PREPARATION, CHARACTERIZATION OF DATE STONES, CORNCOBS (YELLOW) ACTIVATED CARBON USING Fecl$_3$ AS ACTIVATING AGENT AND REMOVAL OF TRANSITION METAL IONS

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Abstract : Agriculture waste materials, which impact negatively on environment have been commonly applied over the adsorbent due to low or zero cost materials. Activated carbon (AC) is amorphous form of carbon and this is comparative study on properties of Activated carbon (AC) prepared from Date Stones (DS) and corn cobs (yellow) (CCY) by using ferric chloride as a activating agent. It is easily available waste which is used in removal of Ni^{2+} and Fe^{3+} metals by process of adsorption. The Activated carbon (AC) characterized by determining the apparent density, Acid insoluble matter, water soluble matter, p^H, conductivity, Iodine No. The physical morphology was studied by analyzing Scanning Electron Microscopy, X-ray Diffraction and Fourier Transform Infrared Spectroscopy

Keyword: Activating agent,Adsorption,Date stones, Corn Cobs.

Introduction

As we know that now a day's environment is not peaceful because of increasing pollution. Agricultural waste can be thermally and chemically treated wide range of voluble products such as bio-solids, biofuels considered as energy storage medium. The ecological crisis of environmental pollution has been blamed on different issues, of which pollution due to metals or their species in the environment is the major one. Heavy metal pollution affects flora, fauna and other abiotic components of the ecosystem. As these toxins build up in our bodies, they block the receptor sites for essential minerals, so that minerals such as iron, calcium and magnesium cannot be utilized and absorbed to serve body and enzymes functionalities causing enzyme dysfunction, nutritional deficiencies, hormonal imbalances, neurological disorders, damages brain chemistry [1].

Activated carbon is one of the most versatile adsorbents to be used for removal of heavy metals known as the most effective but purification and separation technique used in industry and useful adsorbents. There is batch experiment and column type laboratory experiment carried. This is due to properties of activated carbons which can provide high adsorption capacity and mechanical properties [2].

A study of the effect of preparation conditions on the yield and quality of activated carbon (AC) produced from dates' stones was made using zinc chloride as an activator [3]. Activated carbons are highly porous and adsorbent materials. They have wide application in domestic, commercial and industries. The chemical activation technique has more advantages over the physical activation technique since the chemical reagents enhance the yield and increase the surface area of the resulted product [4].

Basically, there are two different processes for the preparation of activated carbon, the so called physical or thermal and chemical activation. The first step is carbonization of the raw material. According to Sang et al. (1997), activation can be physical or thermal with the use of air, carbon dioxide or water vapour at high temperature or a chemical process employing activating agents such as phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$) [5]. The adsorption was by chemisorption and the external mass transfer was the rate-determining step involves. The adsorbent are characterized by SEM, TEM, XRD, VSM, surface functionality and zero-point charge. The activated carbon is a crude form of graphite having porous structure and high surface area. For these reason, activated carbon is also well suited as an electrode for supercapacitor [6,7]. The activated carbons produced in powdered form as such in order to make them into tablet forms circular ring of a hydraulic press are used. The adsorbents are mixed with water (just enough to cause homogeneous mixing) and manually compacted into the ring[8] .There are different technologies used for removal of heavy metals from waste water mainly precipitation, ion exchange, membrane processes, evaporation chemical oxidation or reduction, solvent extraction and biological materials.

The heavy metals and minerals in wastewater is one of the most serious problems in India. Due to extensive androgenic activities and disposal of industrial waste materials. The concentration increase to dangerous levels in industrial effluent nickel, chromium, lead, zinc, arsenic, cadmium, selenium, and uranium[9].

Objectives of Present Work

From literature survey we came to know that adsorption experiments are carried out to investigate the removal of heavy metal like Nickel(II),Lead(III) and Chromium(II) from coconut shells, corncobs and date stones by using phosphoric acid and Zinc chloride.

