. Samples taken at certain time intervals (0–120 min) were centrifuged (3000 rpm at 5 min), and the concentration of MB remaining in solution was analyzed at 664 nm by UV–vis spectrophotometer (Thermo Scientific, ABD). The adsorption capacity (q_t or q_e) per unit weight of the adsorbent was determined using the Eqs. (3–4) [46].

$$q_t = \frac{(C_o - C_t)}{m} V \quad (3)$$

$$q_e = \frac{(C_o - C_e)}{m} V \quad (4)$$

C_o , C_t , C_e , m , and V represent the initial dye concentration (mg/L), the dye concentration in the solution at any time

(mg/L), the equilibrium concentration (mg/L), the amount of AC (g), and the solution volume (L), respectively.

3 Results and discussion

3.1 Optimization of OAC synthesis

Nine experiments were performed according to the L_9 Taguchi orthogonal array. The removal efficiency gives an estimate of the surface area and microporosity of AC [47]. Therefore, R (%) was chosen as the response variable to determine the effect of the parameters on the ACs produced. The experimental design, values of R (%) and SN_{Lm} are summarized in Table 3. Adsorption experiments were repeated twice. R_{main} (%) was the average of R (%) values obtained from two experiments.

To determine whether the data were normally distributed, SN_{Lm} values (Table 3) were subjected to the Anderson–Darling test, and the results are given in Fig. 1. The p value was determined as 0.190, with the significance level calculated above 0.05. Therefore, it can be seen that the data are normally distributed, and the null hypothesis result is satisfied. Levene and multiple comparison tests were used to assess data homogeneity (for 0.05 standard deviation), and the results are given in Fig. 2. The results of both tests, the p values were greater than 0.05, and the bars did not overlap, indicating that the data had a homogeneous distribution. This result showed that the null hypothesis was supported and the data was normally distributed [48].

ANOVA was performed to calculate the effects of the parameters on AC synthesis. Analysis results were evaluated according to F and p values ($p < 0.05$, 95% confidence level). As a result of the ANOVA created to examine the effects of all parameters, it was seen that the effect of parameter A (impregnation time) was insignificant (0.34%). Thus, this parameter was pooled, and its effect on other parameters

Table 3 Experimental design and values of R (%) and SN_{Lm}

A	B	C	D	R_1 (%)	R_2 (%)	R_{main} (%)	SN_{Lm}
Impregnation time (h)	Impregnation ratio (g/g)	Activation tem- perature (°C)	Activation time (h)				
1	1/1	350	1.0	22.29	21.36	21.82	26.77
1	2/1	500	1.5	31.26	32.22	31.74	30.03
1	3/1	650	2.0	85.73	83.82	84.77	38.56
2	1/1	500	2.0	29.32	28.25	28.78	29.18
2	2/1	650	1.0	80.44	82.46	81.45	38.22
2	3/1	350	1.5	28.91	27.44	28.18	28.99
3	1/1	650	1.5	81.79	83.76	82.78	38.36
3	2/1	350	2.0	16.94	16.63	16.78	24.50
3	3/1	500	1.0	55.09	53.63	54.36	34.70

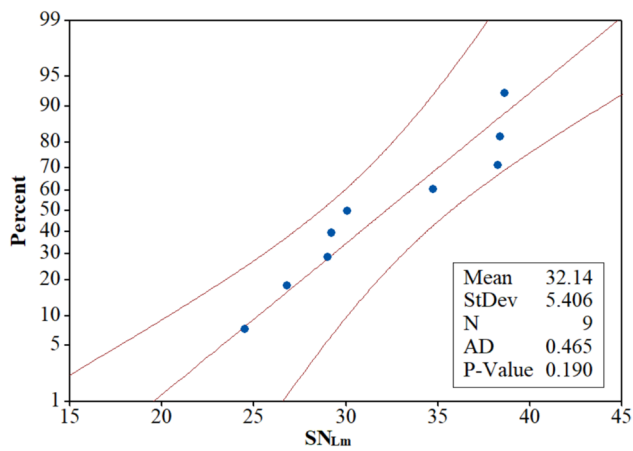


Fig. 1 Probability plot for SN_{Lm} ratios

was adjusted [49]. The ANOVA recreated after the pooling process is shown in Table 4.

Since $F_C > F_B > F_{Table}$ [$F_{(2,2)} = 19$], it can be said that the parameters that most affect AC performance were activation temperature and impregnation ratio, respectively. The most effective parameter on the performance of AC was the activation temperature with a contribution of 88.09%.

Impregnation ratio and activation time had a relatively low impact. The contribution of impregnation ratio and activation time on AC performance was 7.42% and 4.15%, respectively.

The impact of each parameter on performance results is stated in Fig. 3. Delta and rank were used to determine the most effective parameter on the response variant.

From Fig. 3a, it was seen that the impregnation time did not have an important effect on MB adsorption. This indicates that the rate of penetration of zinc chloride into the depths of the biomass is high, and the penetration is significantly complete within 1 h. Açıkyıldız et al. (2014) reported similar results for activated carbons produced with zinc chloride from plant wastes [50]. Increasing the impregnation rate increased the MB removal efficiency (Fig. 3b). Zinc chloride creates an electrolytic effect called swelling in the cellulosic material and causes the cellulose to break down. Increasing the amount of $ZnCl_2$ reaches more cellulosic substances and increases the amount of decomposition. Thus, it causes more tar and volatile substances to move away from the structure and creates a more porous structure [21]. Activation temperature has the greatest effect on MB adsorption capacity. The increase in activation temperature positively increased MB adsorption (Fig. 3c). This

