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Research Article

PREPARATION AND CHARACTERIZATION OF PORE STRUCTURE BY PHOSPHORIC ACID ACTIVATED CARBON FROM UNUSED WOOD OF CITRUS SHRUB

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ABSTRACT

Present study aimed to prepared large surface area activated carbon from unused wood of citrus with 45%w/w concentration of phosphoric acid as activating agent after maintaining optimum condition related to activation time of 25-minute, activation temperature at 550°C and impregnation ratio 4:1 during chemical activation process by means of two stage process. The effect of optimum condition related to activation parameter was studied, the surface and pore structure of activated carbon was characterized by nitrogen adsorption isotherm method. The pore and surface properties of the resultant carbon including Langmuir surface area, BET surface area, pore size distribution, micropore volume and average pore radius were identified by nitrogen adsorption isotherm data using the BET, DFT, DA and BJH method. BET surface area, Langmuir surface area, micropore volume and average pore radius were obtained as high as 649m^2/g, 3015m^2/g, 0.34cc/g and 1.34 nm respectively which exhibit resultant carbon has high surface area and with well-developed micropores.

Keywords: Activated carbon, BET method, Adsorption isotherm, Impregnation ratio.

1. INTRODUCTION

Activated carbons (ACs) are used as effective adsorbents in adsorption process due to high surface area and well developed micropore volume [1, 2]. The preference of precursor mainly depends on its availability, manufacturing process and application of product [3]. ACs is prepared from lignocellulosic precursor for micro porosity, high surface area and well-developed surface functional group. Organic waste material is better choice for the production of ACs. ACs produced from organic waste material reduces the pressure on forest. Many agricultural by products such as coconut shell [2], Chestnut wood [4], fruit stones [5] have been used as suitable material for production of AC. Agricultural by products are considered to be a very important precursor because of low cost material and renewable resources [3]. Unused wood of citrus shrub have no economic value but its conversion into AC would increase their economic values and provide low cost raw material for production of AC. The main application of ACs in industries and environmental process is to separate and purify various types of chemicals in solution [6]. ACs which prepared from coal precursor has the disadvantages related to emission of greenhouse gases so we required decreasing use of fossil fuels in future and search about environmentally friendly inexpensive bio resources to prepare AC such as crop and forestry residue [7]. There are two methods physical and chemical for the activation of carbon which is prepared from precursor.

Thermal activation process does not properly affect the pore size distribution [8] and it requires higher activation temperature while chemical activation process is most suitable due to controlled porosity development and it requires moderate activation temperature. Other advantage of chemical activation is the yield of product which is higher than physical activation process [9]. Development of porosity and adsorption surface area are better in chemical activation process [10]. Chemical activation is carried out at 400-550°C by using KOH, H_3PO_4 and $ZnCl_2$. During the carbonization process, shrinkage in dimension of lignocellulosic material occurs. In chemical activation process, if activating agent is a dehydrating compound than it will change the thermal degradation of lignocellulosic precursor leads to change in the development of porosity [11]. Chemical activation method is mainly used for preparation of AC in powder

form by lignocellulosic materials [12].

The porosity in activated carbon is arise due to the loss of all volatile compounds and reorganization of the remaining structure, after evolution of volatile compound the basic pore structure in resultant carbon is created. The objective of this study is to present general view for production of ACs from unused wood of citrus shrub that was collected from the field by phosphoric acid activation. The raw precursor is hardwood and lignocellulosic in chemical nature with thin stem so lower energy was required during carbonization process. Chemical activation by phosphoric acid helps us to analyses comparison of different method of activation for porosity development. Impregnation ratio (IR) is most important factor among activation temperature, activate time and IR revealed by earlier study [13]. The adsorption behavior of AC is not only depending on its porous structure but also by the developed functional group on its surface. In this study, surface area and pore characteristics of ACs are characterized by N_2 adsorption method at 77°K because of their crucial role in adsorption. The structural heterogeneity of activated carbon is important parameters for adsorption process. Now a day's numerous methods have been developed for the characterization of surface property of AC. In the present study we selected Nitrogen adsorption isotherm for it.

