

Preparation Activated Carbon of From Iraqi Reed**Najat J. Saleh ^{*}, Mohammed I. Ismaeel ^{**}, Raheek. I.****Ibrahim ^{**}, Mummtaz A. Zablouk ^{*}, and Ali amer ^{*}****Received on:31/5/2006****Accepted on:11/1/2007****Abstract**

In this work activated carbon (AC) was successfully prepared from local raw material namely Iraqi Reed .This source is cheap and available and in this work AC is prepared from it for the first time. A chemical method using zinc chloride was used in the activation process. The proper carbonization temperature was found to be 450 °C and the time required for carbonization was one hour. The adsorption capacity for acetone of the prepared AC was measured and found to be 15.6%. Some important properties were also studied such as: apparent density (0.451 g/cm³), ash content (9.4%), moisture content (4.8%). The x- ray diffraction also showed that AC exhibited a poorly crystalline structure, with a little amount of silica and graphite.

Decolorization capacity (DC %) of AC on: (a) Caramel dye solution (b) Potassium permanganate solution, were studied. The effect of quantity Of AC and contact time was investigated using UV- spectrophotometer. It was found that decolorization capacity DC% of KMnO₄ solution (93%) and it was better adsorbed within one hour, while DC% of caramel dye solution was (87%) and it was a better adsorbent for the color within two hours. It is concluded that AC prepared in this work has a good specification compared with standard sample thus it is suitable for industrial uses.

Keywords: activated carbon, Iraqi reed, decolorization**الخلاصة**

(
450
15.6
(%9.4) 0.451
(3.8 %)
() ()
(87) (93)

*Chem. Eng. Dep., Univ. of Tech., Baghdad –Iraq

** Applied Sci. Dep. Univ. of Tech., Baghdad –Iraq

1. Introduction

The terms of activated carbon, charcoal, wood charcoal, active or activated charcoal, bone coal and animal charcoal are synonyms for forms of carbon, which all having marked adsorptive properties; all possess a readily accessible internal surface area (porosity) greatly in excess of the superficial surface^{1,2}. On the other hand Juhola³ defined activated carbon (AC) as a microcrystalline, non graphite form of carbon has been processed to developed internal porosity. All AC posses a porous structure with a small amount of chemically bonded oxygen and hydrogen, also AC can contain up to 20% of mineral matter⁴. Nearly all carbon containing material can be used for manufacture of AC such as nut shell, coal count shells, leather waste, peat, oil shale, rubber waste, sawdust and wood.¹

During the 19th century many studies were made to develop Commercial decolorizing carbon^{5, 6}. The chemical activation of sawdust with zinc chloride producing AC was first described by Osterr⁷ which was then operated by Bayer. Repik et. al⁸ described a process in a fluidized bed which includes continuous activation in the bed, while Ninomiyal et.al⁹ used coconut shell, sawdust as a carbon starting material in production of the coarse granular AC by means also of fluidized bed in reactor. Oda et. Al¹⁰ used a shift kiln for producing AC. Whiten and co-workers¹¹ described a method for producing AC employing a moving grate stoker. The starting material may be any one or more of various carbonaceous materials Alford¹²

described a process for production of high yield AC particles of high activity using a multiple heat furnace. Barnebey and co-workers¹³ described a combustion method for particular material in furnace structure.

Shiral et.al¹⁴ described a process for preparing AC by carbonizing and then activating cellulose material. Many authors described production of AC using phosphoric acid as activating agent.¹⁵ Mcmillan¹⁶ used foamed polymers for preparation of light weight porous carbon Watanabe et. al.¹⁷ provided a process for producing granular AC form a waste tire pyrolysis residue Some works were carried out in Iraq¹⁸ AC was prepared form locally available raw materials such as walnut peelings and date stone , Also sulfur residual and asphalt's binder material were used to prepare AC.¹⁹

In recent years the interest was increased in studying adsorption properties and application of AC.Cooney and co-workers²⁰ used four commercially available AC to evaluate their abilities in adsorbing phenobarbital, chlorpheniramine maleate and theophylline in vitro,Attapolitou et.al studied the adsorption characteristics of chlorpromazine on AC.