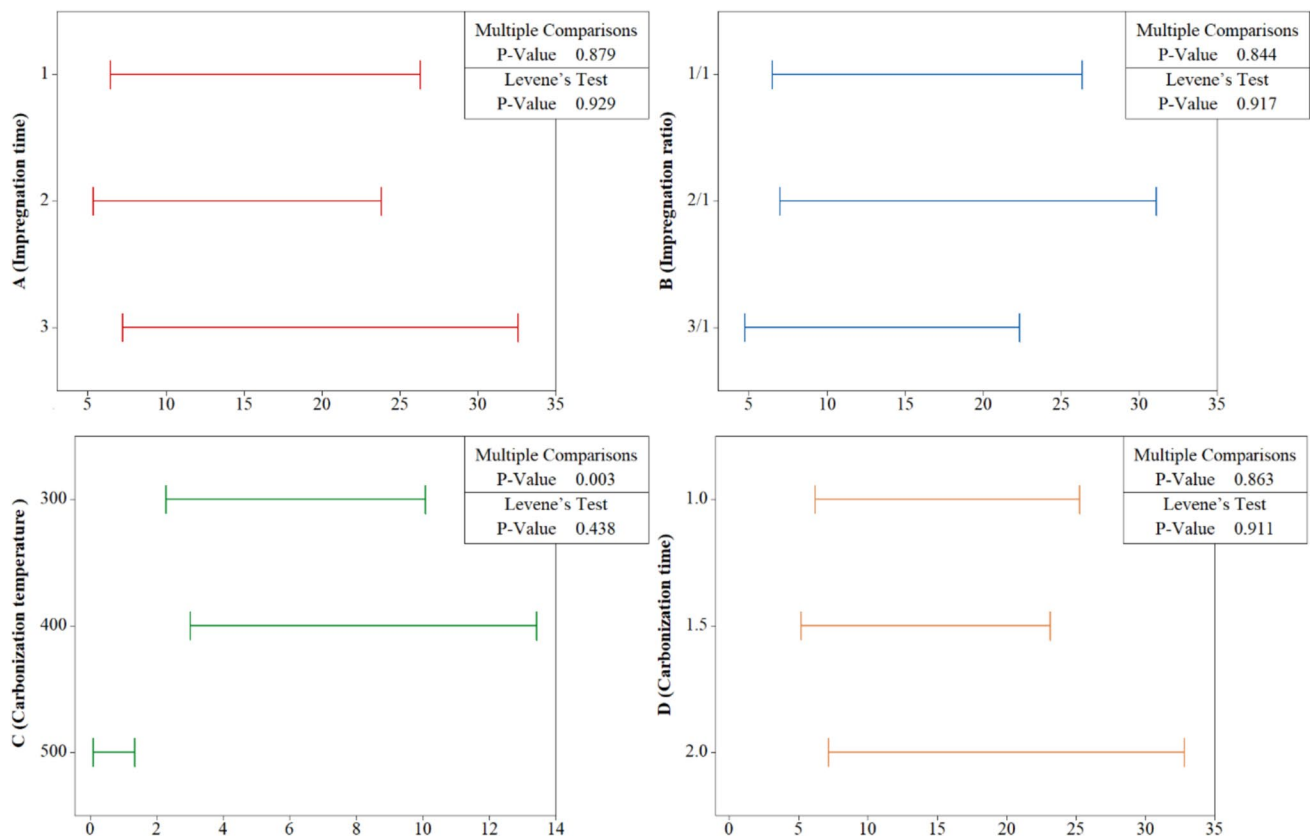
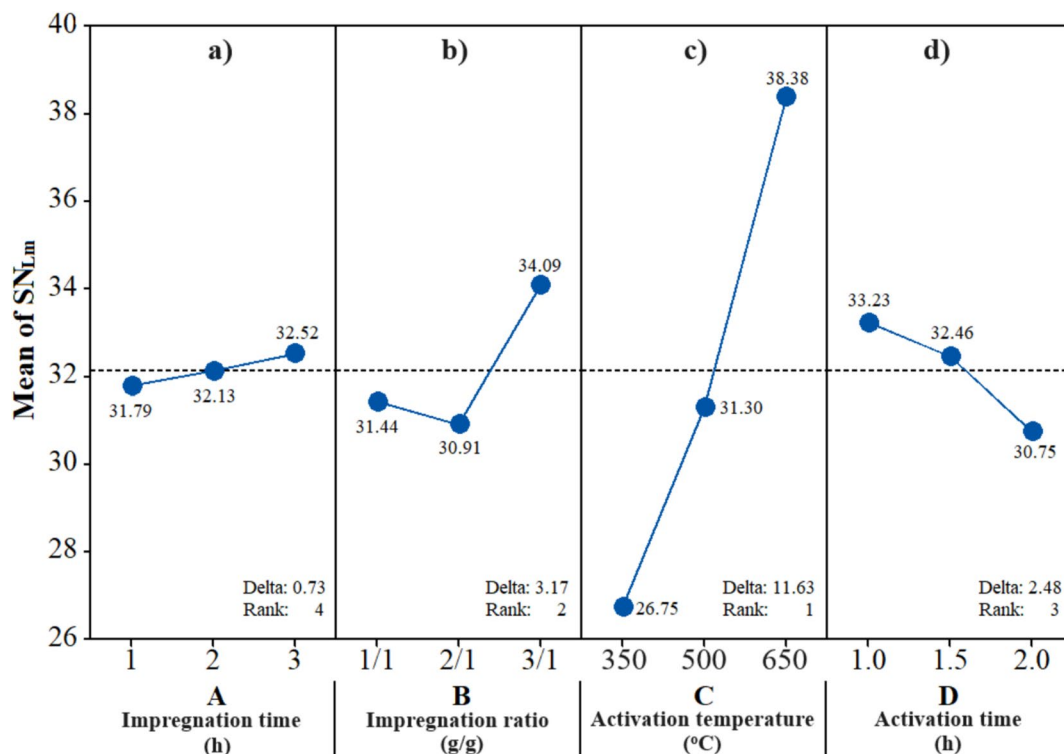


Fig. 2 The homogeneity (Levene and multiple comparison) test for SN_{Lm} ratios

Table 4 The analysis of ANOVA

Source	DF	Seq SS	Adj MS	F value	p value	Contribution %
A	-			Pooled		
B	2	17.35	8.68	21.64	0.044	7.42
C	2	205.93	102.97	256.79	0.004	88.09
D	2	9.70	4.85	12.09	0.076	4.15
Error	2	0.80	0.40			0.34
Total	8	233.78				100.00

**Fig. 3** The main effect of each parameter on the performance statistics

effect can be described as increasing thermal decomposition by rising temperature and rising the formation of a porous structure with volatile components evaporation [51]. Increasing the activation time decreased the MB adsorption of AC (Fig. 3d). The thermal stress on the thin walls of the porous structure, which remains under the influence of temperature for a longer period, increased. Collapse of pore walls as a result of increased thermal stress leads to the transformation of micropores into macropores or the closure of pores [52].

The largest peak value of each main effect graph represents the most optimum value for the given parameter [53]. It can be seen from Fig. 3 that the optimum operating conditions were the impregnation time: 3 h, impregnation ratio: 3/1, activation temperature 650 °C, and activation time: 1 h (A3B3C3D1). As a result of ANOVA analysis, it was seen that the impregnation time was not important.

Therefore, the impregnation time was taken as 1 h to save time. In this case, the optimum conditions were arranged as the impregnation time: 1 h, impregnation ratio: 3/1, activation temperature 650 °C, and activation time: 1 h (A1B3C3D1). When the experimental plan (Table 4) was examined, it was seen that there was no experimental set suitable for this combination. Therefore, a validation experiment was conducted for optimum conditions, and then the MB removal efficiency of AC obtained on the optimum conditions was determined. The results are given in Table 5. The MB removal efficiency of OAC was obtained to be 98.78%.

As given in Table 5, the experimentally found removal value is within the confidence interval. This result shows that the internal interactions between the experimental parameters are insignificant and the accuracy of the established model [54].

