



Production of activated carbon from local raw materials using physical and chemical preparation methods

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ABSTRACT

This study was concentrated on the preparation of activated carbon from local raw material (Rice husk & waste plastic), as they are available in large quantities. A comparison between physical and chemical preparation methods and their efficiency were investigated. Results are shown that the preparation by chemical method is more efficiency than physical method due to bigger surface area of AC, except treatment with NaOH. The optimum preparation conditions together with the effected of these conditions on the yield & efficiency of produced AC have been studied. The maximum surface area of produced AC from rise husks is 201.15 m²/gm in physical method and the maximum surface area in chemical method is 329.8714, 280 and 59.0532 when treated with H₃PO₄, ZnCl₂ and NaOH respectively. While the surface area of produced AC from waste plastic is nill that indicate the porosity is not available. Also the characteristic of produced AC were determined such as surface area, bulk density, particle density, porosity, pH, pore volume and FTIR.

Key words: Activated carbon, Rice Husk, Waste Plastic, Chemical Preparation method of AC, Physical Preparation method of AC.

INTRODUCTION

Active carbons (AC) in the form of carbonized wood charcoal have been used for many centuries as an adsorbent for medicinal purposes and also as a purifying agent. Due to it's excellent surface properties, high porosity and low cost of manufacturing, these properties make activated carbon a good adsorbent in spite of the presence of many adsorbents such as silica gel, bentonite, and saw dust [1]. Humphrey and Keller (1997) were estimated of worldwide sales of AC 1 billion \$[2]. AC can be widely used as industrial adsorbents for separation, purification, recovery processes. catalytic supports, chromatography columns, electrode materials for batteries and capacitors. Also an adsorbents in treating drinking water, food industry ,Medicinal uses and pharmaceutical [2,3,4,5,6,7]. Therefore, in recent years, this has prompted a growing research interest in the production of AC from renewable and cheaper raw material such as date pits[8] bamboo[9] oil palm fibre[10,11] coconut shell[12]apricot stones [13]sugar beet bagasse [14] waste tires[15,16,17] coconut husk, seed shell [18] dates stones [19] pistachio-nut shells[2] sun flower [20]Asphaltic carbon[21] marine algae[22] Henna Leaves [23] nilgiri (eucalyptus globulus) leaves[24] TerminaliaCatappa Linn fruit shells[25]. According to FAO, about 500 million tons of rice are processed in the world which give a100 million tons rice husk. Thus, its utilization poses serious ecological and technological problems. The RH contain 74.5% organic matter which consists of about (32% cellulose, 21% hemicelluloses, 21%lignin, 20% silica and 3% crude protein), and the rest is inorganic matter containing 20% SiO₂ and 5.5% mixture of the following oxides: CaO, Fe₂O₃,MgO, Al₂O₃, Na₂O,K₂O, MnO₂, as well as traces of Cu and Pb[26,27].

In this study, we attempted to produce an activated carbon from local raw material (RH, WP) by physical and chemical preparation methods, which gives economic and environmental advantages. To be used later for removal the heavy metal ions from aqueous solutions.

EXPERIMENTAL SECTION

Materials

Zinc Chloride with purity (97%) and Sodium Hydroxide with purity (97.5%) was supplied from THMAS BAKER (Chemicals) Company. Nitrogen gas with purity (90%) and Carbon Dioxide gas with purity (95 - 99 %) was supplied from Basrah Factory, Phosphoric acid purity (85 %) was supplied from GFS Company. Rice Husks were collected from Al-mshgab City, Al-najaf ALashraf, Iraq, which had been discarded as waste from rice cultivation. Thousands of tonnes were disposal in the above place causing a big problem to environment. A waste plastic bottles were used in this research as a raw materials for activated carbon production. This kind of raw materials causing environmental problem and from this point it is a very cheap raw materials.

Physical Method

Initially, the (RH,WP) were well washed with distilled water and dried in electrical oven for 24 hours. The carbonization step was carried out in electrical furnace at heating rate of 30 °C/min in absence air using nitrogen (N₂) at flow rate is 200 L/min.

In the activation step, the product from carbonization step was activated by passing carbon dioxide (CO₂) instead of nitrogen. The different temperature and time of carbonization and activation steps were used.