Nakamura et.al²² studied invitro adsorption characteristic of parquet and diquat with AC. and they found that the adsorption depends on the particle size of carbon Baski from et.al²³ studied the preparation of AC from Bamboo and the development of AC produced towards commercialization

Recently AC was prepared using three types of Iraqi raw

*Chem. Eng. Dep., Univ. of Tech., Baghdad –Iraq

** Applied Sci. Dep. Univ. of Tech., Baghdad –Iraq

materials: date nuts, rice hull and sawdust by chemical method also decolorisation capacity was studied.²⁴

AC is used in various applications such as decolorizing of sugar and sweeteners , drinking water treatment , gold recovery , production of pharmaceuticals and fine chemicals , catalytic processes , off gas treatment of waste incinerators , automotive vapor filters .²⁵ Very recently Jaguaribe et.al.²⁶ studied the performance of AC from sugarcane bagasses, babassu, and cocount shells in removal residual chlorine.

In present work, AC has been prepared using an iraqi raw material, Reed by chemical method, zinc chloride was used as activating agent. Decolorisation capacity on colored solution was studied by using the prepared AC, some important physical and chemical properties were also studied.

2. Experimental part

2.1) Chemicals used

1. Zinc chloride powder ($ZnCl_2$) [Riedel de-Haenag] purity 99.9%.
2. Aceton (Fluka chemika).
3. $KMnO_4$ (Gillman South Australia).

2.2) Instruments used

1. UV- visible Recorder Spectrophotometer UV-160 Shimadza
2. Electronic balance
3. Muffle furnace (Nabertherm, lilienthal. Mod.N54 /E Germany.
4. X-ray diffractometer Philips (type PW1840) Holland.

All the above Instruments available in Chem. Eng.Dept. Univ. of Technology

2.2) Raw materials

Reed was used as a source of carbon for preparation of activated carbon it was collected from Balad city.

2.3) Preparation of activated carbon

1. Reed was cleaned and dried at (80 - 100°C) for one hour then it was crushed and milled into small pieces.
2. By using mechanical mixer 50 g of Reed was mixed carefully with 200 g of zinc chloride solution (40%) then it was impregnated in the solution for 24 hours.
3. The mixture was washed and filtered then dried in an oven at a temperature of 80°C for one hour⁽²⁴⁾.
4. The dried sample was covered with aluminum foil and placed inside a special stainless steel container then it was covered with a layer of graphite powder to avoid oxidation, the lid of container was closed and the container was placed in a muffle furnace and the samples were heated to a temperature range between 300- 700 °C and for various times range between 1-3 hours.
5. Some of dried samples were mixed with Novalac paste and shaped using a special mould prepared for this purpose into circular shape using a pressure of (3 T/cm²) these circular samples were dried also and transferred to the container (s.s.) and covered with a layer of graphite, the container was covered and transferred to a muffle furnace and heated at a temperature as mentioned before (step 4)
6. The AC obtained after heating in a muffle furnace was tested as follows:

2.4) Measurements and Techniques

4.2.1) X- ray diffraction

The standard diffractometric technique was used to study the structure of the prepared AC and also to determine the content of materials.

2.4.2) Apparent density measurements

This measurement was carried out according to ASTM method D2854-83⁽²⁷⁾

2.4.3) Determination of adsorption capacity¹

The test was commenced as follows: two a graduated cylinder (100 ml), 20 ml. of an acetone were transferred and mixed carefully with 1g of dried powdered of activated carbon. Then the cylinder was closed carefully at room temperature, and then the reduction in volume of the mixture was determined. The adsorption capacity of the activated carbon was expressed by the volume of acetone adsorbed.