Table 5 Optimum experimental conditions and experimental and estimated values of MB adsorption capacity of OAC

Parameter	Optimum level	Optimum value
Impregnation time (h)	A 1	1
Impregnation ratio (g/g)	B 3	3/1
Carbonization temperature (°C)	C 3	650
Carbonization time (h)	D 1	1
	Means	
Estimation value (%)	99.10	
Experimentally obtained value (%)	97.52	
Confidence limits of prediction (%)	97.32–100	

Table 6 Ultimate analysis of miswak and OAC

Composition (%)	C	H	N	S	O
Miswak	41.2	5.66	0.63	0.86	51.65
OAC	85.1	3.75	0.93	0.55	9.67

3.2 Characterization

The ultimate analysis of raw miswak and OAC is shown in Table 6. The elemental composition of miswak was determined as 41.20% C, 5.66% H, 0.63% N, 0.86% S, and 51.65% O. The C content of the AC obtained as a result of activation increased from 41.2 to 85.12%. During the activation process, a significant portion of the non-carbon substances in the miswak was removed, so the remaining part had a structure that contained a large proportion of carbon [55]. The H, O, and S contents decreased from 5.66 to 3.75%, from 51.65 to 9.67%, and from 0.86 to 0.55, respectively. The use of ZnCl_2 and the thermal effect cause the removal of atoms such as H, O, and S from the AC structure [56]. The amount of N increased from 0.63 to 0.93%. This increase can be explained that ZnCl_2 provides the release of volatile substances and facilitates the adsorption of N onto C [21].

The thermal behavior of miswak under a nitrogen atmosphere in the range of 20–1000 °C was examined and the TGA curve is given in Fig. 4a. Miswak has a three-stage decomposition zone over a wide temperature range. There was approximately 10.30% weight loss in the first region between 25 and 230 °C. This region can be attributed to the removal of moisture content and slightly volatile components in the miswak. This was followed by the second region, where there was a 49.63% weight loss between 230 and 360 °C. This region, called first pyrolysis or reactive pyrolysis, refers to the process in which lignin, hemicellulose, and cellulose decompose and depolymerize. The third zone is the second pyrolysis zone or passive pyrolysis zone. There was a weight loss of approximately 30.96% in the

range of 360–790 °C. This region can be assignable to the breakdown of lignin and tar [57].

Adsorption–desorption isotherm and distribution of pore size of OAC are given in Fig. 4b. According to the IUPAC adsorption classification, the isotherm obtained complies with type IV [58]. At relative pressures up to $\sim P/P_0 < 0.4$, a sharp rise in adsorbed volume was determined by rising pressure. At relative pressures above this, volume expansion continued to increase at a slower rate with increasing relative pressure. This behavior indicates that OAC has micro and mesopore structures [58]. In addition, the presence of hysteresis at relative pressures greater than 0.4 also confirms that OAC has a mesoporous structure [59]. By analysis, the surface area, the pore volume, and the average pore diameter of OAC were obtained as $1702.11 \pm 4.72 \text{ m}^2/\text{g}$, $1.34 \text{ cm}^3/\text{g}$, and 3.14 nm, respectively. The BET surface area of the raw sample was $40.13 \pm 1.50 \text{ m}^2/\text{g}$. With the activation process, the surface area of the raw sample increased approximately 42 times.

SEM analysis was performed to evaluate the morphological features of raw miswak and OAC. SEM images of raw miswak and OAC are given in Fig. 4c and d respectively. While the raw miswak sample was observed to have a homogeneous flat surface, the synthesized OAC interface was observed to have heterogeneity, roughness, and a distinctly porous structure. In particular, these formed pores facilitate the penetration of MB dye molecules into the inner surface of OAC. This indicates that AC was successfully synthesized from the raw miswak sample to OAC [60].

FTIR spectra of raw miswak and OAC in the range of 4000–400 cm^{-1} are shown in Fig. 4e. Characteristic bands were observed in the raw and AC at 3535, 3094, 1157, and 955 cm^{-1} . As a result of chemical and thermal activation, the peak seen in the band at 2379 cm^{-1} in miswak disappeared in activated carbon, while two new peaks were formed in the bands of 1580 and 758 cm^{-1} in activated carbon. The functional groups predicted at these points are given in Table 7.

The pH_{pzc} value of the produced OAC was found as 4.85 in Fig. 5. At pH_{pzc} , the number of negative and positive charges on the surface of the AC is equal, meaning the surface charge is zero at this value. At values lower than pH_{pzc} , the surface charge of AC is positive, while at higher values, the surface charge is negative. For this reason, it is preferred to work at pH values lower than pH_{pzc} for the adsorption of anions, and at higher pH values for the adsorption of cations [64].

3.3 Effect of some parameters on MB adsorption

3.3.1 The pH

The pH is one of the most significant parameters of the solution for the success of the adsorption as it determines the

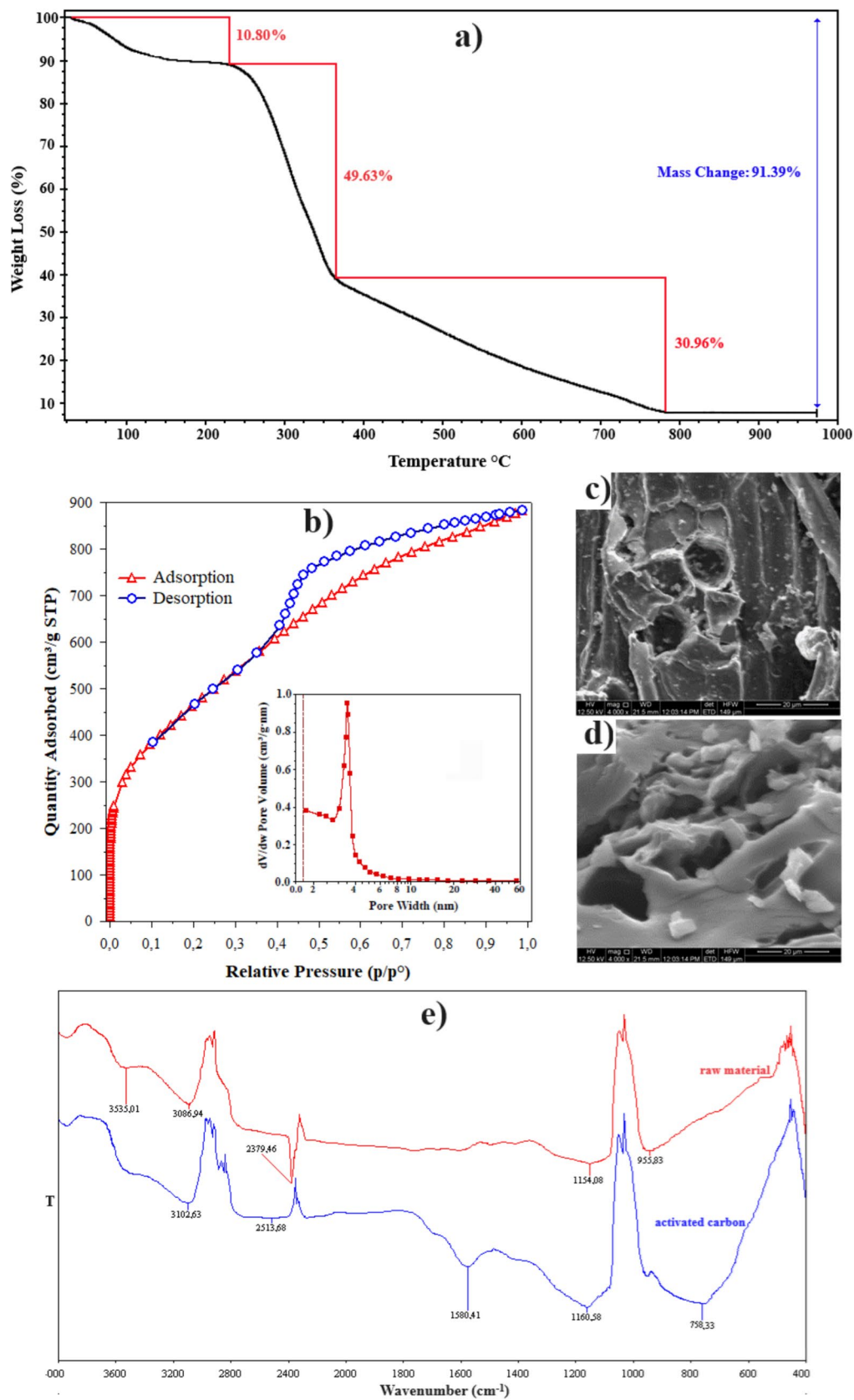
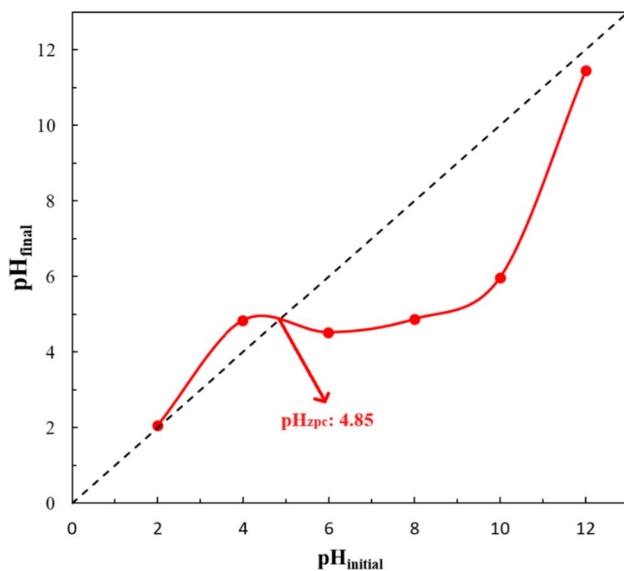


