



RESEARCH ARTICLE

Single-step pyrolysis for producing activated carbon from sucrose and its properties for methylene blue removal in aqueous solution

Omer Kazak¹

¹Necmettin Erbakan University, Department of Environmental Engineering, Meram, Konya, TURKEY

ABSTRACT

Herein, activated carbon was prepared from sucrose, renewable carbon precursor by chemical activation method. Chemical activation process was carried out with KOH at 750 °C. The effects of chemical activation on the structure and morphology of activated carbon products were evaluated using TGA, BET, SEM, FT-IR, and zeta potential techniques. As a result of the activation process, the activated carbon having microporous ($1.138 \text{ cm}^3 \text{ g}^{-1}$) with high specific surface area ($2116.42 \text{ m}^2 \text{ g}^{-1}$) was obtained. The potential of using activated carbon as an adsorbent for removal of methylene blue in water was investigated under several experimental conditions. Langmuir adsorption capacity for methylene blue is $1666.66 \text{ mg g}^{-1}$ and its higher adsorption capacity than other adsorbents. Regeneration studies have shown that the activated carbon can also be used at least ten times for the removal of methylene blue with no change in its adsorption capacity. The performance was tested on real textile wastewater.

Keywords: Activated carbon, sucrose, adsorption, reusability, real textile wastewater

1. INTRODUCTION

Dyes can be used on textiles, paper, rubber, leather, food, etc. it is widely used in various industries and the waste water from these industries is one of the main pollutants. Industrial wastewater containing dyes has high chemical oxygen demand (COD), strong coloring effect, high pH and biologically toxic properties [1]. Discharge of industrial wastewater containing dyes to streams, lakes, marine and other receiving environments constitutes an important environmental problem and many of the dyes have carcinogenic and mutagenic properties for humans as well as aquatic life [2]. Therefore, industrial wastewater containing dyestuffs should be treated before discharging to the receiving environment.

In recent years, many techniques are used for the treatment of industrial wastewater containing dyes, including coagulation [3], photocatalytic degradation [4], membrane separation [5], biodegradation [6], advanced oxidation [7] and adsorption [8,9]. Among these methods, due to the ease of application and high removal efficiency of the adsorption method, it is

accepted as an effective method for removing dyes from wastewater [10]. Recent studies for the treatment of wastewater containing dyes by adsorption method have focused on the preparation of efficient, cheap and renewable adsorbent materials. One of the most commonly used adsorbents for the treatment of wastewater containing dyes is activated carbon. Activated carbon is known as carbon based materials with its highly porous structure and wide surface area [11]. In particular, the large surface area and chemical structure of activated carbon provide high removal of dyes from wastewater. In recent years, there has been an increasing interest in studies for the production of activated carbon from renewable and inexpensive starting materials [12]. Low-cost many biomass wheat bran [13], popcorn [14], waste vinasse [8], *thuja orientalis* cone [15], starch [16] were used as starting materials to prepared activated carbon. Although the reported activated carbon products are used in dyes adsorption, it is observed that the adsorption removal capacities are insufficient and have low regeneration efficiency. Also, few studies on the performance of activated carbon products were tested with real textile wastewater.

Corresponding Author: okazak@erbakan.edu.tr (Omer Kazak)

Received 6 April 2021; Received in revised form 4 May 2021; Accepted 24 May 2021

Available Online 15 June 2021

Doi: <https://doi.org/10.35208/ert.910576>

© Yildiz Technical University, Environmental Engineering Department. All rights reserved.

Compared to different starting materials, sucrose is considered a very attractive precursor material for obtaining activated carbon due to its low-cost, recyclable and rich carbon content [17]. With its simple molecular structure, sucrose can be obtained with high surface area with practical processes and provides less dangerous emission release during the pyrolysis process. This study, activated carbon production was carried out by simple chemical activation with KOH from sucrose. The structural and morphological properties of the products are characterized by Thermal Gravimetric Analysis (TGA), Brunauer Emmet and Teller (BET) (specific surface area, pore volume and pore size distribution), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), techniques and zeta potential analysis. The removal of activated carbon with the highest surface area, pore volume and size distribution were evaluated using model contaminant methylene blue in the aqueous solution. The effect of different pHs and contact time on activated carbon efficiency was investigated. Isotherm analysis and regenerability of activated carbon was presented. The adsorption capacity of activated carbon was compared with the literature. Finally, the adsorption mechanism was explained and activated carbon tested with real textile wastewater.

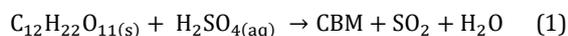
2. MATERIALS AND METHOD

2.1. Materials

Sodium hydroxide, Hydrochloric acid (30%), Sulfuric acid (98%) Sodium chloride, Potassium hydroxide, Methylene blue, Sucrose, Ethanol, were purchased from Merck Co. (Darmstadt, Germany).

2.2. Activated carbon preparation from sucrose

Firstly, starting carbon-based material was obtained from sucrose. To obtain the carbon-based starting material, 50 g of sucrose and 50 mL of 98% H₂SO₄ were added to the glass beaker in a controlled manner and mixed quickly with a glass stick for 30 seconds. With this method, according to the reaction given in Eq. (1), sucrose sulfuric acid was dehydrated and carbon-based starting material (CBM) was obtained.



CBM was washed with pure water until the pH of the wash water was 6.5-7. The washed material was dried at 105 °C and ground in agate mortar. KOH was used to activate of CBM. The CBM was homogeneously mixed with KOH in 1:1, 1:2, 1:3, 1:4, and 1:5 (w/w) ratios by mass. The mixture prepared in the stainless-steel reactor oven (Ptf Protherm 12/75/800) under a nitrogen atmosphere (200 mL/min) activation by heat treatment at 750 °C for 1 hour was performed. The activated carbons obtained were washed with pure water until the wash water is about 6-7, and dried in an oven at 105 °C. The activated carbons obtained are named as AC-x (x = 1, 2, 3, 4 and 5 KOH mixture ratio).

2.3. Characterization studies

The thermal behavior of CBM was analyzed with thermal gravimetric analyzer (Setaram, Setsys Evolution, France) under argon atmosphere at 25 mL/min flow rate, in the range of 40-800 °C with a temperature increase of 5 °C min⁻¹. FT-IR spectra of the products were recorded by FT-IR spectrophotometer (Perkin Elmer 1600, USA) in the range of 500-4000 cm⁻¹ wavelength. The surface morphologies of the products were obtained using FESEM (Zeiss, Geminisem 500, GERMANY). Using the BET analyzer (Quantachrome Quadrasorb evo, USA), the BET surface area and pore size distribution from N₂ adsorption isotherms were determined at 77K. Total pore volume (V_{total}) was obtained from the amount of N₂ adsorbed at P/P₀=0.95 according to the NLDFT (Non Local Density Functional Theory) method. The zeta potential of the product used in the adsorption studies was determined by using a Nanoplus 3 (Japan).

