



CHARACTRIZATION OF PHOSPHORIC ACID ACTIVATED CARBON FOR POROSITY AND SURFACE CHEMISTRY

Pradeep Dwivedi*, Ankit Gawshinde and Rashmi Singhai

Department of Chemistry, Regional Institute of Education, Bhopal

Email- dpradeepmbk@gmail.com, ankit.gawshinde@gmail.com

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Abstract: In this study, activated carbon that prepared from unused wood of citrus shrub by chemical activation method using phosphoric acid as activating agent was characterized by SEM and FTIR method. The chemically modified adsorbent was identified by observing developed active functional group and porosity on surface of resultant carbon. These qualities are essential for effective adsorption of adsorbate and removal of pollutants from aqueous solution. In this study SEM images indicated developed micro and mesopores while FTIR graphs were represented formation of active phosphorous and oxygen containing functional groups such as P-O-P, P- O-C and P=OOH etc. On surface of AC. Based on these results the resultant carbon is promising adsorbent for removal of polar and non-polar pollutants from aqueous solution.

Keywords: - Activated carbon, SEM, FT-IR, Adsorbents, Adsorption

Introduction

Activated carbons (AC) are commonly produced from various organic materials such as biopolymers, agriculture residue, coconut shell, wood etc [1-5]. Adsorption is one of the most promising technique by AC among the other technique such as ion exchange, reverse osmosis and chemical precipitation due to high efficiency and easily operability for treatment of waste water [6-10]. Various organic materials such as biochar, carbon nanotubes and AC have been used as an adsorbent for purification and separation process in liquid and gaseous mixture [11-15]. The transformation of raw precursor into AC through activating agents such as phosphoric acid and zinc chloride are generally used because of low cost and feasibility [16-18]. The carbonization of the raw organic material may be followed by chemical activation method by using chemical reagents such as phosphoric acid, zinc chloride and potassium hydroxide for growth of porosity and increase surface area of the char or by thermal activation in inert atmosphere [19-22]. These chemical reagents decompose the organic materials and induce the aromatization resulting formation of pores. Activating agent H₃PO₄ oxidize the carbonaceous materials resulting generation of active functional groups on the surface of AC [23-27]. Raw precursor and method of preparation determine the surface chemistry and porosity of AC [28-31]. By changing the activation method, the characteristics of resulting carbon can be different. The advantage of chemical activation in comparison to physical activation are that it can be carried in only one step and require low temperature and produces may higher yield [32-33].

Developed heterogeneity in the framework of activated carbon is an important property of AC during adsorption method. Methods such as SEM can be used for the characterization of

the heterogeneous property of AC. In the case of lignocellulosic raw material weight loss is generally completed at or above 550°C during pyrolysis process. Along with weight loss porosity continuously develop at or above 550°C activation temperature by the shifting of carbon in a disordered way in the vicinity of pore. Well-developed pore size distribution was observed after a partial blockage of large pore opening in AC during pyrolysis at optimum temperature which would allowed to check the accessibility of adsorbate molecule of different sizes to the inner pores. An optimal temperature is required for the carbonization of raw material which provides the highest adsorption quality and this optimal temperature control adsorption properties of the lignocellulosic precursor. Factors such as rate of heating process, activation time, carbonization process and activation in inert atmosphere control properties of AC. Activation method and characteristics of raw material decide the qualities of activated carbon [34]. Chemical activation method gives a better yield than the other activation process and decreases mineral matter in resultant activation carbon [20].

Activated carbon with its large surface area is used mainly in purification and chemical recovery process in industries. Earlier researches explain relation between the creating porosity and precursor by using many parent organic raw precursors and chemical activating agent [35-36]. In previous work from researcher it has been observed that carbon prepared by phosphoric acid activation of organic raw precursor show acidic behaviour which has been utilized in purification process and elimination of particular metals ion from aqueous medium [37]. Phosphoric acid activation is a well-known process for the production of activated carbon. Phosphoric acid activation of organic materials produces better adsorbent qualities such as better pore structure and surface chemistry in AC [38- 40]. In this study we selected unused wood of citrus as a starting material for the preparation of activated carbon by phosphoric acid activation. The unused wood of citrus was identified as hardwood. The adsorption properties of resultant carbon are analysed not only by their heterogeneity and porosity of surface of carbon but also by generation of chemical functional groups on its surface after chemical activation process. The modification of concentration of surface functional group and the nature suitably carried by thermal or chemical treatment of precursor. The adsorption characteristics of prepared ACs specially for metal ion and pollutants based mainly on the presence of acidic/polar functional groups containing oxygen and other heteroatom in carbon skeleton [41]. Activated carbon which produced from unused branches of citrus shrub by phosphoric acid activation was examined in both two steps in this study [42]. Due to incorporation of phosphorus into carbon skeleton form active functional group which show cation exchange properties [43]. The generated surface functional groups of resultant carbon influence its chemical interactions with adsorbate that indicates creation of chemical group on surface of ACs which has an important role in adsorption method. A detailed knowledge of surface chemical group of AC enables production of adsorbent with desired qualities for environmental applications.

