Research Article

FTIR, XRD, AFM, AND SEM SPECTROSCOPIC STUDIES OF CHEMICALLY MW- WASTE COOKED TEA ACTIVATED CARBON

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ABSTRACT
Microwave–induced activation process with or without ultrasonic technique was performed to produce activated carbon from waste cooked tea. This material was activated by using Clorox or concentrated H_2SO_4- HNO_3 mixture as individual activating agent. Different spectroscopic (FTIR, XRD, SEM, and AFM) techniques were applied to qualify the resulted properties as results of activation process and applied activating agent. The qualitative and quantitative analysis with statistical information of several prepared samples were summarized, discussed, and compared with our recently published paper that demonstrated the existence of micro- and nano- structural particles.
Our selection of waste cooked tea as a starting material subjected to microwave irradiation or ultrasonic as eco-friendly activation process beside different chemicals as activating agents with their spectroscopic results suggested that the prepared activated carbon representing an economically promising material with wide spectrum of applications.

Keywords: Activated carbon, consumed black tea, FTIR, XRD, SEM, AFM, microwave, ultrasonic.

INTRODUCTION
Microwaves are considered as a form of electromagnetic energy with many applications through domestic or industrial ovens [1,2] providing several advantages compared with conventional heating methods such as energy source type, energy transfer mechanism, environmental – health consequences, method efficiency, engineering design, possibility of heat controlling, and uniform temperature distribution conjugated with rapid temperature rise [3].
Activated carbon as amorphous carbon with high qualities in porosity, surface area, penetration, adsorption capacity, and regenerations can be prepared from agricultural, food processes, and human consumption wastes as friendly environmental material with less cost by applying chemical, physical, and physico - chemical activation methods [4-23].
Chemical activation process based on prior material and accomplished with thermal decomposition of the raw agricultural industrial residues with acidic or basic reagents [6].
The aim of this study was directed to prepare activated carbon from largely consumed product in Iraq that is black tea after cooking with different activation agents and procedures, and characterize it with available FTIR, XRD, SEM, and AFM techniques that may be compared with our published works.

Experimental part
Chemicals (used as received)
Sulfuric and nitric acids were from BDH. Clorox bleaching solution containing 5% sodium hypochlorite was purchased from Baghdad, Iraq. Black tea samples were purchased from local market in Baghdad city, Iraq with different commercial marks.

Equipment and Instruments
The following equipment and instruments were used to achieve our goal:
1. Domestic microwave oven type DAEWOO, China.

2. Ultrasonic bath, F5200b Decon Laboratories Ltd., East Sussex, United Kingdom.
3. FTIR spectra were recorded using infrared spectrophotometer, Shimadzu, Japan.
4. X-Rays Diffraction also recorded using a Lab X (XRD-6000), Shimadzu, Japan and using the operational details of the following: Target: Cu Kα radiation, Wave: 1.54060 A, Voltage: 40.0 kV, Current: 30.0 mA, Speed: 5.0000 deg. / min.
5. Scanning Electron Microscope (SEM) type VEGAS III Tescan Algiua origin. Atomic Force Microscope, AA3000, 220V, Angstrom Advanced Inc., USA.
6. To obtain a clear quantitative image of grain size and surface roughness, AFM measurements of several prepared samples of activated carbon with different applied conditions were conducted with an AFM – AA3000 of Angstrom advanced Inc., USA) in ambient conditions.

Modified Multistep Preparation of activated carbon
Our modified multistep preparations of activated carbon samples are summarized in Figure -1- for our published work [24] and Figure -2- for the present paper. The details for both were as following.

Sample A
Cooked or consumed black tea was dried in open air vessel at room temperature then in electrical oven at 70 ^{o}C for five hours then grinded with domestic grinder to fine powder.

Sample A1
unweight quantities of sample A were heated in muffle furnace at 500 ^{o}C for (15 minutes) the cooled to room temperature.

Sample B
7.5 gm of sample A1 were impregnated in 70 mL of Clorox solution for 24 hrs. then filtered off, washed several times with deionized water to neutral pH, and dried.

Sample C
20 gm of sample A1 were 20 mL of H_2SO_4:HNO_3 concentrated mixture (1:1) by adding 10 mL of concentrated sulfuric acid then 10 mL of concentrated nitric acid. The resulting paste was left to stand at lab temperature with occasionally stirring for more than 100 hrs. then diluted with deionized water, filtered off, washed with deionized water to pH 7, and dried.

Sample D
The same procedure of preparing sample C was repeated except that the resulted diluted mixture with deionized water was left for 48 hrs. at lab temperature, filtered off, washed with deionized water to pH 7, and dried.

Sample E
Sample A was heated with domestic microwave oven for 10 minutes.

Sample F
2.26 gm of sample E were impregnated in 25 mL of Clorox solution for 24 hrs., filtered off, washed several times with deionized water to pH 7, and dried.

Sample G
5.1 gm of sample E with concentrated acids were mixed with the same steps of sample C preparation.

Sample H
For this sample, the same procedure for sample D was repeated except using sample E as a primary source for activation step.

Sample I
0.36 gm of sample A1 and 5 mL of Clorox solution were mixed for one hour with ultrasonic apparatus, filtered off, washed with deionized water to pH 7, and dried.

Samples (J, K, and L) were prepared with the same procedure of sample I for (5, 15, and 60) minutes respectively and starting with sample E and Clorox solution.

