



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH

RESEARCH ARTICLE

Whether To Worry With Waste: A Review On Activated Carbon Precursors From Various Waste Materials**Priti Malhotra^{1*}, Ritu Payal¹, Arti Jain¹**

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Manuscript Info**Manuscript History:**

Received: 15 November 2015

Final Accepted: 22 December 2015

Published Online: January 2016

Key words:

Activated Carbon, adsorption, carbonization, acid and base treatment, and impregnation.

Abstract

The phenomenon of adsorption is an important surface activity and its exploration for the purpose of treating waste has attracted a great deal of attention in the recent past. Employing agricultural waste to produce activated carbon which are further used in various fields, is not only a promising exploration but also economically viable and sustainable for the environment.

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Introduction:-

The world is progressing every minute and with the technological advancements reaching a pinnacle, amount of waste produced in the environment is equally growing tremendously. The world seems to be living on “***I take, I use and I throw***”, which should strictly be not allowed. The massive waste collected on the planet is biggest danger to the future and sustainability of the planet earth. Therefore, the most vital subject of today's progressive world is disposal of waste and its recycling to ensure sustainability and protection of the environment (Gidde and Jivani, 2007). The prime focus of every innovation ought to be the waste management so as to generate wealth from waste and proving that “***someone's trash is another's cash***”.

Majority of the waste produced in today's age possess a wide range of carbon content leading to the preparation of activated carbon (AC) from its elemental carbon source (Suzuki *et al.*, 2007). AC is high-grade carbonaceous product, is highly porous and adsorptive and is usually prepared by carbonization and chemical activation (Sekaran *et al.*, 2007). The adsorptive efficiency of activated carbon majorly depends on the resource material, the method and temperature of activation, heating rate, activation time and types of inclusions as well as impregnations (Cheenmatchaya and Kungwankunakorn, 2014).

Utilization of waste materials obtained from various sources in the preparation of highly porous activated carbon has been very common as it has high sustainability, economic viability and ecofriendly approach. Among the various types of wastes which can be productively utilized for generating activated carbon, agricultural and food wastes are of prime significance as they are commonly available, have massive carbon content and their exclusion from the surroundings will help to keep the environment benign. Carbonaceous adsorbents, as they are also referred to, are particularly utilized owing to their large surface capacity, fast kinetics of adsorption and their recovery (Rajoriya *et al.*, 2007).

This current review aims on utilizing organic waste materials as precursors for preparing AC, who's physical and chemical activation leads to its potential adsorption capacity. The cost of obtaining AC from waste materials is low, enables the recycling of organic waste and its extremely versatile absorbing characteristics enhances its industrial significance (Ioannidou and Zabaniotou, 2007). This review article focuses on the various methodologies involved

in the preparation and carbonization of activated carbon from a range of industrial and agricultural waste materials and its specific applications in adsorbing both organic and inorganic contaminants (Alvim-Ferraz *et al.*, 2007). The efficiency of adsorption, the pore size and the rate of adsorption of the AC depends on the following factors: (a) types of waste materials which include agricultural waste, industrial waste and food waste, (b) the heating temperature while converting the carbon rich material to pure carbon by pyrolysis and, (c) activating this generated carbon by either physical or chemical methods (Bouchelta *et al.*, 2008 and Hayashi *et al.*, 2000).

The properties of active carbon have been found to be greatly influenced by the physical and chemical methods of activation (Sriuttha *et al.*, 2011). High porosity, high adsorptive capacity, high mechanical strength, large surface area, high degree of surface reactivity, are the prominent features associated with AC. They are also classified as microporous (<2 nm), mesoporous (2-50 nm), macroporous (>50 nm) depending on the diameter (or size) of the pores within these porous solids. Furthermore, gas phase AC usually consist of micropores whilst liquid phase AC have more number of mesopores due to lesser diameter range of 0.4-0.9 nm in the former case (Martins *et al.*, 2008).

1. Procedures for the Synthesis of Activated Carbon

The high degree of surface activity of AC has not been explored for adsorption but also for various catalytic activities besides catalytic support mechanism. As such, many studies have been conducted to develop activated carbon from waste materials following different methodologies and then using them for removal of pollutants from aqueous as well as gaseous phase (Ayranci, 2005; Kouimtzis *et al.*, 1995 and Allen, 1995).

Mainly two procedures are used for the preparation of AC. The first one involves agricultural residues as starting material whose pyrolysis, temperature and heating rate, nitrogen flow rate and pyrolysis residence time are important parameters to be considered. Carbonaceous agricultural solid are cost effective and have low inorganic content which increases the yield of activated carbon. The formation of AC usually involves two stages: Initially, the starting materials are carbonized under an inert atmosphere of nitrogen or helium gas at moderate temperature producing chars of primitive pores which are further activated in the subsequent stage (Barroso-Bogeat *et al.*, 2014; Yang and Lua and Haykiri *et al.*, 2006).