2. MATERIAL AND METHODS

2.1. Preparation of Activated Carbon

The unused wood of citrus plant is the raw material for AC, which was collected, cleaned and washed with distilled water to remove all impurities. The cleaned wood was kept in oven for 10 h at 110°C for drying. After that dried pieces of wood were reduced in size for production of AC. The elemental analysis of this raw precursor was carried using Perkin Elmer CHN elemental analyzer with ASTM standards and was found to be 7.20, 56.27 and 40.24% for ash, fixed carbon and volatile matter respectively.

Phosphoric acid was used to activate the raw carbon by chemical activation process. Eighty five grams of raw precursor and 45 wt. % concentration of phosphoric was taken for impregnation. Fixed impregnation ratio 4:1 was adjusted for getting better result. Approximately 85 grams of small pieces of wood was initially carbonized at optimum temperature for 550°C for 20 minutes after cooling in the nitrogen flow the char was grounded and impregnated with selected acid concentration for 20 hours at 100°C. The resulting mixture turned black as reported by earlier researcher [14-16].

The impregnated char was then activated under a continue nitrogen flow of 90 cm^3 per min STP for 50 minutes. The activated carbon after two stages of activation process was collected and kept in a desiccator for cooling. The resultant product was then washed with the distilled water until normal pH of the solution was acquired. Finally, the resultant carbon was dried in a vacuum oven at 120 for 20h.

2.2. N_2 adsorption method

The main characteristics of activated carbon are large surface area and well-developed porosity on surface of AC which was identified by N_2 adsorption isotherm technique at 77°K by an ASIQ instrument. For the analysis, sample was taken in powder form. First of all, sample was degassed at 100°C in a vacuum condition for gas sorption process for 6 hr. N_2 adsorption isotherm was measured over a relative pressure (P/P^0) range from 0.1 to 1.0. The BET surface area was calculated with the help of standard BET equation in relative pressure range from 0.1 to 0.3. With the help of N_2 adsorption data which was provided by gas adsorption analyzer, various properties of activated carbon such as porosity, BET surface area, Langmuir surface area, total surface area and V_{micro} can be determined using BET, BJH method [17, 18]. By t-plot method, the microporous and mesopore value were calculated. The pore radius distribution of the resultant carbon was identified from adsorption isotherm using Density Functional Theory (DFT) method and BJH method [19-21]. The total pore volume was calculated at a relative pressure of approximately 0.98 which indicates all pores were completely filled with nitrogen gas at this ($P/P°$). The BET surface area, Total surface area, pore size distribution and V_{micro} of AC was obtained based on nitrogen sorption isotherm using Quanta chrome 6.0 software.

3. RESULTS AND DISCUSSION

3.1. Carbon content

Proximate analysis of unused wood of citrus plant reveals that the raw material used in this research has high carbon content approximately 48% and low Ash content about 4% explain that it is preferable precursor for preparation of AC.

The reaction of phosphoric acid with lignocellulosic starts after mixing component, initially phosphoric acid reacts with hemicellulose and lignin then after cellulose

molecule. It was found that cellulose show more resistance towards hydrolysis in acidic medium [22]. The glycoside linkage will be hydrolyzed in lignocellulose and aryl ether bond cleavage in lignin by phosphoric acid. At higher temperature of 550°C, dehydration aromatic condensation and the degradation reaction also take place in the lignocellulosic precursor for chemical transformation. After chemical treatment, there is a decrease in the yield of resultant carbon due to evolution of gaseous product from the precursor.

Impregnation ratio is second critical factor that check the quality of carbon. Here IR 4:1 was maintained for getting proper yield of carbon because yield of AC decreases as the IR increases. Higher acid concentration will induce gasification of carbon and increase the weight loss of resultant carbon. The earlier research shows the same result [22, 23]. The yield of AC obtained is 56.5%. The results of earlier research are shows [14, 15, 24] *i.e.* 46.63% for rubber wood AC, 31.9- 48.5% for fruit Stone AC and 42-51% for cellulose activated carbon.