In this research work we are going to perform adsorption experiment to investigate the removal of heavy metal but by using $FeCl_3$ which is yet not used. The significant feature of activated carbon that makes it a unique and particularly economical adsorbent is that it can be produced from waste materials for environmental and ecological reasons. The innocuous disposal of these wastes has become immensely important. The main objective of the work is to removal of heavy metal ions and elemental analysis and also the scanning electron microscopy and Fourier transform infrared spectroscopy and X-ray diffraction analysis is to be carried out characterization of the prepared activated carbon do by using various analyses such as apparent density, acid insoluble matter, water soluble matter, pH value ,conductivity, iodine test etc.. The prepared activated carbon compared with commercially available activated carbon.

Experimental

Materials:

Date stones and Corncobs selected from the local farms, market. Activated carbon is prepare taking 20%, 40% and 60% concentration

Fig - Datestone

Fig - Corncob

Preparation of the activated carbon

The precursor used for the preparation of the activated carbon is the Date stones and Corncobs. These are purchased from local market and seeds are separated. The separated seeds are then washed with distilled water to remove any dirt or impurity present and dried overnight. The swollen or the bad seeds are discarded. The selected batch of seeds was then dried to remove the water in an oven at 110 ^{0}C for 1hr. The seeds selected were put on a petri dish and inserted into a muffle furnance 300 ^{0}C for 1hr.

The carbonised samples are crushed in mortar and pestle to produce the uniform sized crushed particles of tamarind seeds. The crushed were then washed several times to remove other impurity, The washed samples particle is then dried overnight. On the other day the particles were further dried at 110 ^{0}C for 1hr. The carbon produced is then put in the desiccators to cool them to the room temperature. The cooled particles are then stored in the air tight containers.

The another batch then impregnated with the (w/w) of ferric chloride in 1:4 ratio by weight and mix well. The mixture formed is then left for 24 hrs. The mixture is then put in oven at 160^{0}C for hrs. The activated material is kept desicater and cooled to room temperature. The mixture is then washed several times with deionised water until the pH of the washing equilibrates to 6.5-7. The carbon was soaked in 1% sodium carbonate solution for 24 hour. Then it is washed with distilled water to remove excess sodium carbonate and dried at 110 ^{0}C for 1hr. The dried carbon is then cooled in desicater and then stored in air tight container.

Characterization

Properties :

1. Apparent density:

A specific gravity bottle of 25 ml capacity was filled with the adsorbent and packed well by tapping with a rubber stopper. The weight of the adsorbent was determined. The weight (g) divided by the volume (ml) gives the apparent density (g/ml) of the adsorbent.

2. Acid insoluble matter:

The adsorbent (0.5 g) is placed in an evaporating dish, mixed with distilled water to a thin slurry 5 - 10 ml of concentrated HCl is added and digested by warming until sample is nearly dry. The digestion is repeated three times with 5 ml of the acid. Then it is diluted with 100 ml water, filtered using a previously weighed sintered crucible and the weight of the insoluble matter is calculated after drying for a constant weight at 103 °C.

3. Water-soluble matter:

0.5 gm of each adsorbent is added to 50 ml Of distilled water and is shaken thoroughly for about 30 minutes and filtered. The residue i.e. adsorbent is dried, cooled and weighed.

4. pH :

Apparatus and material:

1. pH meter : ELICO LI120 is used for measurement of pH,where temperature is set on 20^{0}C .glass electrode and reference electrode Cl 51 B use.
2. Distilled water
3. Buffer solution at pH 9.00
4.Buffer solution at pH 4.00

Procedure-

Weight out 0.5g of sample in 250ml beaker, add 50 ml of distilled,CO_2 free(boiled out)water, cover with watch glass and boil on the hot plate for 5minute.

Insert the thermometer and set aside for a few movement to allow the bulk of the activated carbon particle to settle. Pour off supernanent as soon as possible and before its cool to 60 ^{0}C.Cool the decanted portion to the room temperature and measure the pH to one decimal place.

scope-

Activated carbon carring inorganic and organic groups on the surface may alter the pH of the liquid to which it added a predictive standard test giving a good approximation of the actual condition.

5. Conductivity:

0.5g of the carbon was weighed and transferred into a 250 ml beaker and 50 ml distilled water was added and stirred for 1hour. Samples were allowed to stabilize. This solution is used to measure the electrical conductivity (EC)measurements of the ACs and results read .

