



Research article

Sustainable production of activated carbon from indigenous *Acacia etbaica* tree branches employing microwave induced and low temperature activation

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ABSTRACT

Growing demand for activated carbon as an efficient and cost effective means of treating environmental pollution necessitates the economical production of good quality activated carbon. It is possible if it is done using low cost precursor materials and economical production methods. In the present study, two types of activated carbon were produced from *Acacia etbaica* tree branches while employing phosphoric acid as an activating agent. The first sample underwent carbonization by microwave irradiation (AC-MWI), while the second sample was carbonised in a furnace (AC-CA). Characterization of the formed activated carbon samples was executed by proximate and ultimate analysis adopting standard ASTM procedures. In addition to the elemental analysis, hardness, bulk density, pH, moisture and ash content, surface morphology, BET specific surface area, pore volume, volatile matter, fixed carbon, and iodine number were determined. Characteristics of both activated carbon samples were compared with the characteristics of activated carbon available in the literature and activated carbon available commercially in the market. The comparison revealed that the characteristics of the produced activated carbon samples was well comparable with the activated carbons produced from other species of *Acacia* tree and activated carbon available commercially. Results showed that the produced activated carbon demonstrated high activation efficiency of 39.8% and 48.7% for AC-CA and AC-MWI, respectively. Furthermore, AC-MWI has a BET specific surface area higher than that of AC-CA (1065 m²/g and 773 m²/g respectively). It was found that the BET specific surface area and pore volume of AC-MWI was higher by 37.7% and 12.7%, respectively, as compared to the values acquired for AC-CA. Additionally, activated carbon could be produced by microwave irradiation in about 48% less time as compared to traditional low temperature heating. The adsorption study of produced the activated carbon was performed utilising methylene blue (MB) as a contaminant, and the data was fitted to Langmuir, Freundlich, as well as Harkins–Jura isotherm showing comparable correlation. However, Freundlich isotherm was found to be the best to elaborate the MB adsorption on the produced activated carbon. The results confirmed the viability of microwave irradiation in producing good quality activated carbon from *Acacia etbaica* tree branches, which demonstrated comparable characteristics with commercially available activated carbon. The strategy could be beneficial for the country in order to produce high quality activated carbon and strengthen its self-reliance.

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1. Introduction

Saudi Arabia is considered a barren and arid country. However, it is home to a broad diversity of floras in the region. Furthermore, in many parts of the country, diversity in shrubs, plants and trees can be observed. A thorough study ‘The flora of Saudi Arabia’ reported that the “country has about 2282 species in 855 genera; of which 9 species are Gymnosperms and 27 species are Pteridophytes. A total of 131 families have been reported from all over Saudi Arabia; among these 33 families are represented by a single species each” [1]. Acacia are the most prevailing flora in Saudi Arabia and in general in the Arabian Peninsula. Acacia is generally known as whistling thorn or thorn tree, which is a genus of shrubs and trees belonging to the subfamily Mimosoideae of the family Fabaceae-Leguminosae. Around 1300 species of Acacia are reported globally. However, among them 10 species of Acacia trees including *Acacia etbaica* are abundantly found in deserts and other lands of Saudi Arabia [2]. Maintenance of these trees and plants by cutting and shaping produces huge quantities of solid waste annually, especially in rural regions [3].

Studies show that Saudi Arabia is generating about 15.3 million tons of municipal solid waste per annum, including the agricultural solid waste coming from pruning, cutting and farm maintaining activities. The disposal of massive quantities of waste is becoming a rising problem with time. If the cutting and pruning waste of the trees could be utilised for a beneficial purpose, it may reduce the increasing solid waste quantities and provide economic benefits [4].

Activated Carbon (AC) is a product of carbonaceous material, which has been treated by physical and chemical processes to convert it to an extremely porous material, which possess enormous surface area available for adsorption, or separation of components. It is estimated that only 1 g of activated carbon may have a surface area more than 3000 m² [5]. Due to inherent advantages of AC as an adsorbent, its global use is increasing rapidly [6]. Activated carbon can be prepared from various precursor materials containing carbon, including coal, lignite, peat, and biomass sources such as wood, sawdust, bagasse, and coconut shells [7–10]. *Acacia etbaica* is an abundant desert plant available in Saudi Arabia and its cuttings and prunings during maintenance and weathering are considered a waste material like that of other similar trees [11].

Acacia etbaica tree branches could be used as raw material as they are financially more viable as compared to other materials whose procurement entails additional financial burden for the manufacturers. Currently, there is inadequate information existing about *Acacia* tree species utilised as a precursor material for the preparation of AC. In fact, *Acacia etbaica* has never been used in the past to produce activated carbon. In the present study, *Acacia etbaica* was utilised to produce activated carbon to evaluate the possibility of utilising it as a precursor material. Generally during preparation of AC, precursor material is carbonised by heating in a furnace to obtain extra-porous material, and chemical agents (generally, acid and base) are used as catalysts to activate the carbonaceous material [12]. Use of phosphoric acid gained the attention of researchers because it has various economic and environmental benefits; its energy cost is relatively low, it has a higher yield of char, and it is easier to recover the spent acid as compared to other activation agents [13]. Furthermore, phosphoric acid is a strong dehydrating agent, providing excellent synthesis of mesopores and micropores during the activation of carbonaceous material [14].