2.4. Adsorption studies

The most suitable product was used as a result of structural characterization (specific surface area, total pore volume and others) processes in adsorption studies. To study the adsorption performance of the product, the batch adsorption experiments were carried out using aqueous solution of methylene blue (λ_{max}= 660 nm).

Adsorption experiments, 0.01 g of product was put into the 20 mL of methylene blue solutions at various concentrations in the range of 250-1500 mg L⁻¹, the mixtures were shaken at 210 rpm over a period of time at 25 °C. After separation of each solution by simple filtration, the initial and remaining dye concentrations of each solution were determined by using a UV-visible spectrophotometer (Hach Lange, DR 5000, Germany) at each corresponding λ_{max} mentioned above. The pH of the solutions was adjusted with 0.01 M HCl and/or 0.1 M NaOH. Ionic strength of the mixtures was kept down as 0.01 M with NaCl. The amount of methylene blue adsorbent by product was determined using Eq. (2).

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (2)$$

where *q* is sorbed amount of methylene blue by product (mg g⁻¹); *C*₀ and *C*_{*e*} are the initial and equilibrium concentrations of methylene blue (mg L⁻¹); *V* is the solution volume (L); *m* is the mass of product (g). The effects of experimental parameters studied are pH (3-11), contact time (5-180 minutes), initial methylene blue concentration (250-1500 mg L⁻¹) and its reusability by using washing with 20 mL ethanol for 10 minutes was performed.

2.5. Real textile wastewater application

Real textile wastewater without any treatment was used in experimental studies. Physico-chemical characteristics of the the real textile wastewater used for study were pH: 9.80- 10.87, COD: 487 mg L⁻¹, Conductivity: 1987 μS cm⁻¹. Real textile wastewater

was supplied from a textile factory in Konya (Turkey). The color and chemical oxygen demand (COD) change of the real textile water at different pH (3, 7, 11) was observed.

3. RESULTS AND DISCUSSION

3.1. Determination of activation temperature

The effectiveness of the activation process depends on the interaction of the oxidizing agents used in the process with the carbon-based materials and the activation temperature. The activation process is generally carried out at temperatures where the mass loss of the starting material stabilizes [18]. Therefore, firstly, thermal behavior of CBM in argon atmosphere was evaluated and activation temperature was determined. The thermogram of the CBM obtained as a result of TGA is shown in Fig 1.

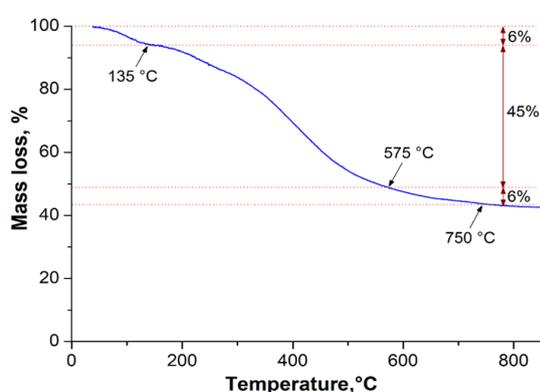


Fig 1. Thermal behavior of the carbon-based material (CBM)

With the increase in temperature, mass loss in CBM was determined to occur in three stage. The first stage, the 6% mass loss in which the temperature reaches 135°C is caused by the loss of moisture in the CBM [12]. The mass loss (45%) between 135-575 °C in the second stage may be due to the loss of oxygen-containing functional groups within the CBM as CO and CO₂ [19]. In the third stage, the mass loss (6%) at

the temperature increase after 600 °C slowed down considerably and became stable. As a result of the TGA of the CBM, it was observed that there was no significant mass loss in the mass above 600 °C. Therefore, the temperature of 750 °C was chosen for activation of CMB with KOH.

3.2. Characterization of ACs

The nitrogen adsorption-desorption isotherms and pore size distribution of the activated carbon products obtained with different amount of KOH (CBM: KOH, w/w) were compared, shown in Fig 2a-b. According to Fig 2a, AC-1, AC-2 and AC-3 show an isotherm with low porosity material properties, while AC-4 and AC-5 show an isotherms classified as type 1 according to the IUPAC classification and have microporosity [20,21]. It is seen that AC-4 and AC-5 have DFT pore size distributions (Fig 2b) less than 20 Å and microporous structure.

Surface areas, total pore volumes and micropore volumes of activated carbon products were examined and the results are presented in Table 1. As can be seen in Table 1, while the amount of KOH is increased from 1 to 4, the surface areas, total pore volumes and micropore volumes of activated carbon products increased from 756.24 to 2116.42 m² g⁻¹, from 0.412 to 1.199 cm³ g⁻¹, from 0.404 to 1.138 cm³ g⁻¹, respectively, above 1:4 these values decreased. KOH amount above 1:4, excessive metallic potassium on the carbon surface might cause blocking and collapsing in the pores which leads to a reduction in the surface area and pore volume [22]. According to these results, the amount of KOH appears to significantly affect the change in the surface area and pore structure. The fact that activated carbon has a large surface area and high pore volume means that higher adsorption efficiency will occur [23]. Consequently, the activated carbon product (AC-4), which is most suitable for adsorption, has been tried to be determined with the highest surface area (2116.42 m² g⁻¹) and total pore volume (1.199 cm³ g⁻¹).

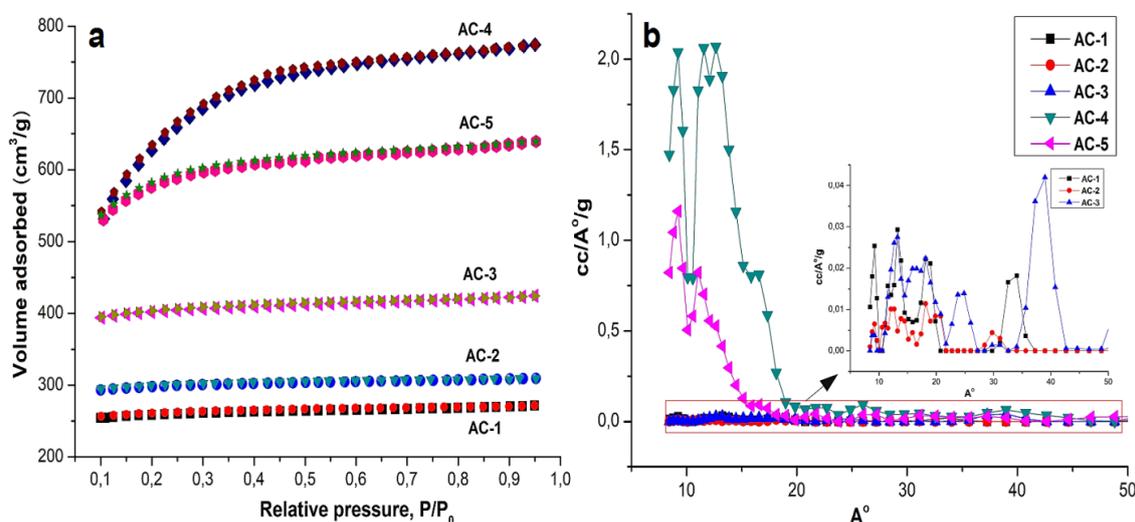


Fig 2. N₂ adsorption-desorption isotherms (a) and the DFT pore size distribution (b) of activated carbon products

Surface morphology of products obtained were examined by SEM technique and the images obtained are shown in Fig 3. It can be observed that the surface of the CBM is quite smooth and there are no pores. The porous structure of the products obtained as a result of activation of CBM with KOH appears to improve. When Fig 3 is examined, it is seen that

increasing the amount of KOH causes the development of porous structure on the surface of activated carbon products. The development of the products in the pore structure is due to the reaction between the carbon atoms and KOH, and the effect of the activation temperature [24].