RESULTS AND DISCUSSION
Its well-known that non-crystalline or porous activated carbon material with surface area ranged (300-5000) m^2/gm used in adsorption processes, surface reactions, ion exchange, and mechanical filtration [25] can be prepared from raw materials with varying in quality and composition depending on chemical treatment methods based upon hydrogen removal linked to raw materials {Dates stones and walnut shells (as primary carbon materials) Asphalt (binding material) [26]; Waste Tar refineries, Baiji / Iraq [27]; Petroleum charcoal [28], waste cooked tea [24, 29].
Figures -1- and -2- show the modified multistep preparation of activated carbon from waste cooked black tea with different activation agents (Clorox solution and mixture of concentrated sulfuric and nitric acids) and using muffle furnace [24] and microwave oven in carbonization step beside ultrasonic bath for activation step with Clorox solution.
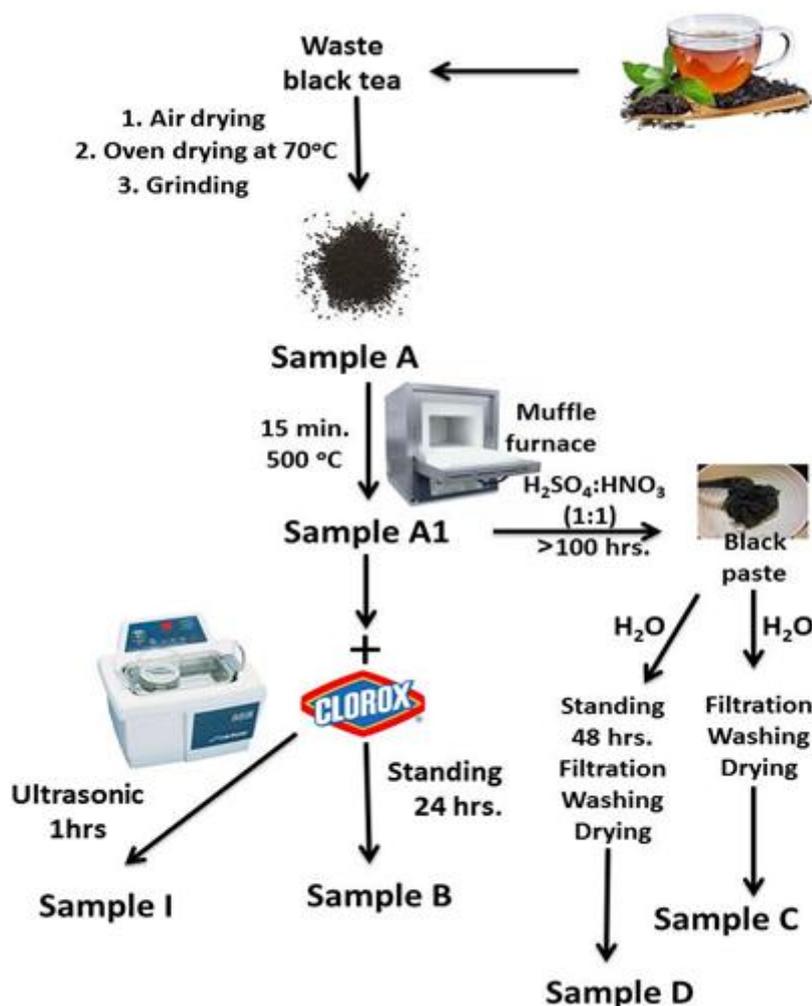
Fig. 1: Modified multistep preparation of activated carbon from waste cooked black tea with different activation agents and muffle furnace [the same figure from our previously published paper [24]]
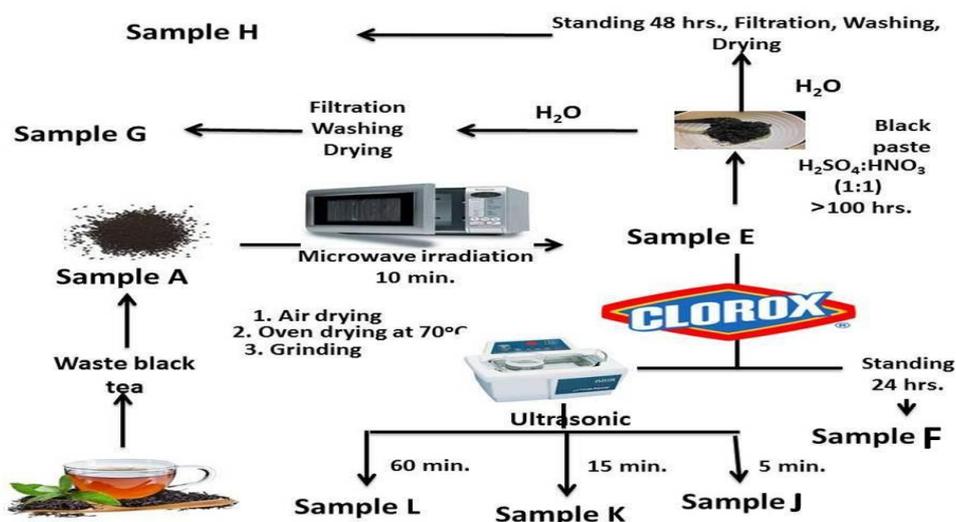
Fig. 2: Modified multistep preparation of activated carbon from waste

cooked black tea with different activation agents and microwave oven [present work]

Clorox solution as a commercial bleach trade mark of 5.25% of sodium hypochlorite or mixture of concentrated sulfuric and nitric acids was chosen for the second time by our team to be applied as an activation agent for preparation of activated carbon.

Also, nonconventional (microwave oven) replaced conventional (muffle furnace) to achieve this modified multistep work. Microwave oven is considered as eco-friendly tool to achieve many chemical reactions including preparation of activated carbon may be used in this work and compared with muffle furnace as a conventional tool mentioned in various published articles.

The effect of applying the above multistep was tabulated in Table -1- through residual percentage calculated from the difference between material weights after and before each identical single step in percentage state.

