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# Physico-Chemical Characterization and Freundlich Isotherm studies of Adsorption of Fe(II), from aqueous solution by using Activated carbon prepared from *Doum* fruit waste

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**ABSTRACT**

*Doum fruit is one of the common tradition plants grown in many agriculture area in Sudan, the wastes of the Doum fruit were use to prepare activated carbon through chemical activation method with 1 M KOH and under temperature of 600 $^{0}C$ for 1 hr , the product of the activated was examined for its proximate composition ; ash (4.9%) , moisture (2.2%), carbon content (35.15%) , volatile matter (24.43%) , porosity (60.08%) , iodine number of 15.42 and methylene blue value of 200 mg/g. XRF study on activated carbon prepared from Doum fruit (ACD)shows different concentration of inorganic elements the major elements in the sample are Potassium (1.04%) ,Calcium (1.25%) and Zinc(5.26%).XRD analysis showed the presence of highly organized crystalline structure of raw activated carbon for ACD sample , Carbon with crystalline structure Rhombohedral and Carbon Supplied with crystalline structure Orthorhombic were detected. The result showed a strong and broad adsorption peak at 1577.66 $cm^{-1}$, which corresponds to the lactone in ACD samples While other strong and broad adsorption peak appeared at 1253.64 $cm^{-1}$, which corresponds to the aromatic C===O and aromatic structure , conjugate carbonyl was observed at 1595.02 $cm^{-1}$ for the same sample . The kinetics of adsorption of $Fe^{2+}$, $Cr^{3+}$ and $Co^{2+}$ from aqueous solution has also been investigated. The adsorption process was carried out in isothermal container at $30^{O}C$. the effect of dose of activated carbon prepared from the sample on percentage removal metals indicate that the maximum dose of adsorbent was at concentration of 0.8 g/l for sample , The contact time was in 80 min for the samples . The adsorption decreased as the pH increase the optimum pH for the adsorption was attended at 6 for .The experimental isotherm data were analyzed using Freundlich equations. The adsorption process follows the Freundlich order kinetic, having a correlation coefficient ($R^2$) of 0.97. Adsorption capacity with value of 1.36 and Adsorption intensity of 0.13 .*

**Key words:** activated carbon , Doum Fruit , Proximate analysis , XRF , FT-IR , XRD ,Adsorption kinetic.

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## INTRODUCTION

These agricultural by-products and waste have little economic value, and their disposal not only is costly but may also cause environmental problems. Conversion of these agricultural waste into carbonaceous adsorbents that can be used in food applications such as sugar refining or wastewater treatments or in pharmaceuticals industry would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbonaceous adsorbents. activated carbons (AC), on the other hand, are prepared from a variety of local raw materials of vegetable origin, such as wood and peat, The by-products include soft lignocellulosics such as rice straw, soybean hull, sugarcane bagasse, peanut shell and harder materials such as pecan and walnut shells [(1),( 2)]. AC is prepared and activated by various methods, including thermally and chemically, with acids and various salts. Pervious study mentions that activated carbon and the method of activation determine the effectiveness of the carbon as a decolorize of sugar syrup and many other applications. The world production of AC

in 1990 was estimated to be 375,000 ton, The demands of AC were increase over the year and market growth was estimated at 4.6% per year [3]. The strong market position held by AC relates to their unique properties and low cost compared with that of possible competitive inorganic adsorbents like zeolites. Heavy metal is a term, given to the group of metals and metalloids with atomic density greater than 5g/cm3, usually associated with pollution and toxicological problems [4]. Toxic metals have adverse effect on the health of human, when they penetrated through the human organ and tissue as well as the entire systems.[5]

Adsorption technique is widely used in environmental management applications throughout the world. There are different types of adsorption techniques such as gas –gas adsorption and Liquid – solid adsorption systems which are based on the ability of certain solids to preferentially concentrate specific substances from solutions on to their surfaces. The main objective of the study was to determine the chemical and physical properties of activated Carbon prepared from Doum fruit and to investigate the adsorption characteristics of the Ferrous ion from aqueous solution with respect to Freundlich Isotherm studies, adsorption kinetics, effects of pH , Contact time and Adsorbent doses

## MATERIALS AND METHODS

### Material

**Doum fruit:**Doum , *Hyphaene thebaica* is native to upper Africa. It is found along the Nile River in Egypt and Sudan, in the Inner Niger Delta. A doum dates is made in Egypt and believed good for hypertension. In Diu, Una and Saurashtra region of Gujarat (India), the tree is known as Hoka Tree and the red ripe edible fruit is known as Hoka[6].The sample of Doum was obtained from local market in Khartoum state-Sudan.

