Elemental Analysis of Activated Carbon by EDS Spectrophotometry and X-Rays Diffraction

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Summary: Low cost material (*Corncobs-CC, Paulownia tomentosa-PT, Populus caspica-PC* and *Animal bones-ABC)* were utilized for the preparation of activated carbon. Carbon samples were activated chemically and by thermal means (400-1000 °C). The samples were characterized by surface area, EDS analysis showed high carbon contents in the samples activated at high temperature as compared to raw and 400 °C activated samples while the content of oxygen was found to decrease with the increase in activation temperature. Other elements like, chlorine, silica, iron, magnesium etc were found in trace amounts. The XRD analysis using ORIGIN-50 computer software showed that carbon, hydrogen, nitrogen, oxygen. boron, chromium, fluorine and nitrogen were present in the carbon samples.

Introduction

Activated carbon prepared from low cost precursors with high carbon content is the most significant option to clean environmental pollution (gases and liquid impurities). Agriculture by-product (corncobs) and fast growing trees are commonly used as a starting material for preparing activated carbon [1]. Basically, activated carbon can be prepared by physical and chemical activation methods and occasionally by combination of both types of methods. Physical activation consists of reaction of a carbonized product at temperatures in the 350-550 °C (air) and between 800 and 1100 °C (steam and carbon dioxide) [2]. Chemical activation is the process where carbonization and activation of a precursor material occur simultaneously in the presence of dehydrating agents (*i.e.* H_3PO_4, $ZnCl_2$, H_2SO_4, KOH), which influence the course of the pyrolysis, between 400 and 800 °C [3]. Chemical activation using KOH has been reported by many researchers. Several materials [4-10] have been used in the preparation of activated carbons by KOH activation. Also, it has been reported that activated carbons with a very large surface area and great micropore volume can be prepared by KOH activation of pre-carbonized carbonaceous materials such as pistachio-nut shells [11, 12], coffee grounds and macadamia nut shells [13] and rice straws [14]. The KOH-activation method has been regarded as a mixed process of physical and chemical processes [15, 16]. *Corncob*, which is an agricultural residue and are generated abundantly, *Paulownia tomentosa (PT) and Populus caspica (PC)* are the fast growing trees having low economic values. Activated carbon is prepared in the present study by chemical and thermal activation with KOH. The influence of carbonization temperature on carbon contents, organic and in organic phases has explored in this study.

Results and Discussion

The surface area of the carbon samples were determined by BET and DR methods and are given in Table-1. The BET surface area ($m^2\ g^{-1}$) is one of the most widely known methods associated with carbon. The BET equation is given by [20].

$$\frac{1}{W\left(\frac{P_\circ}{p}-1\right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C}\left(\frac{P}{P_\circ}\right) \qquad (1)$$

Where W is the weight of gas adsorbed at a relative pressure, P/P_o and W_m is the weight of adsorbate constituting a monolayer coverage. The term C is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent/ adsorbate interactions. The standard multipoint BET

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Table-1: Surface area and pore size distribution of carbon samples.

Carbon sample	Raw/ Degassing	Surface area (m^2/g) Methods		Pore size distribution BJH method	DR method	
		BET	DR	Pore volume (cc/g)	Micropore volume (cc/g)	Average Pore width (Å)
Paulownia tomentosa (PT)	Raw	79.8	85.1	0.05	0.03	13.3
	400 °C	165.8	241.4	0.05	0.09	52.3
	800 °C	219.9	311.2	0.1	0.11	65.3
Populus caspica (PC)	Raw	37.8	41.8	0.01	0.01	10.2
	400 °C	360.8	528.7	0.04	0.19	50.1
	800 °C	398.3	644.6	0.13	0.23	52.6
Animal Bones	600 °C	38.8	131.3	0.02	0.05	42.2
	800 °C	140.2	276.1	0.04	0.10	82.0
	1000 °C	280.0	398.3	0.05	0.17	90.3

method requires a minimum of three points in the appropriate relative pressure range. The weight of a monolayer of adsorbate W_m can then be obtained from the slope and intercept of the BET plot. From equation (1):

$$S = \frac{C-1}{W_m C} \qquad (1a)$$

$$i = \frac{1}{W_m C} \qquad (1b)$$

Thus, the weight of a monolayer (W_m) can be obtained by combining equations (1a) and (1b).

$$W_m = \frac{1}{S+i} \qquad (1c)$$

The total surface area (S_t) of the sample can be expressed as:

$$S_t = \frac{W_m N A_{CS}}{M} \qquad (1d)$$

Where N is Avogadro's number (6.023×10^{23}) and M is the molecular weight of the adsorbate and C is cross sectional area of nitrogen gas (16.2 $Å^2$/mol). The nitrogen adsorption isotherms for all carbon samples were determined and it was found that all curves exhibit type I isotherm which are characterized by unimolecular adsorption and applies to microporous adsorbent with small pore sizes [20].

Surface area (S_{BET}) [20] of the all carbon samples were obtained by plotting $1/W[(P_o/P)-1]$ against P/P_o of the N_2 adsorption and the values are given in Table-1. The surface area of other carbon activated at 800 °C are, PT carbon (219 $m^2.\ g^{-1}$), PC (398.29 $m^2.\ g^{-1}$), and animal bone charcoal (140.23 $m^2.\ g^{-1}$). The surface area (S_{BET}) was found to increase with the increase in activation temperature (Table-1). During activation the blind pores opened, which in turn increase the porosity and surface area of the samples. A high non-polar surface at high temperature is another reason for high surface area is due to the fact that polar functional groups situated at the pore opening emit and leaving the surface with wide pore volume [20].