Table 1: Residual percentage of the prepared materials according to their conditions

Process direction	Used equipment	Activation agent	Residual percentage, %
E to F	Microwave oven	Clorox	70
E to J	Microwave oven, ultrasonic (5 min.)	Clorox	60
E to K	Microwave oven, ultrasonic (15 min.)	Clorox	78
E to L	Microwave oven, ultrasonic (1 hr.)	Clorox	78
E to O and P	Microwave oven	Acid mixture	59

- **Analysis of Infrared spectroscopy (FTIR)**
The prepared activated carbon samples were characterized with FTIR instrument and showed different vibration modes before applying our selected activating agent with some shifting in wavenumbers after activation step Figure -3-. The shifting or disappearance reflected the influence of the acting step (carbonization, activation, and using assistant tool (ultrasonic irradiation bath).

Several characteristic vibration bands can be noticed in Figure -3-. Sample (A) showed hydroxyl group, carbonyl, bending of (C-O) group, stretching of (N-O) group, and stretching vibration of (S=O and Si-O-Si) that were marked in references [24,29, 30] with almost the same spectral identification of asymmetrical and symmetrical vibrations of (C-H) and broad (OH) band indicated high degree of hydrogen bonding.
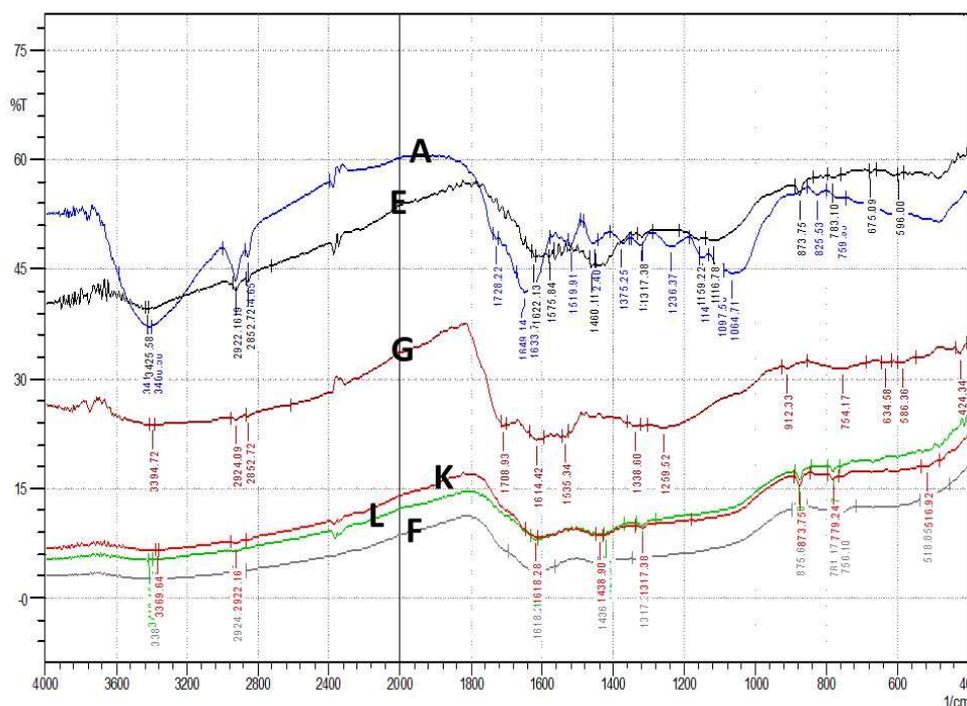
Fig. 3: FTIR spectrum of activated carbon after carbonized tea residues with microwave oven with different activation agents and processes

The presence of N, S, and O as hetero-functional groups with demand oxygen in tea structure represented the effective centers in surface interactions and activated carbon behavior [24, 29, 31-36] after applying potassium carbonate, potassium acetate with tube furnace, or sodium hydroxide or carbonate with microwave irradiation or sodium hypochlorite as Clorox solution and mixture of concentrated sulfuric and nitric acids heating with muffle oven.

- Analysis of X-rays diffraction (XRD)
XRD patterns (Figure -4-) shows three different Bragg angle (2θ,deg.) with maximum intensity in all measured samples (24-29) degrees and around (44) degrees corresponding to (002) and (100) diffraction of the disordered stacking of the microstructures. Also, the obtained results of prepared activated carbon samples (Figure -4-, Table -2-) illustrated that spaces between interlayers with weak crystalline character as non-graphitized carbonaceous structure are larger than graphite as calculated by Scherrer equation [37]:

$$d = k \lambda / \beta . \cos \theta$$

where:
d= average crystallite size (or mean size of the ordered crystalline) in (nm).

λ= X-ray wavelength in (nm)
β= the peak width of the diffraction peak profile (or the line broadening) at half maximum (FWHM) in (radius); [β(radian)=2π β(deg.)/360].
K= shape factor (or constant related to crystalline shape= 0.91).
θ= Bragg angle in (radius); θ (radian) = 2π θ (deg.)/ 360.
Microwave irradiation **(sample E, 20.6 nm)** was more effective in producing less average size (d) than applying muffle furnace (**sample A1, 26.7 nm**) in carbonization stage (Table -2-).

The ultrasonic irradiation time put its fingerprint on the obtained results (Table -2-) where (15) minutes gave the lowest size (**sample K, 18.9 nm**) compared (60) minutes (**sample L, 27.6 nm**) or (5) minutes (**sample J, 42.7 nm**).

Clorox as activation agent was more influence with sample A1 (muffle furnace [24]) as average size function than microwave irradiation (sample E) with the same experimental conditions (muffle carbonization [24]- **sample I, 41.4 nm** while microwave irradiation-**sample L, 27.6 nm**) (Table -2-).