### Methods:

### Chemical activation

**Carbonization:** The carbonization of the materials was done at 350$^{O}$C for two hours and allowed to cool at room temperature according to the method of Ekpete. and Horsfall [7].

**Activation:** The method of Hassan and Ashfaq [8] was used. After sample preparation, 200 grams of the each sample was mixed with 250 ml of KOH . The samples were impregnated in muffle furnace at 600 °C for 1 hour. Washing of prepared sample was carried to clean the base content of the prepared AC. The washing process was continued until pH 7 was attained. The samples were then dried in oven at 105 °C to remove any moisture content .

### Physical and chemical properties of activated Carbon

The pH was measured by using pH meter (HACH 103),for Moisture Content**;** 0.5gm from the activated carbon was placed, weighed at once to the nearest 0.5gram. and then placed in a preheated oven at 105$^{0}$C.

After cooling in desiccators to ambient temperature and the weight was measured again. The moisture content was determined using the following formula mentioned by Ekpete. and Horsfall [7]

$M_n = ((W_w-W_d)/W_w) \times 100$

in which:
$M_n$ = moisture content (%) of material
$W_W$ = wet weight of the sample
$W_d$ = weight of the sample after drying.

### Ash Content:

A crucible containing 1 gm from each sample was ignited in the muffle furnace at 650$^{0}$C for 1h. It was then placed in the desiccator, cooled to room temperature and weighed.

The ash content was determined using the method of Ekpete. and Horsfall [7] followed by calculation using the formula:

Ash % = $(W_1/W_2) \times 100$

Where: $W_1$ = weight of ash.
$W_2$ = initial weight of dried sample.

**Carbon content and Iodine number:**
Carbon content was determined according to the method mentioned by Malike [9]. ASTM[10] (D4607-94) was used to determine the iodine number.

**Determination of porosity/ bulk density and Carbon content :**
The method described by Ekpete and Horsfall [7]was used to determine of porosity/ bulk density The bulk density and porosity were calculated using the following expressions

Bulk density = mass of wet sample/mass of volume
Porosity = Vv/Vt
Where Vv = volume of void, Vt = total volume

**Calculation of decoloring efficiency DE(%):**
The decoloring efficiency DE (%) is used to determine the decoloring capacity of AC. The following Equation was employed to quantify the DE (%). The absorbance of original liquor was taken as A0 and that of filtrate was taken as A . [11]

DE (%) = (A0-A)/A0 × 100 %

**XRF analyzer :**
The sample was analyzed using the technique of X-ray fluorescence (XRF).The samples were first crushed into fine powder and then they were pressed into a pellet form using a 15 ton pressing machine The diameter of each pellet was about 2.5 cm and a mass about 1.0g.The pellets were subjected the XRF spectrometer system were each of them was measured for 2000 sec .The spectra obtained as a result of X-ray excitation using Cd-109 x-ray source were transferred to a computer. The absorption spectra were then analyzed and concentration of the element present in the samples were obtained using AX1L –XRF software.

**FTIR analyzer :**
The samples were grinded and milled with 100 mg KBr to form a fine powder. This powder was then compressed into a thin pellet under 7 tons weight for 5 minutes. The sample was then analyzed using Fourier Transform Infrared (Shimadzu 8300) spectrometer and the spectrum was recorded in a spectral range of 400-4000 $cm^{-1}$.

**XRD analyzer :**
The sample was prepared using bulk mineralogy method given in Fauzi"S guide on X – ray diffraction mineralogy of sedimentary rock. The water was chilled at temperature $20^{O}C$ and pressure 400 PSI. The XRD diffractometer was switched on at initialization power 15 kV and 5mA. The sample was then analyzed using the xpert -pro system.

**Adsorption properties.**
**Dosage of adsorbents:**
Different doses of the adsorbent were mixed with the metal ion and the mixture was agitated in a mechanical shaker. The percentage of different adsorption doses was determined by keeping all other factors constant.

**Initial concentration:**
In order to determine the rate of adsorption, different initial concentrations of metal ion ranging from 0.1-0.1gram were used. All other factors are kept constant.

**Contact time**:
The effect of period of contact linking the adsorbent and adsorbate on the removal of the metal ion in a single cycle was determined by keeping initial concentration, particle size, pH, dosage, and temperature constant.