Porosity can also be predicted from the N_2 adsorption isotherms. Type-I isotherms were obtained for all carbon samples (Table-1). Such types of isotherms are concave to the P/P_o axis and N_2 uptake is governed by accessible micropores volume rather than the internal surface area. Such behavior was observed for all the samples indicating the porous structures. The result in Table-1 shows that activation temperature has a significant effect on pore volume and increases with the increase in activation temperature. The micropore volume ($cm^3.g^{-1}$) of all 800 °C activated carbon samples were found as 0.23 for PC > 0.11 for PT > 0.100 for ABC. The increase in pore volume with rise in activation temperature is due to by removal of the tar as volatile matter that was trapped in the porous structure.

The surface area of all carbon samples was determined by applying the DR equation by plotting volume adsorbed ($cm^3.\ g^{-1}$) *vs.* $\log^2 (P/P_o)$ and the results are given in Table-1. The surface area ($m^2\ g^{-1}$) of 800 °C activated carbon samples were compared and found as, $PC_{644.68} > BC_{398.35}$. The micropore volume was evaluated by applying the DR equation and was estimated from the intercept of straight lines. The results are given in Table-1. The data shows that when the activation temperature increases the micropore volume increases. At 800 °C activation

temperature the PT carbon samples was found to be a high micropore volume (0.230 cm^2 g^{-1}). The micropore volume (cm^2 g^{-1}) of other samples were found as, $PT_{0.11} > BC_{0.1}$.

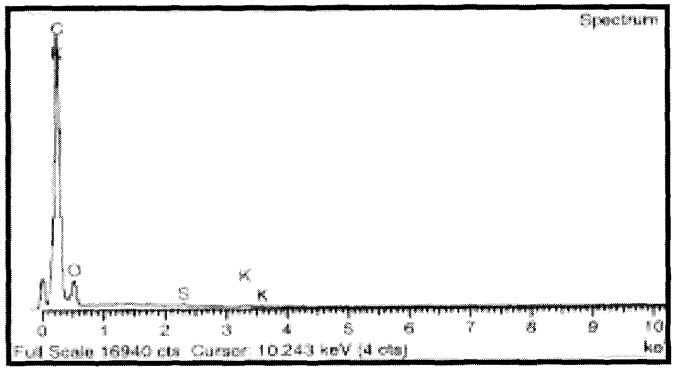
The energy dispersive spectral studies give a semi-quantitative analysis of the carbon samples. The results of EDS analysis (both % weight and % atomic) for PT, PC, CC, carbon samples are given in Table 2 and Fig. 1-4, which shows that high carbon contents (% atomic) were found in 800 °C activated PT sample (92.59). Rest of the samples show the carbon contents (% atomic) as 88.30 (CC) and 85.89 (PC), respectively. The concentrations of oxygen in all the samples were found to be decreasing with the increase in activation temperature. Some other elements were present in the same samples in trace quantities [17].

In the bones charcoal activated at 600 °C, 800 °C and 1000 °C both organic and inorganic composition is evident in Fig. 4. The samples activated at different temperatures as, carbon: 25.29 % (600 °C), 22.94 % (800 °C), 43.85 % (1000 °C); oxygen: 53.09 % (600 °C), 54.04 % (800 °C), 34.85 % (1000 °C); calcium: 13.08 % (600 °C), 14.16 % (800 °C), 10.890 % (1000 °C); phosphorus: 7.610 % (600 °C), 7.740 % (800 °C), 6.3700 % (1000 °C), respectively. Other elements like magnesium, sodium, aluminum and chlorine were found in trace quantities. Bone is composed of about 70 % inorganic substance called hydroxyapetite [$Ca_{10}H_{12}(PO_4)_6$] that has no carbon atom. The organic phase consisting of about 30 % of bone is collagen with a tiny fraction of other compounds like chondroitin sulfate, Keratin sulfate and phospholipids. The results confirm that the contents of phosphorus and oxygen in the samples decrease with the increase in the activation temperature, and that these may have evolved as volatile substances during the carbonization [18].

XRD spectra of the raw and activated carbon samples are given in Fig. 5-8. The d values of the samples were matched with the d values of standard spectra in the ORIGIN 50 software of the spectrophotometer. The XRD profiles for Raw PT carbon (Fig. 5a) show distinct absorption bands at d

Table-2: EDS analysis of carbon samples.