6. Iodine No.

Iodine Number is defined a the number of milligrams of iodine absorbed by one gram of activated carbon powder. Iodine Number is a measure of micro-pore content of activated carbon. A higher iodine number signifies higher micro-porosity.

Scope-The determination of the iodine number is a simple and quick test. giving an indication of internal surface area of activated carbon.

Tables

Date Stones-

Unactivated carbon	Apparent density g/ml	Acid insoluble matter gm	Water soluble matter gm	pH	Conductivity	Iodine test
Date stones	10.22	0.07	0.43	2.82	0.37×10^{-3}mhos	846.966

Table 1.-charactrization of unactivated carbon of Date stones

Chacterization	20%	40%	60%
Apparent density g/ml	8.35	8.55	9.62
Acid insoluble matter gm	0.11	0.10	0.09
Water soluble matter gm	0.42	0.37	0.39
pH	2.64	2.51	2.30
Conductivity	1.02×10^{-3}mho	2.15×10^{-3}mho	2.44×10^{-3}mho
Iodine test mg/g	720.9	799.47	824.022

Table 2 .-charactrization of activated carbon of Date stones (Activated)

Corncobs-

Unactivated carbon	Apparent density g/ml	Acid insoluble matter Gm	Water soluble matter gm	pH	Conductivity	Iodine test mg/g
corncobs	5.32	0.12	0.44	2.71	0.36×10^{-3}mhos	871.58

Table 3.-charactrization of unactivated carbon of corncobs

Characterization	20%	40%	60%
Apparent density g/ml	6.31	5.38	7.29
Acid insoluble matter Gm	0.08	0.10	0.09
Water soluble matter Gm	0.30	0.32	0.35
pH	2.62	2.25	2.37
Conductivity	1.31x10 $^{-3}$mhos	2.24x10 $^{-3}$mhos	2.44x10 $^{-3}$mhos
Iodine test mg/g	747.16	764.34	788.89

Table 4. charactrization of activated carbon of corncobs (Activated)

Date Stones

ppm	20%	40%	60%	Unactivated
1000	14.16	13.36	15.84	15.84
800	8.72	12.4	14.00	10.16
600	7.28	11.28	8.24	8.64
400	5.12	8.64	8.00	8.00
200	4.48	5.28	6.48	7.68

Table 5-% Removal Of Ions- (Fe^{3+})

ppm	20%	40%	60%	Unactivated
1000	13.76	14.00	14.48	14.8
800	13.6	13.28	14.00	14.00
600	12.88	12.88	13.76	13.84
400	12.72	12.80	13.04	13.12
200	7.28	12.72	12.88	12.96

Table 6-% Removal Of Ions- (Ni^{2+})

Corncobs

ppm	20%	40%	60%	Unactivated
1000	13.36	14.88	15.28	10.56
800	11.84	10.56	12.96	8.56
600	7.76	6.88	12.32	5.52

400	6.72	5.76	7.68	4.08
200	6.56	4.88	7.52	2.56

Table 7-% Removal Of Ions- (Fe^{2+})

ppm	20%	40%	60%	Unactivated
1000	14.08	15.28	13.76	14.56
800	8.64	14.72	12.64	14.08
600	5.76	14.56	11.36	13.68
400	4.88	14.32	10.40	13.12
200	4.32	12.08	9.12	12.96

Table 8-% Removal Of Ions- (Ni^{2+})