3.2. N_2 Adsorption Isotherm: (For identifying surface area and pore structure of AC)

The results of the adsorption isotherm are shown in fig. 1 indicates volume of N_2 adsorbed from relative pressure 0.1 to 1.0 of the carbon without activation with phosphoric acid activating agent. The fig. clearly shows that low value of adsorbed nitrogen by resultant carbon at higher relative pressure indicating lower surface area and porosity of carbon and need to enhance porosity and surface area of carbon.

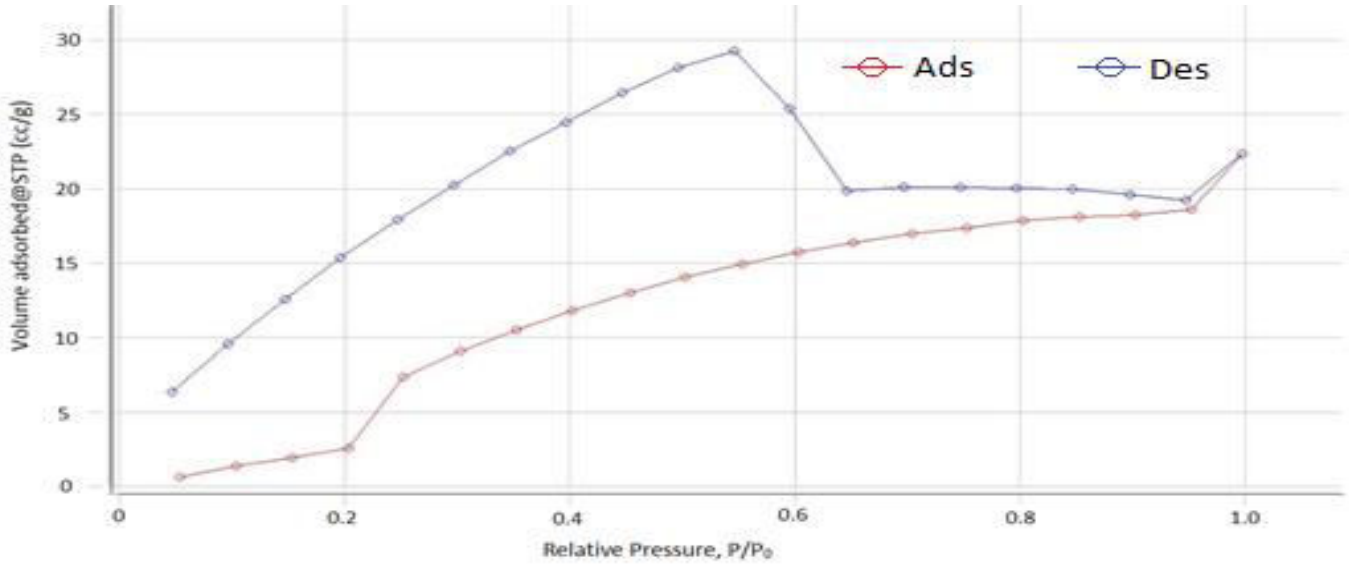

Fig. 1: N_2 adsorption isotherm for non-activated carbon

Fig. (2) illustrates the adsorption isotherm of N_2 of AC in same relative pressure range 0.1 to 1.0. The amount adsorbed at low relative pressure is low and rapidly increases up to $P/P^{o=}0.6$, therefore, it is concluded that carbon has a larger adsorption capacity due to micro porosity with a wider pore size distribution (fig. 2). Various parameters such as activation time temperature and IR at optimal level which affect the quantities of AC at highest level were studied. The optimum temperature for preparation of AC was 550°C because, as the temperature increases above this optimum temperature instead of increasing value of surface area and porosity goes decreasing [16, 25-27]. An activation temperature around 550°C has been proved to be optimum temperature for getting better result in chemical activation of unused wood by phosphoric acid reagent [5, 28]. The presence of phosphoric acid at this optimum temperature promotes the decomposition of biopolymer after that polyphosphate and phosphate bridges formation takes place in lignocellulosic biopolymer material which connects the fragment of polymer avoiding the shrinkage of the carbon. It was found that at higher temperature *i.e.* above 550°C, porosity and surface area of activated carbon decreases due to continue formation of polyphosphate after reaction with cellulose and hemicellulose molecule with phosphoric acid during activation process which covered the space led to reduction in size of pore structure of