**pH**:
Adsorption experiments were carried out at a range of pH 1-10.The acidic and alkaline pH of the medium has been maintained by adding the necessary amounts of hydrochloric acid and sodium hydroxide solutions.

**Temperature:**
The adsorption experiments were carried out at constant temperatures, 30ºC in a thermostated shaker machine. The constancy of the temperature was maintained with an accuracy of ± 0.5º C.

**Equilibrium adsorption isotherms**

The adsorption data was evaluated using Freundlich model. The fitting parameter and calculated constants as well as graphical representation was obtained by linear regression analysis .The Freundlich model is represented by the following equation; [12]

$qe = K_f Ce^{1/n}$

qe = quantity adsorbed per gram of carbons in (mg/g), Kf = adsorption capacity, 1/n =adsorption intensity.

The $Fe^{2+}$ concentration retained in the adsorbent phase was calculated according to equation **[12] ;**

$$Qe = \frac{(Ci-Cf)/V}{W}$$

where *Ci* and *Ce* are the initial and equilibrium concentrations (mg/L) of $Fe^{2+}$ solution respectively; *V* is the volume (L); and *W* is the mass (g) of the adsorbent.

**Data Analysis:**

Using Statistical Packages for Social Sciences (SPSS) program analyzed results. Comparison between adsorbents and other parameters was completed by single and two-factor ANOVA. Percent relative standard deviations were computed for all replicate samples.

## RESULTS AND DISCUSSION

**Table (1): Proximate analysis of the activated Carbon Prepared from Doum fruit by chemical activation**

| Parameter* | Doum Fruit (**ACD**) |
|---|---|
| pH | 7.8 |
| Bulk Density g/ml | 0.71 |
| Moisture% | 2.2 |
| Ash % | 4.9 |
| Iodine number | 15.42 |
| Porosity (%) | 60.08 |
| Volatile matter (%) | 24.43 |
| Carbon content(%) | 35.13 |
| Methylene Blue mg/g | 200 |
| Decoloring efficiency DE(%) | 85.8 |

**An average of triplicate sample*

**proximate analysis of activated carbon papered from Doum Fruit**

Qualitative and quantitative analysis of activated carbon give useful data about the activated carbon produce. Proximate analysis is one of the most important analysis techniques. Table (1)shows chemical composition of prepared activated carbon from the plant. carbon content of the sample was 35.13 % , amount of carbon content is related to the raw materials [13].lignin, cellulose , are lignocellulosic material consists of plant and extractives are known to vary in chemical structure and initial carbon content. The cellulose is a linear polymer of glucose with a theoretical carbon content of 44.4 %. Lignin is a three dimensional polymer of aromatic alcohols with a carbon content of 60 – 63%. As a result the carbon content of a lignocellulosic material is dependent on the relative abundance of its constituents. Thus the yield of carbon from each component is directly related to the carbon content of the respective components. Thus the carbon yield upon pyrolysis of lignocellulosic material is dependent on the composition of the precursor material. In general, greater the aromaticity and molecular weight of the precursor, greater will be the char yield. The low carbon yield in the case of cellulose is due to the fact that significant amount of carbon is lost from the glucose derivatives due to volatilization and as a result the char yield is low. the char yield from cellulose is known to be enhanced by the presence of inorganic compounds (mineral matter). In plants $Na^+$ and $K^+$ ions are of physiological important. Plant cells are intelligent in differentiating $Na^+$ and $K^+$ by some complexing mechanism.