These results (Table -2-) coincide with many published documents of preparation and characterization of activated carbon [3, 24, 28-29].
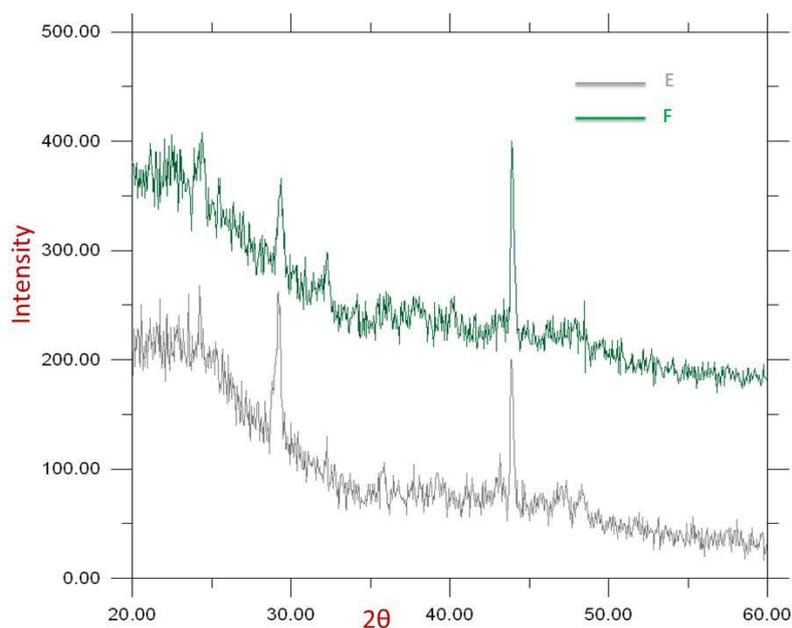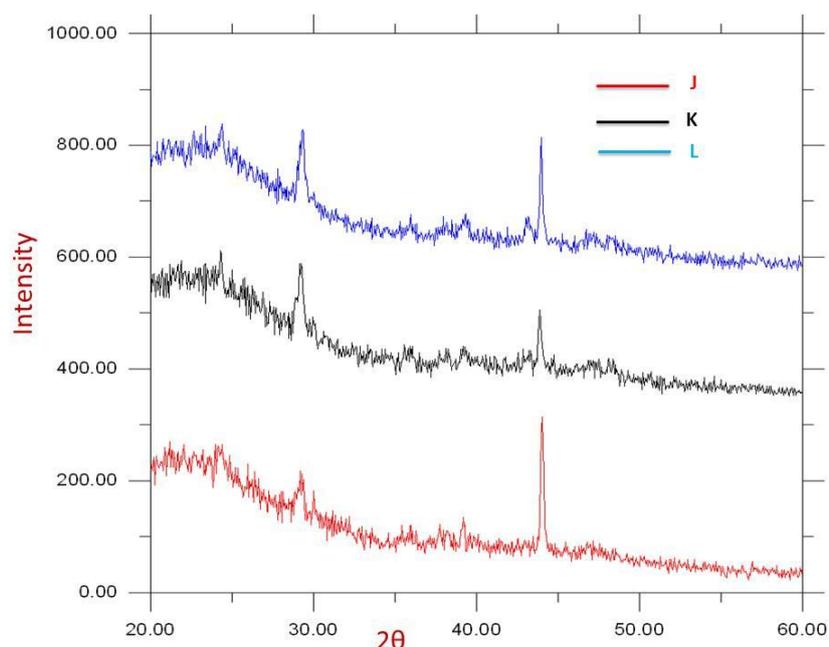
Fig. 4: XRD analysis of prepared activated carbon with microwave carbonization (E), and Clorox activation agent (F) with ultrasonic assistance (J, K, and L)

Table 2: XRD results according to Scherrer equation

Sample	2θ, deg.	β(FWHM), deg.	d=kλ/β. cosθ	Ref.
A1	29.4088	0.3105	26.74646	Previous published work [24]
B	29.2844	0.4041	20.54545	Previous published work [24]
C	43.9521	0.2346	36.92305	Previous published work [24]
D	43.9727	0.3098	27.96248	Previous published work [24]
E	29.1854	0.4021	20.64299	Present work
F	43.9335	0.3149	27.50581	Present work
I	43.9923	0.2090	41.45155	Present work
J	44.0469	0.2026	42.76922	Present work
K	29.2215	0.439	18.9094	Present work
L	43.9899	0.3136	27.62532	Present work

- Analysis of Scanning Electron Microscopy(SEM)
Analysis of Scanning Electron Microscopy (SEM) of the prepared activated carbon samples after treatment with Clorox or concentrated acid mixture depicted in Figures -5- and -6- had been done for both previous [24] and present work respectively.
Figure -6- shows the effect of microwave irradiation on tea residues with concentrated acid mixture (sample F) or Clorox (sample L) where Clorox- ultrasonic influence is more remarkable in microscopic porous characterization than concentrated acids mixture. By comparing Figures (-5- and -6-), it can be noticed that carbonization with muffle furnace (sample D) is more proposal of gaps, channels, and/ or slits than microwave irradiation (sample F). This note can be affirmed by comparing both sample (B) and sample (L).