The aim of activation process is to develop porosity and generate active functional groups on the surface of resultant carbon that depends on various conditions such as optimum temperature, concentration and time during process of preparation. The surface area and pore volume of the resultant carbon was determined by using BET method [44]. In the present paper surface chemistry worth to be examined by FT-IR characterization method that play

major role in the uptake of polar adsorbate during adsorption process [45]. FT-IR technique is more preferable to monitor the surface functional group that develop on the surface of ACs under phosphoric acid activation process in oxidizing condition. The development of pores on the surface of resultant carbon are another important characteristic for adsorption of organic pollutants from waste water was examined by using SEM technique.

2. Experimental technique

2.1 Preparation of activated carbon

The precursor used for the production of ACs was unused wood of citrus and phosphoric acid of concentration of 45wt% used as activating agent for chemical activation method. This concentration of phosphoric acid produced better qualities in ACs. The optimum temperature for carbonization of precursor was at 550°C impregnation ratios of phosphoric acid and raw precursor 4:1 was selected. Factors related to chemical activation of carbonized char such as temperature, impregnation ratio and activation time were increased above optimum condition then oxidation and gasification process increases which decreases not only yield of carbon but number of functional groups on the surface of activated carbon also. The washed and dried small pieces of wood was kept in phosphoric acid solution for impregnation for 22 hours at 110°C. After impregnation of raw precursor, it was carbonized at optimum temperature 550°C for activation of carbon. The activated carbon after activation process was collected and kept in desiccator for cooling. The resultant product was then washed with distilled water. Lastly the resultant carbon was dried in a vacuum oven at 120°C for 12 h.

2.2 Scanning Electron Microscope (SEM):

The morphology of the resultant carbon was determined using SEM instrument. Scanning electron micrograph was recorded by using JEO/EO version JSM 6390 SEM instrument of the resultant carbon at widening distance 21mm, working voltage 15kV, magnetic field 5000, spot size- with 500x different magnification. The coated samples of AC were then transferred to the SEM specimen chamber and analysed at an accelerating voltage of 15 kV.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The surface chemistry of the AC was characterized by Fourier Transform Infrared Spectroscopy (FTIR) to study its surface chemical active group both quantitative and qualitative. The surface chemical groups of AC were studied by obtaining transmission spectra of resultant carbon sample by KBr technique. The technique was carried by using grinded KB powder and the powder surface was evened using the attach the sample passing bar. Next the resultant carbon sample was diluted with the KBr powder with the ratio of 10% and grounded until it become fine particle to mix the both of them The KBr reagent treated sample of resultant carbon gave FTIR spectra in wave number range of 4000-500cm⁻¹, with 2 cm⁻¹ resolutions of resultant carbon sample by KBr technique.

3 Result

The surface qualities developed in resultant carbon was investigated by a SEM and FTIR technique.

3.1 Yield-

The optimum condition was maintained during chemical activation by phosphoric acid reagent related to factors such as activation temperature and impregnation ratio. The

activation optimum temperature was maintained at 550°C and used phosphoric acid with impregnation ratio 4:1 for getting highly developed surface qualities of resultant carbon with good yield. In this study the yield of resultant carbon obtained is 47% which is same as mentioned in earlier studies [46-47].