Microwave heating technology has also gained popularity and finds wide applications in material science, food processing and analytical chemistry applications. Microwave heating in the production of AC shows promising results as compared to conventional activation; however, its application is still in the investigation phase [15]. The cost of activated carbon is one of the key limitations in using such a versatile material in pollution abatement applications, such as water and wastewater treatment [16]. Therefore, it is wise to produce activated carbon from low-cost waste material, and utilise easy and low cost preparation methods. Use of waste tree branches could be an attractive option [17].

Although several studies have been done in the past to produce good quality AC, most of the studies come up with relatively expensive products by utilising conventional preparation methods. Limited information is available about the production of AC by microwave irradiation, which has been demonstrated as an economical and good quality AC production method [15]. In order to evaluate the said method, the present study utilised abundantly available solid waste (local *Acacia* tree branches)—several species of which have been used by the author and some other researchers—and obtained promising results to produce an economical and good quality product. Therefore in the present study, AC was produced with locally available waste material of *Acacia etbaica* tree branches, using chemical activation with phosphoric acid (H₃PO₄), followed by carbonization via low temperature thermal and using microwave irradiation (MWI) on separate chemically activated carbon samples. Comparison between the produced ACs was made. Hardness, bulk density, pH, moisture and ash content, surface morphology, BET specific surface area, pore volume, volatile matter, fixed carbon, and iodine number were determined. Characterization of produced ACs was done and major characteristics were compared with the activated carbon supplied in the market and reported in literature. Finally, adsorption isotherm evaluation was executed utilising methylene blue dye as a contaminant and data fitted to prominent adsorption models.

2. Materials and methods

2.1. Preparation of activated carbon samples

Precursor material *Acacia etabica* tree branches were collected from Jubail Industrial City area. After cleaning, washing and cutting, the material was readied for AC preparation as described by Saleem and co-workers (2017). In the chemical activation with phosphoric acid, 1 kg of precursor material was added, with the phosphoric acid keeping an impregnation ratio of 1:1.5 based on studies performed on other acacia species as raw material and phosphoric acid as an activating agent [17]. The Reagent Grade phosphoric acid (Thermo Scientific Chemicals) having a purity of 85.8 wt% was utilised. The mixture was kept in the drying oven at 110 ± 5 °C. After one day, two samples were prepared from the mixture; the first sample was treated by chemical activation and second by microwave

irradiation. The first sample of the mixture was poured into a cylindrical stainless steel container having 8 cm diameter and 15 cm length. Two narrow exhaust openings of 5 mm diameter each were provided at the ends of the cylinder along with screw caps for filling and emptying the container. Once the cylinder was filled, it was loaded in a High Temperature Intelligent Box Furnace (TMAX-1700, Muffle, China) and heated at a rate of 5 °C/min, to provide swift and free evolution of volatile components until the temperature reached 600 °C. The mixture was kept at 600 °C for 150 min. The second sample was kept in a microwave oven (Panasonic) with a microwave input power of 600 W for 5–15 min (in several runs). After that, the cooled product was washed with hot water to neutralise the samples. The material was then dried at 110 ± 5 °C for 180 min to obtain the final product which was later utilised for characterization and adsorption studies. A step-by-step flow diagram for the production of *Acacia etbaica* tree branches activated carbon is presented in Fig. 1.

2.2. Characterization of activated carbon samples

In addition to proximate analysis, detailed analysis of the produced AC samples was performed. Results were obtained for ball point hardness, bulk density, pore volume, pH, BET specific surface area, Iodine number, and moisture and ash content. The produced ACs were characterised by adopting the standard procedures described elsewhere [18]. The standard ASTM procedures and methods adopted in the presented study for the analysis are summarised in Table 1.

2.3. BET specific surface area analysis

BET specific surface area of the produced activated carbon was determined by utilising BET Specific Surface Area Analyser Macsorb, HM-Model 120, Japan. Equipment was fully automated and used with a liquid nitrogen supply unit.

2.4. FTIR analysis

Surface functional group identification was performed by utilising the Fourier Transform Infrared (FTIR) technique, (Shimadzu – 8400S FTIR spectrometer) which provides results based on infrared spectroscopy with Fourier transform employed for analysis of the spectrum results. The technique is grounded on the identification of functional groups within molecules where such groups vibrate (either through stretching or bending in various ways) when irradiated with specific wavelengths of light.

2.5. SEM analysis

In order to determine the morphological structure of the prepared activated carbon, Scanning Electron Microscopy (SEM) was utilised. Images were acquired using the JSM-IT200 InTouchScope™ Scanning Electron Microscope model.