The obtained results clarify that activated muffle furnace carbonization samples with Clorox and concentrated acids mixture (B and D) respectively have porous structures outputted from heating and activation agents effects on residual tea (Figure -5-) [24]. These (B and D) samples had gaps, channels, or slits of porous structure as Microscopic porous character. This character conjugated with size and shape irregularities was clearly affected with activating materials.
The configuration of pores is linked to the formation of carbon dioxide and carbon monoxide. The formation of these gases resulted from oxidation processes of carboxylic and/or lactone (for CO_2 formation), phenol, carbonyl ether, and/ or quinone (for CO formation), and/or anhydride (for both CO_2 and CO formations) functional groups [38].
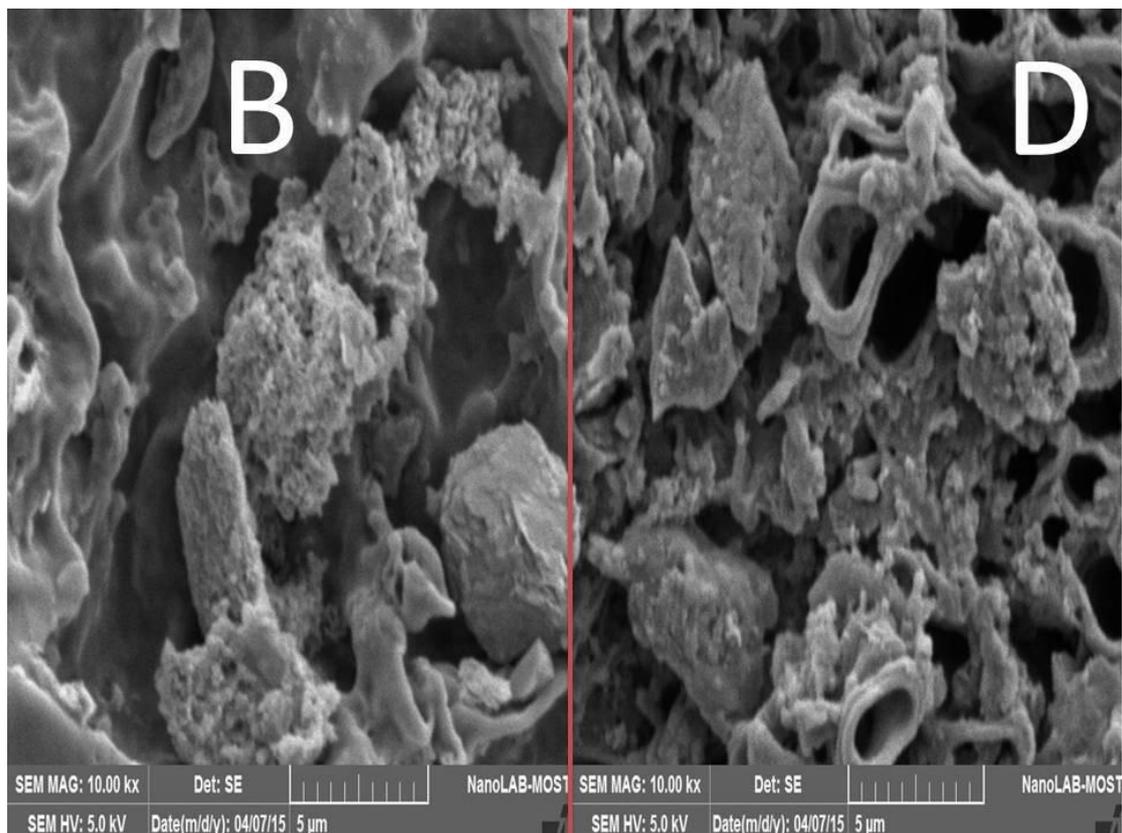
Fig. 7: SEM images of the prepared activated carbon samples after muffle furnace carbonization and activation with Clorox (B) or concentrated H$_2$SO$_4$: HNO$_3$ mixture (D) [24]
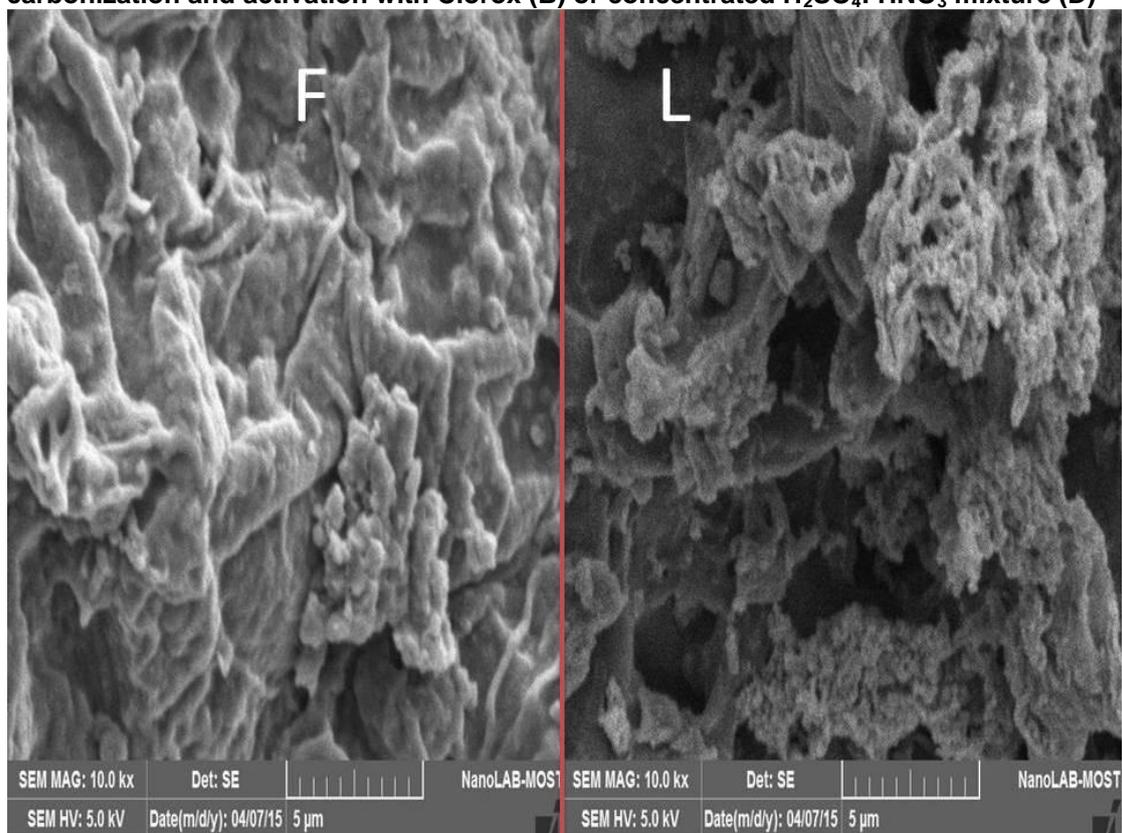
Fig. 8: SEM images of the prepared activated carbon samples after carbonization with microwave irradiation (F and L) and activation with Clorox (present work)