2.4.4) Determinations of total ash contents

This test was carried out according to ASTM – designation D- 2866 – 83⁽²⁸⁾ as follows:

1. An accurately weighed sample (10g) of dried AC was transferred to porcelain crucible
2. The crucible was placed in a muffle furnace and the sample was heated at temperature adjusted to $(650)^{\circ}\text{C} \pm 5^{\circ}\text{C}$
3. The sample was heated for hours until a constant weight was achieved.
4. The crucible was cooled in desiccators to ambient temperature and re-weighed.
5. The weight of ash content is expressed as follows

$$\text{Total ash\%} = \frac{[D-B]}{[C-B]} * 100 \quad (2-1)$$

Where

B= weight of crucible (g)

C= weight of crucible + sample (g)

D= weight of crucible + ash (g)

2.4.5) Determination of moisture content of AC

This test was carried out according to ASTM- method D2867 - 83⁽²⁹⁾. The test was carried out as follows:

1. The weight of dry closed capsule was determined.
2. Ten grams of AC were transferred to the capsule. The weight of capsule with sample was determined accurately
3. The capsule was opened and placed with its lid in a preheated oven (145 to 155°C) for 3 hours.
4. The sample was dried to constant weight then it was removed from the oven with the capsule closed, cooled to ambient temperature, the capsule was weighed again accurately.
5. Moisture contents were calculated as follows

$$\text{Moisture content} = \frac{[C-D]}{[C-B]} * 100 \quad (2.2)$$

where

B= weight of capsule+ cover (g)

C= weight of capsule+ cover+ original sample (g)

D= weight of capsule + cover + dried sample (g)

2.4.6) Preparation of Caramel solution (dye solution samples)

1-The Caramel solution, was prepared from a weighed amount of sugar which was heated until light brown color was obtained, then 100ml of distilled water was added to obtain the original caramel solution which is dark brown²⁴.

2-From solution in step (1) 10ml were diluted to 200ml to obtain the stock solution.

3-Different volumes were taken from stock solution to plot the calibration curve with concentration ranges between (500) ppm to (5000) ppm as shown in Table (1)

4-From the UV-spectrum of each solution it was concluded that λ_{\max} is equal to 310 nm.

5-The absorbance value of each of the five standard solutions at λ_{\max} (310 nm) was measured and plotted against their concentration (ppm) to obtain the calibration curve as shown in Fig (1). Plot falls in the region of applicability of Lambert-Beer's law.

6. This calibration curve was utilized in subsequent quantitative estimation through out the course of this work.(Table (1))

2.4.7) Preparation of KMnO_4 solution

1. The stock solution of KMnO_4 (1000) ppm was prepared from which the following solution were prepared (Table 2)

2. From UV – spectrum of each solution it was concluded that (λ max) equals to 525 nm.

3. The absorbance value of each of the eight standard solution at λ max (525 nm) was measured and plotted against their concentration (ppm) to obtain the calibration curve as shown in fig (2).Plot falls in the region of applicability of Lambert-Beers law.

4. This calibration curve was utilized in subsequent quantitative estimation through out the course of this work.

2.4.8) Determination of equilibrium time of adsorption

Forty ml of (5000)ppm concentration of Caramel solution and KMnO_4 solution were shaken with (1)g of AC , then the concentration of adsorbate solution was determined spectrophotometrically at different intervals (5, 10, 15, 30, 60, 120 ,240 ,480) minute until reaching equilibrium (no further uptake of adsorbate). From the results it can be concluded that the equilibrium time is (1-2) hrs.

2.4.9) Determination

decolorisation capacities¹

A volume of 40ml of Caramel solution and KMnO_4 solutions at ambient temperature (RT) was shaken with 1gm of AC, after the mixture was allowed to settle, the clear solution was filtered using filter paper and the equilibrium concentrations were obtained by the usual manner of comparing the experimental data with the calibration curve. Decolorisation capacity was calculated using the following expression:

$$\text{Decolorisation capacity} = (1 - C / C_0) \quad (2-3)$$

C=the final concentration of the dye

C_0 = the original concentration.

3. Result s and Discussion

3.1) Choice of carbonization temperature

Carbonization temperature: is the temperature at which the matter should be totally pyrolysis. As it was mentioned before in the experimental part ,different temperature were examined(300-700°C) to determined the carbonization temperature, and it was found that the optimum temperature is 450 °C. This temperature at which maximum decolorization has been achieved. Our result in good agreement with result obtained by Jaguaribe and co-workers²⁶, they obtained a carbonization temperature of 500 °C for cane sugar bagasse.