Sample/ Degassed	Elements	*Paulownia tomentosa (PT)* Weight (%)	Atomic (%)	*Populus caspica (PC)* Weight (%)	Atomic (%)	*Corncobs (CC)* Weight (%)	Atomic (%)
Raw	C	73.5	78.8	74.3	79.8	74.05	80.1
	O	26.0	21.0	24.7	19.9	23.25	18.8
	S	0.17	0.07	xxxx	xxxx	xxxx	Xxxx
	K	0.24	0.08	0.630	0.21	1.13	0.38
	Ca	xxxx	xxxx	0.290	0.09	0.24	0.08
	Si	xxxx	xxxx	xxxx	xxxx	0.96	0.44
	Cl	xxxx	xxxx	xxxx	xxxx	0.37	0.14
400 °C	C	79.0	83. 8	80.5	85.4	78.3	84.7
	O	20.0	15.9	17.6	14.0	16.3	13.2
	K	0.89	0.29	0.14	0.05	2.65	0.88
	Cl	xxxx	xxxx	0.14	0.57	0.90	0.33
	Si	xxxx	xxxx	xxxx	xxxx	1.04	0.48
	Fe	xxxx	xxxx	xxxx	xxxx	0.29	0.07
	Mg	xxxx	xxxx	xxxx	xxxx	0.17	0.09
800 °C	C	89.4	92.6	80.7	85.9	81.8	88.3
	O	8.84	6.87	16.4	13.2	11.3	9.14
	Cl	0.17	0.06	0.21	0.08	1.15	0.42
	K	1.53	0.49	2.03	0.66	3.17	1.05
	S	xxxx	xxxx	0.16	0.06	xxxx	xxxx
	Ca	xxxx	xxxx	0.21	0.07	xxxx	xxxx
	Mg	xxxx	xxxx	0.14	0.08	0.250	0.13
	Fe	xxxx	xxxx	xxxx	xxxx	0.38	0.09
	P	xxxx	xxxx	xxxx	xxxx	0.22	0.09
	Si	xxxx	xxxx	xxxx	xxxx	1.31	0.61
	C	15.7	25.3	13.95	22.94	22.9	34.85
	O	43.8	53.1	43.75	54.04	41.71	47.50
	Mg	0.45	0.35	xxxxx	xxxxx	0.52	0.39
	Na	0.68	0.57	0.850	0.740	xxxxx	xxxxx
	P	12.2	7.61	12.14	7.740	10.8	6.37
	Ca	27.1	13.1	28.73	14.16	23.9	10.9
	Cl	xxxx	xxxx	0.28	0.150	xxxxx	xxxxx
	Al	xxxx	xxxx	0.3	0.220	xxxxx	xxxxx



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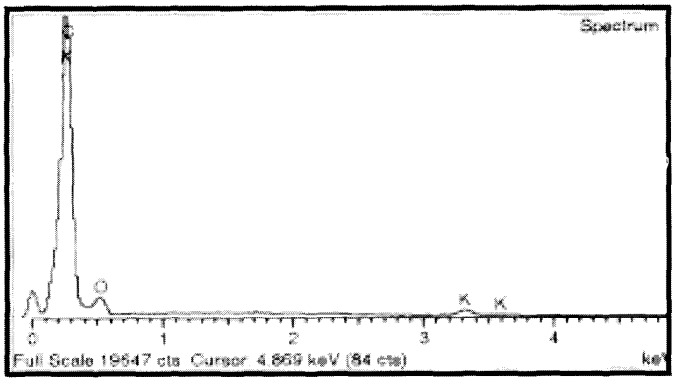

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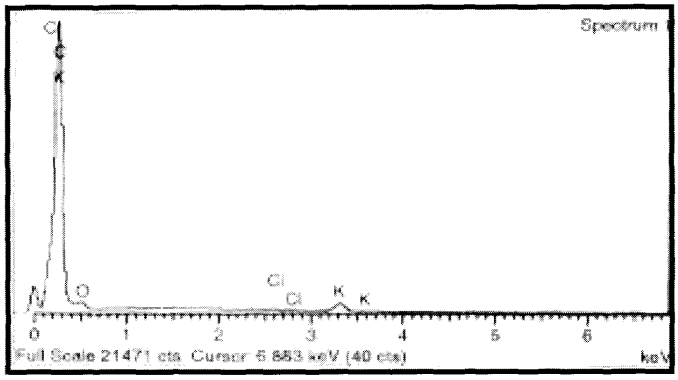
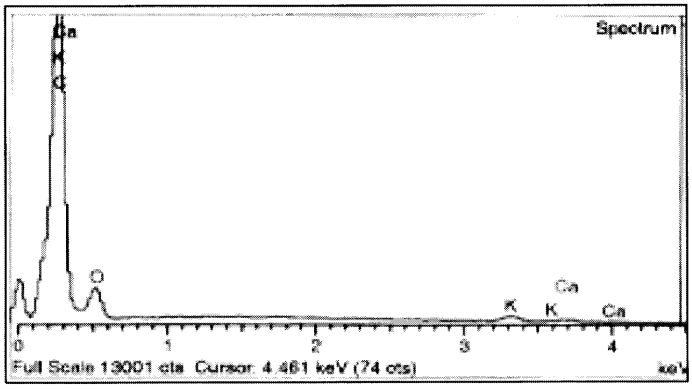


c.

Fig. 1 EDS spectra of *Paulownia tomentosa* (PT) carbon samples. **(a)** Raw and activated; **(b)** 400 °C **(c)** 800 °C.



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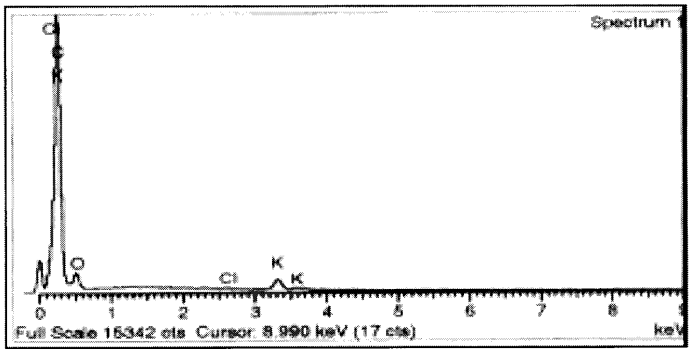