Table 1. Surface area ($\text{m}^2 \text{g}^{-1}$) and pore volumes ($\text{cm}^3 \text{g}^{-1}$) of the products

Carbonaceous product	Specific surface area, $\text{m}^2 \text{g}^{-1}$	V_{total} , $\text{cm}^3 \text{g}^{-1}$	V_{micro} , $\text{cm}^3 \text{g}^{-1}$	V_{meso} , $\text{cm}^3 \text{g}^{-1}$
CBM	5.54	0.012	nd*	nd*
AC-1	756.24	0.421	0.406	0.015
AC-2	894.72	0.479	0.468	0.011
AC-3	1216.22	0.657	0.632	0.025
AC-4	2116.42	1.199	1.138	0.061
AC-5	1756.25	1.014	0.940	0.074

* V_{meso} was determined by subtracting V_{micro} from V_{total}

*nd: could not be determined

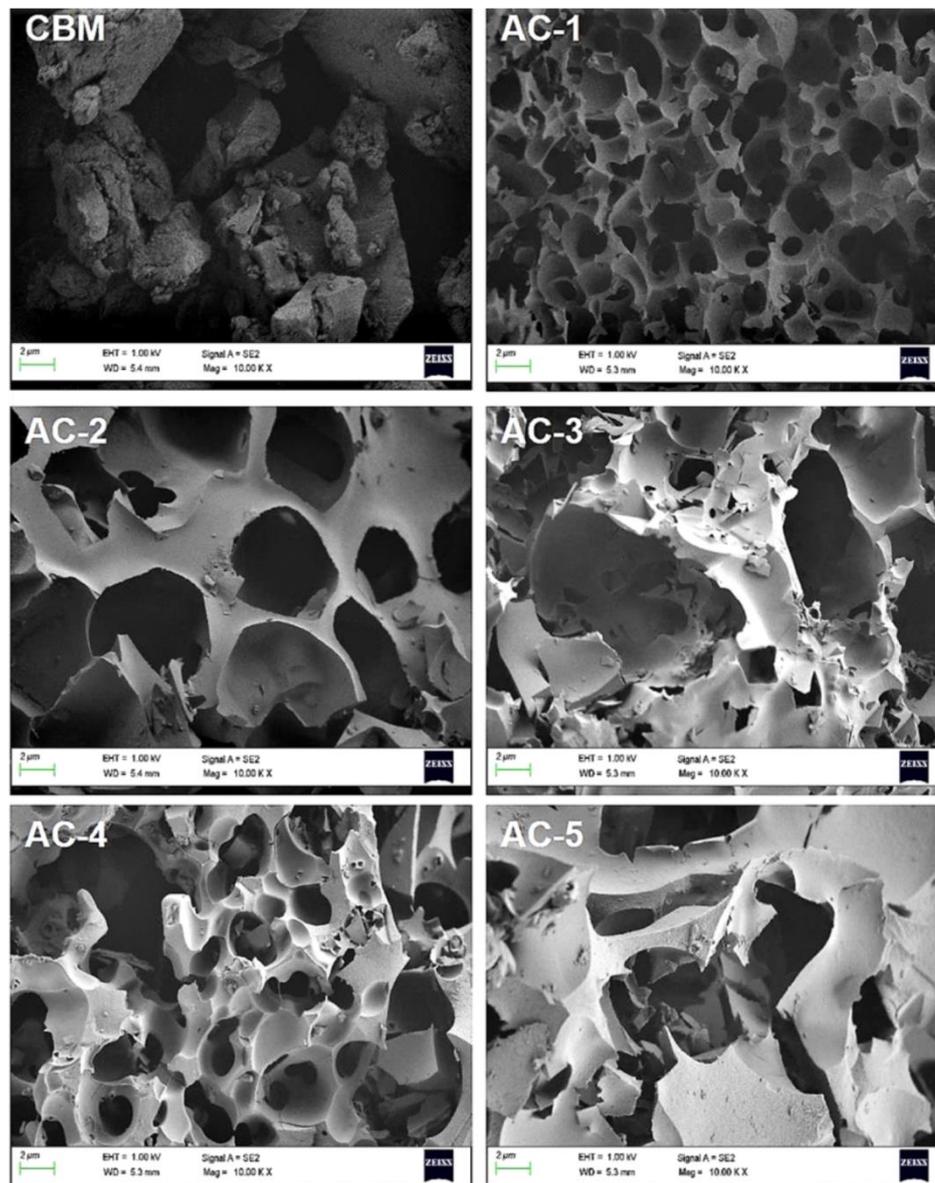


Fig 3. Surface morphologies of CBM and activated carbon products

Changes in the chemical structure of the activated carbon (AC-4) obtained by activation of the CBM product with KOH were examined by FT-IR analysis and the results are shown in Fig 4. In the FTIR spectrum of CBM, it originates from the band -OH group at 3375 cm^{-1} [25]. The bands seen in 1697 and 1242 cm^{-1} can be linked to the stretching the C=O and C-O-C groups, respectively [26]. The band seen at 1600 cm^{-1} comes from C=C vibrations [27]. As a result of the activation process applied, there is a decrease in the intensity of the bands in the FT-IR (Fig 4) spectrum of CBM.

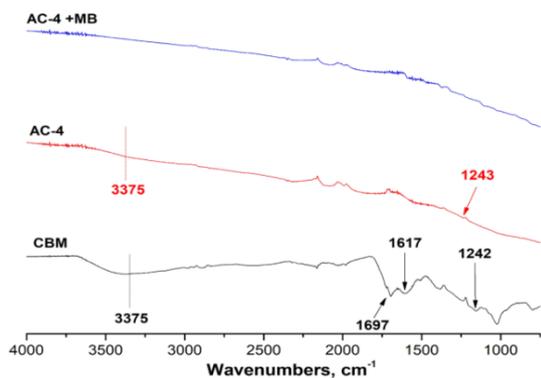


Fig 4. FT-IR spectra of the CBM and AC-4 before and after adsorption

3.3. Adsorption Studies

In the first studies conducted with methylene blue, the performance of the activated carbons (AC-x) obtained with different KOH ratios was tested with 500 mg/L methylene blue solution. The results obtained are shown in Fig 5. As shown in Fig 5, AC-4 product has been determined to have the highest methylene blue removal efficiency. This result is due to the higher surface area and total pore volume of the AC-4 product than the surface area and total pore volumes of other products. The results obtained from this preliminary experiment with methylene blue and the characterization studies, it was confirmed that it would be more appropriate to use the AC-4 product in adsorption studies.