2.6. Equilibrium adsorption studies

Equilibrium adsorption studies were conducted using methylene blue as an adsorbate and AC-MWI as an adsorbent in six 250-mL

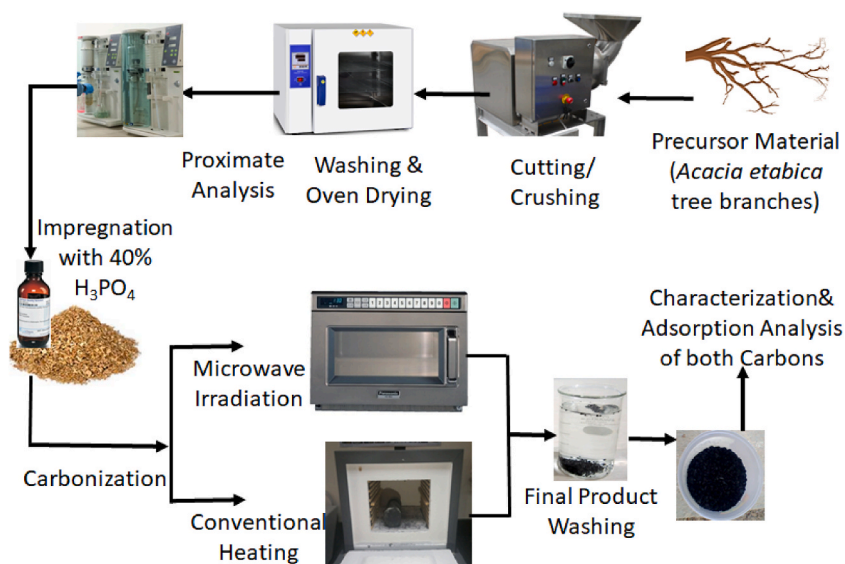


Fig. 1. Flow diagram describing the activated carbon production steps.

Table 1
List of standard ASTM procedures and methods utilised in the study.

Type of analysis	Method/ASTM standard procedure
Bulk density	ASTM D2395
Moisture content	ASTM D4933-99, 201
pH	ASTM D1293-12-2018
Fixed carbon	ASTM D3172; ISO 1350
Volatile matter	ASTM D5832-98
Hardness	ASTM D3802
Ash content	ASTM D2866-94, 2004
S _{BET} -Surface area	Brunauer-Emmett-Teller, BET specific surface area
Pore volume	ASTM D4641-17
Iodine number	ASTM D4607-94

Erlenmeyer flasks. Each flask contained 100 mg of activated carbon in 200 mL of methylene blue solutions with various initial concentrations ranging from 10 mg/L to 50 mg/L. The set of flasks were agitated in an Orbital shaker OS-1400 at 120 rpm and 30 °C. Shaking continued for a period of 2 days in order to allow the system to attain equilibrium. After equilibrium was reached, the samples were passed through 0.45 µm Millipore filter paper (Hach, UK), and evaluated for the methylene blue concentrations remaining in the solution utilising the UV-6000 UV Vis spectrophotometer (A51119700DPC, Thermo Fisher Scientific, USA) at a wavelength of 664 nm. Methylene blue standard solutions between 10 and 50 mg/L were prepared and used to obtain calibration curves.

2.7. Adsorption isotherm studies

Generally, adsorption processes are evaluated through graphs known as adsorption isotherms. These isotherms show the amount of adsorbate on the adsorbent as a function of its concentration or pressure at a constant temperature. The amount adsorbed is practically always normalised by the amount of the adsorbent in order to make comparison of various materials. In the current study, equilibrium data was produced by utilising AC-MWI sample, as it demonstrated better characteristics than the AC-CA. The data was fitted to three famous isotherm models, namely the Langmuir, Freundlich and Harkin–Jura isotherm models.

2.7.1. Freundlich Isotherms

In 1894, a mathematical fit to an isotherm was published for the first time. It was published by Freundlich and Küster and the formula of the adsorption model was a purely empirical relationship [19]. Freundlich Isotherm is described by:

$$q_e = K_F C_e^{1/n} \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate in the solution (mg/L), q_e is the amount adsorbed (mg/g) on the surface of adsorbent, and K_F and n are Freundlich constants. The value of 'n' gives an indication of how favourable the adsorption process is and K_F (mg/g)(L/mg)^{1/n} is the adsorption capacity of the adsorbent. For non-linear isotherms, the data can be plotted in linear form as shown in equation (2), by taking the log of both sides of equation (1), [19].

$$\log(q_e) = \log(K_F) + (1/n)\log(C_e) \quad (2)$$

2.7.2. Langmuir Isotherms

It is a monolayer model based on the assumptions that adsorbed molecules do not interact by any other mechanism, adsorption takes place through the same mechanism, the surface of the adsorbent is uniform and at the maximum adsorption capacity, molecules of adsorbate do not attach on already adsorbed molecules of adsorbate, and they only attach on the free surface of the adsorbent [20]. The Langmuir Isotherm is described by the following equation (3);

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

where, q_m is the saturated monolayer adsorption capacity and K_a is the adsorption equilibrium constant. Linear form of Langmuir Isotherm can be produced as shown in equation (4), [19];

$$(C_e / q_e) = (1 / q_m) C_e + 1 / (K_a q_m) \quad (4)$$

2.7.3. Harkin–Jura isotherm model

Harkin–Jura isotherm is a multilayer adsorption model and considers the presence of a heterogeneous pore distribution. Harkin–Jura model is represented as shown in equation (5), [21];

$$\text{Log } C_e = \alpha + \beta / a^2 \quad (5)$$

where, C_e is the equilibrium concentration, α is the specific adsorption, and a and β is the Harkins–Jura isotherm parameter and isotherm constant, respectively. According to equation (5), a plot of $\log C_e$ against $1/q_e$ will give a straight line with a slope b , which

is associated with the specific surface area of the adsorbent by equation (6), [22];

$$1/q_c^2 = (\beta/a) - 1/a(\log C_c) \quad (6)$$

In order to maintain quality control in the characterization and adsorption analysis, quality control (QC) samples (duplicate samples) were prepared and analyses were performed on both samples in parallel. All the analyses were performed under strict quality control and utilising standard ASTM procedures and methods (Table 1). As such, blanks were prepared accordingly in the preparation of calibration curves for methylene blue.