Chemical method

After the (RH) was well washed and dried ,the immersion step carried out by immersing a 100 gm in solutions of (NaOH, ZnCl₂,H₃PO₄) in different concentrations (0.1 N ,0.16 N ,0.2 N) for 48 hours individually, the samples dried for 4 hours at 120°C to remove the moisture content.

The activation step carried out in electrical furnace at temperature 650°C for 1.5 hour and a heating rate of 30 °C/min. In this step (CO₂) was used at flow rate is 200 lit/min.

Adsorbent Characterization

Surface Area (S.A.)

Adsorbents surface areas were measured in the Petroleum Research and Development Center Baghdad, Iraq, using Surface Area and Porosity analyzer, micromeritic model ASAP 2020 . The results are listed in Tables(1 to 3)

Fourier transform infrared spectroscopy (FTIR)

The surface functional groups of the prepared activated carbon were detected by Fourier Transform Infrared spectroscopy in State Company For Petrochemical Industries basrah using Shimadzu FTIR 8400S, A spectrum was recorded in the mid-IR range from 4000 to 400 cm^{-1} with a resolution of 1 cm^{-1} . The results are shown in Figure(7) and Table(10).

Bulk Density (ρ_b)

Laska method was used to determine the values of bulk density ρ_b . For determining ρ_b the glass beaker was emptied, desiccated and tared , then filled to overflowing with each adsorbent. tapping lightly the sides of the beaker ten times with glass rod, then leveled by rolling the rod across the top edge of the beaker six times. Then reweighing of the beaker and calculating of the medium density is carried out according to [28]:

$$\rho_b = \frac{M_f}{V_f} \quad (1)$$

The results are listed in Table(5).

Particle Density (ρ_p)

The method described by Chenxi Li [29] was used to determine the density of particle. A 100 ml volumetric flask and stopper were tared. adding four grams of each adsorbent to the tared flask with 32 ml distilled water. plastic stopper was used to seal the flask, and heated the solution on a hot plate to boiling. The solution was boiled for 5 minutes, cooled to room temperature, and then filled to a 100 ml volume with pre-boiled and cooled distilled water. Cleaning and drying the outside of the flask. Then reweighing the flask. emptying cleaning, drying the flask then filling to a volume of 100 ml with pre-boiled distilled water and reweighing. calculating of the particle density is carried out according to :

$$\rho_p = \frac{\rho M_s}{M_s - (M_{s+f+w} - M_{f+w})} \quad (2)$$

The results are listed in Table(6).

Porosity (ϵ_a)

The porosity values were calculated by using the following equation[29] :

$$\epsilon_a = 1 - \frac{\rho_b}{\rho_s} \quad (3)$$

The results are listed in Table(7).

Pore Volume (V_a)

To find the pore volume of Activated Carbon drown, one gram from A.C drown in water then boiled until all the trapped in the pores air must be excluded. Then all the moisture on the surface must be removed, and reweight .The different in weight must be divided by the water density to find the pore volume[30]. The results are listed in Table(8).

Adsorbent pH

Measuring of Adsorbent pH was executed according to the following procedures[29].placing five grams of each adsorbent in a 100 ml flask with 25 ml of distilled water individually. The flask contains were mixed 100 rpm for 30 minutes. Measuring of the PH by using a calibrated *PH Meter*, after filtration, using *Whatman4* filter papers. The results are listed in Table(9)

RESULTS AND DISCUSSION

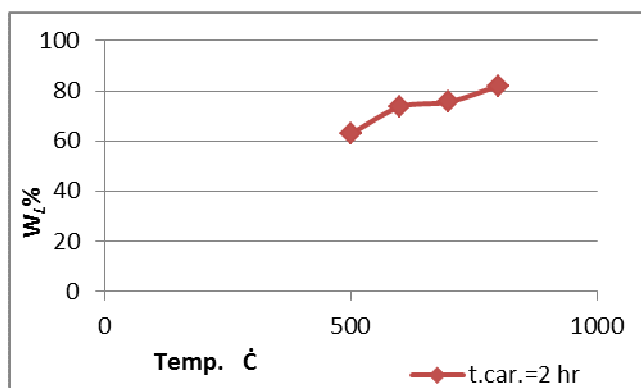
Effect of Time and Temperature of Carbonization on AC produced by physical method:

The figures (1 to 4) showed that the overall weight loss increased with increasing both temperature and time of carbonization, also the overall weight loss increased with increasing both temperature and time of activation, resulting in decreasing yield, while the more losses in weight of produced AC in carbonization step. Similar observations were reported by other researchers [31]. At low burn off, the surface area is small that lead to a low adsorption capacity, and at height burn off the ash content is increased which not desirable which considered an impurity, the materials with the lowest ash content produce the most active adsorbent.

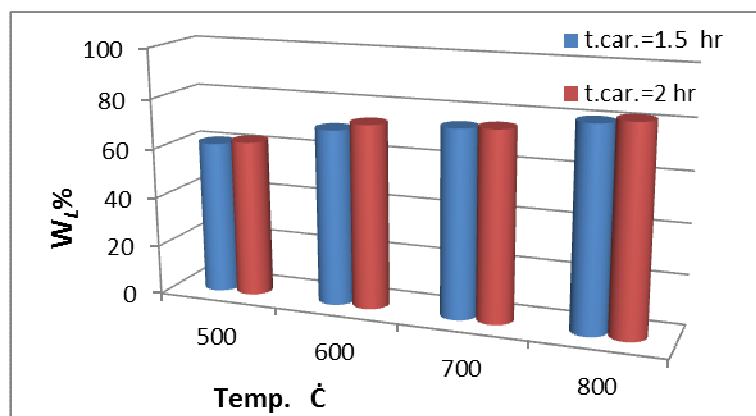
In the carbonization step, the raw material was converted, by progressive heating. And the porosity was created by removal of small molecules are eliminated from the raw material such as(the volatiles, hydrogen and oxygen atoms). The percentage of loss of weight can be calculated from equation:

$$W_l \% = \frac{w_1 - w_2}{w_1} * 100 \quad (4)$$

Where : $w_l\%$, w_1 and w_2 (gm) are percentage of loss of weight , weight before carbonization or activation and weight after carbonization or activation, respectively.



Figure(1): Effect of Carbonization Temperature on weight loss



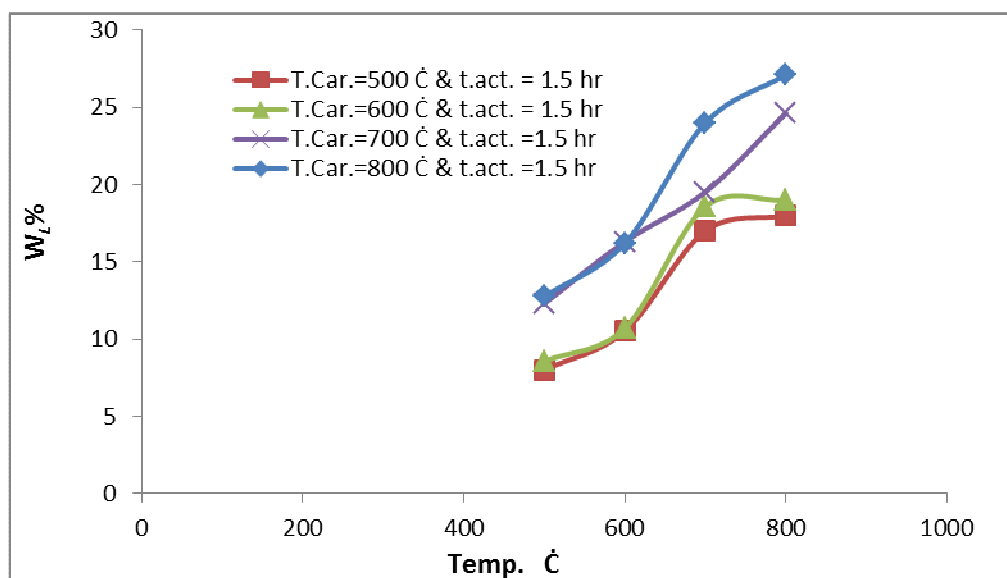
Figure(2): Effect of Carbonization Time on weight loss