3.4. Effect of pH

The pH of the solution, are important parameters that can affect the adsorption of substances from solution media. The adsorption of methylene blue (500 mg L^{-1}) from the aqueous solution with the AC-4 product was carried out at a different pH in the range of 3-13, and the results obtained are shown in Fig 6. As seen in Fig 6, the highest methylene blue removal capacity was obtained at pH 7. The zeta potential values of the AC-4 product in the range of pH 3-13 range between (24.86 and -34.08 mV respectively). According to these results, the increase in the pH of the solution increased the negative surface loads of the adsorbent. Adsorbent has a negative surface charge in the $\text{pH} > 5$. As expected, the adsorption performance of the MB solution at $\text{pH} > 5$ was significantly increased due to the electrostatic interaction between the positively

charged methylene blue molecules and the negatively charged adsorbent surface [28]. Then the adsorption performance increased insignificantly with further increase of $\text{pH} > 7$, probably because the adsorption has reached saturation. It can be stated that due to the lower removal capacities determined for $\text{pH} < 7$, the adsorption zones are partially covered with hydronium ions, the regions to absorb the methylene blue molecules are reduced and the removal capacity decreases accordingly [9]. The ability to be used as an adsorbent with high adsorption efficiency without the need for pH adjustment can be considered as an advantage for environmental and practical applications. Therefore, no adjustment of the solution pH was made in the next stages of the adsorption.

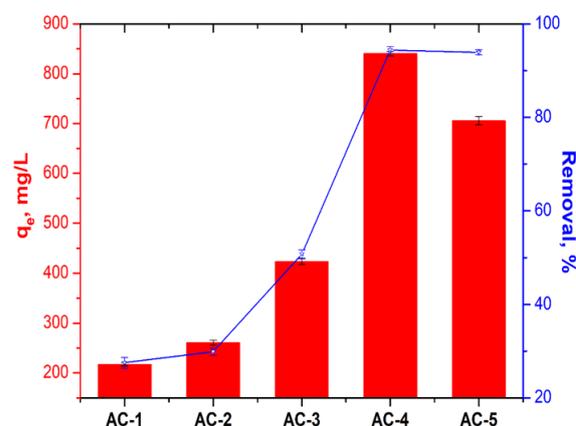


Fig 5. The removal of methylene blue from aqueous solutions with concentrations of 500 mg L^{-1} by using AC-1, AC-2, AC-3, AC-4 and AC-5 (pH of solutions: 7.03, amount of adsorbent: 0.5 g L^{-1} , contact time: 2 h, ionic strength: 0.01 M , shaking speed: 210 rpm , temperature: $25\text{ }^\circ\text{C}$)

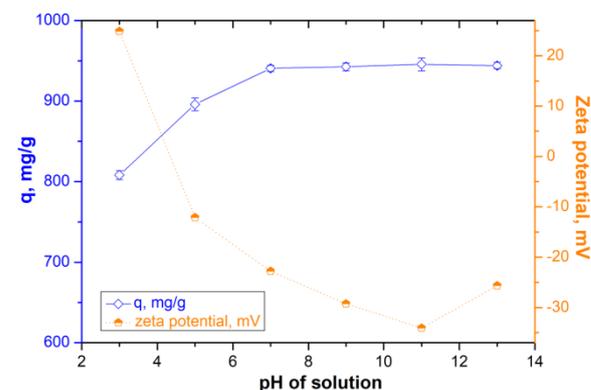


Fig 6. Effect of solution pH on the adsorption of methylene blue by AC-4 (Concentration of methylene blue: 500 mg L^{-1} , amount of adsorbent: 0.5 g L^{-1} , contact time: 2 h, ionic strength: 0.01 M , shaking speed: 210 rpm , temperature: $25\text{ }^\circ\text{C}$)

3.5. Effect of contact time

The effect of contact time on methylene blue (250 and 500 mg L^{-1}) adsorption with the AC-4 product is shown in Fig 7(a). It was found that the adsorbent adsorbed a significant amount of methylene blue in the first 5 min for two different concentrations (250 and 500 mg L^{-1}). In this short time, high removal of methylene blue can be attributed to the large surface area of the adsorbent and thus to a large amount of

areas where adsorption will occur. The methylene blue removal rate decreased after 5 min and reached equilibrium in 90 min. It has been observed that the required contact time (90 min) is comparable with the studies in the literature on the subject [10]. The decrease in removal rate for the adsorbent after the first 5 min may be caused by the intra-particle diffusion effect [29]. The role of diffusion in adsorption was examined according to the intraparticle diffusion model expressed by Eq. (3) [30].

$$q_t = k_i \times t^{1/2} + C \quad (3)$$

where, k_i is a constant of the intra-particle diffusion rate [$\text{mg} (\text{g}^{-1} \text{min}^{-1/2})$], C is a constant about the boundary layer (mg g^{-1}).