3. Results and discussion

In the present study, Phosphoric acid was used as an activating agent with the precursor material (*Acacia etbaica* tree branches) as it can increase the porous structure, provide high surface area and total pore volume, which in turn increases the yield, adsorption capacity, active free valences, surface reactivity, and thermal stability [23,24]. Furthermore, it was easy to treat the wastewater produced during the washing of activated carbon, either by addition of metal salts to precipitates that were removed by solids separation processes, by evaporation in treatment basins or by neutralisation with calcium salts [25].

3.1. Characterization of precursor material and produced activated carbon

3.1.1. Results of proximate analysis

The elemental analysis of the raw material (*Acacia etbaica* tree branches) was performed and the result of the analysis was compared with the result of other *Acacia* tree species mentioned in the literature. The result presented in Table 2 shows that the dominating constituent of the sample is carbon (53.6%). The comparison with other studies shows that *acacia* trees generally have high carbon content, which is in the range of 48%–53%, making them an appropriate candidate to prepare good quality adsorbent.

3.1.2. Characterization of activated carbon

Results of the proximate and ultimate analysis of both ACs (prepared by thermal and MWI processes) are presented in Table 3. It can be seen from the results that the properties of both types of ACs (AC-CA and AC-MWI) are comparable with the properties of AC produced from other species of *Acacia* trees and the properties of ACs being supplied commercially on the international market. Both ACs produced in the present study had similar hardness, low values of moisture content and high BET-Surface area which ranked the produced activated carbon as of good quality. Higher fixed carbon value is a desirable quality for commercial AC. The low value of ash content also provides a high value of fixed carbon. Values of fixed carbon for both ACs were comparable with the values of fixed carbon reported in the literature [27].

While comparing the results of AC-CA and AC-MWI, it can be seen that activated carbon produced from microwave irradiation has a lower ash content and moisture that may be attributed to the microwave induced vibration at the molecular level, which effectively reduced the moisture content from the material matrix and produced less ash during carbonization.

3.1.3. Surface properties

3.1.3.1. BET specific surface area. BET specific surface area is one of the most important characteristics of AC that indicates the performance of activated carbon in adsorbing impurities; the larger the surface area of AC, the more will be the capability to remove pollutants and vice versa. BET specific surface area obtained for *Acacia etbaica* tree branches using low temperature carbonization (AC-CA) and microwave irradiation (AC-MWI) was found to be 773 m²/g and 1065 m²/g, respectively. These pores and cavities result from evaporating the H₃PO₄ molecules during carbonization, leaving the spaces previously occupied by H₃PO₄ on the surface of AC [28]. It can be seen from Table 2 that the values are well comparable with the BET specific surface area of AC reported in literature produced from other species of *Acacia* tree [17,24,29,30]. Furthermore, the BET specific surface area of AC-MWI is even higher than the commercially available high quality activated carbons (Table 2).

Table 2

Comparison of elemental analysis results of precursor *Acacia etbaica* tree branches with the values mentioned in the literature.

Constituent (%)	<i>Acacia etbaica</i>	<i>Acacia seyal</i> [17]	<i>Acacia asak</i> [24]	<i>Acacia nilotica</i> [26]
C	53.6	51.3	52.7	48
K	1.50	1.82	0.93	–
Al	0.09	0.17	ND	–
N	0.39	0.33	0.42	0.4
H	5.6	5.8	5.3	6
Zn	<0.1	0.01	0.01	–
S	<0.1	0.03	0.02	–
P	<0.1	0.09	0.1	–
O	41.3	32.9	41.5	44

Table 3

Comparison for the characteristics of AC-CA and AC-MWI with ACs produced from other species of Acacia and commercial AC available on the market.

Property	<i>Acacia etbaica</i> (AC-CA)	<i>Acacia etbaica</i> (AC-MWI)	<i>Acacia seyal</i> [17]	<i>Acacia asak</i> [24]	<i>Acacia nilotica</i> [26]	*Filtrisorb® 400	*QAC-400
Ball Point Hardness	91	92	91	95	Low	High	95
Ash (%)	5.6	4.5	5.9	3.21	5.8	5–6	6
Bulk Density (g/cc)	0.37	0.39	0.3	0.51	–	0.44	0.55
Moisture Content (%)	4.3	4.1	4.2	2.9	4.1	–	5
pH	6.4	7.0	6.5	6.7	7.0	6.2	9–10
BET-Surface Area (m ² /g)	773	1065	762	1037	590	944	400
Pore Volume (m ³ /g)	4.74	5.33	4.92	5.26	4.4	0.6	–
Volatile Matter (%)	3.97	2.15	–	2.42	5.12	–	–
Fixed Carbon	90.6	92.3	–	91.47	–	–	–
Iodine Number	813.6	892.4	827	927	480	1000	400

* Calgon Carbon Corporation, Pennsylvania, 15205 USA.

Quantum Active Carbon Pvt Limited (2016).