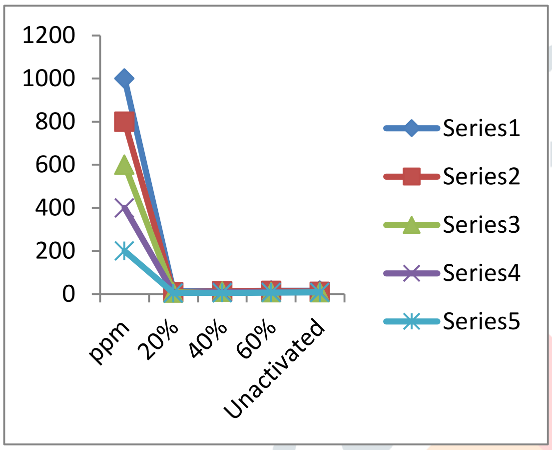

Fig 1-% removal of (Fe^{3+}) from Date Stones

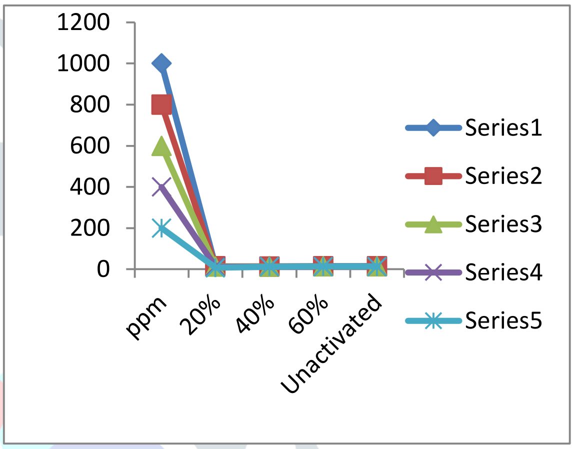

Fig 2-% removal of (Ni^{2+}) from Date Stones

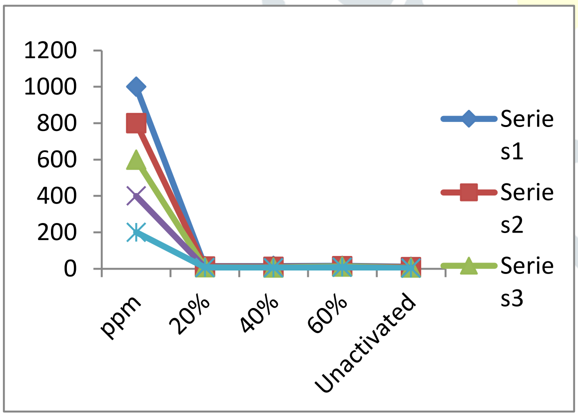

Fig 3-% removal of (Fe^{3+}) from corncobs

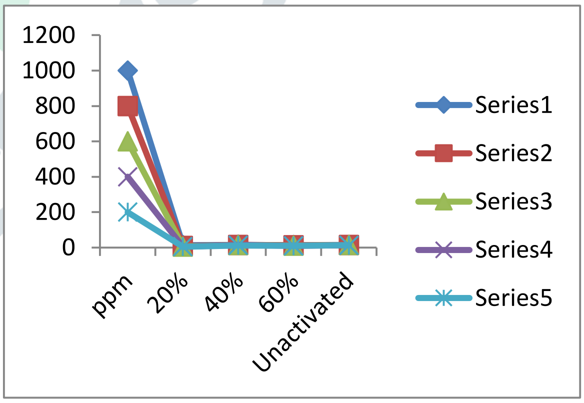

Fig 4-% removal of (Ni^{2+})

Result and discussion

1.1 SEM analysis-The morphology of activated carbon analysed by using ZEISS machine.The activated carbon is known as a good adsorbent because of its high degree of porosity and an extensive surface area.

Date stones

Fig.5-6 shows the surface morphology of raw activated Date Stones and unactivated DateStones no or minimal pores on the surface. In corncobs activated and unactivated fig.7-8. Shows lot of grooves,cracks and crevices in surface matrix.