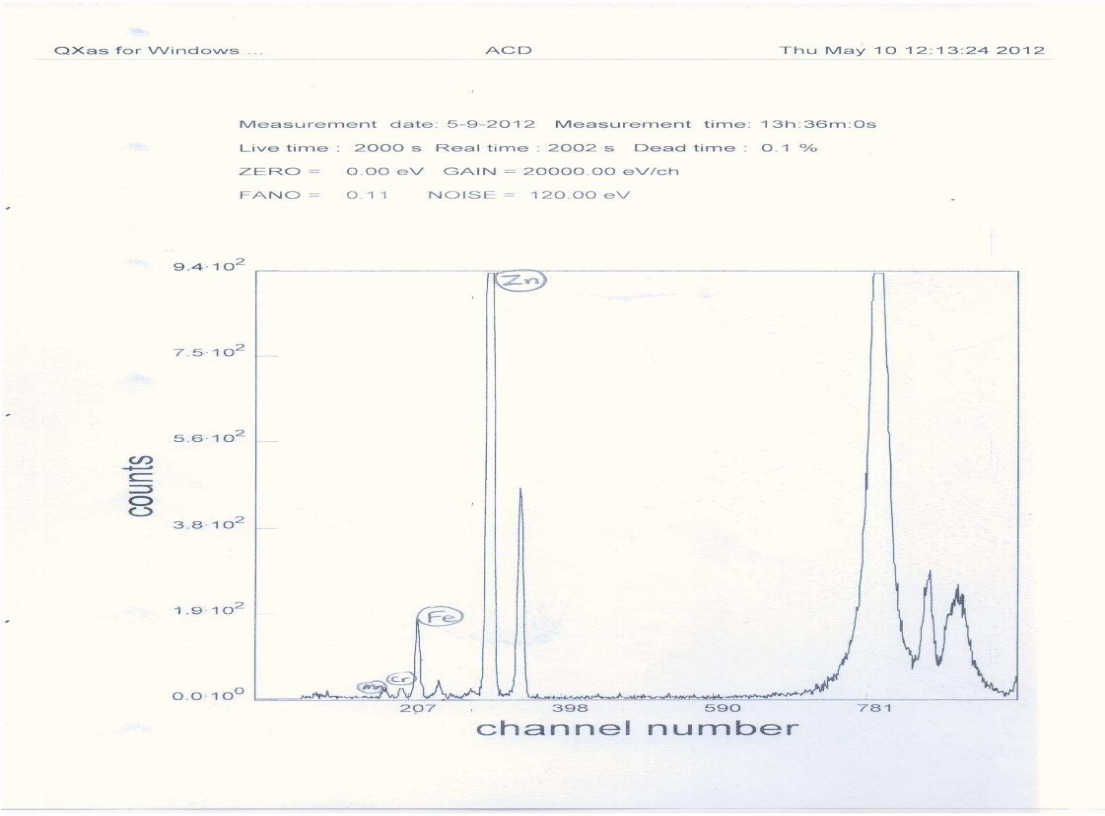
The porosity percentage of the samples ACD prepared by Chemical activation of KOH which had porosity of 60.08%, Iodine number is a fundamental parameter used to characterize activated carbon performance. It is a measure of the micro pore content of the activated carbon and is obtained by the adsorption of iodine from solution by the activated carbon sample. The micro pores are responsible for the large surface area of activated carbon particles and are created during the activation process [7]. ACD has value of iodine number of 15.42 $mgI_2/g$,

Rajeshwari [14] reported a value range from 12.000, 12.750, 13.500, 13.500 and 14.250 at 400,500,700, 600, and 800 $C^0$ respectively for activated carbon prepared form *Parthenium* seed some authors reported high iodine number, from table (1) moisture content of activated carbon prepare from Doum Fruit (ACD) was 2.2% , moisture content is factor that affect on the activity of activated carbon The presence of even small amounts of water vapor, on the other hand, considerably inhibited the activity. The decrease in activity was to the extent of about 25% with a moisture content of 5% as compared to the activity in the dry air. [15].High moisture content may be due to plant origin , while some author reported a low value moisture content of 0.3255% for Activated carbon. Subhashree[16] reported moisture content of 0.4 and 14.9 % for Rice husk and paper sludge respectively. ACD has Methylene blue number of 200 mg/g .Methylene blue test give an indication of the adsorption capacity for large molecules having similar dimensions to methylene blue; it is a quick test for medicinal and other carbons prepared to adsorb large molecules, high value of methylene blue indicate to characterize carbons for their surface area and microporous structure.

The power of activated carbon to remove the color is measure in term of decoloring efficiency and expressed as percentage. Decoloring efficiency DE(%) of activated carbon prepared from Doum fruit ACD sample was found to 85.8 for $Fe^{2+}$ (Table 1)