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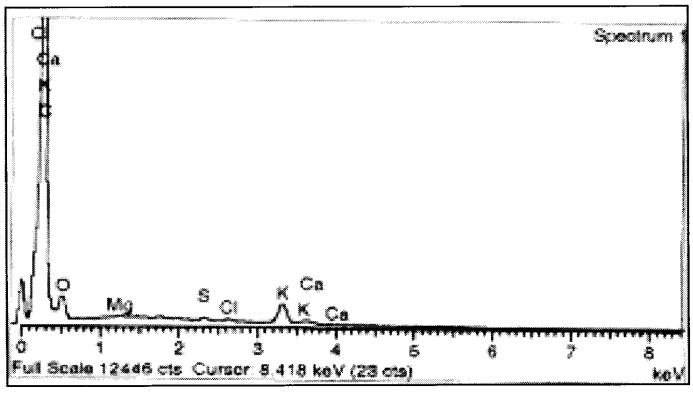

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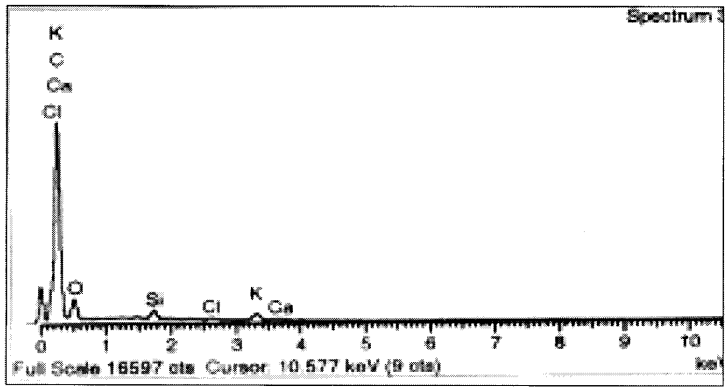
Fig. 2: EDS spectra of *Populus caspica* (PC) carbon samples. **(a)** Raw and activated; **(b)** 400 °C (c) 800 °C.



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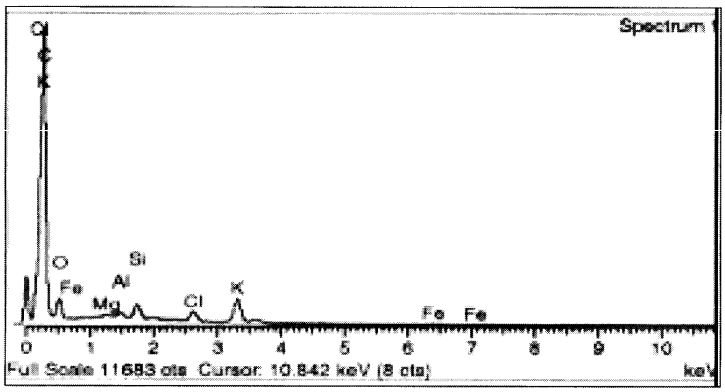

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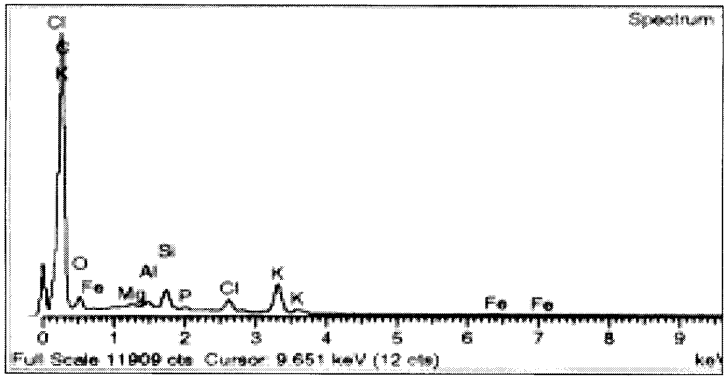

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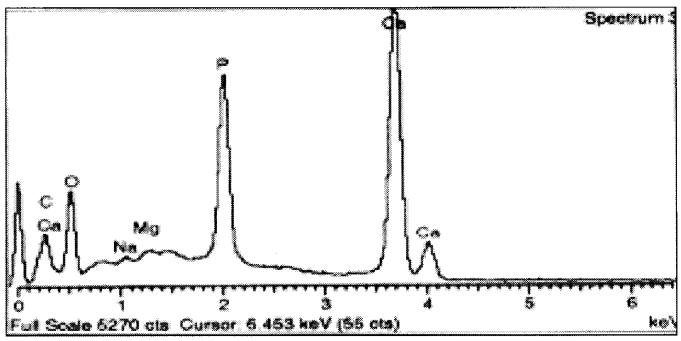
Fig. 3: EDS spectra of *Corncobs* (CC) carbon samples. **(a)** Raw and activated; **(b)** 400 °C **(c)** 800 °C.



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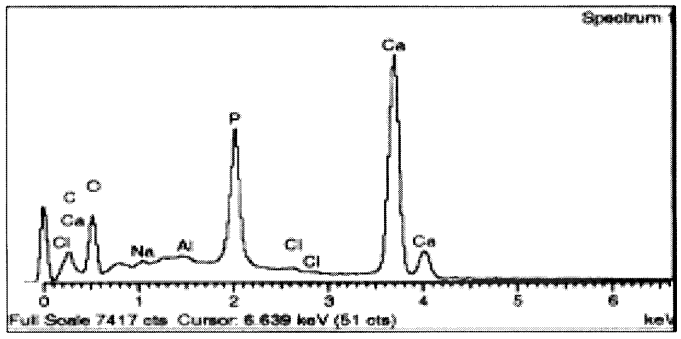

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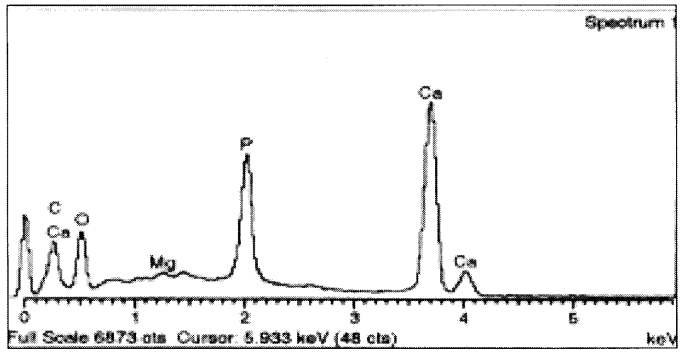

c.