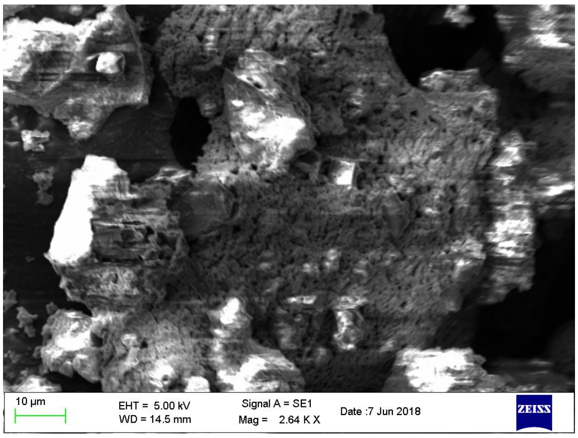

Fig.5- SEM of Date Stones activated 60%

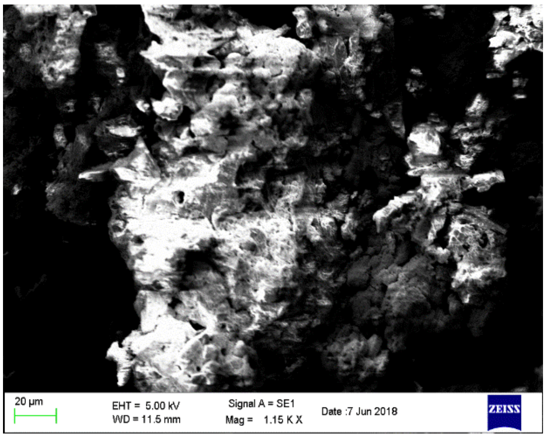

Fig 6- SEM of Unctivated Date Stones

Corncobs

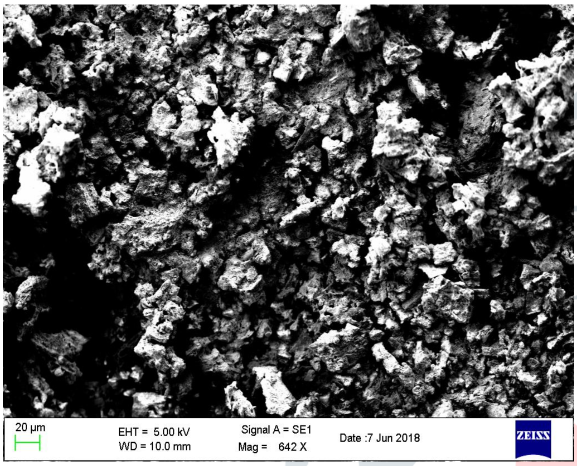

Fig 7- SEM of Corncobs activated 60%

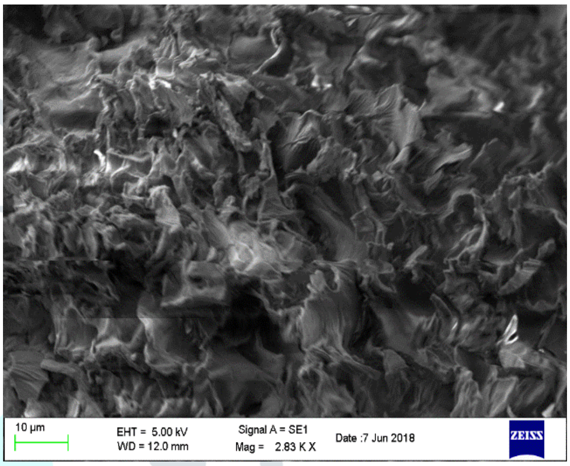

Fig 8- SEM of Unctivated Corncobs

1.2 FT-IR analysis-

Details of functional groups present on surface of carbon materials are obtained from FT-IR studies as shown in fig 9-10 .The main hydrophilic group detectd in FTIR specta are O-H and N-H at 3424,3734 cm-^{1}. Absorption bands characteristics of CH_3 or CH_2 are observed at 2928 cm^{-1} . Similarly unactivated Date stoned existence of aliphatic species on carbon at 1546,1462 cm^{-1}. In case of corncobs activated 60% and unactivated (fig 11-12)O-H stretching aty 35445,3418 cm^{-1}. A carbonyl group C=O stretching is at 1604 and 1693 cm^{-1}.