resultant carbon [22, 29]. Second critical factor is activation time that influences the quality of resultant carbon [14]. The IR of 4:1 at 550°C the optimum activation time is 25 minutes. If activation time increases with 45wt% H_3PO_4 at 550°C then surface area gradually decreases. Similar trends have also been found for the influence of activation time on the BET surface area and porosity of resultant carbon obtained through H_3PO_4 activation of other lignocellulosic raw material [30]. The activation time *i.e.* 25 minutes, for preparation of resultant carbon was the optimum for getting such result. Another important factor is impregnation ratio (IR) that was found of 4:1 for phosphoric acid and organic material as the optimum value for getting good surface area and porosity in resultant carbon. If the value of IR increases, then excess of phosphoric acid promotes depolymerization of bio polymer with formation of polyphosphate which blocks the pore space resulting decreased surface area of AC and porosity also. At this selected IR, the resultant carbon had predominantly micropores and mesopores to some extent. The same observation was reported by several researchers [28, 31-33].

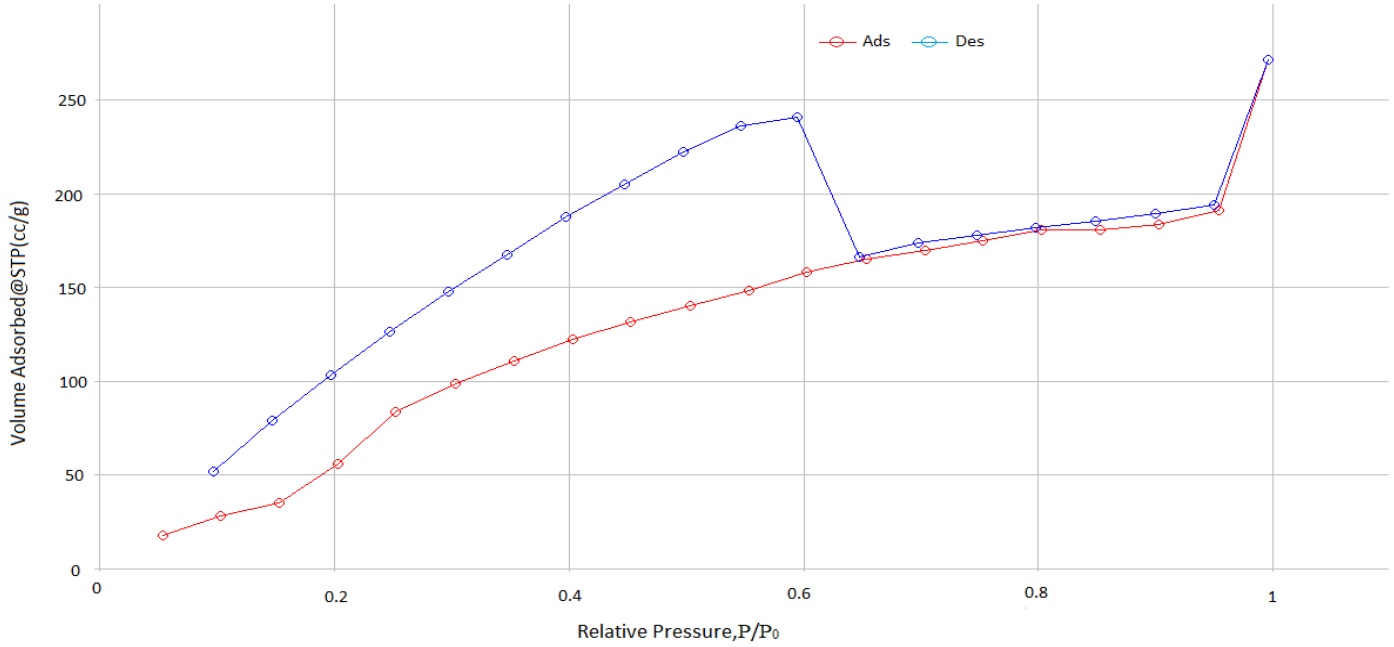

Fig. 2: N_2 adsorption isotherm for activated carbon at activation temperature 550°C