3.1.3.2. Surface functional groups (FTIR analysis). The surface functional groups of the produced activated carbon were analysed by utilising FTIR techniques, and it was found that the FTIR spectra for both produced activated carbon samples were almost the same. The similarity in shape may be attributed to the use of the same precursor material. However, the difference in strength indicated that the activated carbon had some different contents of functional groups on their surface due to the difference in treatment [31].

Figs. 2 and 3 show the FTIR spectra of AC-CA and AC-MWI, respectively. As shown in the figures, the FTIR spectra of the produced AC exhibited three main absorption bands in the region from 1020 to 3400 cm⁻¹. In the case of AC-CA, the dominating functional groups are carboxyl functional groups with Alkanes, Ketones and Alkyl halide spectra. The FTIR analysis of AC-MWI showed that the dominating functional groups are Amines and Amides bonded N–H/C–H/O–H. Other peaks also show presence of Ketone and Alkyl groups.

The band that appears around 3400 cm⁻¹ is related to the stretching modes of N–H/C–H/O–H bonds. The alcohol bonding is a strong and broad link with intermolecular and intramolecular hydrogen links [32]. The band that appears around 3200 cm⁻¹ represents the carboxyl group –COOH. In the band of 2275 cm⁻¹ to 2250 cm⁻¹, presence of N=C=O is indicated. Similarly, the band which appears around 1600 cm⁻¹ represents the ketone R-(C=O)-R' bonds [33]. Another band around 1020 cm⁻¹ can be assigned to the stretching vibrations of C–O bonds [34]. In both activated carbon samples, there were weak peaks around 400 cm⁻¹ indicating the presence of the unsaturated alkyne C=R stretching modes. These peaks show that both types of AC have practically the same oxygenated surface functional groups that are attached to the surface of the produced AC. However, presence of characteristic carboxylic and anhydride groups appears to be more effective in adsorbing the cationic contaminants [35]. The presence of carboxyl, ketone and alkynes indicate the active contribution of these functional groups in adsorption of methylene blue dye. In brief, presence of these functional groups indicates that the adsorption on the produced ACs may include ion exchange, interaction with π -electrons and surface functional groups complexation with the pollutants as reported elsewhere [36].

3.1.3.3. Surface morphology (SEM image). As the adsorption capacity, pore volume and adsorption efficiency of activated carbon is strongly dependent on the surface morphology of produced activated carbon samples, SEM analysis was performed in this study [37]. The scanning electron microscopy (SEM) was performed for both activated carbon samples to investigate their morphological structure as shown in Fig. 4(a and b).

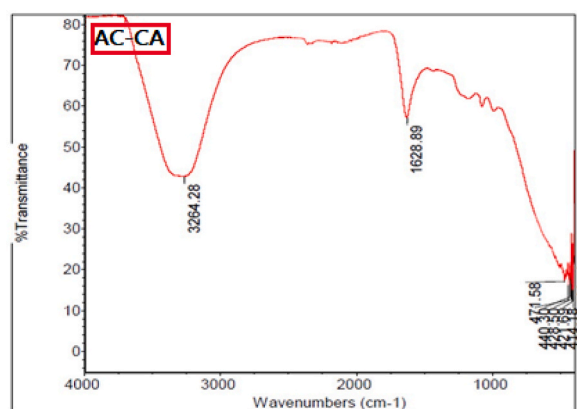


Fig. 2. FTIR analysis of AC-CA produced from Acacia etbaica tree branches.

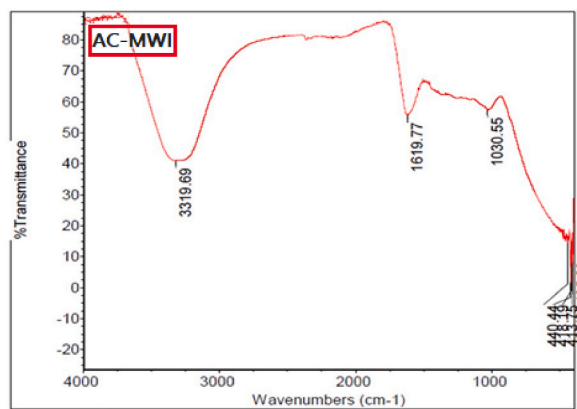


Fig. 3. FTIR analysis of AC-MWI produced from *Acacia etbaica* tree branches.