Effect of Time and Temperature of Activation on AC produced by physical method:

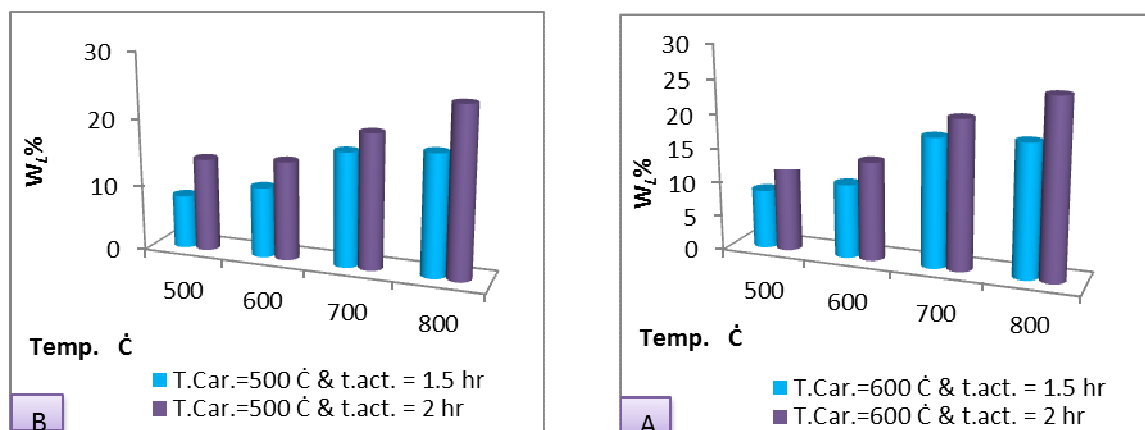
When activation temperature low, the reaction between char and CO₂ was slow, so that the surface area, total volume and micro pore volume were relatively small. With increasing activation temperature, the surface area, total volume and micro pore volume were increased because of the higher reaction rate between carbon and CO₂, and higher rate of releasing of volatile matter. At highest activation temperature, the reaction between C and CO₂ was very faster, so the speed of widening pores was faster than that of developing pores, resulting in increases in pore diameters and formations of meso pores, so that, the surface area, micro pore volume and micro pore percentage were decreased[6].

The time of activation effected on the development of the porous carbon. The time should just be enough to eliminate all the moisture and most of the volatile components, activation time should be limited up to that point. The surface area and the adsorption capacity of activated carbon prepared could reduce at very long or very short activation time, with longer activation time might destroy the pore structure formed previously while shorter activation time could not be enough develop the porosity.

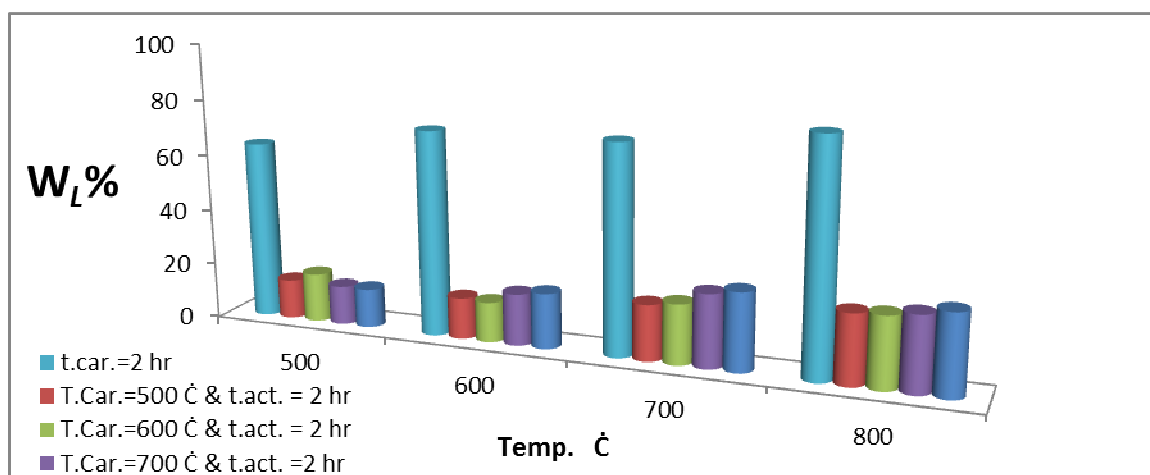
The surface areas of AC produced by physical method are shown in Table (1).