Fig. 2 illustrated that N_2 adsorption isotherm of these unused wood of citrus plant by phosphoric acid activation belong to type (IV) with a hysteresis loop of H4 of IUPAC classification which is associated with mixture of mesoporous and microporous material. The initial part of the isotherm at low relative pressure explained to the significant uptake of nitrogen by resultant carbon related to adsorption of nitrogen within its micropores and coverage of monolayer sites. At intermediate relation pressure, the isotherm shows along with monolayer, multilayer adsorption begins in mesopore of resultant carbon. Adsorption isotherm of activated carbon exhibits the significant monolayer as well as multilayer adsorption followed by capillary condensation by well-developed pore of activated carbon at high relative pressure. It was clearly demonstrated that the uptake of nitrogen was found initially increased rapidly at low relative pressure then it intermediate relative pressure indicating resultant carbon has micropores with different size. Moreover, the hysteresis with narrow loops develops when desorption isotherm is plotted along with the adsorption isotherm proves poor development of mesopore and large development of micropores with different sizes. Development of micropores with different size development of micropores and mesopores are also proved by adsorption isotherm which has a wider knee at low relative pressure and the amount of nitrogen adsorbed slightly increases at higher relative pressure. Porosity development occurs at optimum temperature of 550°C with a maximum surface area of 649.75m^2/g in resultant carbon which was prepared from unused

wood of citrus plant by phosphoric acid activation process. The same result was observed with lignocellulosic materials in earlier studies [12, 30, 34].

By Density Functional Theory (DFT) model the pore size distribution (PSD) of AC was ascertained the PSDs exhibit to higher peak at 1.3nm and 1.7nm.

Results (fig. 3) showed that contribution of micropore is high but contribution of mesopores is small in resultant carbon. Fig. 4 shows that the porosity range is between pore radius 1 to 3 nm. The AC prepared at 550°C has mesopores with size more than 2 nm along with micropores due to widenings of micropore to mesopore. The DA micropore volume was found 0.33m per gram. Fig. 5 shows the pore size distribution (PSD) of AC obtained by BJH method. The PSD shows sharp peak in the micropore range with the maximum around 1.3 and 1.7 nm for resultant carbon sample. The pore diameter distribution of the AC mostly lies between 1.3 to 7 nm which clearly indicate that the pores are manly micropore and mesopore to same extent. The maximum BJH micropore volume is 0.33cc/g, pore surface area 176 m^2/g and BJH average pore radius is 1.54nm.

The result of resultant carbon prepared at optimal condition by phosphoric acid activation process is summarized in table 1.