Fig. 4 **a** TG curve of raw miswak. **b** Adsorption/desorption isotherm and pore size distribution of OAC. **c** SEM images of raw miswak. **d** SEM images of OAC. **e** FTIR analysis of raw miswak and AC

Table 7 Functional groups of the raw material and AC [61–63]

Band (cm ⁻¹)	Raw material	Activated carbon
	Functional groups	
3535	Hydroxyl groups O–H stretching	Hydroxyl groups O–H stretching
3094	C–H stretching of methyl and methylene groups	C–H stretching of methyl and methylene groups
2379	C≡C of functional groups	-
1580	-	N–H stretching vibration or O–H stretching
1157	C–O stretching of oxidized carbons as alcohols, phenols etc	C–O stretching
955	C–O stretching of ether groups	C–O stretching
758	-	Out of plane bending in benzene derivatives

**Fig. 5** Point of zero charge of OAC

degree of ionization of dye and the surface charge of activated carbon. The interaction between the adsorbent and the adsorbate may occur through electrostatic attraction–repulsion forces, van der Waals forces, or hydrogen bonds during the adsorption process, [65]. The effect of pH on MB adsorption was examined in the range of pH 2–10 (2.0 g/L adsorbent amount in 100 mL, 25 °C, 1000 mg/L initial MB concentration, 120 min, 250 rpm). The results are shown in Fig. 6a. MB adsorption increased in the pH range of 2–6. This situation is relevant to the values of pK_a and pH_{zpc}. The pK_a value of MB is 5.80 [66]. When the pH value of the solution is lower than 5.80, the dye molecules are anionic, and at pH values higher than this value, they are cationic. pH_{zpc} value was found to be 4.85 for this study, meaning that the surface charge of activated carbon was neutral at this value. When pH_{solution} < pH_{zpc}, the surface of the activated carbon becomes positively charged due to protonation of acidic groups on the surface. When pH_{zpc} < pH solution, the

surface of the activated carbon becomes negatively charged due to dissociation or ionization of acidic oxygen groups on the surface. This increased adsorption as it caused the electrostatic attraction between AC and MB molecules [43, 65]. As seen in Fig. 6a, MB adsorption increased in the range of pH 2–6. In the figure, while the adsorption capacity was 250 mg/g and the removal rate was 50% at pH 2, it was 430 mg/g and 88.3% at pH 6, respectively. No significant change in MB adsorption was observed at pH values greater than pH 6. This indicates that adsorption has reached the optimum level [43].

3.3.2 The initial concentration and contact time

The effect of time on MB adsorption at different initial concentrations (500–1500 mg/L) was examined (a dosage of 2.0 g/L adsorbent in 100 mL, 25 °C, pH 6, and 250 rpm), and results are given in Fig. 6b. As seen in Fig. 6b, the amount of q_t and the adsorption rate increased with increasing initial concentration. With increasing concentration, the number of MB molecules in the unit volume of the solution increases. The rises in the number of molecules rises the driving force and allows MB molecules to move faster to the AC surface. As a result, both the adsorption rate and the q_t value increase [67]. Depending on the adsorption rate, three regions were seen in this graph. In the first region between 0 and 30 min, the adsorption rate was high because the active centers of the adsorbent were empty and driving force of mass transfer was high. In this region, q_t values increased in the range of 223–495 mg/g with increasing initial concentrations, respectively, while removal rate values were found in the range of 89.2–66%. In the second region between 30 and 90 min, the adsorption rate slowed down considerably as the occupancy rate in the pores increased. Again, in this region, q_t values increased in the range of 241–540 mg/g with increasing initial concentrations, respectively, while removal rate values were found in the range of 96.6–72%. In the third region between 90 and 120 min, the adsorption rate was a constant period and reached equilibrium [68].