3.2) Choice of carbonization time

Heating treatment was carried out at different period of time ranged between (1-3) hours and the optimum time of heating was one hour.

Accordingly all experiments were commencing at optimum temperature of 450 °C and heating treatment time of one hour.

3.3) X- ray Diffraction

As it is well known that when cellulose material subjected to sufficient heat in an inert atmosphere, it will crack thermally to carbon. Carbon is an amorphous and can easily be detected by x- ray diffraction. Figure (3) shows the diffractogram of carbon obtained from the Iraqi Reed material, from this figure it is shown that: Firstly: carbon is poorly crystalline. Secondly: the lattice structure of Reed contains silica along with carbon. Thirdly: it has two graphite peaks in the lattice structure. Finally: our result in good agreement with result obtained by Muhammad⁽²⁴⁾ and Finch³⁰.

3.4) Apparent Density measurement:

The density of AC derived from Iraqi Reed source is: 0.451 g/cm³. Apparent density of AC; as it was mentioned before in method of determination is the weight per unit volume of it, thus it including the pores and voids between particles. Therefore the smaller the density, the greater the pores and accordingly the higher the surface area available with AC that means the adsorption capacity proportional inversely with the increase in density. Our result is not far from the result obtained by Wennerberg et.al.³¹ (0.32 g/cm³), Baski and co- workers²³ (0, 28 g/cm³) and Muhammad²⁴ (0.32 g/cm³) for carbon prepared from date nut.

3.5) Adsorption capacity

The result of adsorption capacity of AC measured in the experimental part for Iraqi Reed is 15.6%. From this result it is clear that Iraqi Reed sample yield AC having a higher surface area as result of higher pores inside the bulk of AC, our result in good agreement with result obtained by Muhammad⁽²⁴⁾. (Who

obtained 15% for adsorption capacity of AC prepared from Rice hill and Fujiwara et.al⁽³²⁾.

3.6) Decolorization experiments

3.6.1) Effect of contact time

Table (3) shows the results of decolorization of Iraqi Reed and contact time, also figure (4) shows the relation between percent DC For caramel dye solution (A) and KMnO₄ (B) and contact time. From this figure it is clearly seen that: there is a rapid adsorb of color by AC in a contact time of less than hour and almost reach a steady state at 60 minutes in the case of KMnO₄ dye solution and 120 minutes in the case of Caramel dye solution. This indicates that Caramel dye solution is better adsorbed the color within one to two hours while KMnO₄ dye solution is better adsorbed the color within one hour, and the isotherm equilibrium was established above this time. Also this may be attributed to the higher pores area posses by the AC. prepared from Iraqi Reed.

3.6.2) Effect of AC quantity

Table (4) shows the result of increasing AC quantity on decolorization capacity. Also figure (5) shows the relation between quantity of AC and %D.C. It can be seen that the decolorization capacity is increased with increasing the quantity of activated carbon. This behavior is similar to that recoded by Muhammad.²⁴

3.7) Determination of total ash content

The amount of ash content in our Reed as a raw material is found to be 9.4%. As it is well known that the inorganic constituents of carbon are usually reported as being in the form in which they appear when carbon is ashes⁽¹⁾. As raw material contains mineral component which

becomes more concentrated during the activation process. Moreover, the inorganic chemicals of activation are often only incompletely removed.

The amount of ash obtained seems to be high, this may be attributed to the inorganic constituent present with carbon: such as SiO₂, as shown in fig. (6), which shows the x-ray diffractogram of ash after five hours of heating. Our results are in good agreement with the result obtained by Whitten and co-workers⁽¹¹⁾, and Yokogama and co-workers.³²

3.8) Determination of moisture content

The result of moisture content of AC prepared from Iraqi Reed in this work is .As it is well known that the permissible range <10% (1) our result indicates, that the moisture content is in the permissible range. Moisture content does not affect the adsorptive power, but it dilutes the AC this additional weight of moist carbon is required to provide the required dry weight. Our results are in good agreement with the result obtained by Muhammad²⁴.