Previous mentioned notices of our prepared activated carbon were similar in characteristic properties with others that prepared from tea or vegetarian sources [28, 29, 36, 40-42].

- Analysis of atomic Force Microscopy(AFM)
To understand the small scale phenomena, micro- and / or nano- tribological studies are needed to be applied especially with Atomic Force Microscopy instrumentations. In order to establish the effect of muffle-MW, Clorox – concentrated acids mixture, conventional – ultrasonic mixing, and exposure time to concentrated acid mixture on the morphology of our newly prepared samples, AFM technology was applied. The AFM morphological results are presented in Table -3- and Figures (9-11).

The effects of the applied conditions (type of carbonization process (muffle or MW), activation agent, time with same activation agent, ultrasonic, …) on the obtained characteristics were summarized in Table -3- through AFM surface roughness parameters [roughness average (S_a, nm), root mean square (S_q, nm), surface kurtosis (S_{ku}), Surface area ratio (S_{dr}, nm), Fractal dimension, Avg. diameter in nm] beside other calculated data from the AFM images and the instrument software [$\sum$ of volume (%), highest volume (%)]. These tabulated data cannot consider as representative absolute surface values because of sample, image, and instrument processing.

From amplitude or height parameters of all measured samples with AFM instrument, the increasing sequence of roughness average (S_a) which depends on the average profile of heights was [S_a **(K) >** S_a **(D) >** S_a **(H) >** S_a **(F) >** S_a **(I) >** S_a **(G) >** S_a **(B)].** Root mean square (S_q) as a function of the square root of the measures is more sensitive to peak and valley than roughness average (S_a) because S_q represented the standard surface height deviation (as square root) not the height deviation. Sq increasing series was [S_q **(K) >** S_q **(D) >** S_q **(H) >** S_q **(I) >** S_q **(F) >** S_q **(G) >** S_q **(B)].** Also, Sq to Sa ratio as an indication to the Gaussian distribution of surface was less than 1.31 (ranged from 1.197 to 1.153) [43, 44].

With muffle furnace carbonization and two different types of activation agents [Clorox and concentrated H_2SO_4-HNO_3 mixture], the resulted acid mixture sample (**D**) gave the higher roughness average (S_a) value compared with (**I or B**) and this notice reflects the importance of activation time. These observations can be repeated in their effects with root mean square (S_q) value.

Microwave irradiation with Clorox (**K**) was with highest roughness average S_a value of all samples and subsequently higher than conventional heating with muffle furnace (**F, I, or B**). Also, root mean roughness (S_q) direction, in this point, was the same of roughness average (S_a).

The distribution of the spikes above and below a mean line for all measured samples, which is represented by roughness kurtosis (S_{ku}), were less than 3 as bumpy or flat surface (Platykurtic surface) not spikes or surface with more peaks than valleys(S_{ku} value is higher than 3) or perfectly random surface as Gaussian amplitude distribution (Mesokurtic surface, S_{ku} = 3). S_{ku} increasing sequence were [**S_{ku} (I) > S_{ku} (G) > S_{ku} (D) > S_{ku} (F) > S_{ku} (B) > S_{ku} (H) > S_{ku} (K)**]. This numerical increasing sequence of S_{ku} (or flatness parameter) is more apparent to eye by observing the obtained AFM images especially as 3D (Figures -9- and -10-) [45-47].

Surface area ratio (S_{dr}) as a hybrid parameter increased with different sequence that was [**S_{dr} (K) > S_{dr} (D) > S_{dr} (I) > S_{dr} (G) > S_{dr} (F) > S_{dr} (H) > S_{dr} (B)**]. From this parameter, roughness ratio can be calculated with (r=1+S_{dr}/100) equation [47]. Our calculated (r) was more than (1) as another indication of roughness.

The resulted fractal dimensions were varied from **2.3 to 2.79; close to 3**; with increasing sequence of our prepared activated carbon (**D > K > I > H > F > B > G**) which another characteristic of rough three dimensional surface not of high self-affinity smooth surface when fractal dimension is close to 2.

To understand the effects of the applied conditions on the resulted activated carbon samples, other main values came to light with AFM science and technology that are sum of volume (%) and highest volume (%) that computed with nano – diameter (or less than 100 nm), beside average diameter as presented in Table -3- and Figures (9-11).