Figure(3): Effect of Activation Temperature on weight loss.

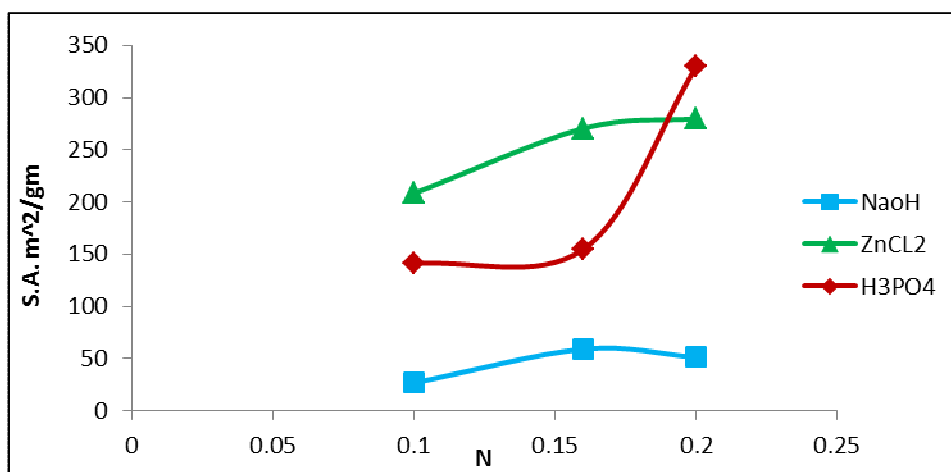


Figure(4): Effect of Activation Time on weight loss.



Figure(5): A comparison between effect of carbonization & activation temperature on weight loss.

Effect of type and concentration of activation agent on AC produced by chemical method:



Figure(6):Effect of type and concentration of activation agent on the surface area of AC produced by chemical method.

The figure (6) showed that the use of zinc chloride as an activation agent was strongly effective in creating well-developed pores and large surface area. The activated carbon yield was also affected by the chemicals concentration where increasing chemicals concentration decreased the yield, because with higher concentration, the weight losses increasing due to release of volatile products, as resultant the surface area and porosity of AC increased.

NaOH removes natural fats, waxes and low molecular weight lignin compounds from the rice husk surface thus revealing chemically reactive functional groups like –OH. The removal of the surface impurities also improves the surface roughness of the fibers or particles thus opening more hydroxyl groups and other reactive functional groups on the surface[32].

Phosphoric acid leads to an increase in the volume of micro pores by widening of micro porosity, with all pore sizes being developed, thus leading to activated carbons with different volumes of micro pores. The surface areas of AC produced by chemical method are shown in table (3).

The Properties of Produced Activated Carbon

Table(1):Surface area of RHAC produced by physical method

Sample	T. Car. °C	t. Car. hr	T. Act. °C	t. Act. hr	S. A. m ² /gm
B 12	500	2	700	2	201.1518
B 16	500	2	800	2	144.809
B 32	600	2	800	2	139.44
B 39	700	1.5	600	2	174.703
B 48	700	2	800	2	196.637
B 60	800	2	700	2	133.265
B 64	800	2	800	2	165.107

Table (2):Surface area of AC from waste plastic produced by physical method.

Sample	T. Car. °C	t. Car. hr	T. Act. °C	t. Act. hr	S. A. m ² /gm
A8	500	2	700	2	4.7
A23	600	2	800	2	Null
A27	700	2	700	2	Null
A28	700	1.5	800	1.5	Null
A35	800	2	800	2	Null

The above results showed that the surface area of AC prepared from waste plastic is null, this because the plastic during carbonization and activation steps converted to liquid causing no porosity and the activation gas cannot enter in to atoms.

Table (3):Surface area of RHAC produced by chemical method.