Conclusion

1-Iraqi Reed was used as a new source for preparation of activated carbon for the first time Reed is cheap, available in nature and gives a higher decolorizing capacity. The carbonization temperature of AC was determined, also time required to reach carbonization temperature was established.

2- Decolorizing capacity of caramel solution and KMnO₄were determined, also the adsorption capacity of prepared AC was measured.

3- Some important characterization was determined.

4- From all previous results and characterizations obtained, it is

concluded that the prepared AC is suitable and can be used in industry.

5- The Iraqi reed may be invested to build up a factory for producing AC commercially.

References

- 1-Hassler, J.W. "Purification with Activated Carbon" Chemical Publishing Co., INC New York (1974).
- 2- American Standard Testing Method (ASTM) Designation: D 2652-76 (1987).
- 3- Juhola, A.J., Carbon 13,437 (1975).
- 4- Smisek, M. and Gerny, S., Active Carbon, Elsevier Publishing Co., INC, New York (1970).
- 5- Warring, R.H. "Filters and Filtration Hand book" the Trade and Technical press Ltd, UK (1981) P:31.
- 6-Ostrejko, V., British Patent 14224 (1900). 18040 (1900); German Patent 136,792 (1901).
- 7-Osterr, V. fur chem. and metal produkle AT 68 196(1913).
- 8-Repik, A.J., Miller, C.E. and Johnson, H.R., U.S., Patent 3,976,597; Aug 29 (1976).
- 9-Ninomiyal, W. and Kunil, D.; U.S. Patent 3,852,216; Dec. 3 (1974).
- 10-Oda, T., Manaka, J. and Minaniyama, K.; U.S. Patent 3,541,025; Nov. 17 (1970).
- 11-Whitten, C.M. and Hagstrom, R.G.; U.S. Patent 3,870,652; Mar. 11 (1975).
- 12-Alford, H.E.; U.S. Patent 3,994,829; Nov. 30 (1976).
- 13-Barnebey, H.L.; U.S. Patent 4,038,154; Jul. 26 (1977).
- 14-Shiral, Y., Lchikawa, H., Yoshida, A., Uchidd, N., Tsuji, M. and Matsumoto, Z.; U.S. Patent 3,676,365; Jul. 11 (1972).

- 15-Shinomiya , T. , Tarui , Y. and Enomoto , E. , U.S. Patent 3,835,064; Sep. 10 (1974) .
- 16-Mcmillan , W.J. ; U.S. Patent 3,342,555; Sep. 19 (1967) .
- 17-Watanabe , Y. and Miyaiima , T. ; U.S. Patent 4,002,587; Jan. 11 (1977) .
- 18- ليث ياسين قاسم ؛ تحضير الفحم المنشط من المصادر النباتية ؛ أطروحة ماجستير – كلية العلوم – جامعة الموصل (1991)
- 19- ليث ياسين قاسم, طه سلمان كاظم, صباح جاسم احمد, عيسى حسن مطر, هاشم محمد جعفر, براءة اختراع رقم 2679 (1992)
- 20-Cooney , D. J. Toxicol . Clin . Toxicol . (1995) ,33,3, P 213-217
- 21-Atta-Politou , J. , Macheras , P.E. and Koupparis , M.A., J. Toxicol . Clin . Toxicol (1996) ,34,30, P: 307-316
- 22-Nakamura , T. ; Kawasaki , N. , and Tamura , T. Bull , Enuron contam – Toxicol (2000) 64,3, p:377-382
- 23- Baski, S. , Biswas, S.and Mahajan , S., Tifac, news and Views, org.in , internet (2003)
- 25-Activated Carbon Production Plant , Asian and Pacific center for transfer of Technology ,<http://www.tifac.org.in/offer/tsw/apctt 27.htm> (2004) .
- 24-Muhammed , S.S. , M.Sc. thesis , College of Education (Ibn. Al-Haitham) Baghdad University (2004) .
- 26- Jaguaribe, E.F., Medeiros, L.L.Barreto, M.C.S. and Araujo,L.P.,Braz. J.Chem. Eng.vol.22 no.1(2005)
- 27- American Standard Testing method (ASTM) Designation: D2854- 83
- 28- American Standard Testing Method (ASTM) Designation :D2866-83.
- 29- American Standard Testing Method (ASTM) Designation :D2867-83.
- 30-Finch,H.E., U.S.Patent 3,451,944;Jun.24(1969)
- 31- Wennerberg,A.N.,and Grady,T.M.O.,U.S. Patent.4,082,694,Apr.4(1978).
- 32- Yokogam , A.,Mitooka , M. and Shima; U.S. Patent.3,940,344;Feb.24(1976).