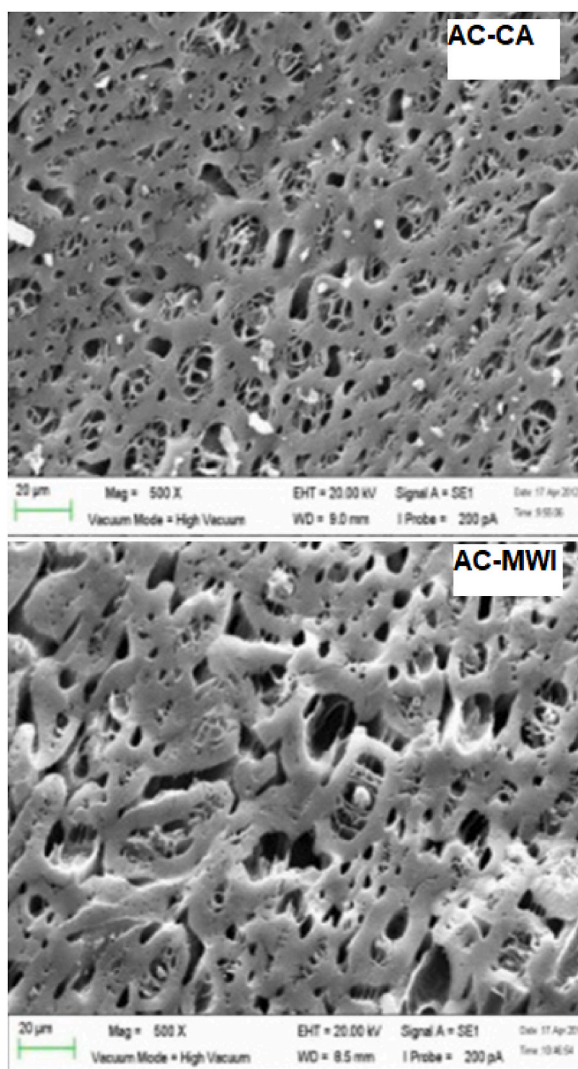


Fig. 4. The SEM images of a) AC-CA and b) AC-MWI produced from *Acacia etbaica* tree branches.

The SEM images of both ACs show similar pore structure; however, AC-CA shows smaller pores as compared to AC-MWI which is seen having a mix of larger and smaller pores. The property of wide range of pore sizes in AC-MWI could be responsible for higher adsorption capacity as contaminants of various sizes will have more probability to adsorb during passage through the distributed sizes of pores. Due to that, AC-MWI also demonstrated higher BET-Specific Surface area and better adsorption capacity [31].

The AC-CA had dominating pore openings ranging from 0.5 μm to 10 μm , while AC-MWI pore openings ranged from 2 μm to 20 μm . This may be due to the ability of microwave irradiation to penetrate deeper into the precursor material and produce more and wider range of pore structures.

3.1.4. Activation efficiency

The activation efficiency of both carbon samples was also determined in the study. The activation efficiency R (%) is defined as the ratio of the mass of activated carbon obtained after completing the activation process to the mass of the precursor material used in the activation process. The activation efficiency values can be estimated by utilising equation (7) as shown below [38];

$$R (\%) = \frac{\text{mass of activated carbon produced}}{\text{Initial mass of precursor mass}} \times 100 \quad (7)$$

It was found that the activation efficiencies of AC-CA and AC-MWI are 39.8% and 48.7%, respectively. The higher activation efficiency obtained by AC-MWI may be attributed to the reason that although both carbons were produced by H_3PO_4 activation, the conversion to activated carbon by microwave irradiation provides higher fixed carbon and low ash content. This may be due to heating of precursor material at the molecular level as microwaves cause molecules to vibrate; this increases the friction between the molecules, which results in heating the material, unlike the bulk heating of material in a furnace, and produces a more fixed solid final mass.

3.1.5. Total ash content

For good quality activated carbon, minimum ash content is a required parameter [39]. A small increase of ash content in an activated carbon causes a reduction in its adsorption properties. Activated carbon produced from *Acacia etbaica* tree branches using low temperature carbonization and MWI have ash contents of 5.6% and 4.5%, respectively (as mentioned in Table 2). The ash content is comparable with the values reported by researchers in the literature. This may be attributed to the higher heating rate and ultimate temperature (i.e. 600 $^\circ\text{C}$). Furthermore, the impregnation ratio (i.e. 1:1.5) also plays an important role as depolymerisation reactions between the volatile materials and phosphoric acid during the carbonization are affected. Although phosphoric acid (H_3PO_4) restricts the formation of tar, high heating rate and high impregnation ratio increases the formation of tar, so it is expected that as tar formation increases, ash content of the sample increases [28]. However, this can be overcome by using a lower heating rate and by regulating the impregnation ratio [40,41]. Still, the value of ash content obtained by microwave irradiation is lower than most of the reported values in the literature (Table 2). This may be attributed to the same reason discussed in the formation of fixed carbon in the above paragraphs.

3.1.6. Moisture content

Moisture content affects the porosity of activated carbon; as the moisture content increases, the porosity of AC also increases and vice versa [42]. It can be seen from Table 2 that the moisture content of AC-CA and AC-MWI are comparable (i.e. 4.3% and 4.1% respectively) with the typical values reported in the literature which were produced from other species of *Acacia* tree. Similarly, these values are also comparable with the commercially available activated carbon on the market as shown in Table 2. Acid washed, impregnated or chemically activated carbons normally have high moisture content as they are wetted during processing and then dried [43].

3.1.7. pH value

Largely, the value of pH for commercial AC is neutral or slightly alkaline. The reason for this is that generally, activated carbon is widely used in the water industry for purification purposes, so if the pH is away from neutrality range then there is a chance that the water being purified may become acidic/basic. However, final pH of produced AC in the present study is within the range of pH for commercially available AC (i.e. AC-CA and AC-MWI are 6.4, and 7.0, respectively).

3.1.8. Iodine number

The iodine number is a relative indicator of porosity in an activated carbon. Generally, iodine number is used as a rough estimate of surface area for some types of activated carbons. However, this relationship between iodine number and surface area cannot be generalised because it differs with the type of raw material, pore volume distribution, processing method and conditions [44]. The values of iodine number in the present study for AC-CA and AC-MWI were found to be 813.6 mg/g and 892.7 mg/g, respectively, as compared to the typical values mentioned in Table 2 (480–927 mg/g) and the values of commercial grade activated carbon also mentioned in Table 2 (400–1000 mg/g).