Fig. 4: EDS spectra of *animal bones charcoal* (ABC) samples activated at (**a**) 600 °C (**b**) 800 °C (**c**) 1000 °C.

values of 11.0, 7.49, 6.91, 6.36, 5.44 (2θ) etc. These d values match with the phase of β-chromium, 1.10 phenanthroline chloride boron fluorides ($C_{24}H_{16}BCl_2CrF_4N_4$), which corresponds to carbon, hydrogen, boron, chromium, fluorine and nitrogen, present in the sample. The d values of 400 °C activated sample (Fig. 5b) are 7.8, 7.13, 6.75, 5.21 and 5.05 (2θ) which match the strychnine nitrate ($C_{21}H_{22}N_{202}.HNO_3$) phase and is indicative of the occurrence of carbon, hydrogen, nitrogen and

oxygen. Fig. 5c (800 °C activated) depict calcium tartrate hydrate ($C_4H_4CaO_6.4H_2O$) like phase having carbon, hydrogen, calcium and oxygen.

The X-ray diffraction patterns of PC carbon (Fig. 6) have a peak at $2\theta \approx 22^{\circ}$ showing the disordered graphitic 002 planes [19]. All the carbon samples (Raw, 400 °C and 800 °C activated) match the phase of 2-methyl-2-(4-isopropoxyphenyl} propane-dioic acid ($C_{13}H_{16}O_5$), corresponding to elements like carbon, hydrogen and oxygen.

Fig. 7 a-c shows the XRD profile of CC carbon obtained over the angular range of 8-30° (2θ). The d values were found to be matching the phases of trans- dichlorobispyridine platinum ($C_{10}H_{10}C_{12}N_2Pt$), potassium oxide (K_2O_2) and chlorine (Cl_2). It indicates that the surface of all sample *i.e.* Raw and activated at 400 °C and 800 °C have the elements of carbon, hydrogen, nitrogen, platinum, oxygen, potassium and chlorine.

The X-ray diffraction patterns of bones charcoal obtained at 2θ of 20 - 44° are given in the (Fig. 8 a-c) showing distinct peaks. The peaks for 600 °C degassed charcoal are matching to the phase of calcium phosphate ($Ca_x+2P_{2x}O_6+2$) [file number 44-0752], magnesium oxide (MgO_4) [File No. 27-0759] and sodium [File No. 01-0832]. The 800 °C and 1000 °C degassed charcoal indicate the existence of several elements when spectral peaks were matched with the standard spectra of computer software ORIGIN-50. The elements in the phases are of calcium, magnesium, sodium, hydrogen, phosphorus, carbon oxide, chloride, fluoride $(CaMgNaH_3)_5(PC)_3O_{12}(OH.ClF)$ [File No.12-0529]; sodium, calcium, hydrogen, carbonate, phosphate, hydrate Ca_8H_2 $(PO4)_6$. H_2O-$NaHCO_3$-H_2O [File No. 47-0261] and sodium, calcium, hydrogen, carbonate, phosphate, hydrate Ca_8H_2 $(PO_4)_6$. H_2O-$NaHCO_3$-H_2O [File No. 47-0262].

Experimental

Preparation of Carbon

Agricultural waste material, wood of fast growing trees and *Animal bones* were collected and heated continuously for 8 hours on a flame burner in an iron container with an outlet for the emission of volatile matter. Carbon obtained was cooled in the container and ground with the help of pestle and mortar and screened with US standards mesh 150-180 μ m. It was then treated with 0.5 M aqueous solution of KOH for 24 hours with occasional stirring. The mixture was then filtered and washed with double distilled water for the complete removal of basicity. The carbon was then leached with 0.2N solution of HNO_3 : HCl (1:1) and allowed to stand for 24 hours at room temperature with regular mixing. It was then filtered and washed with double distilled water until free from Cl^- and NO_3^- ions. The carbon thus obtained was then air-dried in an oven at 105 ± 2°C. This treated carbon was then extracted with n-hexane for two hours in a soxhlet extractor and allowed to dry for 8 hours in a vacuum oven. The sample was then degassed by placing in silica (SiO_2) tubes and heated at 400 and 800 °C in a tube furnace (FS. 215 Gallenkamp England) with a vacuum facility. The samples thus obtained were allowed to cool and stored under nitrogen atmosphere.

Surface Area

BET-N_2 adsorption experiments were carried out manometrically at -196 °C using Quantachrome NOVA 2200 surface area and pore size analyzer. Surface area was obtained by applying the standard BET equation to the adsorption data in the relative pressure (P/P_o) range: 0.05 - 0.85. The values of 0.81 g cm^{-3} and 16.2 × 10^{-20} m^2 were used for the density of liquid nitrogen and the molecular area of adsorbate nitrogen at -196 °C, respectively. The pore size distribution was determined by DR method using the NovaWin2 data analysis software [19].

Energy Dispersive Spectrum (EDS)

Energy Dispersive Spectrum of the samples were obtained by mounting the sample on aluminum discs (1 cm × 0.25 cm) and by using scanning electron microscope (SEM-Model-JSM-5910, Japan JEOL) with energy dispersive spectrum (EDS -INCA 200 Oxford Instruments) for elemental analysis.