3.2 External surface of resultant carbon using SEM-

The SEM micrographs of AC which presented in Fig 1 and Fig 2 indicate transformation in resultant carbon after activation process at different magnification. SEM images exhibit a irregular structure with cracks and crevices on the surface which confirmed heterogeneous structure of activated carbon. The surface morphology of sample of the resulting carbon are given in figure (1). Figure (1) shows the resultant carbon prepared at optimum condition each porous carbon having cavities on its external surface. The creation of pores on external surface of AC is due to the evaporation of the phosphoric acid molecule after carbonization leaving the space which previously occupied by the activating reagent 48. The wide range of pores on surface of AC was demonstrated by SEM micrograph of resultant carbon which belong to micropores and mesopores

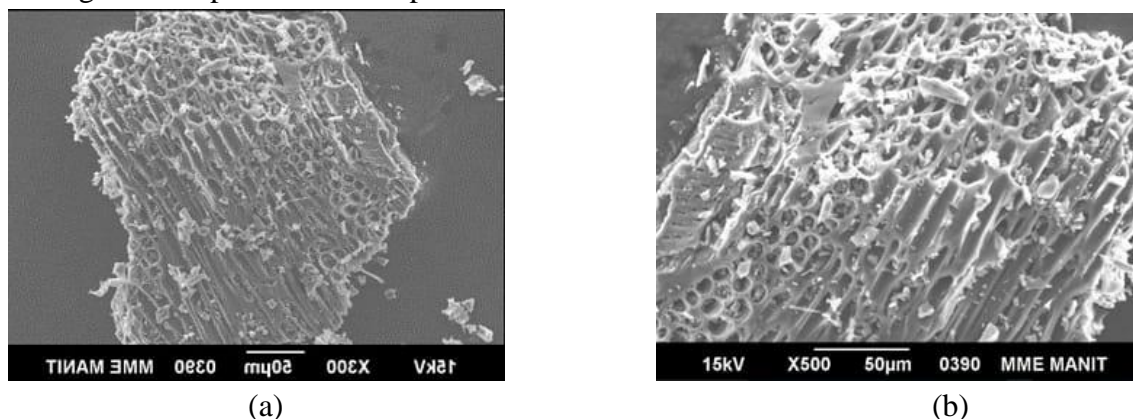


Fig.1 (a) and (b) SEM images of activated carbon at 300X and 500X magnification

Scanning Electron images of the surface structure of sample of the resultant carbon is given in figure (1). From the figure (1) it is observed that carbon produce at this optimum temperature is porous carbon and has cavities on its external surface. The texture quality of the resultant carbon having the greater surface area from phosphoric acid activation process is shown in figure. The nature of the raw material and process for activation decide the porosity of the activated carbon. Micropore volume of activated carbon produced by phosphoric acid is very high. Pore development in the activated carbon during pyrolysis process was also important as this would enhance the surface area and volume of activated carbon by promoting the diffusion of phosphoric acid molecule into the pores. At optimum temperature or above, development of pore increases during activation due to increasing the phosphoric acid carbon reaction via acid hydrolysis process which would then create more pore after hydrolysis of glycosidic linkage in hemicellulose and cellulose molecule along with cleavage of aryl bond in lignin [49-50].

Figure 2 illustrate that the external surface of AC has large cavities and irregularity indicating high porosity was produced by attack of the reagent H₃PO₄ during activation. Chemical activation at 550°C with phosphoric acid resulted in the creation of irregularity in surface and more pores as observed same by other chemical reagent after activation 51]. It can be seen

from the micrographs that the external surface of the activated carbon has particle size cracks, gray sizes and crystals of various sizes in large holes. The particles in micropore are most likely the decomposed compound of precursor which formed during activation process. The phosphoric acid activated carbon image shows partially developed honey comb like morphology and some micro holes observed on the surface. After activation some amount of these compound remain in the surface skeleton of resultant carbon. Figure 3 illustrated there the surface of activated carbon became rough and some irregular pore formed due to removal of volatile matter after activation process. Activation at 550°C with phosphoric acid resulted in the production of well-developed micropores and after substantial removal of various volatile matter in the activated carbon. This was agreed by earlier research where the surface porosity of activated carbon increased after activation process produces large surface area with different types of voids on the surface [52-53].