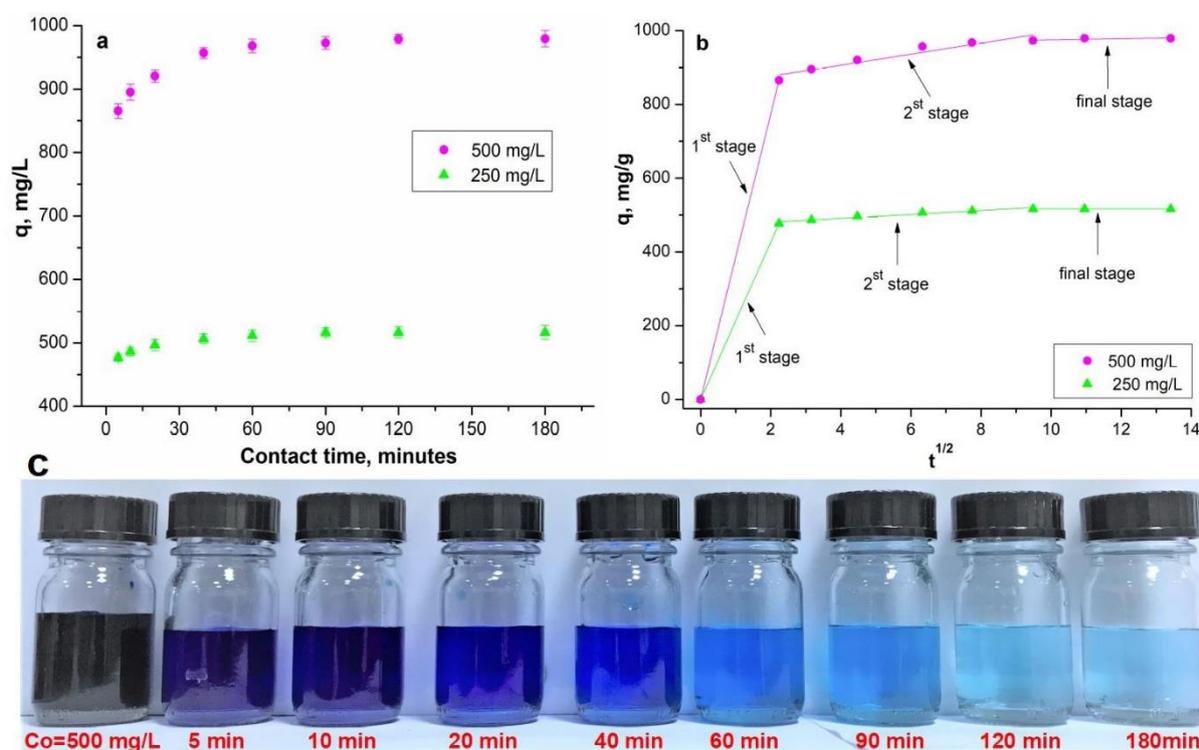


Fig 7. Effect of contact time on the adsorption of methylene blue by AC-4 (a), the plots of intra-particle diffusion model (b) and the change in the color of 500 mg L⁻¹ of methylene blue solution as a function of contact time (c)

3.6. Isotherm analysis

The change of concentration (C_e , mg L^{-1}) remaining in the solution after the adsorption of methylene blue with AC-4 product with the amount of methylene blue (q_e , mg g^{-1}) per unit adsorbent mass is shown in Fig 8(a). Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models, which are widely used to perform isotherm analysis for adsorption data. Isotherm graphs formed by applying the adsorption data obtained for the AC-4 product to the isotherm equations given between Eq. (4-6), respectively.

$$q_e = \frac{Q_0 \cdot b \cdot C_e}{(1 + b \cdot C_e)} \quad (4) [31]$$

$$q_e = k \cdot C_e^{1/n} \quad (5) [32]$$

Fig 7 (b) showing the plots of q_t vs $t^{1/2}$ for the concentrations of 250 and 500 mg L^{-1} have three stages. The first stage is due to the diffusion (film diffusion) of methylene blue molecules to the adsorbent surface. The second stage consists of intra-particle diffusion of methylene blue molecules. The final stage, it is possible to mention that the adsorption has reached equilibrium. From the results obtained in this study, it can be concluded that intra-particle diffusion is effective in adsorption, but it is not the only mechanism controlling adsorption [10]. The change in the color of the 500 mg L^{-1} methylene blue solution is shown in Fig. 7(c) and the consistency of the obtained result was checked.

$$\ln q_e = \ln X_m - K \cdot \varepsilon^2 \quad (6) [33]$$

where q_e is the amount of methylene blue adsorbed by AC-4 (mg g^{-1}) at equilibrium, C_e is the equilibrium concentration of methylene blue (mg L^{-1}), Q_0 is the Langmuir adsorption capacity of the AC-4 (mg g^{-1}) and b is the adsorption constant of Langmuir isotherm (L mg^{-1}), k is an indicator of the Freundlich adsorption capacity [$(\text{mg g}^{-1}) \cdot (\text{mg L}^{-1})^{-1/n}$], n is an empirical parameter.

For the D-R isotherm, X_m , adsorption capacity (mmol g^{-1}), K , constant the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), ε , Polanyi Potential, which is calculated from the Eq. (6). Average energy of adsorption (E) was determined on the basis of Eq. (7) [34].

$$R \cdot T \cdot \ln \left(\frac{C_e + 1}{C_e} \right) \quad (7)$$

$$E = (-2 * K)^{-0.5} \tag{8}$$

where R is ideal gas constant [8.314 J (mol.K)⁻¹] and T is temperature (K). The constants of each parameters and R^2 values were obtained from linear graphs of isotherm models (Fig 8 (b-d)) and listed in Table 2.

Langmuir adsorption capacity (Q_0) and isotherm constant (b) for AC-4 methylene blue adsorption were calculated as 1666.66 mg g⁻¹ and 0.060, respectively. From the Freundlich isotherm model, adsorption capacity (k) and isotherm constant (n) were found as (822.24 (mg g⁻¹). (mg L⁻¹)^{-1/n}) and (9.680), respectively. According to the D-R isotherm model, the adsorption energy (E) was determined to be 7.332 kJ mol⁻¹. In the adsorption process, it is possible to state that E value is between 8-16 kJ mol⁻¹, ion exchange is effective in removal, and if it is less than 8

kJ mol⁻¹, physical adsorption is effective in removal. According to this information, it is possible to say that physical adsorption has a role in methylene blue adsorption with AC-4 product. As shown in Table 2, the R^2 values of these isotherm models indicate that the adsorption data fit more with the Langmuir isotherm model. This result shows that the AC-4 surface is homogeneous and the methylene blue molecules are adsorbed in a singel layer on the adsorbent surface. Langmuir adsorption capacity of AC-4 product for methylene blue was compared with Table 3 in methylene blue removal capacities of activated carbons obtained from different starting materials in the literature. It has been determined that AC-4 product has higher adsorption capacity than others.

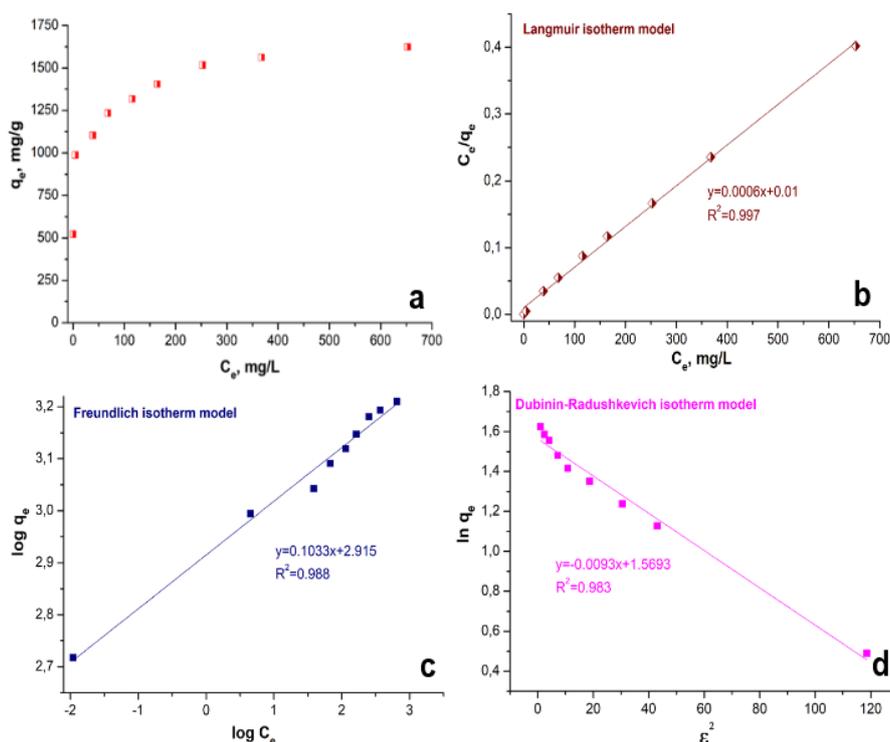


Fig 8. Variation of q_e (mg g⁻¹) as a function of equilibrium concentration (C_e) of methylene blue (mg L⁻¹) (a) Langmuir (b), Freundlich (c) and Dubinin-Radushkevich (d) isotherm model for the adsorption of methylene blue by AC-4 (pH of solution: 7.05, amount of adsorbent: 0.5 g L⁻¹, contact time: 2 h, ionic strength: 0.01 M, shaking speed: 210 rpm, temperature: 25 °C)