**XRF , FT-IR and XRD OF Activated carbon prepared from Doum Fruit**

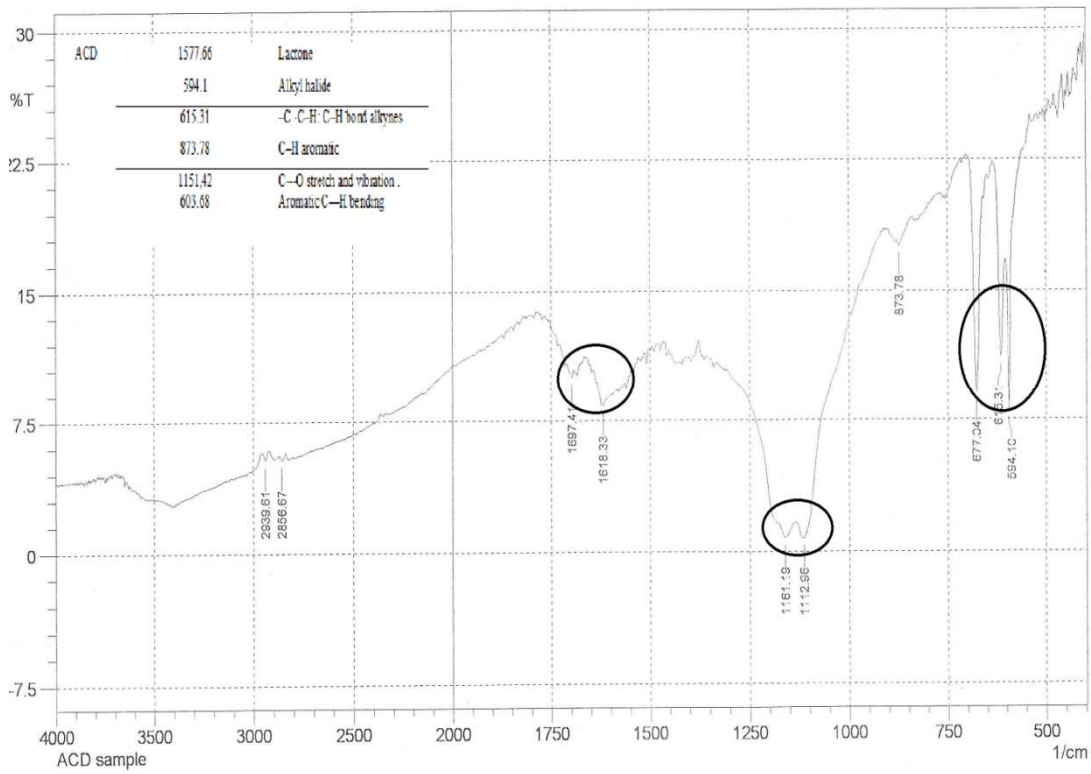
XRF analysis is made to predict type and concentration of elements emdaded with crystallographic structure , the result indicate that the elements Potassium , Calcium , Manganese , Iron , Copper ,Zinc and Chromium with concentration range between 0.01-1.5%. while was found in ACD sample only.(Figure1).these elements have improve the adsorption process when the activated carbon used as adsorbent , The transition metals and their compounds, are used as catalyst because of their ability to change oxidation state or in the case of the metals, to adsorb other substances on their surface as catalyst. Transition metals are often used to catalyze redox reactions [17].