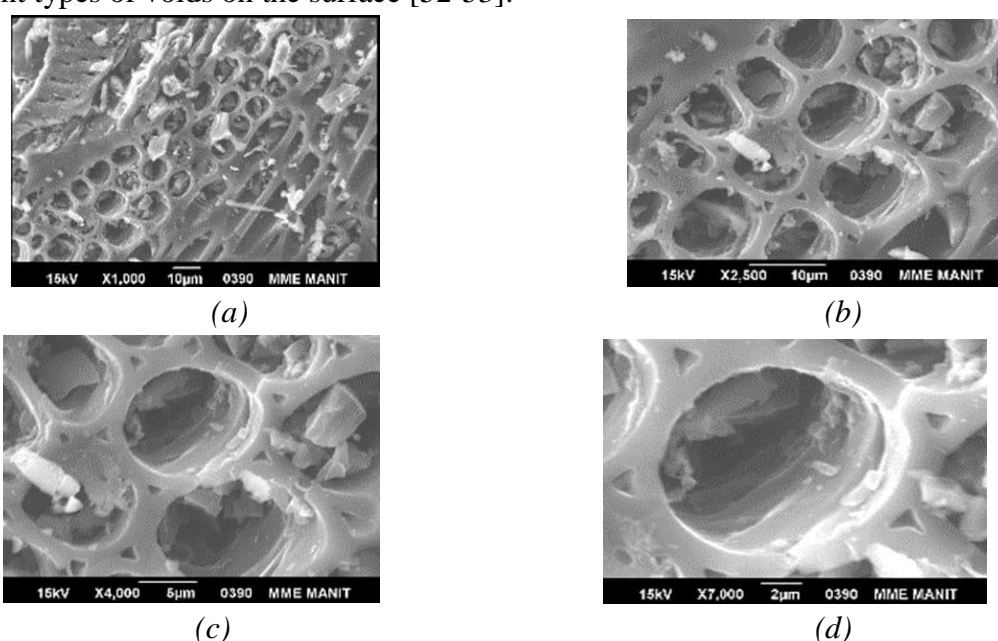


Fig.2 (a) and (b) SEM images of activated carbon at 1000X to 7000X magnification

3.3 Surface chemistry of the activated carbon

The carbon matrix is made up of carbon with other heteroatoms like hydrogen, phosphorus, nitrogen, oxygen etc. These heteroatoms combine with carbon atom and form specific functional group on surface of AC after activation process. The surface chemistry of activated carbon is mainly determined by the acidic and basic nature of its surface [54-55]. The presence of surface chemical groups such as carboxylic, anhydride lactone, carboxyl etc are associated with acidity of surface. The presence of functional groups such as carboxyl, phenolic and other acidic functional groups which developed on surface of activated carbon after activation process are responsible for acidic nature of surface of AC. Surface chemistry of the resultant carbon: The FT-IR spectra of without activated carbon showed in figure (1)

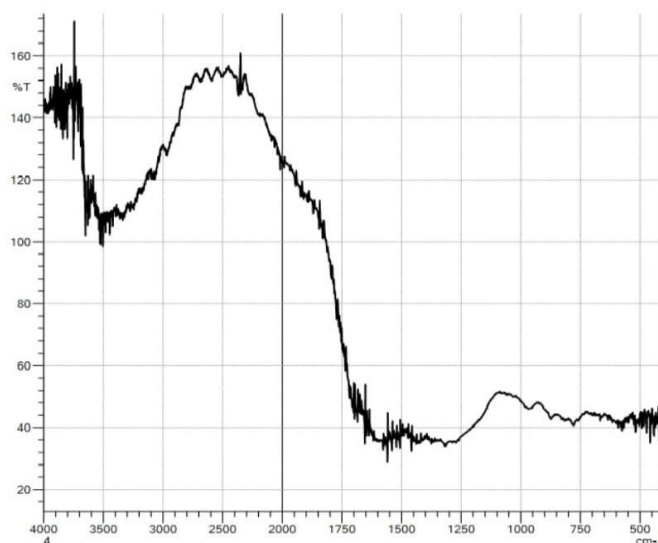


Fig. 3 FTIR spectra of non-activated carbon at 550°C activation temperature.

Which indicate development of chemical active group on the surface of carbon is required by phosphoric acid activation process. The carbon skeleton consists of not only carbon atom but heteroatom like hydrogen, oxygen, nitrogen, halogen and phosphorus also. The surface chemistry of resultant carbon is governed by bonded these heteroatoms the to the edges of the carbon skeleton. The surface chemistry of activated carbon is mainly determined by the acidic and basic nature of its surface. The presence of surface chemical groups such as carboxylic, anhydride lactone, carboxyl etc are associated with acidity of surface. The activation of carbon at optimum temperature 550°C produce sufficient amount of acidic functional group. Similar result was reported with previous research with phosphoric acid activation [56]. FTIR spectra of resultant carbon that prepared from unused wood of citrus with impregnation ratio 4:1 at optimum activation temperature 550°C is exhibited in Fig (2).