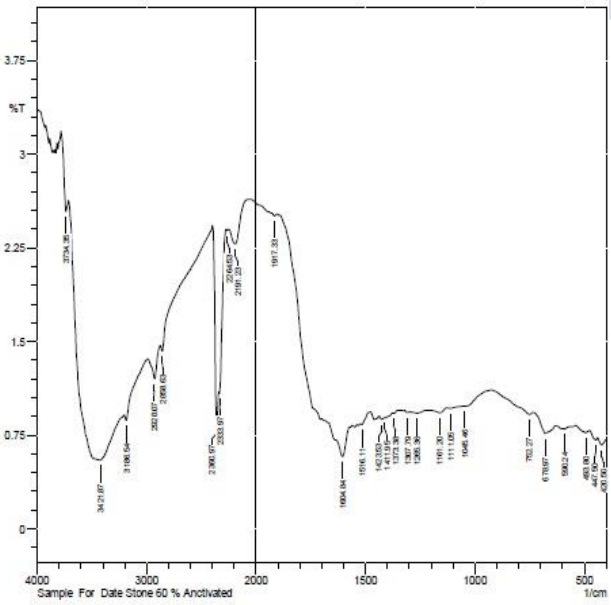

Fig.9- FTIR of Date Stones activated 60%

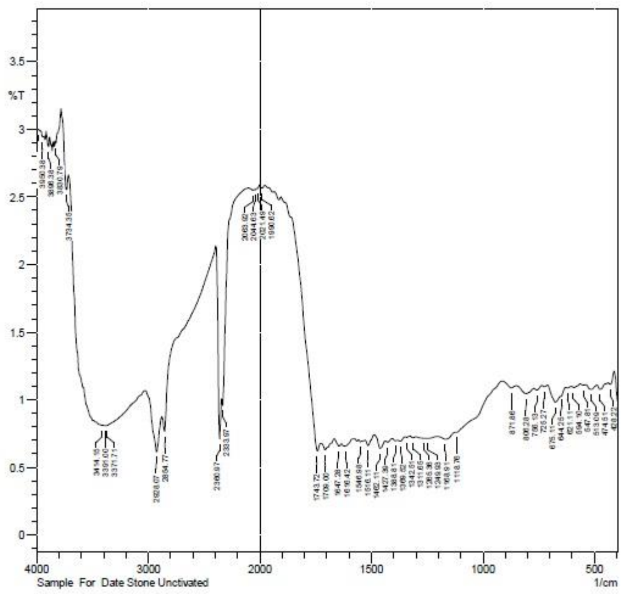

Fig 10.-FTIR of Unctivated Date Stones

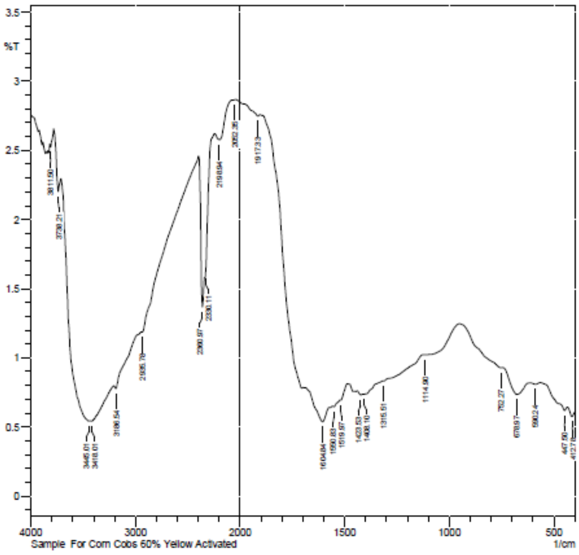

Fig.11- FTIR of Corn Cobs activated 60%

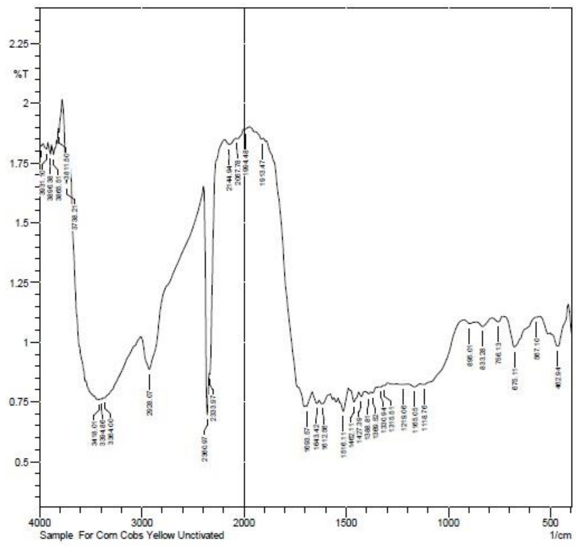

Fig 12.-FTIR of Unctivated Corn Cobs

1.3 -XRD

Date Stones

Following figures : Illistrates the XRD pattern of activated carbon prepared from coconut shell by activating agens $FeCl_3$ The activated carbon of coconut Shells 60% exhibited peaks around $2^{\theta}= 25^0,30^0$ and unactivated