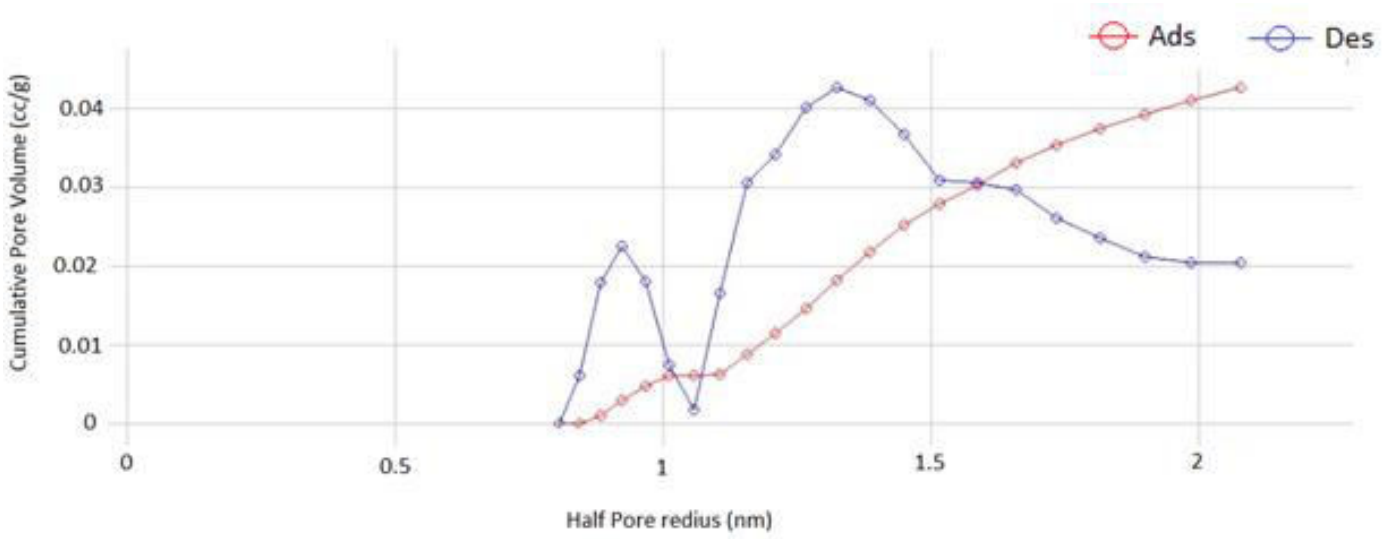

Fig. 3: DFT based pore size distribution of activated carbon produced at activated temperature at 550°C

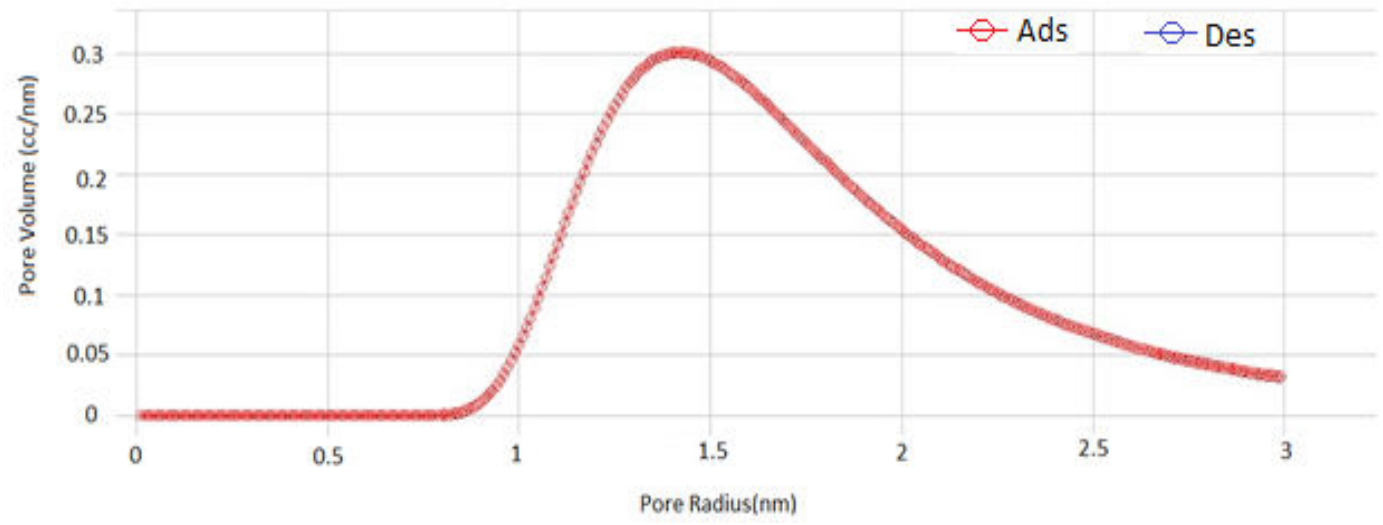

Fig. 4: Pore radius distribution of the activated carbon based on D.A method at 550°C activation temperature