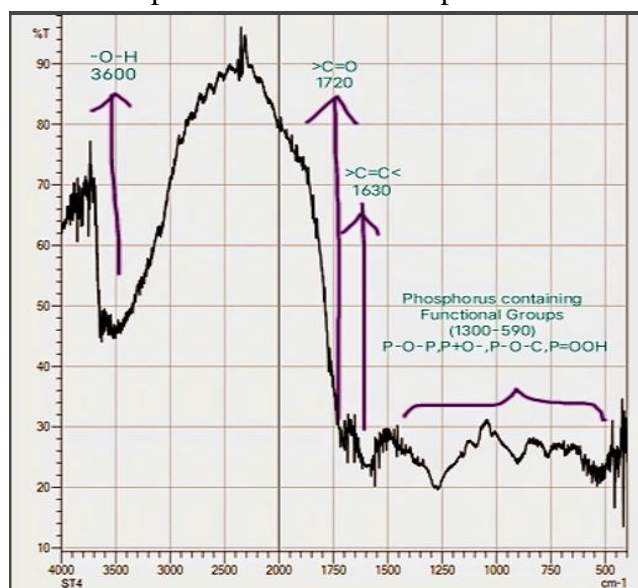


Fig. 2 FTIR spectra of activated carbon at 550°C activation temperature.

A peak around 1720 cm^{-1} indicate the presence of C=O functional group of ketone, lactose and carbonyl. A broad band around 3400-2400 cm^{-1} and peak near 1710 cm^{-1} shows the

stretching vibration of carboxylic acid [57]. A low intensity peak near 3100 cm^{-1} indicates the presence of -OH functional group in phenol. Very weak peak near 2900 cm^{-1} indicates presence of methyl group due to C-H stretching vibration. A band near 1630 cm^{-1} represent C=C stretching vibration of aromatic ring [58]. A peak at 1460 cm^{-1} attributed to the aliphatic carbon chain. A peak at $1230-1170\text{ cm}^{-1}$ can be attributed to the stretching vibration of hydrogen linked P=O, O-C stretching vibration in P-O-C bonding and the P=OOH. The shoulder near 1080 cm^{-1} correspond to the P+-O- linkage in acid phosphate and symmetrical vibration of P-O-P chain [59-60]. At optimum temperature various phosphorus and oxygen containing functional groups were developed on the surface of AC which become dominant around $1110-1220\text{ cm}^{-1}$. At optimum temperature at 550°C , the FT-IR spectra of the activated carbon shows as number of changes. The band at $1666-1532\text{ cm}^{-1}$ indicates presence of unsaturated C-C bond of aromatic functional group that produced by H_3PO_4 activation method [61-62]. The FTIR spectra of phosphoric acid activated carbon clearly different from without activated carbon due to development of new signal at $1110-122\text{ cm}^{-1}$ in FTIR spectra after activation process. Information related to the surface chemical group and surface structure of the produced activated carbon was analysed by FT-IR Spectroscopy [63-64]. A band at approximately 1720 cm^{-1} is the $>\text{C}=\text{O}$ stretching vibration in ketone aldehyde lactone and carboxylic group. All bands with low intensity indicate oxygenated functional groups on the surface of phosphoric acid activated carbon [65-66].

Conclusion

Activated carbon prepared from unused wood of citrus using phosphoric acid during chemical activation process the effect of optimal condition related to activation factors on porosity and development of surface active functional group of resultant carbon was also investigated. With the help of SEM technique, the pore structure of resultant carbon was analysed and surface chemistry of AC was explained by FTIR technique. Porous carbon was prepared at optimum activation temperature of 550°C with the well-developed various type of pores. The acidic behaviour of surface of resultant carbon was due to presence of acidic functional group on its surface after impregnation of resultant carbon with phosphoric acid. It can be seen from micrograph which were obtained from SEM technique that the surface of the resulting carbon has cracks and some crystals of various size in large micropores exhibit decomposition of biopolymer during activation process. Phosphoric acid activation at optimum condition of unused wood of Citrus provides heterogeneous structure to adsorbent after developing various types of pores and cracks on surface with additional qualities like developed functional groups on surface for increasing adsorption capacity for specific use related to removal of pollutants from river water.

References:

- 1) Tan X, Liu Y, Zeng G et al (2015) Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* 125:70–85.
- 2) Angin, D (2014) Production and characterization of activated carbon from sour cherry stones by zinc chloride. *Fuel* 115:804–811.
- 3) Nguyen, C. and Do, D.D. (1995). 33,1717.