Quantity AC. (mg)	%Decolorization capacity of AC
250	85
500	86
750	87
1000	88
1250	89
1500	90

Table (3) Decolorization capacity as function of contact time for Iraqi Reed

A. Caramel dye

B- $KMnO_4$

Table (4) Decolorization capacity as function of AC quantity of Iraqi Reed

Sample No.	Concentration (ppm)
1	500
2	1500
3	2500
4	3750
5	5000

Table (1):

Caramel solutions with different concentration

Sample No.	Concentration (ppm)
1	5
2	10
3	15
4	20
5	25
6	30
7	35
8	40

Material	Time (min)	Adsorption	Conc. (PPM)	C/C ₀	DC%
Iraqi Reed	5	0.104	60	0.150	85
	10	0.089	5.2	0.130	87
	15	0.087	5.0	0.125	87.5
	30	0.082	4.6	0.115	88.5
	60	0.079	4.4	0.110	89
	120	0.075	4.2	0.105	89.5
	240	0.061	3.4	0.061	91.5
	480	0.050	2.8	0.070	93

Material	Time (min)	Adsorption	Conc. (PPM)	C/C ₀	DC%
Iraqi Reed	5	0.50	2188	0.43	56.2
	10	0.448	1950	0.39	61
	15	0.4	1750	0.35	65
	30	0.351	1575	0.32	68
	60	0.311	1350	0.27	73
	120	0.276	1150	0.23	77
	240	0.226	1000	0.20	80
	480	0.148	650	0.13	87