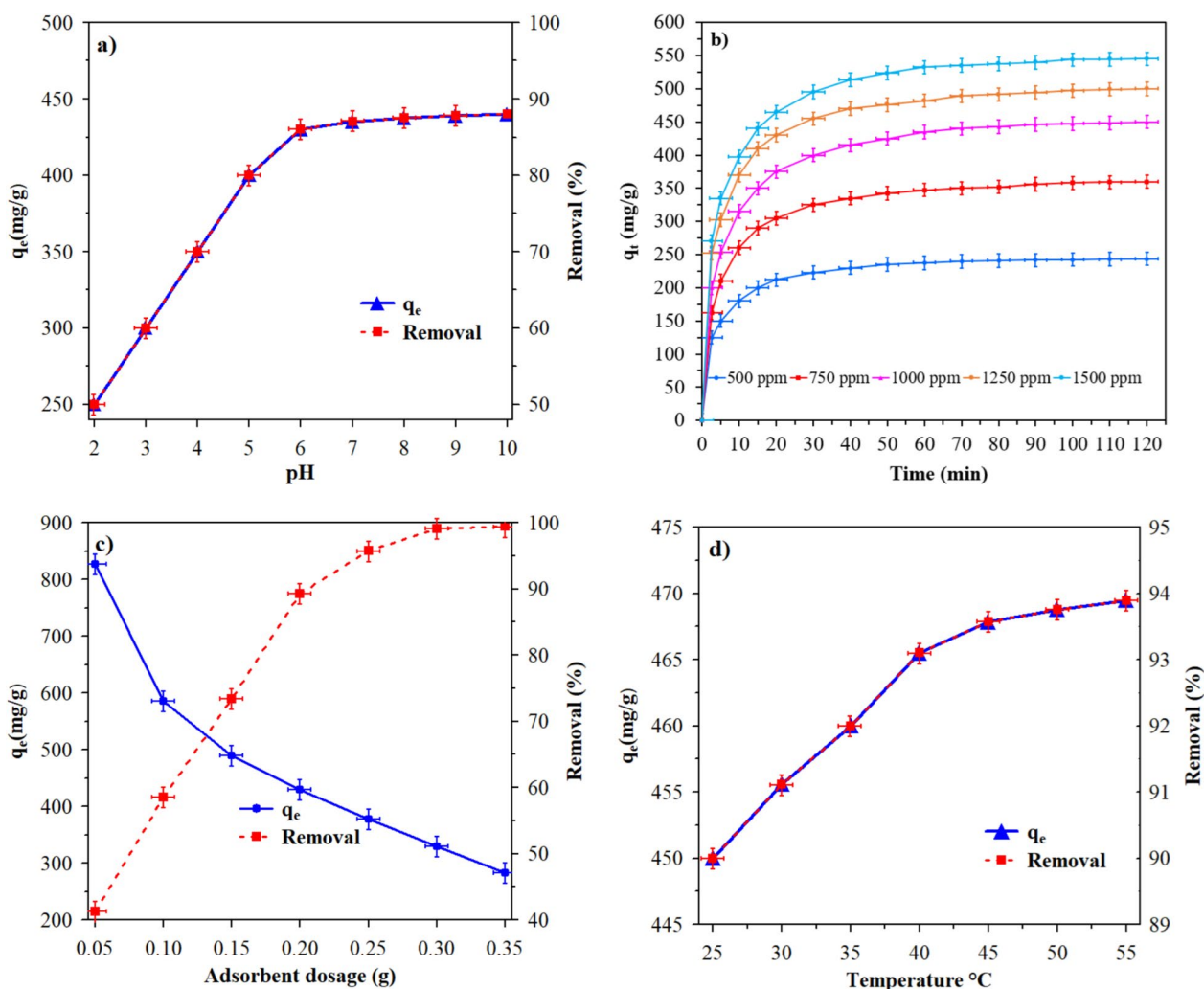


Fig. 6 **a** Effect of pH on the adsorption of MB. **b** Effect of contact time and initial MB concentration on the adsorption of MB. **c** Effect of adsorbent dosage on the adsorption of MB. **d** Effect of temperature on the adsorption of MB

Values of q_e varied between 243.7 and 545 mg/g, and the removal rate varied between 97.4 and 72.7%.

3.3.3 The adsorbent dosage

Determining the optimum amount of adsorbent is important to prevent waste of AC. The effect of the amount of adsorbent on adsorption was examined using OAC in the range of 0.05–0.35 g/L in 100 mL (25 °C, pH 6, 1000 mg/L, 250 rpm, and 120 min), and the results are given in Fig. 6c. When the amount of adsorbent increased from 0.05 to 0.35 g, the dye removal percentage increased from 41.33 to 99.39%. This can be explained by the rise in empty active centers with rising amounts of AC [43]. The adsorption capacity declined from 826.5 to 283.4 mg/g. There will be more usable active sites when the amount of AC increases. Since the number of MB molecules in the solution is the same, fewer

MB molecules will be adsorbed per unit mass [67]. In the figure, it is seen that there is a break in the graph slope at the adsorbent amount of 0.2 g (removal approximately 90%), and the shape becomes a plateau at values greater than 0.2. Therefore, in Fig. 6c, the point of 0.2 g, where this plateau is first seen, was determined as the optimum adsorbent amount.

3.3.4 The temperature

The effect of temperature on the adsorption process was examined in the range of 25–55 °C (0.2 g OAC in 100 mL, dye concentration of 1000 mg/L, pH 6, 120 min, 250 rpm), and the results are given in Fig. 6d. Adsorption efficiency, adsorption capacity, and dye removal were determined as 450 mg/g and 90% at 25 °C, respectively, while at 55 °C, they were determined as 469.49 mg/g and 93.90%, respectively. Adsorption efficiency increased with increasing

temperature. Therefore, it can be said that the adsorption mechanism of MB by OAC is endothermic. The rise in adsorption efficiency with temperature can be explained by factors such as the decrease in solution viscosity and the increase in the kinetic energy of dye molecules. As the temperature increases, the viscosity of the solution decreases. Thus, the resistance to the movement of MB molecules in solution decreases which makes it easier for dye molecules to reach the AC surface. In addition, the solution with reduced viscosity penetrates through the active carbon pores faster, allowing its molecules to come into contact with more surfaces. The rise in the kinetic energy of MB molecules with rising temperature raises the diffusion coefficient in both solution and solid. This allows the MB to move faster and reach more surfaces in less time [69].

3.4 The adsorption equilibrium isotherms

Adsorption isotherms express the balanced relationship established between the amount of substance adsorbed on the AC surface and the amount of the substance remaining in the solution. Three different isotherm models, namely Langmuir, Freundlich, and Temkin, given in Table 8, were used to study the adsorption mechanism of MB adsorbed by OAC [70].

The fit of the equilibrium values obtained from the adsorption experiments with the model equations was examined using the non-linear analysis method (OriginPro 2019b). Nonlinear isotherm graphs of Langmuir, Freundlich, and Temkin models are given in Fig. 7.

Model fits were checked statistically using the correlation coefficient (R^2), the reduced chi-square (χ^2), and the root mean square error (RMSE). The indicator of the statistically most appropriate model is the highest value of R^2 and the smallest value of χ^2 and RMSE values. Model constants with statistical results are given in Table 9.

According to the statistical results, the Langmuir isotherm was determined as the most suitable model with the R^2 (0.9941) and the lowest χ^2 (241.33) and RMSE (14.53) values. This showed that adsorption occurred in certain specific regions on the adsorbent surface, and that there was single-layer adsorption on the surface [71]. Additionally, an important feature of the Langmuir isotherm is the

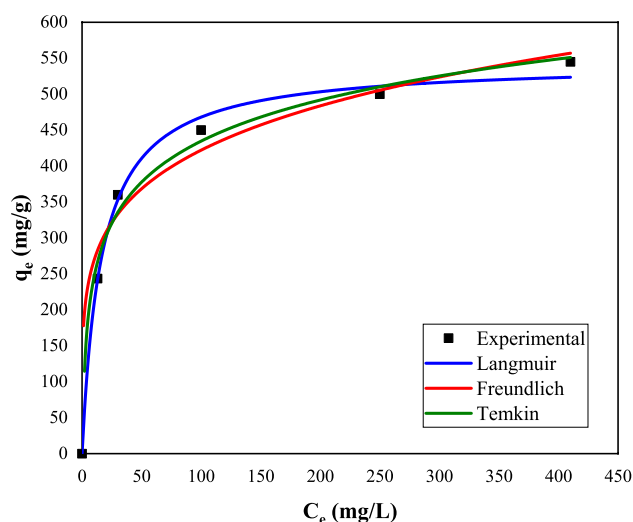


Fig. 7 The fitting curves of nonlinear isotherm models of adsorption (pH: 6, temperature: 25 °C, OAC dosage: 0.2 g, and contact time: 120 min)

separation factor (R_L) it defined to determine the feasibility of the adsorption process. R_L is defined as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad (8)$$

where C_o and K_L express the initial dye concentration and equation constant, respectively.