- 4) Ma, X., Ouyang, F. (2013) Adsorption properties of biomass- based activation Carbon prepared with spent coffee grounds and pomelo skin by phosphoric acid activation. *Appl. Surf.Sci.*280: 1-7.
- 5) Gao R, Fu Q, Hu H et al (2019) Highly-effective removal of Pb by co-pyrolysis biochar derived from rape straw and orthophosphate. *J Hazard Mater* 371:191–197
- 6) Li, D., Ma, X., Liu, X., Yu, L. (2014) Preparation and characterization of nano- TiO₂ loaded bamboo- based activated carbon fibres by H₂O activation. *Bioresources* 9:602-612.
- 7) Angin, D. (2014) Utilization of activated carbon produced from fruit juice industry solid waste for the adsorption of Yellow 18 from aqueous solutions. *Bioresour Technol* 168:259–266.
- 8). Awad FS, AbouZied KM, Abou El-Maaty WM et al (2018) Effective removal of mercury(II) from aqueous solutions by chemically modified graphene oxide nanosheets. *Arab J Chem.*
- 9) Daguerre, E., Guillot A., Py X. (2000). *Carbon*, 38, 59-64.
- 10) Banerjee M, Basu RK, Das SK (2018) Cr(VI) adsorption by a green adsorbent walnut shell: adsorption studies, regeneration studies, scale-up design and economic feasibility. *Process Saf Environ Prot* 116:693–702.
- 11) Sajjadi SA, Mohammadzadeh A, Tran HN et al (2018) Efficient mercury removal from wastewater by pistachio wood wastes derived activated carbon prepared by chemical activation using a novel activating agent. *J Environ Manag* 223:1001–1009.
- 12) Hong, B., Xue, G., Weng, L. and Guo, X. (2012). Pre-treatment of moso bamboo with dilute phosphoric acid. *Bio. Resources* ;7 (4) 4902-4913.
- 13) Chen Z, Jing Y, Wang Y et al (2020) Applied Surface Science Enhanced removal of aqueous Cd(II) by a biochar derived from salt-sealing pyrolysis coupled with NaOH treatment. *Appl Surf*
- 14) Deng R, Huang D, Wan J et al (2020) Recent advances of biochar materials for typical potentially toxic elements management in aquatic environments: a review. *J Clean Prod* 255:119523.
- 15) Fernandez ME, Nunell GV, Bonelli PR, Cukierman AL (2014) Activated carbon developed from orange peels: batch and dynamic competitive adsorption of basic dyes. *Ind Crops Prod* 62:437–445.
- 16) Such NV, Trofymenko SI, Poddubnaya OI, Tsyba MM, Sapsay VI, Klymchuk DO, Puziy AM. Porous structure and surface chemistry of phosphoric acid activated carbon from corncob. *Appl Surf Sci* 2012; 261: 75-82.
- 17) Xua J, Chena L, Qua H, Jiao Y, Xiea J, Xing G. Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with H₃PO₄. *Appl Surf Sci* 2014; 320: 674-80.
- 18) Yang J, Qui K. Development of high surface area mesoporous activated carbons from herb residues. *Chem Eng J* 2011; 167: 148-54.
- 19) Kilic, M., Apaydin-Varol, E. and Putuno, A.E. (2010). Preparation and surface characterization of activated carbon from *Euphorbia rigida* by chemical activation with ZnCl₂, K₂CO₃, NaOH and H₃PO₄. *Appl. Surf, Sci.*, 261: 247-54.