Table (2): $KMnO_4$ solutions with different concentration

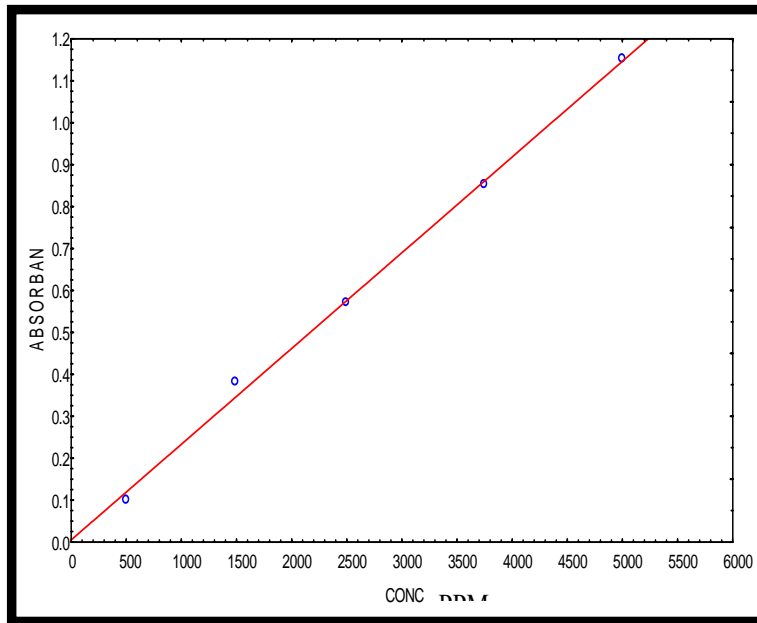


Fig. (1) Calibration curve for standard solutions of Caramel

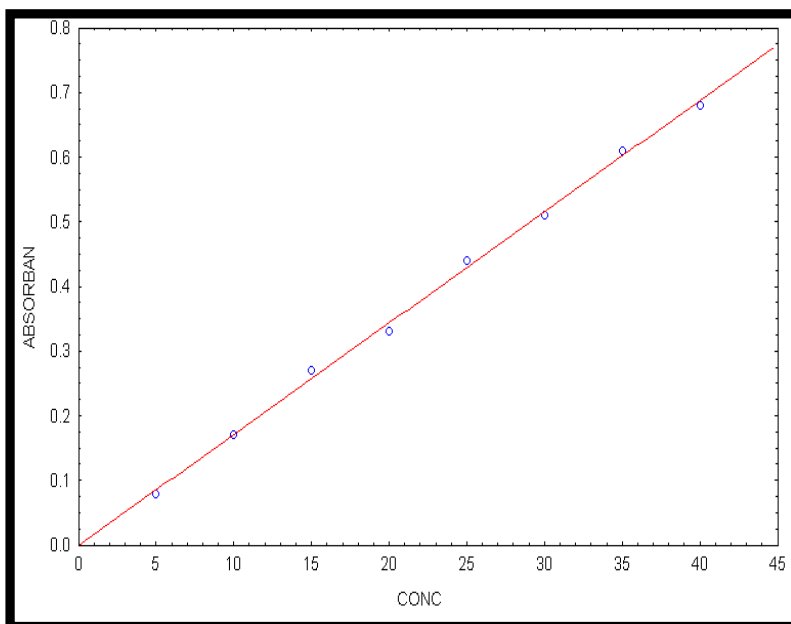


Fig. (2) Calibration curve for standard solutions of KMnO₄

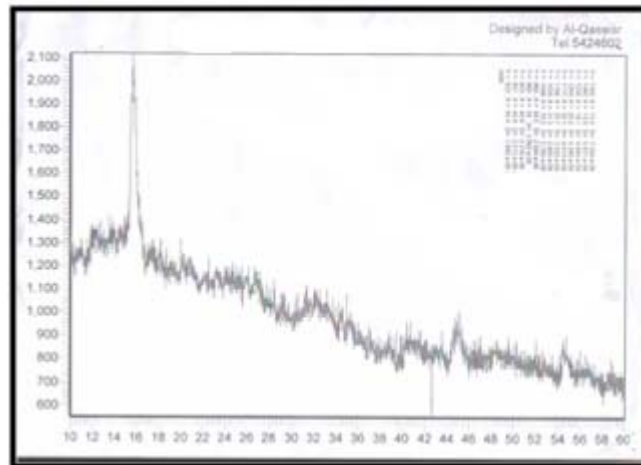