X-rays Diffraction (XRD)

X-rays diffractometer (Rigaku) was used to record X-rays intensities scattered from the examined carbon samples. Cu K_α radiation (35 KV, 20 mA) was used as an X-ray source. Samples were packed

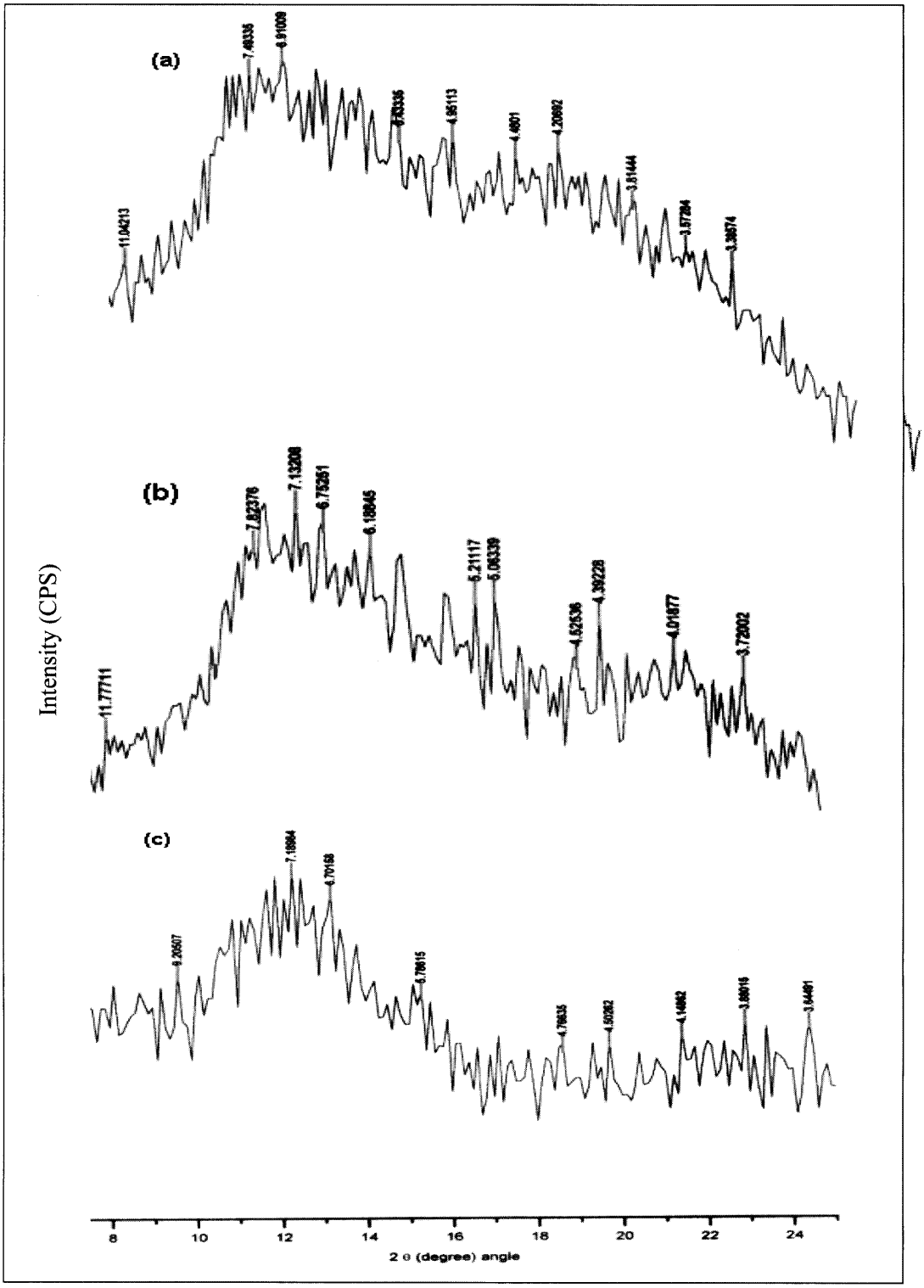

Fig. 5: XRD spectra of *Paulownia tomentosa* (PT) carbon samples.
(a) Raw and activated **(b)** 400 °C **(c)** 800 °C.