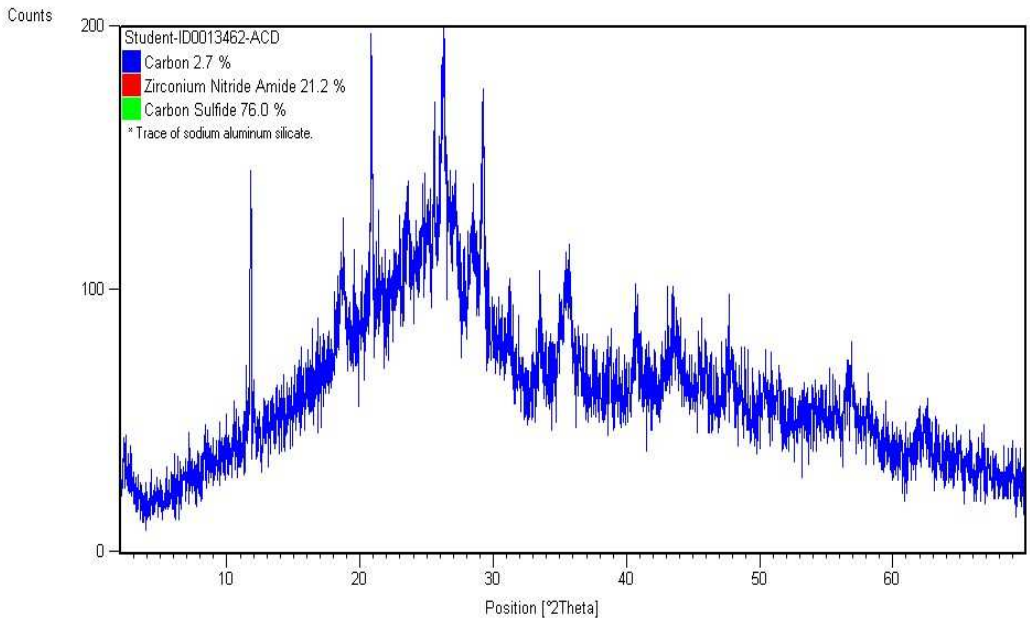

**Fig(1)XRF for activated carbon prepared from ACD**

One of the most important parameters that influence and determine the adsorption of metal ions from aqueous solutions by activated carbon are the carbon-oxygen functional groups present on the carbon surface IR spectroscopy is made for sample ACD.This analysis indicates that the functional groups of Lactone with the frequency 1577.66 $Cm^{-1}$ and C---O at 1151.42 $Cm^{-1}$ and Aromatic C---H at 873 $Cm^{-1}$ were found in ACD sample(Figure 2), in this study KOH activation creates carbon surface rich in oxygen functional groups , The effectiveness of KOH activation relative to either physical activation methods or activation by other chemical agents can be attributed to the ability of K to form intercalation compounds with carbon easily., formation of such

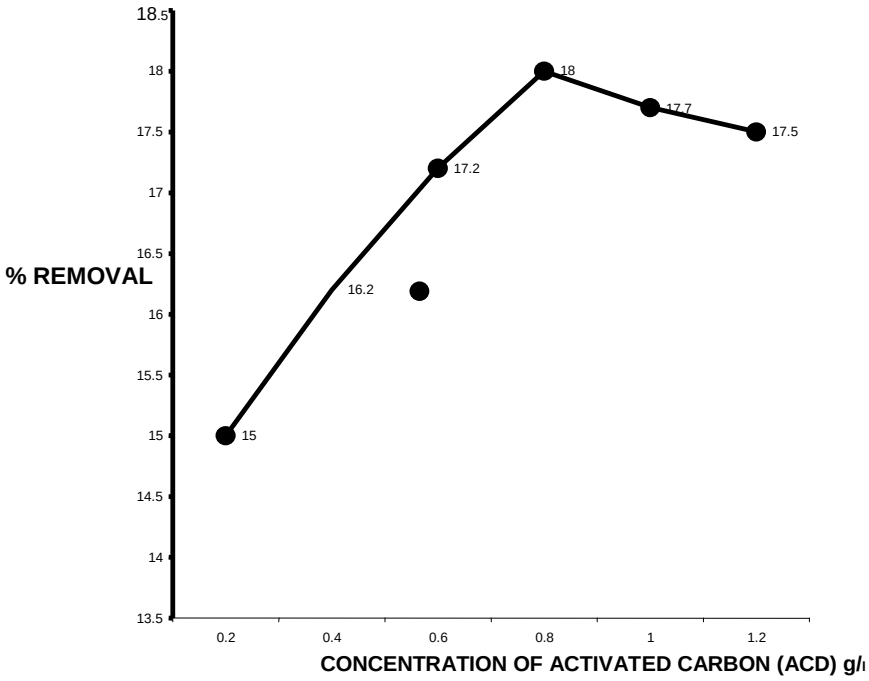
functional group enhance the adsorption capacity as mention by (Roop and Goyal)[15] make such carbon material useful in different application such as catalytic reaction. XRD analysis is made to identify the crystallographic structure of the samples using ICCD standard ACD contains Four crystal system(Figure3),The literature of carbon materials repeatedly refers to the crystallite and to the crystallite size, with its graphitic connotations, in analyses of structure within activated carbon based on XRD data. The XRD diagrams of activated carbon prepared from Doum fruit (ACD) indicate the intense main peak shows the presence of highly organized crystalline structure of Carbon with crystalline structure Rhombohedral and Carbon Supplied with crystalline structure Orthorhombic were detected, this crystalline structure increase the adsorption of metals on to prepared activated carbon ,where the metals adsorbed on the upper layer of the crystalline structure of the carbon surface by means of physisorption .