Table 2. Parameters of Langmuir, Freundlich and D-R isotherm models for removal of methylene blue by AC-4

	Q_0 , mg g ⁻¹	b , L mg ⁻¹	R^2	
Langmuir isotherm model	1666.66	0.060	0.997	
	k , (mg g ⁻¹). (mg L ⁻¹) ^{-1/n}	n	R^2	
Freundlich isotherm model	822.24	9.680	0.988	
	X_m , mol g ⁻¹	K , mol ² kj ⁻²	R^2	E , kj mol ⁻¹
D-R isotherm model	4.803	0.0093	0.983	7.332

Table 3. Comparison of adsorption capacity of AC-4 from Langmuir isotherm model (Q_0) with activated carbons obtained from different starting materials for methylene blue

Adsorbent	BET surface area, $m^2 g^{-1}$	Q_0 , $mg g^{-1}$	Reference
Sucrose	2116	1666.66	This study
Mangosteen peel	1621	1193	[9]
Pecan nutshell	2342	1190.62	[28]
Fox nutshell	2869	968.74	[35]
Coconut shell	2825	916	[36]
Vinasse	832	909.09	[8]
Wheat straw	2263.10	883	[37]
Waste coffee grounds	2407	678	[38]

3.7. Reusability of adsorbent

Desorption processes have been used pH shift and solid-liquid extraction methods for regeneration of adsorbent materials [39]. In this study, solid-liquid extraction method was used for the desorption process. Ethanol was used as solvent in desorption process by solid-liquid extraction method. The advantage of using ethanol is that it can be easily evaporated at room temperature and that desorbed dyes can also be reused.

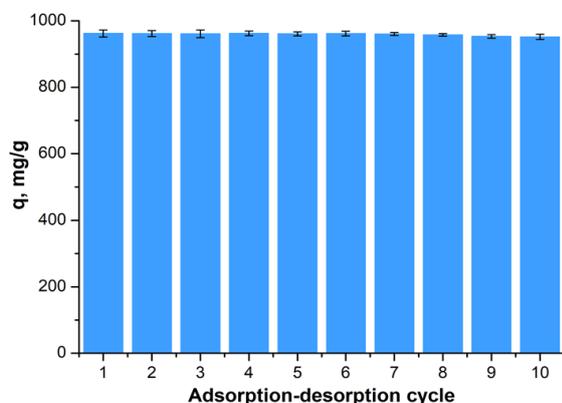


Fig 9. Adsorption performance of AC-4 after each adsorption-desorption cycle (methylene blue concentration: $500 mg L^{-1}$, pH 11.09, amount of adsorbent: $0.5 g L^{-1}$, contact time: 2 h, ionic strength: 0.01 M, shaking speed: 210 rpm, temperature: $25 ^\circ C$)

Desorption of $0.5 g L^{-1}$ amount of AC-4 product used in adsorption of $500 mg L^{-1}$ methylene blue was performed by washing with 20 mL ethanol for 10 minutes. Adsorbents separated from the desorption solution and dried at room temperature were tested in the adsorption-desorption cycles and the results are shown in Fig 9. It has been determined that AC-4 can be used at least ten times in the adsorption-desorption cycle without any change in removal efficiency.

3.8. Adsorption mechanism

Physical and chemical adsorption types can be effective in removing methylene blue from water environment with carbon-based adsorbents. Results of characterization and adsorption studies of AC-4 product, adsorption mechanism of methylene blue was analyzed. The fact that the adsorbent has a large surface area and large pore volume means that the areas where methylene blue adsorption will occur are quite high [40]. In addition, depending on the pH effect, electrostatic interaction between negative surface charge and positive methylene blue molecules can also be important in removal. It showed that the AC-4 product has the highest removal efficiencies. This result is due to the surface area and total pore volume of the AC-4 product being higher than the surface areas and the total pore volumes of other products. In addition, the pore size distribution of AC-4 was compatible with the size of the methylene blue ($14.3 \text{ \AA} \times 6.1 \text{ \AA} \times 4.0 \text{ \AA}$), probably resulting in very high removal efficiency [41]. The density of functional groups did not change after adsorption (Fig 3). The characteristic peaks, which were reported to contribute to the methylene blue removal process, were not observed. There was no chemical change in this case. The highest negative surface charge of AC-4 is pH 7. Accordingly, a large amount of adsorption occurs due to the electrostatic interaction between the positively charged methylene blue molecules and the negatively charged adsorbent surface. Thanks to the effects of these factors, AC-4 has been found to be dominant in physical adsorption. Considering all these results, it has been determined that AC-4 product has a very high methylene blue removal capacity.

3.9. Real textile wastewater application

AC-4 adsorption performance was tested using real textile wastewater chemical composition given in section *real textile wastewater application*. In experiments with real textile wastewater, the removal performance of the adsorbent was evaluated by taking into account the decrease in the COD value of the real

textile wastewater. The change in the color, UV absorbance value and COD of textile wastewater at different pHs (3, 7 and 11) are shown in Fig 10. textile wastewater COD value was determined at the end of 120 minutes contact time decreases by 64%. When this result is compared with the previous reported results, it is determined that it has adsorbent with high removal efficiency [42–44]. According to these results obtained from real textile wastewater applications, it has been determined that AC-4 can be used effectively in the treatment of these wastewater.