- 20) Hu, Z. and Srinivasan, M.P. (1999). Preparation of high surface area activated carbon from coconut shell. *Microporous, Mesoporous, Mater.* 27, 11-18.
- 21) Hashemian S, Salari K, Yazdi ZA (2014) Preparation of activated carbon from agricultural wastes (almond shell and orange peel) for adsorption of 2-pic from aqueous solution. *J Ind Eng Chem* 20:1892–1900.
- 22) Joseph L, Jun B, Flora JRV et al (2019) Removal of heavy metals from water sources in the developing world using low-cost materials: a review. *Chemosphere* 229:142–159.
- 23) Momčilović M, Purenović M, Bojić A et al (2011) Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. *Desalination* 276:53–59.
- 24) Palanisamy PN, Sivakumar P (2009) Kinetic and isotherm studies of the adsorption of Acid Blue 92 using a low-cost non-conventional activated carbon. *Desalination* 249:388–397.
- 25) Solomon O, Adesina K, Oluwapamilerin O, Seun O(2019) Heliyon Functionalized locust bean pod (*Parkia biglobosa*) activated carbon for rhodamine B dye removal. *Heliyon* 5:e02323.
- 26) Wang LG, Yan GB (2011) Adsorptive removal of direct yellow 161 dye from aqueous solution using bamboo charcoals activated with different chemicals. *Desalination* 274:81–90.
- 27) Njoku VO, Hameed BH (2011) Preparation and characterization of activated carbon from corncob by chemical activation with H₃PO₄ for 2,4 dichlorophenoxyacetic acid adsorption. *Chem Eng J* 173:391–399.
- 28) Ning- chuan F, Xue-yi G (2012) Characterisation of adsorption capacity and mechanism on adsorption of copper, lead and zinc by modified orange peel *Trans Nonferrous Met-Soc China* 22: 1224-1231.
- 29) Qin C, Chen Y, Gao J.(2014). Manufacture and characterization of activated carbon from marigold straw (*Tagetes erecta* L) by H₃PO₄ chemical activation. *Mater Lett* ; 135: 123-6.
- 30) Jagtoyen, M.and Derbyshire, F. (1993). Some consideration of the origin of porosity in carbon of chemically activated wood. *Carbon* 31,1185-92.
- 31) Zheng,J., Zhao, Q.,Ye, Z.(2014) Preparation and characterization of activated carbon fibre (ACF) from cotton woven waste.*Appl. Surf. Sci.*299:86-91.
- 32) Ahamadpour, A. and Do, D.D. (1997). The preparation of activated carbon from macadamia nutshells by chemical activation. *Carbon*,35, 1723 -1732.
- 33) Ma, X., Yang,H. Yu, L. Chen, Y.,Li, Y.(2014b) Preparation, surface and pore structure of high surface area activated carbon fibres from bamboo by steam activation. *Materials* 7:4431-4441.
- 34) Jagtoyen, M., Thwaites, M., Stencel, J.M., McEnancy,B.and Derbyshire, F. (1992).Adsorbent carbon synthesis from coals by phosphoric acid activation.*Carbon* ;30 ,1089-96.
- 35) Solum, M.S., Pugmire, R.J., Jagtoyen, M.and Derbyshire, F. (1995). Evolution of carbon structure in chemically activated wood. *Carbon* 33, 1247-1254.
- 36) Tovar AK, Godínez LA, Espejel F et al (2019) Optimization of the integral valorization process for orange peel waste using a design of experiments approach: production of high-quality pectin and activated carbon. *Waste Manag* 85:202–213.
- 37) Molina-Sabio,M.,Rodriguez-Reinosa, F., Caturla,F.,and Selles, M.J. (1995). Porosity in granular carbons activated with phosphoric acid. *Carbon* ;(33), 1105-1113.