The tested samples showed important values with diameter (**≤100 nm**) that were total volume % (2.88-83.55) % and highest volume % (9.66-142.89) in this range with increasing sequence (**F > D > G = I > B > K > H**) and (**H > F > D > B > G = I = K**) respectively. Also, average diameter varied from (**82.61-142.89**) nm with increasing series [**H (142.89 nm) > G (98.07 nm) > K (95.88 nm) > B (92.21 nm) > I (91.28 nm) > F (83.34 nm) > D (82.61 nm)**].
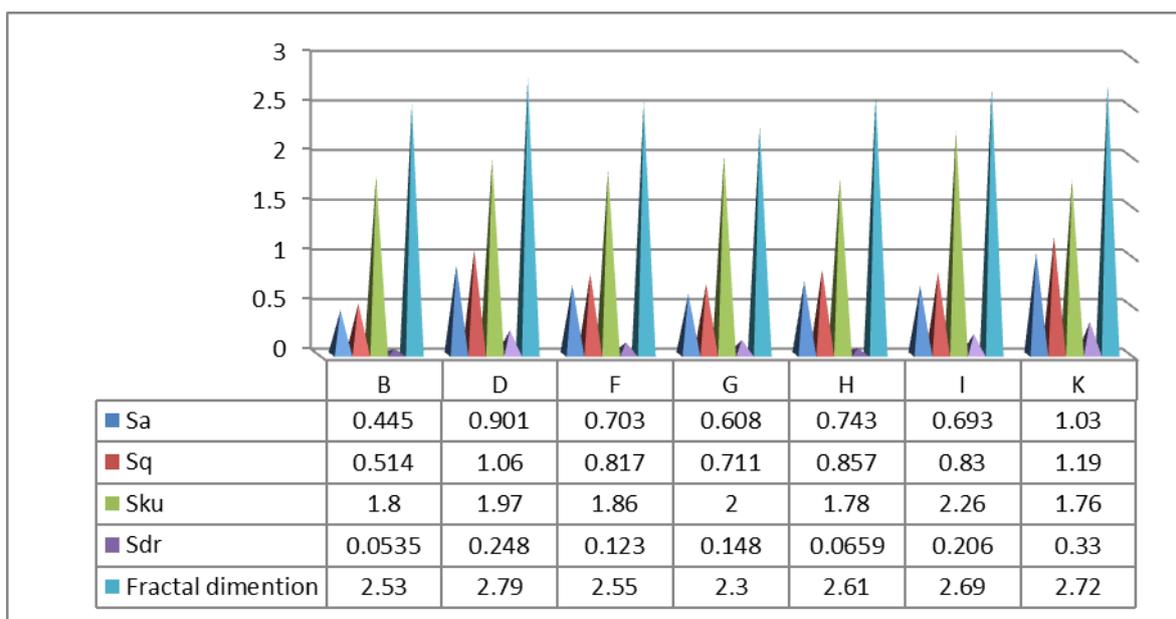
Fig. 9: AFM Fractal dimension, Amplitude (S_a, S_q, and S_{ku}) and (S_{dr}) Hybrid parameters of (B, D, F, G, H, I, and K) prepared activated carbon samples