Activationagent	N	T. Act. °C	t. Act. hr	S. A. m ² /gm
H ₃ PO ₄	0.1	650	1.5	140.796
H ₃ PO ₄	0.16	650	1.5	154.72
H ₃ PO ₄	0.2	650	1.5	329.8714
ZnCl ₂	0.1	650	1.5	208.46
ZnCl ₂	0.16	650	1.5	270.495
ZnCl ₂	0.2	650	1.5	280
NaOH	0.1	650	1.5	26.7276
NaOH	0.16	650	1.5	59.0532
NaOH	0.2	650	1.5	51.1945

Where : T. Car. , t. Car. , T. Act. , t. Act. and N are carbonization temperature, carbonization time , activation temperature, activation time and normality of chemicals .

Table(4):A Comparison between optimum Surface area of Activated Carbon produced by Chemical and Physical methods, and raw RH

Method	Physical method RHAC	Chemical method			RH
		RHACN	RHACZ	RHACP	
S.A. m ² /gm	201.1518	59.0532	280	329.87	0.9672

Where :RH is raw rice husk without any treatment , RHAC is AC produced from RH by physical method, RHACN, RHACZ and RHACP are AC produced by chemical method which treatment with NaOH, ZnCl₂ and H₃PO₄ , respectively.

Table (5):Bulk density (gm/cm³) values of adsorbent .

Diam. mm	RHAC	RHACP	RHACZ	RHACN	RH
0.075	0.3085	0.3402	0.3402	0.3229	0.4119
0.15	0.2753	0.3210	0.3154	0.2979	0.3998
0.3	0.2553	0.2538	0.2656	0.2600	0.3533
0.6	0.2429	0.2444	0.2180	0.2252	0.2913
1	0.1977	0.2269	0.1917	0.2232	0.2569
1.2	0.1762	0.2154	0.1861	0.1966	0.2433

Table (6):Particle density(gm/cm³) values of adsorbent.

Diam. mm	RHAC	RHACP	RHACZ	RHACN	RH
0.075	2.1549	1.9715	2.3351	1.5862	1.4984
0.15	1.6239	1.7861	1.9451	1.3848	1.4077
0.3	1.4369	1.3599	1.5162	1.2901	1.1048
0.6	1.1725	1.2181	1.0267	0.9689	0.8724
1	0.8318	1.1139	0.9307	0.7844	0.7737
1.2	0.6761	0.9546	0.7192	0.6203	0.6875

Table (7):Porosity values of adsorbent

Diam. mm	RHAC	RHACP	RHACZ	RHACN	RH
0.075	0.8568	0.8274	0.8543	0.7964	0.7251
0.15	0.8305	0.8203	0.8379	0.7849	0.7160
0.3	0.8223	0.8134	0.8248	0.7985	0.6802
0.6	0.7929	0.7994	0.7877	0.7676	0.6661
1	0.7623	0.7963	0.7941	0.7155	0.6680
1.2	0.7394	0.7743	0.7412	0.6831	0.6461