3.2. Adsorption studies on the produced activated carbon

3.2.1. Equilibrium adsorption studies

Equilibrium time for methylene blue (MB) dye removal utilising MWI and AC-CA was determined. The equilibrium time for the solutions having concentrations of 10, 30, and 50 mg/L were found to be 28, 45 and 52 h, respectively. The corresponding amount of

MB was found to be 1.22 mg/g, 2.68 mg/g and 3.95 mg/g, respectively. Result shows that with the increase in the concentration of methylene blue, the amount of methylene blue adsorbed per unit mass of AC also increases. This may be attributed to the increase in the initial concentration gradient of methylene blue, which is the main driving force for adsorption. Furthermore, results show that with the increase in the initial concentration of methylene blue, equilibrium time also increases. Initially during adsorption of methylene blue, the dye molecules reach the surface of the adsorbent, then they diffuse into the pores and finally they form a layer on

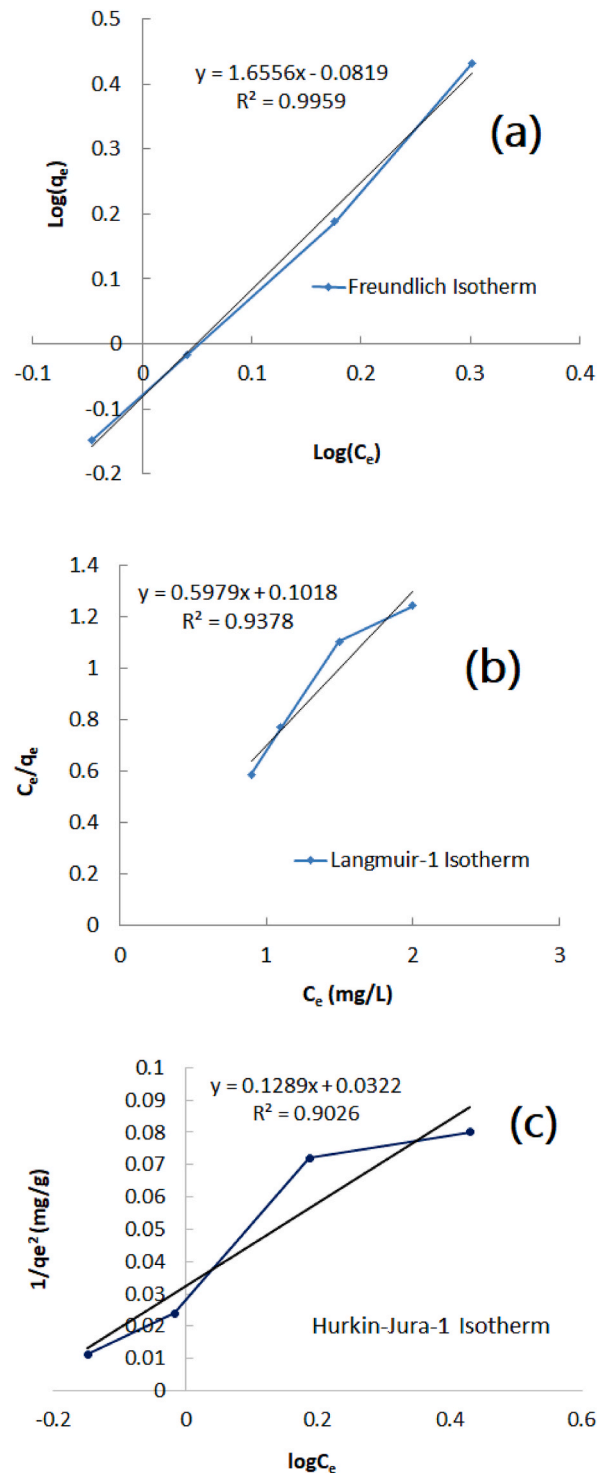


Fig. 5. Adsorption isotherm plots of a) Freundlich, b) Langmuir, and c) Hurkin-Jura models.

the surface of the adsorbent.

3.2.2. Adsorption isotherm studies

The adsorption isotherm indicates the distribution of adsorption molecules between the liquid phase and the solid phase when the adsorption process reaches the equilibrium state. As described elsewhere, adsorption process of the molecules undergoes adsorption from the bulk liquid phase to the adsorbent surface where it will adsorb, and is presumed to be done in three systematic steps: “(1) mass transfer of the adsorbate molecules across the external boundary layer; (2) intraparticle diffusion within the pores of the adsorbent; (3) adsorption at a site on the surface” [45].

Surface analysis of the produced AC indicated that oxygen-containing surface functional groups, including –OH and –COOH, in the active sites of the AC made important contributions to the adsorption of methylene blue dye. Studies in the past also support the presence of this mechanism [37]. The produced AC demonstrated excellent adsorption of methylene blue, which is a cationic dye having heterocyclic molecular structures [46]. The absorption mechanism in the study may also be contributed to by the presence of N–H/C–H/O–H and unsaturated alkyne C=R bonds, as indicated in the FTIR analysis. Furthermore, the existence of the N=C=O bond on the adsorbent surface indicates that the adsorbed MB molecules formed a chemical bond stretching with the active site either directly or indirectly. As mentioned in previous studies, the MB adsorption was not affected by adsorption of water molecules; however, the negatively charged adsorption sites were supported by the water solvent through a multi-step reaction mechanism [47]. Therefore, it is possible that the OH[−] groups on the produced activated carbon surfaces were reversibly ionised groups and became free active radicals and were responsible for generating the N=C=O bond [48].