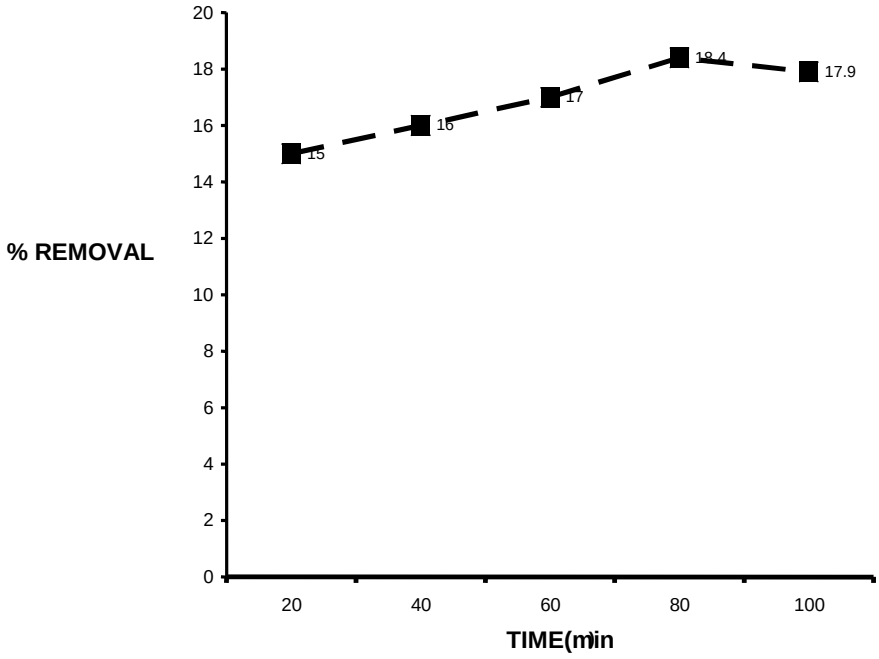

**Fig(2)IR for activated carbon prepared from corn maize (ACD)**




**Fig(3)XRD pattern of ACD sample**




*(Initial pH of 6; Contact time of 80 min; Adsorbent dosage of 0.8 g/L; and Temperature of 30°C.)*
**Fig. (4) Effect of adsorbent dose on the adsorption of ferrous onto ACD**

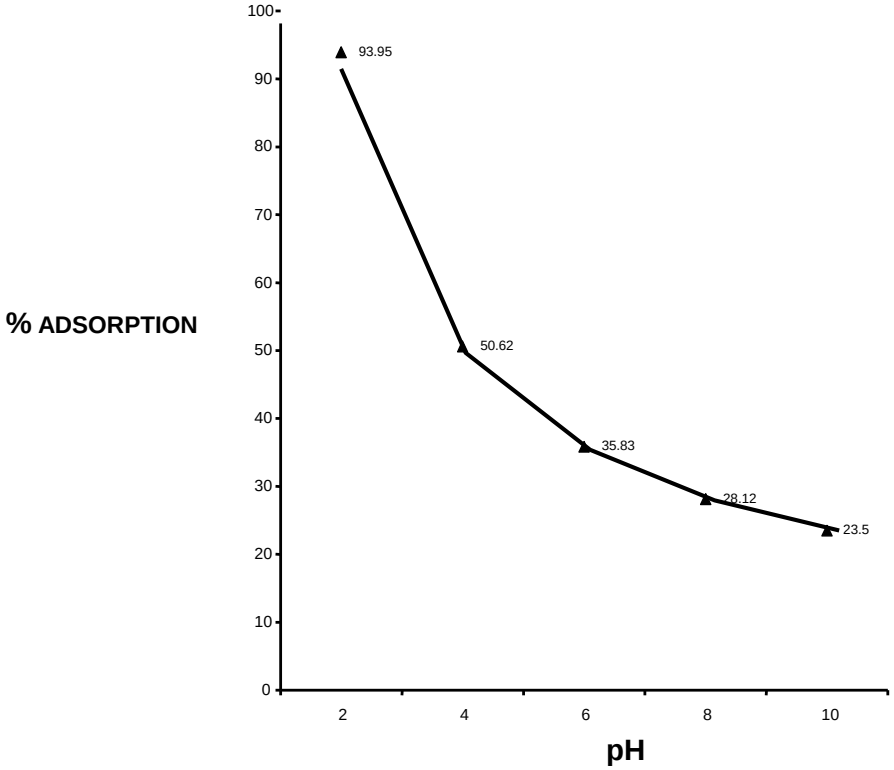



*(Initial pH of 6; Contact time of 80 min; Adsorbent dosage of 0.8 g/L; and Temperature of 30°C.)*
**Fig(5) Effect of contact time on the adsorption of ferrous onto ACD**