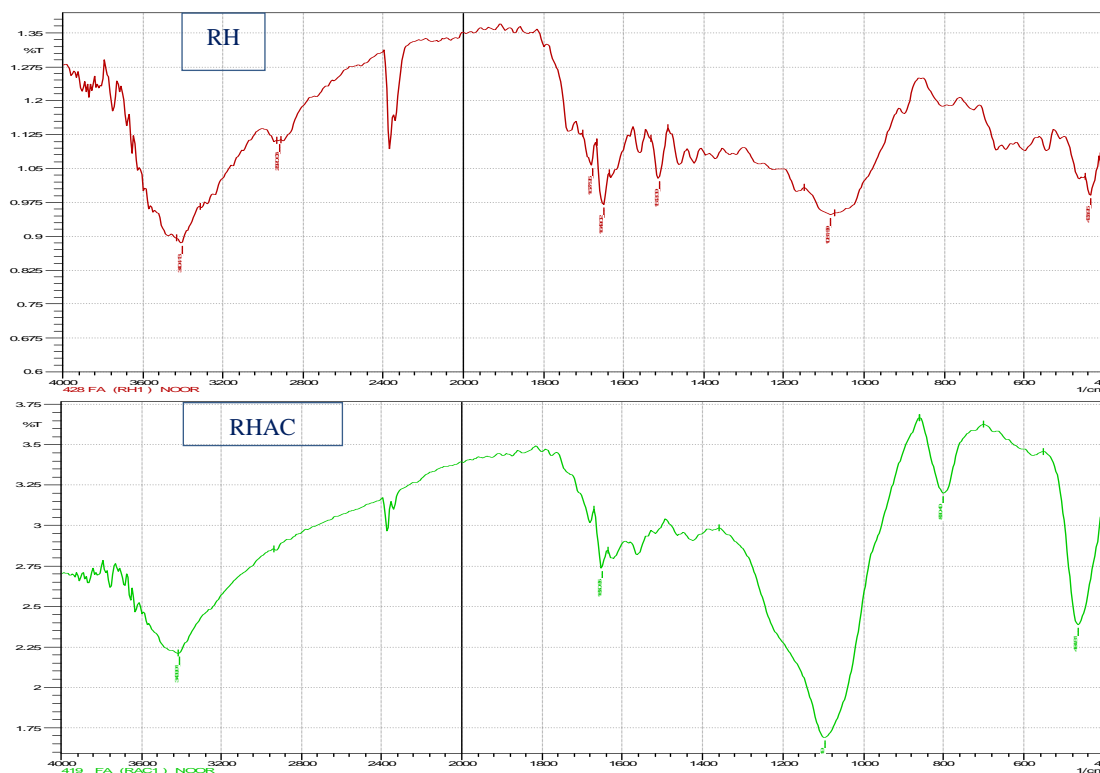
Table (8):Pore volume (cm³/gm) values of adsorbent

Diam. mm	RHAC	RHACP	RHACZ	RHACN	RH
0.075	3.9122	3.743	3.9223	3.2503	2.3897
0.15	3.8649	3.6794	3.8173	3.0474	2.3737
0.3	3.6876	3.4734	3.7802	3.1378	2.2341
0.6	3.1869	3.3292	3.2274	2.5088	2.1374
1	2.8825	2.9051	2.6198	2.1784	1.9072
1.2	2.2099	2.6879	2.1183	1.7121	1.8263

Table (9):pH values of adsorbent

Adsorbent	RHAC	RHACP	RHACZ	RHACN	RH
pH	9.3	6.3	7.02	11.01	7.1

Activated carbons contain both surface acidity and surface basicity. (pH is defined as the minus logarithm of the hydrogen ion (H⁺) concentration). If the value of pH < 7, the acidity from the dissociation of H⁺ from the surface oxygen groups, such as a carboxylic group (—COOH), while for an alkaline solution, the pH has to be >7.0 .