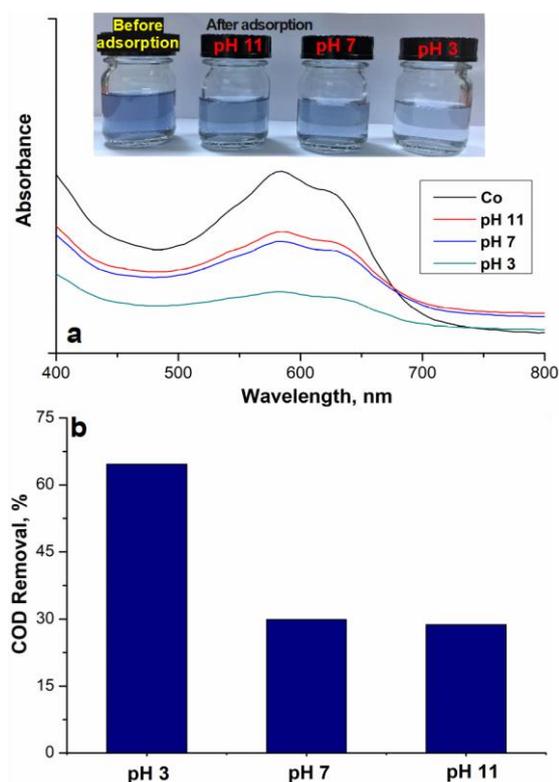


Fig 10. The change in the color and absorbance at wavelength between 400 and 800 nm as different pHs (3, 7 and 11) for adsorption of real textile wastewater by AC-4 (a) and adsorption performance of AC-4 towards of real textile wastewater (COD of real textile wastewater: 368 mg L⁻¹, pH: 3, 7 and 11, amount of adsorbent: 0.5 g L⁻¹, contact time: 2 h, shaking speed: 210 rpm, temperature: 25 °C) (b)

4. CONCLUSION

In the presented study, activated carbon with a high surface area from sucrose was successfully obtained. Activated carbon with the highest surface area (2116.42 m² g⁻¹) and microporous (1.138 g cm⁻³) was obtained at a rate of 1:4 (w/w) KOH at 750 °C. Langmuir adsorption capacity of the activated carbon obtained is higher than many other activated carbon for methylene blue (1666.66 mg g⁻¹). Activated carbon can be used at least ten times in the adsorption-desorption cycle without change in its adsorption performance. Also, it has been determined that the activated carbon obtained can be used successfully in real textile wastewater treatment.

REFERENCES

- [1]. P. Senthil Kumar, S.J. Varjani and S. Suganya, "Treatment of dye wastewater using an ultrasonic aided nanoparticle stacked activated carbon: Kinetic and isotherm modelling," *Bioresource Technology*, Vol. 250, pp. 716–722, 2018.
- [2]. A.A. Mir, A.A. Amooey and S. Ghasemi, "Adsorption of direct yellow 12 from aqueous solutions by an iron oxide-gelatin nanoadsorbent; kinetic, isotherm and mechanism analysis," *Journal of Cleaner Production*, Vol. 170, pp. 570–580, 2018.
- [3]. R. Li, B. Gao, K. Guo, Q. Yue, H. Zheng and Y. Wang, "Effects of papermaking sludge-based polymer on coagulation behavior in the disperse and reactive dyes wastewater treatment," *Bioresource Technology*, Vol. 240, pp. 59–67, 2017.
- [4]. S. Danwittayakul, M. Jaisai and J. Dutta, "Efficient solar photocatalytic degradation of textile wastewater using ZnO/ZTO composites," *Applied Catalysis B: Environmental*, Vol. 163, pp.1–8, 2015.
- [5]. M. Soniya and G. Muthuraman, "Comparative study between liquid-liquid extraction and bulk liquid membrane for the removal and recovery of methylene blue from wastewater," *Journal of Industrial and Engineering Chemistry*, Vol. 30, pp. 266–273, 2015.
- [6]. B.E.L. Baêta, D.R.S. Lima, S.Q. Silva and S.F. Aquino, "Evaluation of soluble microbial products and aromatic amines accumulation during a combined anaerobic/aerobic treatment of a model azo dye," *Chemical Engineering Journal*, Vol. 259, pp. 936–944, 2015.
- [7]. J. Paul Guin, Y.K. Bhardwaj and L. Varshney, "Mineralization and biodegradability enhancement of Methyl Orange dye by an effective advanced oxidation process," *Applied Radiation and Isotopes*, Vol. 122, pp. 153–157, 2017.
- [8]. O. Kazak, Y.R. Eker, H. Bingol and A. Tor, "Novel preparation of activated carbon by cold oxygen plasma treatment combined with pyrolysis," *Chemical Engineering Journal*, Vol. 325, pp. 564–575, 2017.
- [9]. A. Nasrullah, B. Saad, A.H. Bhat, A.S. Khan, M. Danish, M.H. Isa and A. Naeem, "Mangosteen peel waste as a sustainable precursor for high surface area mesoporous activated carbon: Characterization and application for methylene blue removal," *Journal of Cleaner Production*, Vol. 211, pp. 1190–1200, 2019.
- [10]. H. Wang, R. Xie, J. Zhang and J. Zhao, "Preparation and characterization of distillers' grain based activated carbon as low cost methylene blue adsorbent: Mass transfer and equilibrium modeling," *Advanced Powder Technology*, Vol. 29, pp. 27–35, 2018.
- [11]. A.H. El-Sheikh, A.P. Newman, H.K. Al-Daffae, S. Phull and N. Cresswell, "Characterization of activated carbon prepared from a single cultivar