- 38) Kalderis D, Bethanis S, Paraskeva P, Diamadopoulos E (2008) Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. *Bioresour Technol* 99:6809–6816.
- 39) Suarez-Garcia, F., Martinez-Alonso, A., and Tascon J.M.D. (2002). Pyrolysis of apple
- 40) Hadouna H, Sadaouib Z, Souamia N, Sahela D, Toumer I. Characterization of mesoporous carbon prepared from date stems by H₃PO₄ chemical activation. *Appl Surf Sci* 2013; 280: 1-7.
- 41) Yorgun S, Yildiz D. Preparation and characterization of activated carbons from Paulownia wood by chemical activation with H₃PO₄. *J Taiwan Inst Chem E* 2015; 53: 122-31.
- 42) Diao, Y., Walawender, W.P. and Fan, L.T. (1999). Production of activation carbon from wheat using phosphoric acid activation. *Adv. Environ. Res.* ;3(3); 333-42.
- 43) Puziy, A.M., Podderbnaya, O.I., Martinez-Alonso, A., Suarez-Garcia, F. and Tascon, J.M.D. (2002). Synthetic carbons activated with phosphoric acid: surface chemistry and ion binding properties. *Carbon* 40 (9), 1493-1505.
- 44) Singhai, R., Dwivedi, P., Gawshinde, A. (2021). Preparation and Characterization of Pore Structure by Phosphoric Acid Activated Carbon from Unused Wood of Citrus Shrub. *Journal of Advanced Scientific Research*. 12 (3) Suppl: 1: 155-161.
- 45) Boumediene M, Benaïssa H, George B et al (2015) Characterization of two cellulosic waste materials (Orange and Almond Peels) and their use for the removal of Methylene Blue from aqueous solutions. *Maderas Cienc y Tecnol* 17:69–84.
- 46) Srinivasakannan, C. and Bakers, M.Z.A. (2004). Production activated carbon from rubber wood sawdust. *Biomass, Bioenergy*, 27, 89-96.
- 47) Gomez - Serrano, V., Curerda-Correa, E.M., Fernanade Gonzales, M.C., Alexander-Franco, M.F. and Macias-Garcia, A. (2005). Preparation of activated carbon from chestnut wood by phosphoric acid- chemical activation. Study of microporosity and fractal dimension, *Mater. Lett.* 59. 846-853.
- 48) Corcho- Corral B, Olivares- Marin M, Fernandez - Gonzalez C, Gomez- Serrano V, Marcias - Garcia A. Preparation and textural characterization of activated carbon from vine shoots (*Vitis vinifera*) by H₃PO₄ chemical activation. *Appl Surf Sci* 2006; 252:5961-6.
- 49) Liou T (2010) Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation. *Chem Eng J* 158:129–142
- 50) Aik, C.L. and Ting, Y.J. (2004). *Colloid Int Sci*, 274, 594.
- 51) Yakut SM, Sharaf EI- Deen G. Characterization of activated carbon prepared by phosphoric acid activation of olive stones. *Arab J Chem* available online 22 December 2011.
- 52) Lu X, Jiang J, Sun K et al (2014) Influence of the pore structure and surface chemical properties of activated carbon on the adsorption of mercury from aqueous solutions. *Mar Pollut Bull* 78:69–76.
- 53) Mora Alvarez NM, Pastrana JM, Lagos Y, Lozada JJ (2018) Evaluation of mercury (Hg²⁺) adsorption capacity using exhausted coffee waste. *Sustain Chem Pharm* 10:60–70.
- 54) Xu X, Schierz A, Xu N, Cao X (2016) Comparison of the characteristics and mechanisms of Hg(II) sorption by biochars and activated carbon. *J Colloid Interface Sci* 463:55–60.

- 55) Yu J, Yue B, Wu X et al (2016) Removal of mercury by adsorption: a review. *Environ Sci Pollut Res* 23:5056–5076.
- 56) Sabio-Molina, M., Rodriguez-Reinoso, F., Caturloo, F., Selles, M.J.(1996). Development of porosity in combined phosphoric acid carbon dioxide activation. *Carbon* 34, 457-462.
- 57) Ahmad M, Lee SS, Rajapaksha AU et al (2013) Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. *Bioresour Technol* 143:615–622.
- 58) Li X, Shen Q, Zhang D et al (2013) Functional groups determine biochar properties (pH and EC) as studied by two-dimensional ¹³C NMR correlation spectroscopy. *PLoS ONE*.
- 59.) Puziy, A.M., Poddubnaya, O.I., Martínez-Alonso, A., Suárez-García, F. and Tascón,J.M.D. (2002).Synthetic carbons activated with phosphoric acid. I. Surface chemistry and ion binding properties, *Carbon* 40: 1493–1505.
- 60) Socrates, G. (1994). *Infrared Characteristic Group Frequencies*, vol. 2, John Wiley & Sons, New York.
- 61) Puziy,A.M., Podderbnaya, O.I.Martinez-Alonso,A., Suarez Garcia,F. and Tascon,J.M.D. (2005).Surface chemistry of phosphorus containing carbon of lignocellulose origin. *Carbon*; 43,2857-2868.
- 62) Puziy, A.M., Poddubnaya, O.I., Martínez-Alonso, A., Suárez-García, F. and Tascón,J.M.D. (2003).Synthetic carbons activated with phosphoric acid. III. Carbons prepared in air, *Carbon* 41:1181–1191.
- 63) Boonamnuavitya, V., Sae-ung, S. and Tanthapanichakoon, W. (2003). Prepration of activated carbon from coffee residue for the adsorption formaldehyde. *Sep. Purife., Technol.* 42,159-168.
- 64) Olivares-Marin, M., Fernandez- Gonzalez, C., Macias- Garcia, A. and Gomez Serrano, V.(2006). Thermal Behaviour of lignocellulosic material in the presence of phosphoric acid: Influence of the acid content in the initial solution.*Carbon*, 44;2347-50.
- 65) Ahmad M, Lee SS, Dou X et al (2012) Efects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresour Technol* 118:536–544.
- 66)Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Vyvyan, J. A. (2008) *Introduction to Spectroscopy*; Brooks/Cole: Belmont, CA, USA.