Table 3: AFM results of several prepared samples

	Amplitude parameter, nm			Hybrid parameter [Surface area ratio] (S_{dr})	Fractal dimension	Avg. diameter, nm	notes
	Roughness Av. (S_a)	Root mean square (S_q)	Surface kutosis (S_{ku})				
B	0.445 [24]	1.8 [24]	0.514 [24]	0.0535 [24]	2.53 [24]	92.21 [24]	Results of (**65-100**) nm [24] Σ of Volume(%): **65.85** highest volume (%): **12.5** at **85** nm
D	0.901 [24]	1.97 [24]	1.06 [24]	0.248 [24]	2.79 [24]	82.61 [24]	Results of (**55-100**) nm [24] Σ of Volume(%): **82.6** highest volume (%): **13.04** at **75** nm
F	0.703	1.86	0.817	0.123	2.55	83.34	Results of (**60-100**) nm Σ of Volume(%): **83.55** highest volume (%): **14.38** at **75** nm
G	0.608	2	0.711	0.148	2.3	98.07	Results of (**60-100**) nm Σ of Volume(%): **65.9** highest volume (%): **9.66** at **80** nm
H	0.743	1.78	0.857	0.0659	2.61	142.89	Results of (**100**) nm Σ of Volume(%): **2.88** highest volume (%): **142.89**
K	1.03	1.76	1.19	0.33	2.69	91.28	Results of (**60-100**) nm Σ of Volume(%): **65.9** highest volume (%): **9.66** at **80** nm
I	0.693	2.26	0.83	0.206	2.72	95.88	Results of (**25-100**) nm Σ of Volume(%): **50.97** highest volume (%): **9.66** at **90** nm
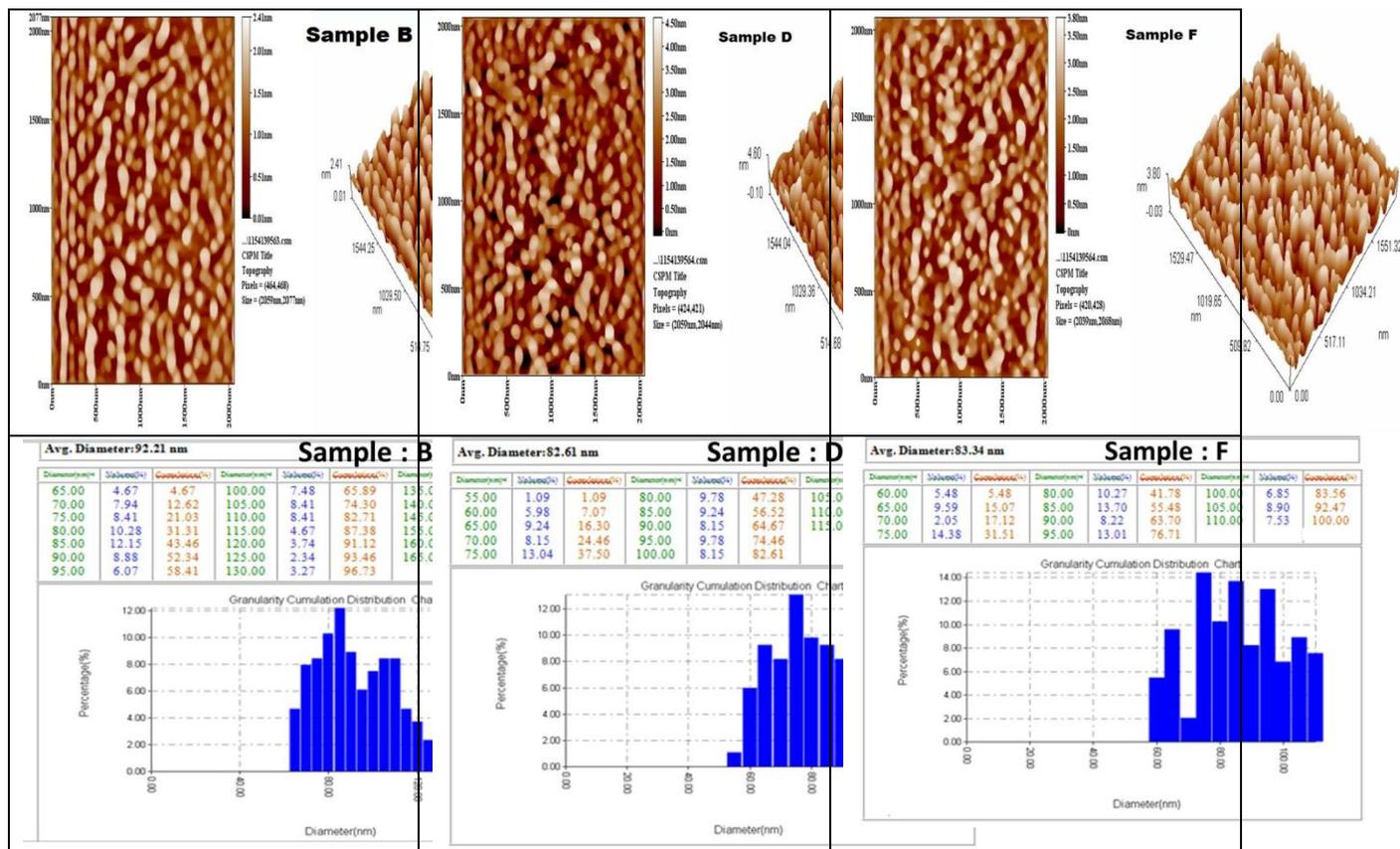
Fig. 10: 2D - 3D images and Granularity-Cumulation Distribution results of B, D, and F prepared activated carbon samples
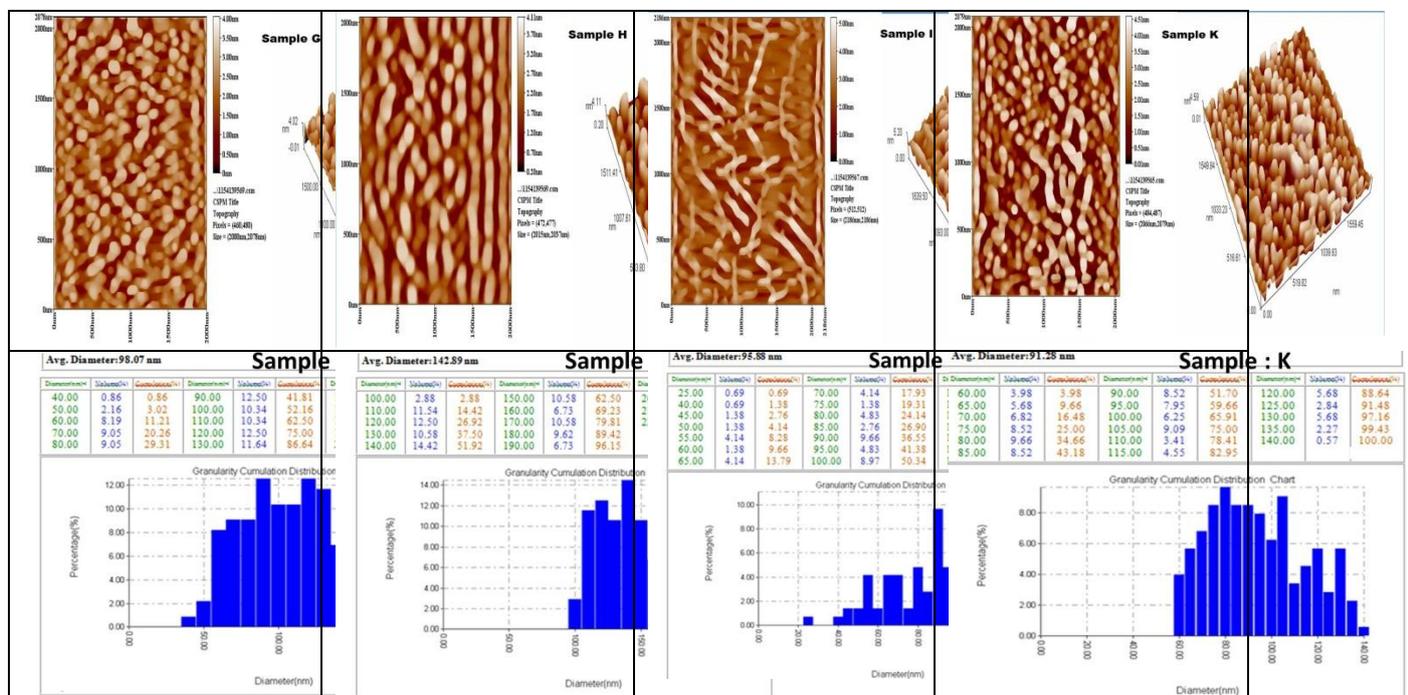
Fig. 11: 2D - 3D images and Granularity-Cumulation Distribution results of G, H, I, and K prepared activated carbon samples

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