If $R_L = 0$, adsorption is irreversible; $0 < R_L < 1$, adsorption is favorable; $R_L = 1$ is linear and $R_L > 1$, adsorption is unfavorable [72]. R_L values calculated from the Langmuir model were found to be between 0.0313 and 0.0106. Since these values are between 0 and 1, it can be said that adsorption is appropriate.

Freundlich isotherm model (Eq. 6) accepts that the adsorption process occurs in multilayers consisting of different structures with various adsorption energies. The constant “ n ” expresses information about the nature of the adsorption. If the n value is less than 1, the adsorption is chemical, if the n value is equal to 1, it is linear, and if the n value is greater than 1, it is physical. Also, “ n ” among 1 and 10 indicates that the adsorption process is suitable [73]. Freundlich constants K_F and n values were calculated as 170.927 mg/g and

Table 8 Mathematical expressions of the nonlinear isotherm models

Models	Equation	No	Equation constants
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ (5)	q_m K_L	Langmuir adsorption capacity (mg/g) Langmuir isotherm constant (L/mg)
Freundlich	$q_e = K_F C_e^{1/n}$ (6)	n K_F	Freundlich exponent Freundlich isotherm constant (mg/g)
Temkin	$q_e = B_T \ln(K_T C_e)$ (7)	B_T K_T	Factor related to the heat of adsorption Temkin equilibrium constant (L/mg)

Table 9 The isotherm parameters and statistical results of MB adsorption onto OAC

Isotherm models	Isotherm constants and coefficients			Model fitting values		
				R^2	χ^2	RMSE
Langmuir	$q_{\max}$ (mg/g)	K_L (L/mg)	R_L			
	544.295 ± 12.17	0.062 ± 0.007	$0.0313 - 0.011$	0.994	241.33	14.53
Freundlich	K_F (mg/g)	n				
	170.927 ± 26.43	5.092 ± 0.03		0.926	1068.53	30.58
Temkin	b (J/mol)	K_T (L/g)	B_T			
				0.991	376.82	18.16

5.092, respectively. Since the n value is greater than 1 and also between 1 and 10, it can be said that the adsorption of MB onto the OAC surface is of physical and the adsorption is suitable.

Temkin isotherm (Eq. 7) examines the relationships among adsorbate and adsorbent in the adsorption. The sorption heat decreases with the amount of substance coated on the adsorbate [74]. Temkin constant b (J/mol), which represents the heat of adsorption, is calculated with the following equation:

$$B_T = \frac{RT}{b} \quad (9)$$

where R represents the universal gas constant that is 8.314 J/mol.K and T represents absolute temperature (K).

b value was found to be 30 J/mol. Since the binding energy is less than 8 kJ/mol, it can be said that the adhesion of MB to the AOC surface is by physical adsorption mechanism, and due to the low adsorption energy, the adsorbate is bound to the AC surface by van der Waals interaction [75].

3.5 The adsorption kinetics

Kinetic models are important tools to understand the rate and mechanism of the adsorption process. These models are used to explain how the adsorption process evolves with time and how the solution of MB binds to the OAC surface. The kinetic models express the amount of dye adsorbed by AC as a function of time. Adsorption experiments to examine the suitability of kinetic models were carried out for

six different dye concentrations (500–1500 mg/L) at pH 6, temperature 25 °C, adsorbent amount 2.0 g/L, and contact time of 120 min. The obtained data were applied to four different kinetic models, including pseudo-first-order, pseudo-second-order, Elovich, and intra particle diffusion models, shown in Table 10 [76].

Analysis of kinetic parameters was calculated by the nonlinear regression analysis method (OriginPro 2019b, 95% confidence level). The fit graphs of the applied kinetic models are presented in Fig. 8, and the coefficients of the kinetic models with their statistical values are presented in Table 11.

From Table 11, the highest values of R^2 and the lowest values of χ^2 and RMSE for all concentrations were provided in the second-order model. Therefore, it can be remarked that the most appropriate kinetic model explaining the adsorption of MB by OAC is the pseudo-second-order kinetic model.

The pseudo-first-order kinetic model is related to the adsorption rate and the amount of dye adsorbed on the OAC surface and is valid in the early stages of the adsorption process. However, the accuracy of this model may be limited, because higher concentrations generally exhibit a behavior more suitable for the second-order-kinetic model. The pseudo-second-order model generally provides better fit at higher concentrations, because this model more accurately reflects the process of adsorption with the surface and the filling of active sites on the surface. In addition, as the concentration increases, the adsorption capacity is reached more quickly, and the adsorption rate is generally more constant [77].

Table 10 Mathematical expressions of the nonlinear kinetic models

Models	Equation	No	Equation constants
Pseudo-first order	$q_t = q_e [1 - e^{-(k_1 t)}]$ (10)	q_e k_1	Adsorption capacity at equilibrium (mg/g) PFO model rate constant (min^{-1})
Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{(1 + k_2 q_e t)}$ (11)	q_e k_2	Adsorption capacity at equilibrium (mg/g) PSO model rate constant (g/mg.min)
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha \beta t)$ (12)	α β	Elovich rate constants (g/mg) Elovich rate constants (mg/g.min)
Intraparticle diffusion	$q_t = k_i t^{1/2} + C$ (13)	k_i C	Model rate constant (mg/g.min ^{1/2}) Kinetic model a constant