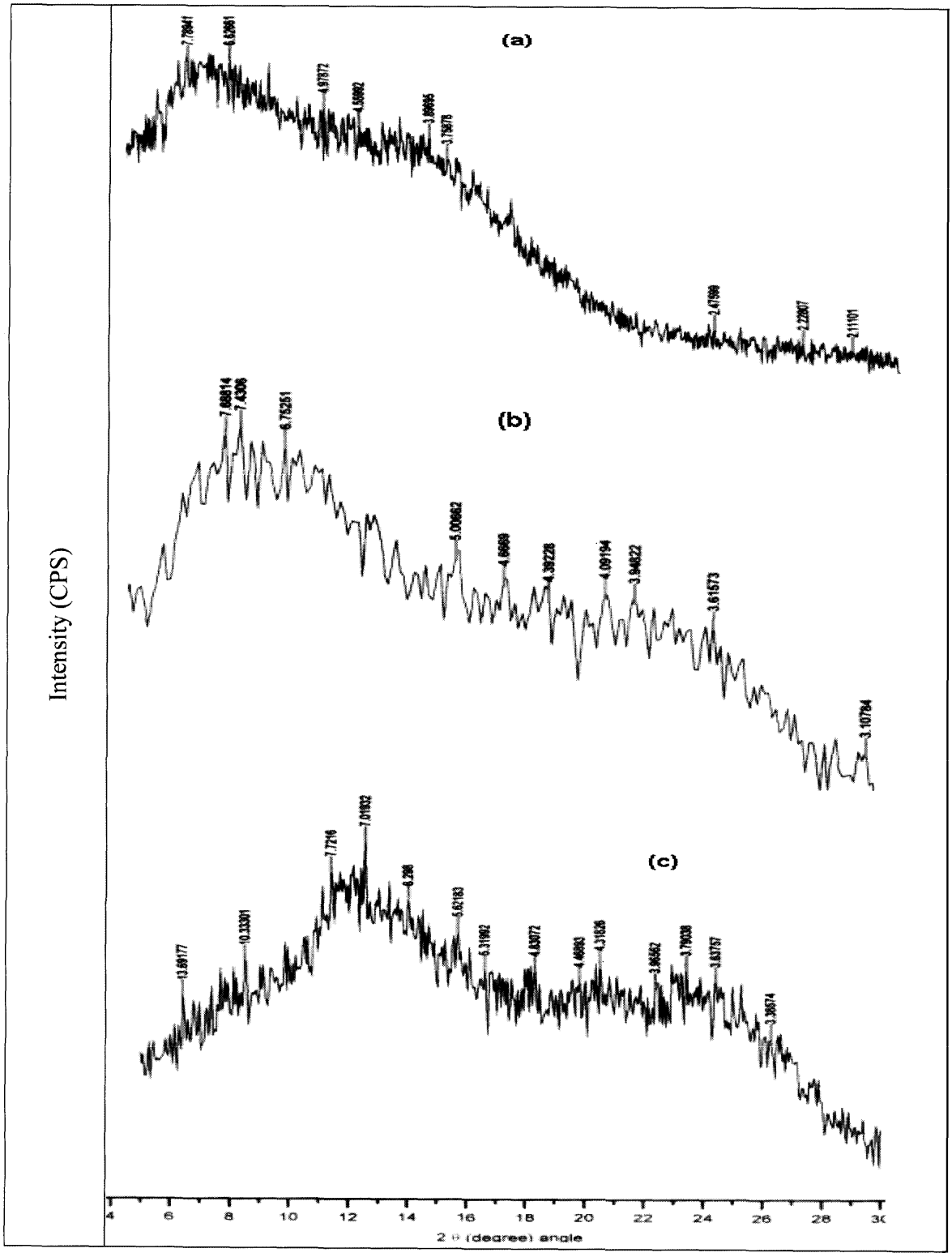

Fig. 6: XRD spectra of *Populus caspica* (PC) carbon samples.
(a) Raw and activated; **(b)** 400 °C **(c)** 800 °C.