- of Jordanian Olive stones by chemical and physicochemical techniques," *Journal of Analytical and Applied Pyrolysis*, Vol. 71, pp. 151-164, 2004.
- [12]. H. Saygılı and F. Güzel, "High surface area mesoporous activated carbon from tomato processing solid waste by zinc chloride activation: Process optimization, characterization and dyes adsorption," *Journal of Cleaner Production*, Vol. 113, pp. 995-1004, 2016.
- [13]. Y. Zhang, X. Song, Y. Xu, H. Shen, X. Kong and H. Xu, "Utilization of wheat bran for producing activated carbon with high specific surface area via NaOH activation using industrial furnace," *Journal of Cleaner Production*, Vol. 210, pp. 366-375, 2019.
- [14]. Y. Yu, N. Qiao, D. Wang, Q. Zhu, F. Fu, R. Cao, R. Wang, W. Liu and B. Xu, "Fluffy honeycomb-like activated carbon from popcorn with high surface area and well-developed porosity for ultra-high efficiency adsorption of organic dyes," *Bioresource Technology*, Vol. 285, pp. 121340, 2019.
- [15]. O. Kazak and F. Sungur, "Preparation of activated carbon from Thuja Orientalis cone and using for removal reactive blue 49 from water," *Eskişehir Technical University Journal of Science and Technology B - Theoretical Sciences*, Vol. 8, pp. 281-292, 2020.
- [16]. O. Kazak, "Preparation of activated carbon from natural starch, its characterization and use as an adsorbent," *Çukurova University Journal of the Faculty of Engineering and Architecture*, Vol. 35, pp. 115-126, 2020.
- [17]. O. Kazak, Y.R. Eker, I. Akin, H. Bingol and A. Tor, "A novel red mud@sucrose based carbon composite: Preparation, characterization and its adsorption performance toward methylene blue in aqueous solution," *Journal of Environmental Chemical Engineering*, Vol. 5, pp. 2639-2647, 2017.
- [18]. W. Suliman, J.B. Harsh, N.I. Abu-Lail, A.M. Fortuna, I. Dallmeyer, M. Garcia-Perez, "Modification of biochar surface by air oxidation: Role of pyrolysis temperature," *Biomass and Bioenergy*, Vol. 85, pp. 1-11, 2016.
- [19]. Y. Lin, Y. Liao, Z. Yu, S. Fang, Y. Lin, Y. Fan, X. Peng and X. Ma, "Co-pyrolysis kinetics of sewage sludge and oil shale thermal decomposition using TGA-FTIR analysis," *Energy Conversion and Management*, Vol. 118, pp. 345-352, 2016.
- [20]. K.C. Bedin, A.C. Martins, A.L. Cazetta, O. Pezoti and V.C. Almeida, "KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue removal," *Chemical Engineering Journal*, Vol. 286, pp. 476-484, 2016.
- [21]. A.H. Basta, V. Fierro, H. El-Saied, A. Celzard, "2-Steps KOH activation of rice straw: An efficient method for preparing high-performance activated carbons," *Bioresource Technology*, Vol. 100, pp. 3941-3947, 2009.
- [22]. H. Saygılı and G.A. Saygılı, "Optimized preparation for bimodal porous carbon from lentil processing waste by microwave-assisted K₂CO₃ activation: Spectroscopic characterization and dye decolorization activity," *Journal of Cleaner Production*, Vol. 226, pp. 968-976, 2019.
- [23]. G.K. Parshetti, S. Chowdhury and R. Balasubramanian, "Hydrothermal conversion of urban food waste to chars for removal of textile dyes from contaminated waters," *Bioresource Technology*, Vol. 161, pp. 310-319, 2014.
- [24]. S. Li, K. Han, J. Li, M. Li and C. Lu, "Preparation and characterization of super activated carbon produced from gulfweed by KOH activation," *Microporous and Mesoporous Materials*, Vol. 243, pp. 291-300, 2017.
- [25]. W. Wang, S. Xu, K. Wang, J. Liang and W. Zhang, "De-intercalation of the intercalated potassium in the preparation of activated carbons by KOH activation," *Fuel Processing Technology*, Vol. 189, pp. 74-79, 2019.
- [26]. D. Wu, H. Xu and M. Hakkarainen, "From starch to polylactide and nano-graphene oxide: Fully starch derived high performance composites," *RSC Advances*, Vol. 6, pp. 54336-54345, 2016.
- [27]. A. Barroso-Bogeat, M. Alexandre-Franco, C. Fernández-González and V. Gómez-Serrano, "FT-ir analysis of pyrone and chromene structures in activated carbon," *Energy and Fuels*, Vol. 28, pp. 4096-4103, 2014.
- [28]. H.H.C. Lima, R.S. Maniezzo, M.E.G. Llop, V.L. Kupfer, P.A. Arroyo, M.R. Guilherme, A.F. Rubira, E.M. Giroto and, A.W. Rinaldi, "Synthesis and characterization of pecan nutshell-based adsorbent with high specific area and high methylene blue adsorption capacity," *Journal of Molecular Liquids*, Vol. 276, pp. 570-576, 2019.
- [29]. H. Li, L. Liu, J. Cui, J. Cui, F. Wang and F. Zhang, "High-efficiency adsorption and regeneration of methylene blue and aniline onto activated carbon from waste edible fungus residue and its possible mechanism," *RSC Advances*, Vol. 10, pp. 14262-14273, 2020.
- [30]. W. Weber, "Kinetics of Adsorption on Carbon from Solution," *Journal of the Sanitary Engineering Division*, Vol. 89, pp. 31-60, 1963.
- [31]. I. Langmuir, "The constitution and fundamental properties of solids and liquids. Part I. Solids," *Journal of the American Chemical Society*, Vol. 38, pp. 2221-2295, 1916.
- [32]. H.M.F. Freundlich, "Über die adsorption in losungen," *Zeitschrift für Physikalische Chemie*, 1906.
- [33]. M.M. Dubinin, L.V. Radushkevich, "Equation of the characteristic curve of activated charcoal," *Proc. Acad. Sci. USSR Phys. Chem. Sect.*, 1947.
- [34]. I. Sargin, G. Arslan, M. Kaya, "Efficiency of chitosan-algal biomass composite microbeads at heavy metal removal," *Reactive and Functional Polymers*, Vol. 98, pp. 38-47, 2016.
- [35]. A. Kumar and H.M. Jena, "Removal of methylene blue and phenol onto prepared activated carbon

- from Fox nutshell by chemical activation in batch and fixed-bed column," *Journal of Cleaner Production*, Vol. 137, pp. 1246–1259, 2016.
- [36]. A.L. Cazetta, A.M.M. Vargas, E.M. Nogami, M.H. Kunita, M.R. Guilherme, A.C. Martins, T.L. Silva, J.C.G. Moraes and V.C. Almeida, "NaOH-activated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption," *Chemical Engineering Journal*, Vol. 174, pp. 117–125, 2011.
- [37]. P. Wang, C. Wu, Y. Guo and C. Wang, "Experimental and theoretical studies on methylene blue and methyl orange sorption by wheat straw-derived biochar with a large surface area," *Physical Chemistry Chemical Physics*, Vol. 18, pp. 30196–30203, 2016.
- [38]. C.H. Chiang, J. Chen and J.H. Lin, "Preparation of pore-size tunable activated carbon derived from waste coffee grounds for high adsorption capacities of organic dyes," *Journal of Environmental Chemical Engineering*, Vol. 8, pp. 103929, 2020.
- [39]. S.M. Alatalo, E. Mäkilä, E. Repo, M. Heinonen, J. Salonen, E. Kukk, M. Sillanpää and M.M. Titirici, "Meso- and microporous soft templated hydrothermal carbons for dye removal from water," *Green Chemistry*, Vol. 4, pp. 1137–1146, 2016.
- [40]. P. Khare and D.K. Goyal, "Effect of high and low rank char on soil quality and carbon sequestration," *Ecological Engineering*, Vol. 52, pp. 161–166, 2013.
- [41]. S. Lei, J. ichi Miyamoto, H. Kanoh, Y. Nakahigashi and K. Kaneko, "Enhancement of the methylene blue adsorption rate for ultramicroporous carbon fiber by addition of mesopores," *Carbon*, Vol. 44, pp. 1884–1890, 2006.
- [42]. K. Santhy and P. Selvapathy, "Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon," *Bioresource Technology*, Vol. 97, pp. 1329–1336 2006.
- [43]. A.A. Ahmad and B.H. Hameed, "Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater," *Journal of Hazardous Materials*, Vol. 173, 487–493, 2010.
- [44]. S.K. Shukla, N.R.S. Al Mushaiqri, H.M. Al Subhi, K. Yoo and H. Al Sadeq, "Low-cost activated carbon production from organic waste and its utilization for wastewater treatment," *Applied Water Science*, Vol. 10, pp. 1–9, 2020.