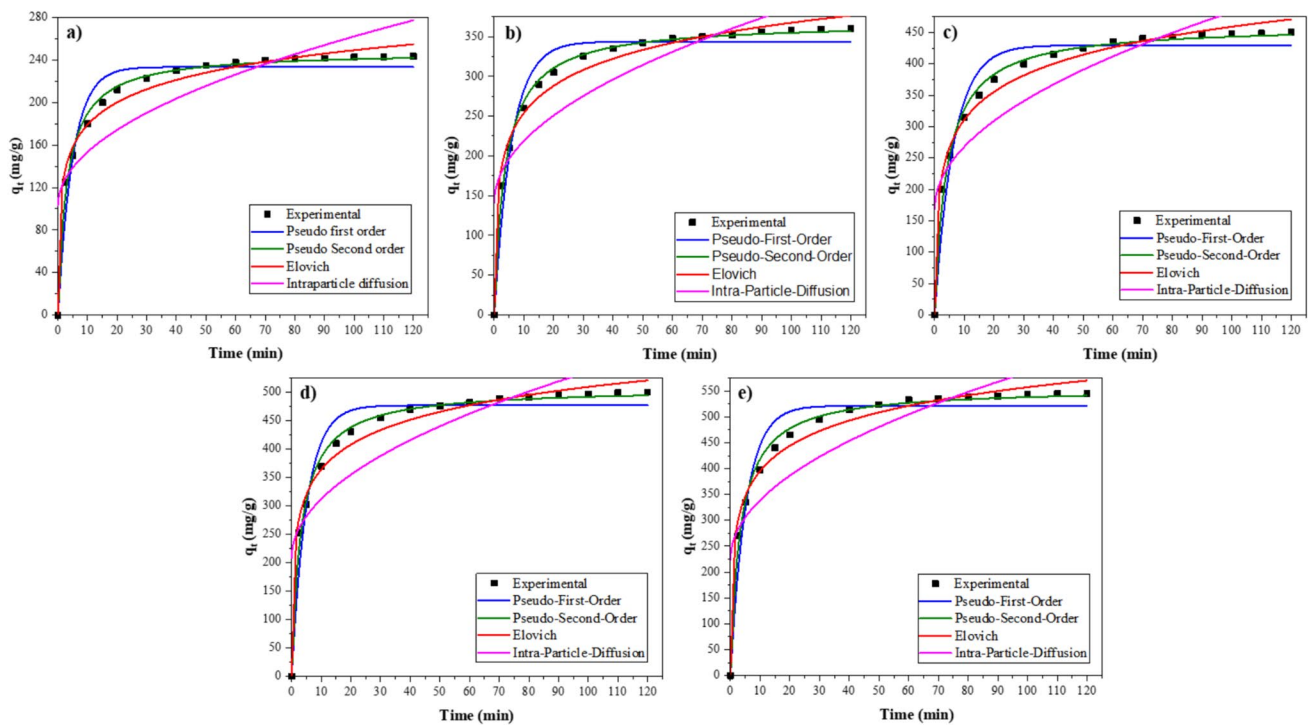


Fig. 8 The nonlinear kinetic curves of adsorption for different initial dye concentrations. **a** 500 mg/L. **b** 750 mg/L. **c** 1000 mg/L. **d** 1250 mg/L. **e** 1500 mg/L

Table 11 The nonlinear kinetic model constants and statistical results of adsorption of MB onto OAC

Kinetic model	Kinetic model constants		Model fitting values		
Pseudo-first-order	q_e (mg/g)	k_1 (1/min)	R^2	χ^2	RMSE
500 mg/L	233.469 ± 4.327	0.201 ± 0.023	0.9505	208.63	13.51
750 mg/L	343.805 ± 5.928	0.172 ± 0.018	0.9605	376.31	18.15
1000 mg/L	429.486 ± 8.292	0.158 ± 0.018	0.9525	718.45	25.07
1250 mg/L	476.988 ± 8.755	0.198 ± 0.023	0.9518	850.94	27.29
1500 mg/L	521.379 ± 10.005	0.192 ± 0.023	0.9482	1102.71	31.06
Pseudo-second-order	q_e (mg/g)	k_2 (g/mg min)	R^2	χ^2	RMSE
500 mg/L	248.202 ± 2.009	$13.1\text{E-}4 \pm 8.7\text{E-}5$	0.9937	26.47	4.81
750 mg/L	367.884 ± 2.110	$7.4\text{E-}4 \pm 3.2\text{E-}5$	0.9971	26.86	4.84
1000 mg/L	461.190 ± 3.794	$6.2\text{E-}4 \pm 3.9\text{E-}5$	0.9945	82.72	8.51
1250 mg/L	507.577 ± 3.950	$5.5\text{E-}4 \pm 3.7\text{E-}5$	0.9943	101.37	9.42
1500 mg/L	555.646 ± 4.628	$5.3\text{E-}4 \pm 3.2\text{E-}5$	0.9936	136.92	10.95
Elovich	β (mg/g min)	α (mg/g min)	R^2	χ^2	RMSE
500 mg/L	0.033 ± 0.002	1081.80 ± 417.87	0.9838	68.18	7.72
750 mg/L	0.020 ± 0.001	846.86 ± 290.43	0.9818	173.17	12.31
1000 mg/L	0.016 ± 0.001	795.01 ± 218.41	0.9962	209.11	13.53
1250 mg/L	0.016 ± 0.001	2018.32 ± 736.26	0.9848	268.48	15.32
1500 mg/L	0.014 ± 0.001	1926.62 ± 656.63	0.9857	304.68	16.33
Intra-particle-diffusion		k_i (mg/g min ^{1/2})	R^2	χ^2	RMSE
500 mg/L	103.191 ± 19.642	15.902 ± 2.774	0.6800	1347.69	34.34
750 mg/L	141.477 ± 27.969	24.449 ± 3.949	0.7133	2732.51	48.90
1000 mg/L	168.910 ± 33.476	31.352 ± 4.726	0.7414	3914.50	58.52
1250 mg/L	208.714 ± 39.750	32.736 ± 5.613	0.6876	5519.45	69.49
1500 mg/L	224.785 ± 42.965	36.148 ± 6.067	0.6970	6448.34	75.12

The Elovich model is particularly effective in adsorption processes on heterogeneous surfaces. α is an indicator of the adsorption rate. A higher value of α indicates that adsorption occurs more rapidly. β is an indicator of the energy inherent in adsorption or the active surface area. This constant depends on the surface properties of adsorption and represents the active surface area of OAC. It also indicates the heterogeneity of the adsorption energy. A lower value of β indicates that the surface is more heterogeneous, and that there is a wider distribution of adsorption energy [78].

The intraparticle diffusion model is used to describe the diffusion of methylene blue from the liquid phase to the OAC surface in the early stages of adsorption. C is a constant and is a parameter that increases the accuracy of the model or reflects the initial conditions. As the dye concentration increases, the amount of dye reaching the OAC surface increases. This may affect the diffusion process. As the concentration increases, the amount of dye reaching the OAC surface increases, which affects the diffusion rate and the C constant. The increase in C represents the differences in the transition stages in the adsorption process and the changes in the initial conditions. Higher concentrations indicate a higher initial concentration and a greater diffusion flux, which increases the C value [79].

3.6 The thermodynamic analysis

The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°), and activation energy (E_a) provide information about the internal energy change of the adsorption process. Thermodynamic parameters were determined using the equilibrium values of adsorption experiments performed at temperatures of 25–55 °C. The equilibrium constant of adsorption (K_c) is determined using Eq. 14.

$$K_c = \frac{C_{Ae}}{C_e} \quad (14)$$

where C_{Ae} is the absorbed concentration at equilibrium (mg/L).

$$\Delta G^\circ = -RT \ln(K_c) \quad (15)$$

Enthalpy and entropy values are determined from the van't Hoff equation (Eqs. 15–16).