**Effect of adsorbent dose , Contact time and pH**

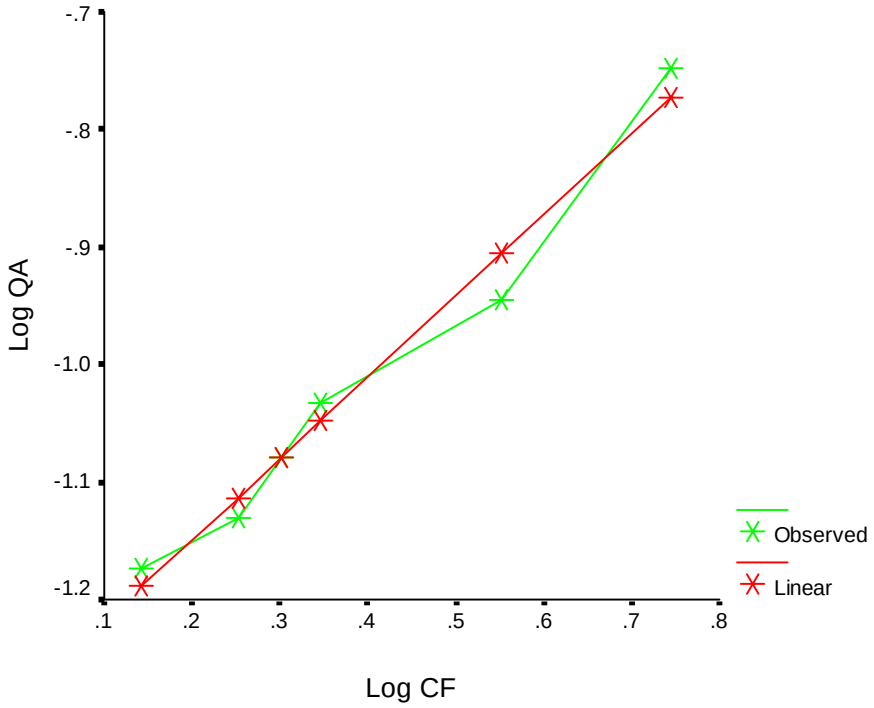
The effect of the adsorbent dose was studied at temperature of (30°C) by varying the sorbent amounts from 0.2 to 1.2 g/L. For all these runs, initial concentration of $Fe^{2+}$ was fixed as 1 mg/L.(Figure 4). The result shows that the adsorption of $Fe^{2+}$ increases rapidly with increase in the amount of Activated carbon prepared from Doum fruit due to greater availability of the surface area at higher concentration of the adsorbent. For sample ACD the significant increase in uptake was observed when the dose was increased from 0.2 to 0.8 g/L. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of

adsorption sites as a result of overcrowding of adsorbent particles [18,19,20], the contact time was in the 80min for the sample (Figure5) . For the pH studies ,the adsorption decreased as the pH increase , the optimum pH was attended at 6 (Figure6) .




***(Initial pH of 6; Contact time of 80 min; Adsorbent dosage of 0.8 g/L; and Temperature of 30°C.)***
**Fig(6) Effect of pH on the adsorption of ferrous onto ACD**

The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log *Ce* vs. log *qe* was employed to generate the intercept value of *K* and the slope of1/ *n*. Good adsorption of metal was record for Activated carbon prepared from Doum fruit




**Fig(7):Freundlich isotherm for the adsorption of $Fe^{2+}$ on to ACD**

**Table (2) Isotherm Models Constants and Correlation Coefficients for Adsorption of Ferrous from Aqueous Solution by ACD .**

| | k | 1/n | $R^2$ |
|---|---|---|---|
| $Fe^{2+}$ | 1.36 | 0.13 | 0.97 |

The Freundlich isotherm model [21] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of nickel adsorbed per unit mass of adsorbent, *qe*, and the concentration of the nickel at equilibrium, *Ce* ([21].

$$q_e = K_f C_e^{1/n}$$

The logarithmic form of the equation becomes,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where *Kf* and *n* are the Freundlich constants, the characteristics of the system.*Kf* and *n* are the indicators of the adsorption capacity and adsorption intensity,respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log *Ce* vs. log *qe* was employed to generate the intercept value of *Kf* and the slope of *n*. From (Fig. 7) the Freundlich constants *Kf* and *n* were found to be 1.36 and 0.13 respectively. The magnitudes of *Kf* and *n* show easy separation of Ferrous l ions from the aqueous solution and indicate favourable adsorption. The intercept *Kf* value is an indication of the adsorption capacity of the adsorbent; the slope 1/*n* indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the correlation coefficient of 0.97.(Table 2)

## CONCLUSION

Preparation of activated carbon from agricultural waste was done successfully.The various properties studied The present research work indicates the applicability of Doum fruit as an effective low cost adsorbent for the removal of ferrous ion from aqueous solution. The adsorption process was highly dependent on solution pH and adsorbent dose, also the results showed goodadsorption capacity and intensity.

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