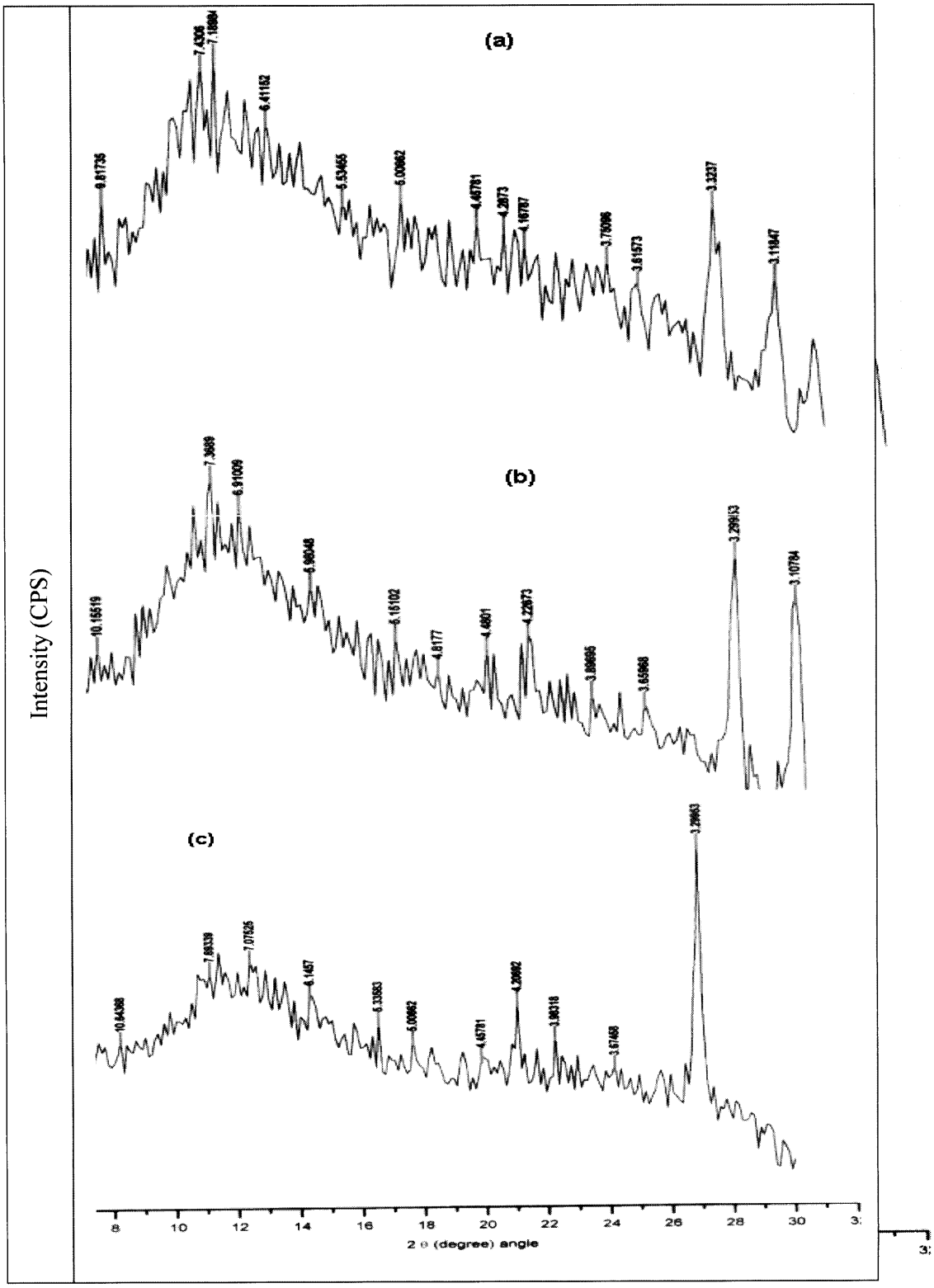

Fig. 7: XRD spectra of *Corncobs* (CC) carbon samples.
(a) Raw and activated; **(b)** 400 °C **(c)** 800 °C.

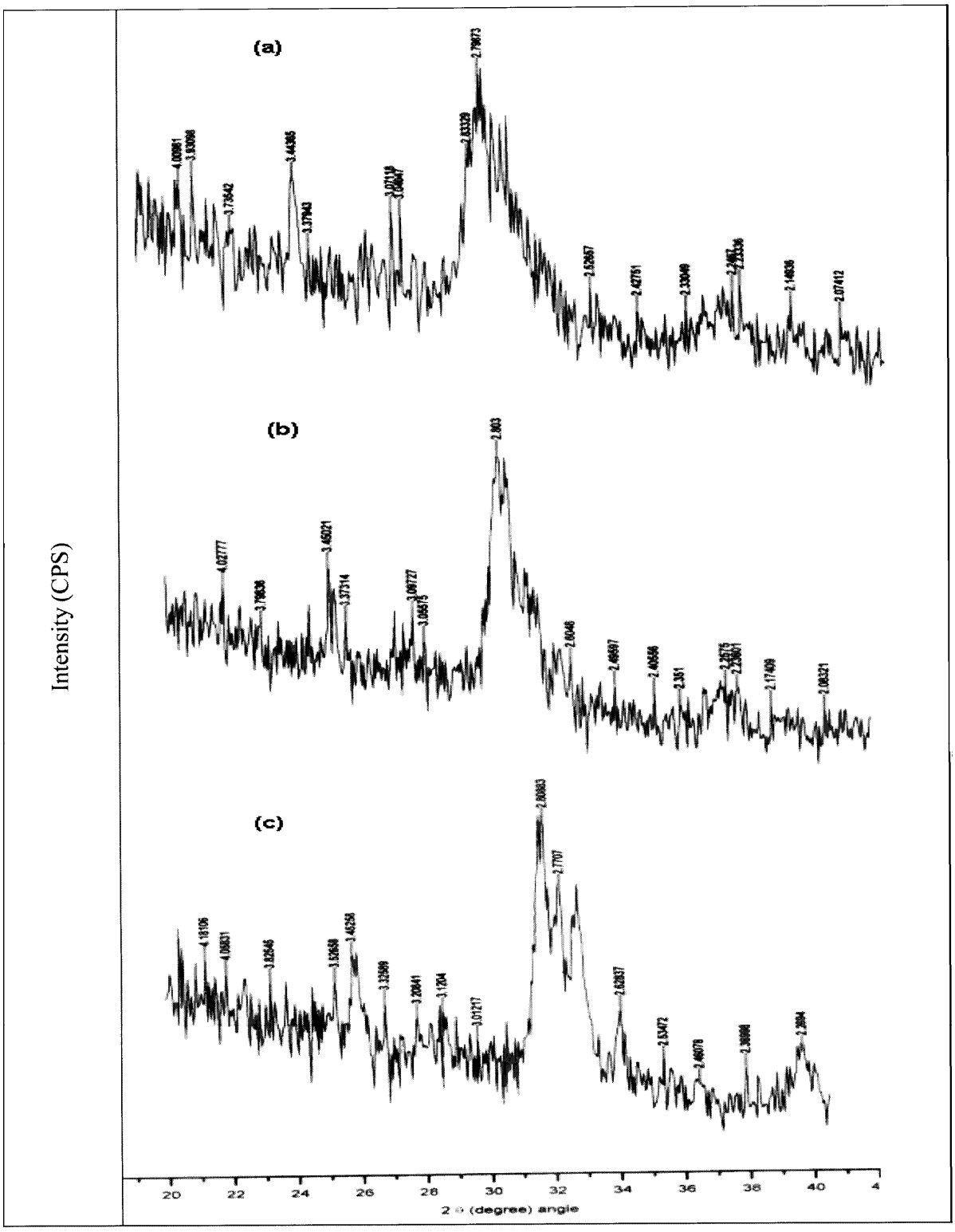

Fig. 8: XRD spectra of animal bones charcoal (ABC) samples activated at; **(a)** 600 °C **(b)** 800 °C **(c)** 1000 °C.

into a rectangular cavity in an aluminum holder and scanned in a step-scan mode (0.05°/step) over the angular range of 7-30° (2θ). The observed intensity curve was obtained in arbitrary unit (CPS). The sample spectra were analyzed with the help of origin-50 XRD computer soft ware.

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