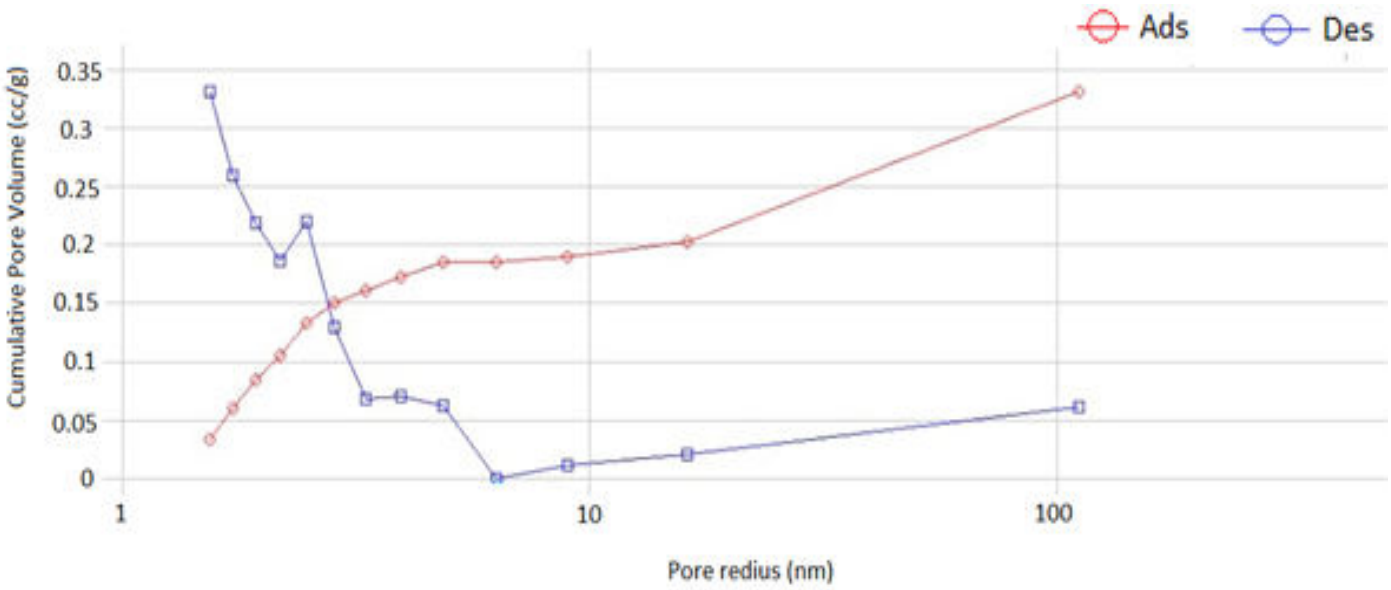

Fig. 5: BJH based micropore volume distribution of activated carbon at 550°C activation temperature

Table 1: Structure characterization of activated carbon

Sorption characteristics	Activated carbon
BET surface area (m^2/g)	649.75
Language surface area (m^2/g)	3015.37
Micropore surface area (m^2/g) (t-plot)	447.32
Micropore Volume cm^3/g (BJH)	0.35
Micropore radius(nm) (BJH)	1.5
External surface area (m^2/g) (t-plot)	202.42
Total pore volume cm^3/g (mp)	0.42

4. CONCLISION

AC was prepared from unused wood of citrus plant using 45wt % concentration of phosphoric acid as activating agent after maintaining optimum condition related to activation time, activation temperature and impregnation ratio during chemical activation process. It also has been found that all important characteristics such as texture quality, porosity, high surface area and heterogenicity which should be present in better adsorbent can be developed after chemical activation of carbon. The use of an inexpensive, easily available unused wood as raw material and selecting a suitable preparation method may be beneficial for preparing low cost activated carbon for its specific application. It was found that unused wood of citrus plant is a good precursor for AC production due to well-developed micropores and mesopores and high surface area 649 m^2/g after phosphoric acid activation process. The phosphoric acid activated carbon produced by two stage preparation method was investigated which exhibit the advantages of a moderate processing time, low energy required and greater adsorption capacity. The present study showed that unused wood of citrus plant can be effectively used as a raw material by phosphoric acid activation of optimum condition for preparation of AC due to development of required qualities such as porosity large surface area and heterogenicity in resultant carbon which makes AC as better adsorbent for specific use.

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Conflict of interset

None declared

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