Fig. (3) Diffraction of AC

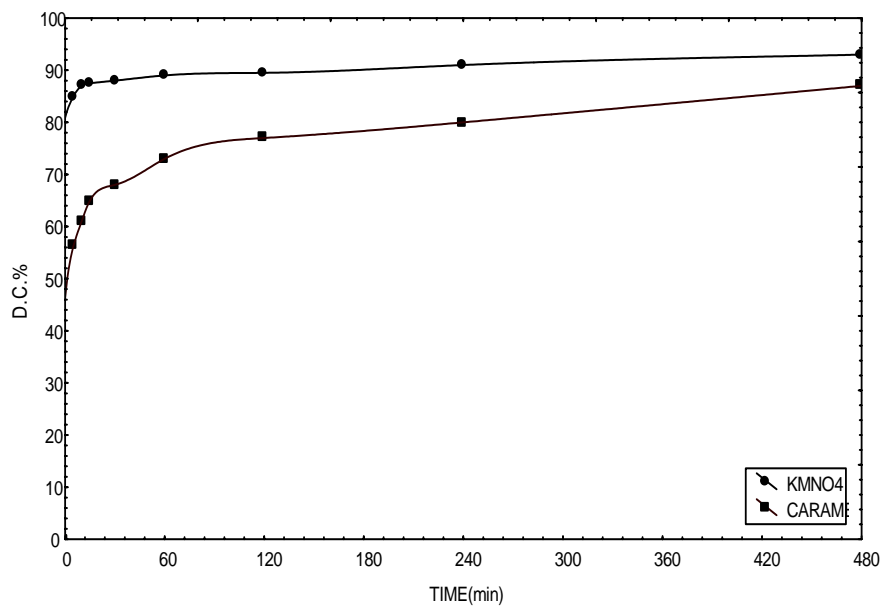


Fig. (4): The effect of time on %D.C. for
A- Caramel solution B- KMnO₄

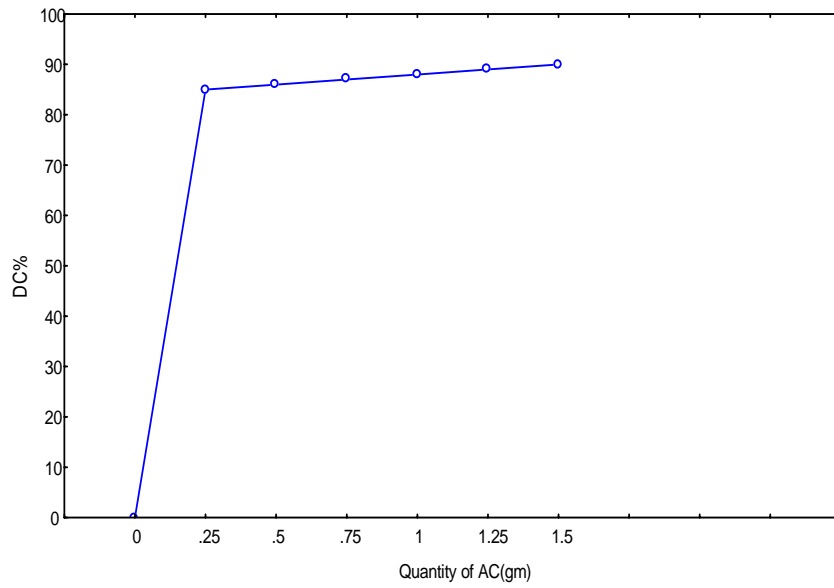


Fig. (5): The effect of Quantity on %D.C. for $KMnO_4$

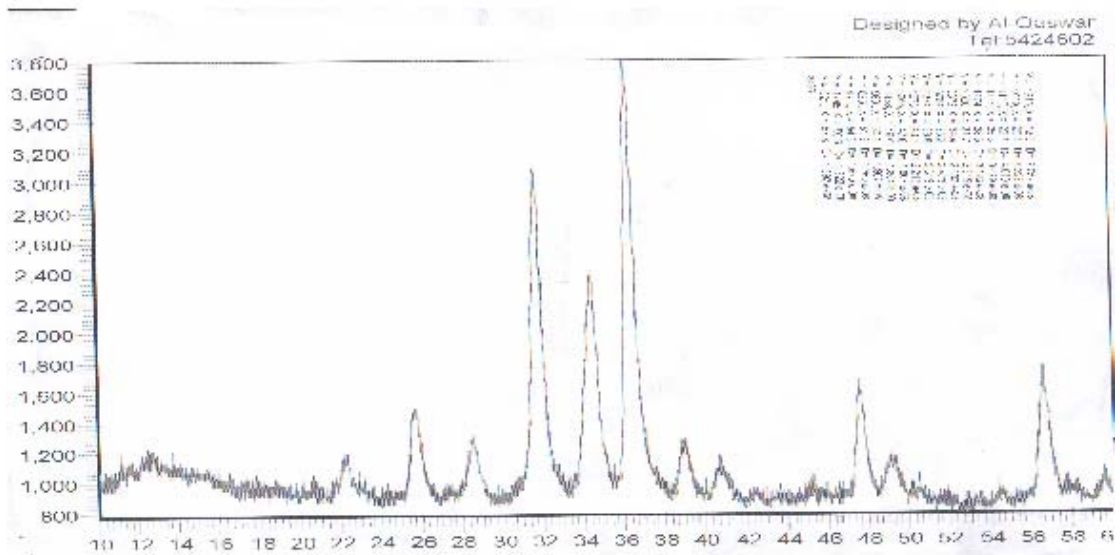


Fig. (6): Diffractogram of ash