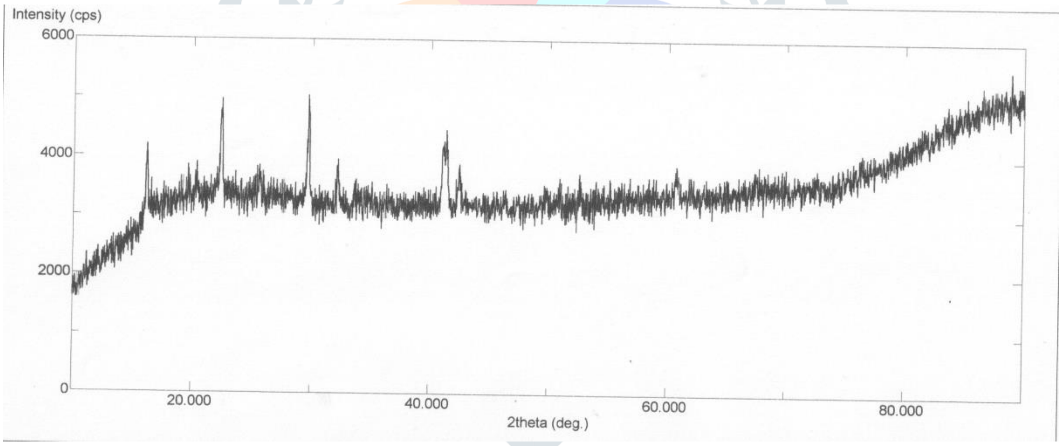

Fig13- XRD of Date Stones activated 60%

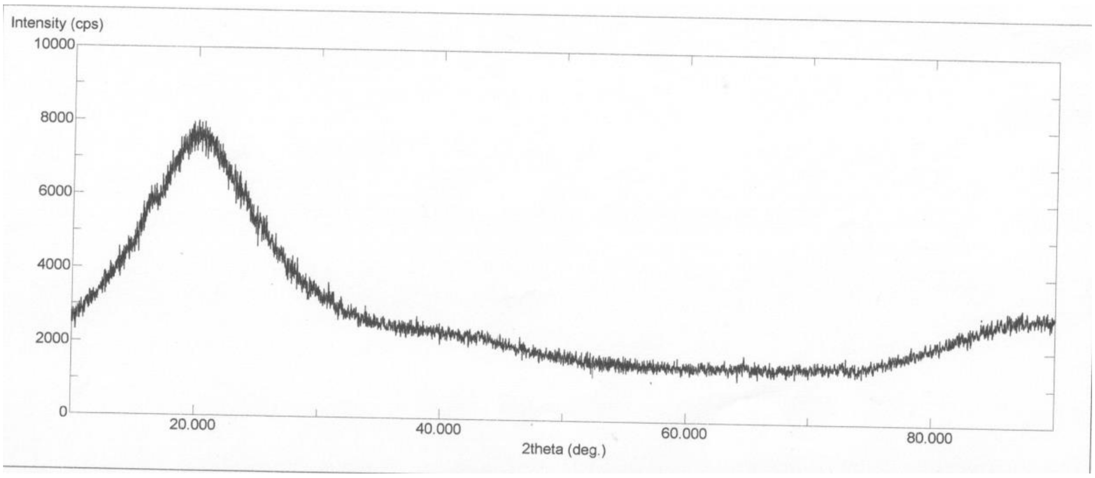

Fig14- XRD of Date Stones unactivated 60%

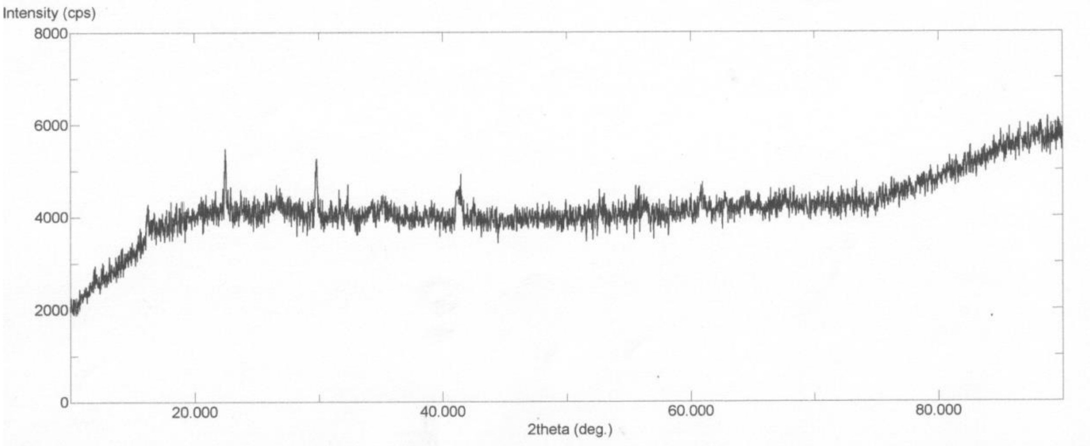

Fig15- XRD of activated Corncobs 60%

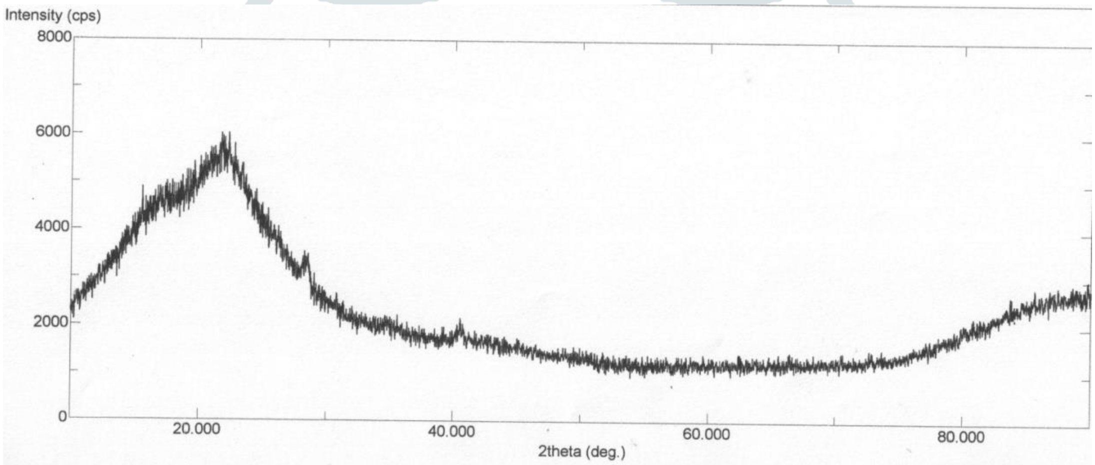

Fig16- XRD of unactivated Corncobs

Conclusion-

The experimental results show much lesser values of bulk density, nutrients and heavy metals than those reported in the literature. The DS,CCY samples can be used in removing these toxic metals . The present study reveal that the variation of physical and chemical properties was found to be depending on the sample collection site.

Based on the results, it is clear that the Iron and Nickel-removal values achieved activated carbon were higher than those unactivated . The main advantages of this removal procedure include (i) simplicity, (ii) cost effectiveness, (iii) rapidity, and (iv) a higher removal efficiency of toxic iron and nickel ions. In this study, activated carbon was successfully synthesized from a coconut shells, Date stones, corncobs with the Ferric chloride activation process. This activated carbon was characterized by XRD, and FTIR. A comprehensive study was performed on its adsorption efficiency for the removal of transition element. XRD analysis proved that the sample had a perfect crystallite structure.

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