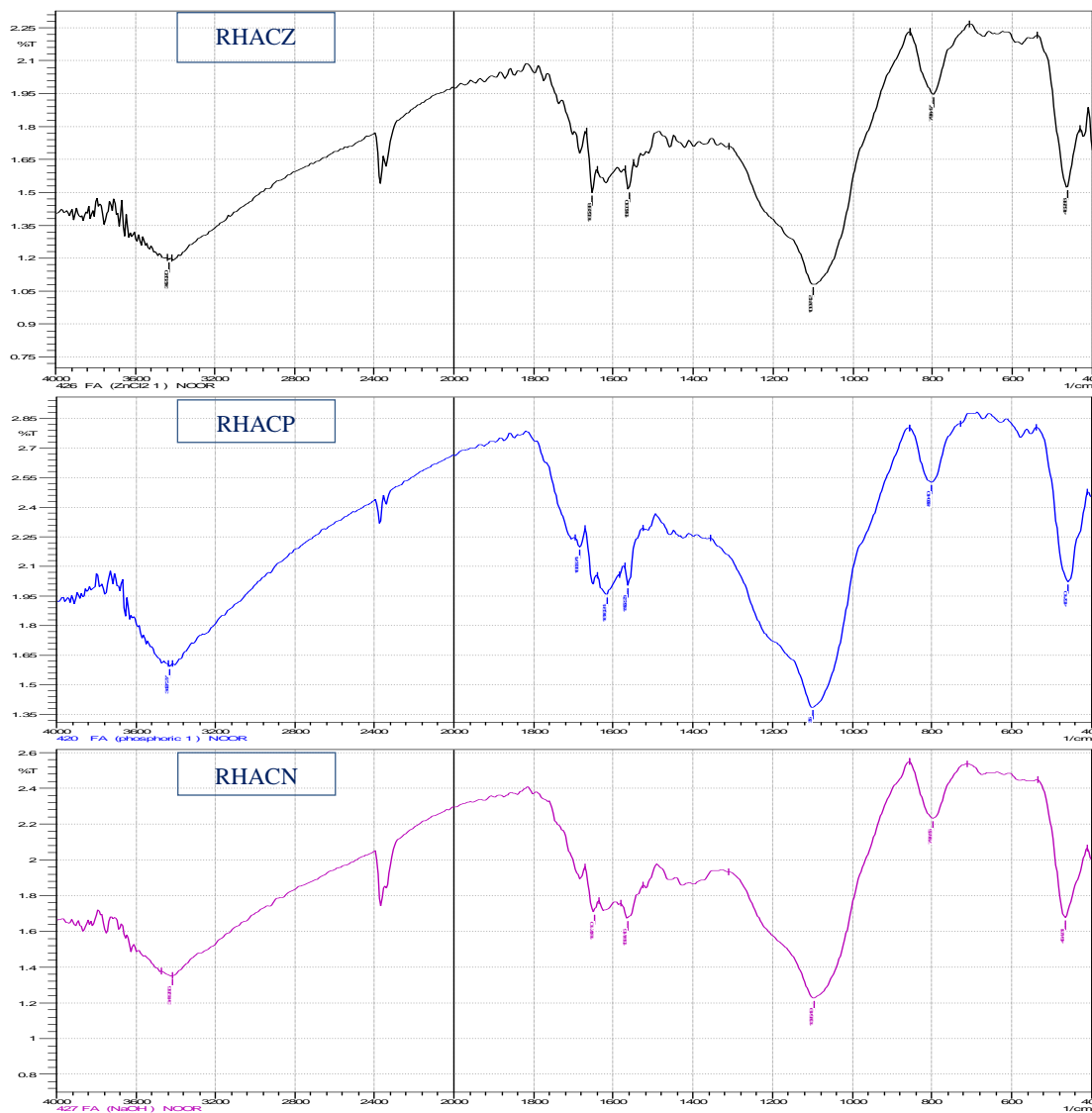


Figure (7): FTIR Spectra of adsorbent

Table (10): FTIR of adsorbent

		RH				
S. V.	3404	2920	1677	1000-1260	1649-1512	1081
F. group	O-H	C-H	C=N	C-O	C=C	Si-O

Table (10):continued

		RHAC		
S. V.	3409	1660	1100	800
F. group	O-H	C=C	Si-O , C-O	Si-H

		RHACZ		
S. V.	3429	1652 - 1560	1097	798
F. group	O-H	C=C	Si-O , C-O	Si-H

		RHACP				
S. V.	3427	1683	1616-1562	1100	1075-1090 & 810-840	800
F. group	O-H	C=N	C=C	Si-O , C-O	PH ₂	Si-H

		RHACN		
S. V.	3419	1647-1564	1096	796
F. group	O-H	C=C, N-H	Si-O , C-O	Si-H

Where: S.V. and F. group are stretching vibrations & Function group, respectively.

CONCLUSION

The results are shown that the optimum conditions of produced AC from RH as 500°C and 2hr of temperature and time of carbonization, respectively. 500°C and 2hr of temperature and time of activation, respectively, in physical preparation method. while in chemical preparation method as 650°C and 1.5hr of temperature and time of activation, 0.2, 0.2 and 0.16 N of H₃PO₄, ZnCl₂ and NaOH, respectively. These conditions were given the maximum surface area of produced AC. The preparation by chemical method is more efficiency than physical method due to bigger surface area of AC, except treatment with NaOH. The AC produced from RH is good adsorbent material due to its height surface area, porosity, pore volume and different surface function groups. The surface area of AC prepared from waste plastic is nill, that indicate the porosity is not available.

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