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (16)$$

$$\ln(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (17)$$

The activation energy of adsorption was determined using linearized Arrhenius equation (Eq. 18).

$$\ln k_2 = \ln k_o - \frac{\Delta E_a}{R} \frac{1}{T} \quad (18)$$

where k_2 is the adsorption rate constant (for the best-fit kinetic model), k_o is a temperature-independent constant [43].

The effect of temperature on the adsorption process was investigated in the range of 25–55 °C (0.2 g OAC in 100 mL, 1000 mg/L dye concentration, pH 6, 120 min, 250 rpm). The k_2 values used in the Arrhenius equation were obtained by applying the data obtained at each temperature to the pseudo-second-order model, which was found to be the best-fitting model in the kinetic study.

Enthalpy (ΔH°) and entropy (ΔS°) values were found from the slope and intercept points of the van't Hoff line (red line in Fig. 9), respectively. The activation energy of adsorption (E_a) was determined from the slope of the linearized Arrhenius plot (blue line in Fig. 9). The values of the thermodynamic parameters are summarized in Table 12. As can be seen in Table 12, ΔG° values were negative signs. This shows that the adsorption process was spontaneous. The positive value of ΔH° indicated that the adsorption of MB onto OAC was endothermic. As seen in Table 12, the numerical value of the Gibbs energy increased negatively with rising temperature, and the MB adsorption tendency increased with rising temperature. This situation supports that the phenomenon is endothermic for the adsorption of MB onto OAC. The positive sign of the entropy value indicates that the MB adsorbate is randomly adsorbed at the solid–liquid interface on the AC [80]. The E_a value was found to be 7.076 (kJ/mol). Since this value is between 0 and 50 kJ/mol, it can be said that the adsorption of MB onto OAC has occurred physically.

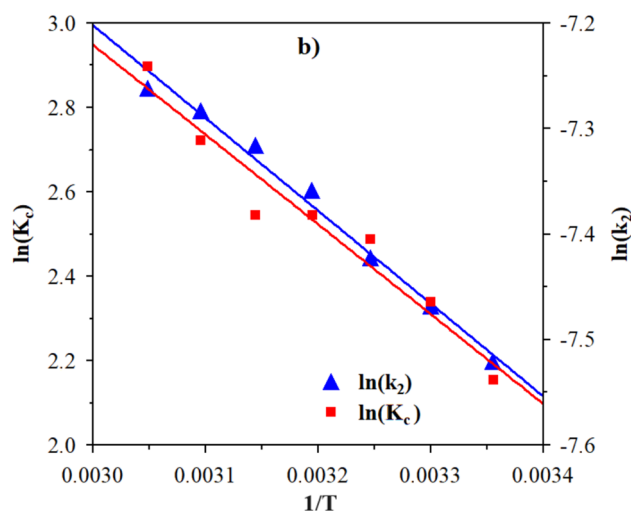


Fig. 9 Van't Hoff plot (red line) and linearized Arrhenius plot (blue line) for the thermodynamic analysis

Table 12 The values of thermodynamic parameters

Temperature (°C)	25	30	35	40	45	50	55	
Thermodynamic analysis	ΔG° (kJ/mol)	−5.44	−5.87	−6.25	−6.77	−7.16	−7.50	−7.76
	ΔH° (kJ/mol)	18.280						
	ΔS° (kJ/mol.K)	0.080						
	R^2	0.987						
Activation energy	k_2 (g/mg.min) $\times 10^4$	5.33	5.26	5.21	5.15	5.11	5.09	5.07
	E_a (kJ/mol)	7.076						
	k_0 (g/mg.min)	9.40×10^{-3}						
	R^2	0.946						

Additionally, the positive value of E_a supports that the adsorption process is endothermic [81].

3.7 Comparison on adsorption of MB

Experimental conditions and adsorption capacities for methylene blue removal of activated carbons produced with different materials are given in Table 13. As can be seen from Table 13, in terms of surface area and adsorption capacity determined in literature studies, the AC produced from miswak presented in this study has higher values in both surface area and adsorption capacity. The results obtained indicate that the synthesized OAC can be used as an effective adsorbent to remove MB dye from aqueous solutions.

4 Conclusion

The optimization of producing AC from miswak using ZnCl_2 as a chemical activator was studied according to the L_9 Taguchi orthogonal design, and the MB removal performance of the produced OAC was examined. Optimum conditions

were found to be impregnation time: 1 h, impregnation ratio: 3:1, activation temperature 650 °C, and activation time: 1 h. The most effective parameter was determined as activation temperature. The BET surface area of AC produced under optimum conditions was determined as 1700.2 m²/g. The characterization of AC produced under optimum conditions has been elucidated by advanced analytical methods such as SEM, FTIR, and BET. The effects of pH, temperature, initial concentration, adsorbate amount, and time on the methylene blue removal performance of OAC were examined. Adsorption data were applied to isotherm and kinetic models. The best-fitting isotherm model was the Langmuir model. The maximum adsorption capacity (q_m) was obtained as 544.30 mg/g. The kinetic model that best represents the adsorption of methylene blue on OAC was determined as the pseudo-second-order kinetic model. The thermodynamic analysis results showed that the adsorption process was spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$). The dye adhered to the OAC surface by physical sorption ($E_a = 7.06$ kJ/mol). In line with our goal, high surface area activated carbon was produced from miswak, which was generally used as a biosorbent in previous studies, under the optimum

Table 13 The comparison of adsorption capacity for different adsorbents in the removal of MB

Adsorbents	pH	T (°C)	t (min)	AC dosage	C_0 (mg/L)	BET (m ² /g)	Langmuir q_m (mg/g)	References
Miswak	6	25	120	2.0 g/L	500–1500	1702.11	544.30	This study
Walnut shells	6	25	120	1.25 g/L	20–100	1.01–3.12	41.40	[82]
Reed	8	25	720	0.005 g	20–200	26–37.50	77.35	[83]
Rapanea ferruginea	7	25	60	0.025 g	20–120	-	99–12	[84]
Stem	6	25	60	0.04 g	25–500	-	110.79	[85]
Sheath palm							162.54	
Pomegranate peel carbon	9.7	49	258	0.18 g	10–300	1.01	161.90	[86]
Corn cob	7	25	120	0.8 g/L	100–500	492.00	333.00	[87]
Coffee husk	7	25	120	1g/L	50–500	743.80	316.50	[88]
Date palm fronds	7.8	40	1050	1.38 g/L	35–540	2085.47	456.62	[89]
Animal dung	6	25	60	1.00 g	20–100	-	24.81	[90]
Scotch pine bark	8	25	60	0.08 g	100–250	1258.24	374.18	[43]

conditions determined, and its methylene blue removal from aqueous media was achieved with high success.

Author contribution Serdar Aral: data curation, writing—original draft preparation, visualization, investigation, supervision, software, validation, writing—reviewing and editing. Gamze Güven Kaya: data curation, writing—original draft preparation, visualization, investigation, supervision, software, validation, writing—reviewing and editing. Ayşe Vildan Beşe: Conceptualization, methodology, investigation, supervision, validation, writing—reviewing and editing.

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Declarations

Conflict of interest The authors declare no competing interests.

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