Three well known adsorption isotherm models were utilised in fitting the equilibrium data, namely the Langmuir, Freundlich, and Hurkin-Jura isotherm models. The produced AC-MWI was used as adsorbate and methylene blue as an adsorbent contaminant simulating the waste effluent from the textile industry [49]. The results exhibited in Fig. 5(a) depicted that the value of the Freundlich constant ‘n’ is smaller than unity (approximately 0.6). Furthermore, the y-intercept was found to be ‘−0.082’, which means that the Freundlich constant K_F has a value of 0.827 which is near to unity. As increasingly large K_F values indicate greater adsorption capacity, results demonstrate that the adsorption process onto AC-MWI is promising for its use as an adsorbent.

Predicted and experimental isotherms show a good agreement between the experimental and predicted values, suggesting that the Freundlich model is valid for the experimental equilibrium data. Application of data on Langmuir and Hurkin-Jura isotherm models is also presented in Fig. 5(b and c).

The best-fit model among those studied was ranked by comparing the correlation coefficients ‘ R^2 ’, and the average percentage error (%Error), shown in Table 4. Based on the fitting results obtained for adsorption of methylene blue, listed in Table 1, the correlation coefficients of the three models (Freundlich, Langmuir, and Hurkin-Jura) were higher than 0.90; however, R^2 value of Freundlich isotherm is the highest (0.9959). Similarly, when %Error is considered, the value of the Freundlich isotherm model was found to be less than the Langmuir and Hurkin-Jura isotherms, as deliberated in Table 4.

Therefore, analysis of adsorption isotherms of methylene blue on AC-MWI produced from *Acacia etbaica* tree branches is following Freundlich, Langmuir as well as Hurkin-Jura isotherm models to a certain extent; however, the data is best fitted to the Freundlich isotherm model, as indicated by the value of correlation coefficient (R^2) which is nearly equal to unity, and minimum %Error as shown in Table 4. These results are in agreement with two different studies done in the past on the adsorption of methylene blue with various adsorbents. Studies revealed that the Freundlich isotherm model had a better fit with the experimental data as compared to the fit shown with the Langmuir isotherm model [37,50].

4. Conclusions & recommendations

The results obtained in this study suggest that the *Acacia etbaica* tree branches found in the Saudi Arabian desert are a suitable precursor material for production of sustainable, good quality activated carbon in the country. The conversion of *Acacia etbaica* tree branches to activated carbon offers a significant potential for reducing the environmental damage, and ultimately reducing the cost resulting from the uncontrolled disposal of these residues. Following are the specific conclusions drawn on the basis of the results obtained from this study.

- Increasing requirement of AC in the country may be fulfilled by producing AC from locally available *Acacia etbaica* tree branch waste material at low cost.
- This strategy will provide two-fold benefit, by providing low cost activated carbon, and reducing the problematic solid waste, which will ultimately aid in reducing environmental pollution.
- Chemical activation with phosphoric acid was found to be a feasible method, which allows AC production at relatively low temperature, and requires simple laboratory setups without skilled or trained manpower.
- Characterization of the produced AC samples (AC-CA and AC-MWI) revealed that both ACs had BET-surface area, pore volume, and iodine number values comparable to commercially available AC.
- The produced activated carbon demonstrated high activation efficiencies of 39.8% and 48.7% for AC-CA and AC-MWI, respectively.
- The produced activated carbon samples are more suitable for water and wastewater treatment as they have very low ash content with higher values of hardness.
- Basic cost analysis of the produced AC shows that the cost of production is less than \$1.2/kg.

Table 4

Comparison of correlation coefficient (R^2), and average percentage error (%Error) values obtained for studied adsorption isotherm models.

Isotherm Model	Correlation Coefficient (R^2)	Average percentage error (%Error)
Freundlich Isotherm	0.9959	2.754
Langmuir Isotherm	0.9378	5.276
Hurkin-Jura isotherm	0.9026	12.026

• Adsorption data of MB fitted to various adsorption models (Freundlich, Langmuir and Harkin-Jura isotherm models) showed reasonable correlation. However, the data is best fitted to the Freundlich isotherm model, as indicated by values of correlation coefficient (R^2) which is nearly equal to one, and the minimum value of % Error.

As in the present study, the microwave used provided uneven heating in microwaved material, which is mainly due to the uneven distribution of microwave energy inside the oven, and somewhat due to the different rates of energy absorption in different parts of the material [51]. Therefore, it is recommended that the application of microwave irradiation for carbonization be further improved when utilising better equipment. As several studies in the past on AC production utilising various *Acacia* tree species demonstrated promising results, it is recommended to catalogue and compile the available scattered data. The inventory will further help in identifying the research gaps and areas to explore in future studies.

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Data availability statement

Data is not available in publicly available repository. Data is included in article/supp. material/referenced in the article.

Authors contribution

Corresponding author is the sole author of the manuscript.

CRediT authorship contribution statement

Muhammad Saleem: Writing - review & editing, Writing - original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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