Various factors among the type of agricultural wastes being used as precursors for generating AC, which largely affects its yield and extent of activation, can be concluded as:

1. The pyrolysis of agricultural residues like wheat straw (Aslan , 2005), olive and rice husks (Lanzetta and Blasi, 1998), grape residue (Encinar *et al.*, 1996) *etc.* produce double char as compared to those produced from wood (Kansa *et al.*, 1977).
2. Low ash contents in AC from almond shells (Marcilla *et al.*, 2000), nut shell (Aygun *et al.*, 2003), apricot (Alvim-Ferraz *et al.*, 2007) and cherry stones (Olivares-Marín *et al.*, 2006) give higher yields as compared to grape seeds (Petrov *et al.*, 2001) which has high ash content and low yield of AC. Generally, it is found that precursor for AC production follows the order: hazelnut shell > apricot stone > almond shell > grape seed.
3. Olive waste, birch and bagasse (Minkova *et al.*, 2001) produce higher yields of AC. Furthermore, other factors governing adsorption and porous characteristics of AC are related to pyrolysis, temperature and time. The proceedings of pyrolysis within 500 °C for a long time reduce carbon having high surface area and high pore volume indicating higher adsorption capacities (Hu and Srinivasan, 2001). Steam pyrolysis reduces large porosity which is further enhanced by chemical activation by ZnCl_2 as compared to KOH. Apart from activation time and temperature, increased surface area of product is also obtained from increased burn off.

In the second stage the gasification of the chars at high temperatures of ~900 °C with steam (H_2O) or carbon dioxide is carried out so that activated mesoporous carbon structures are obtained (Nakagawa *et al.*, 2007). Since, the last step involves activation of carbon, it can be done both by physical and chemical activation. Chemical activating agents are used both as hydrating and oxidizing agents. Separate and sequential of chemical activation can follow various routes using ZnCl_2 with CO_2 or steam, K_3PO_4 with CO_2 and phosphoric acid followed by CO_2 activation, calcium compounds are also known to activate and modify pore size although phosphoric acid treatment prior to physical activation with CO_2 produce highly microporous materials whose pore size are of range (2-50 nm) (Molina-Sabio *et al.*, 2004, 1991).

Mesoporous, granular, high surface area and mesopore content above 70% AC can also be obtained by using inert gases followed by ZnCl_2 treatment. The time of exposure to CO_2 or inert gases and the ratio of waste material to ZnCl_2 further play a significant role in determining the surface area and pore size as well as its activated porosity (Karagöz *et al.*, 2009). The experimental parameters such as carbonization temperature, impregnation ratio, activation protocol *etc.* greatly affect the kinetics and percentage yield of various AC's derived from various agricultural wastes (*e.g.* wheat, nutshells, rice hulls, corn cob and shells, rice husk and rice straw, olive stones, cotton and olive residues, *etc.*).

2. Applications of Activated Carbon

The vast range of uses and applications of AC obtained from different waste materials contain high carbon content are enormous. AC are in form of mesoporous materials having efficient adsorption capacities and their pore size determine their adsorption capacities apart from the type of chemical reaction and polarity parameters of the adsorbates. AC are used for various purposes like waste water treatment, purification of water by removing heavy metals such as Cd^{2+} , Zn^{2+} , Pb^{2+} , Ni^{2+} and dyes from water (Srinivas and Naidu, 2013 and Monser, 2002). AC from hazelnut were found to adsorb phenol and methylene blue (Karagöz *et al.*, 2008), whereas, phenols have been attempted to be removed from activated carbon prepared from beet pulp (Meikap *et al.*, 2005).

Carbonization of corn wastes have great affinity for I^- and Pb^{2+} ions (Tan *et al.*, 2010) and coconut husk generated carbon are found to be capable of removing As(II) from aqueous solution upon addition of copper in the husk (Anirudhan *et al.*, 1998). Temperature activation as well as steam activation along with ZnCl_2 and H_3PO_4 based chemical activations have efficiently removed Cu(II) when prepared from rice husk (Mohamed Latiff *et al.*, 2010) and almonds sheets (Bansode *et al.*, 2003), respectively. Purification of drinking water is achieved by effective removal of Cu^{2+} , Zn^{2+} and Pb^{2+} ions using almond shell based carbon (Husseiny *et al.*, 1998). Local bamboo wastes from construction sites were used to produce granulated activated charcoal and were used for adsorption of heavy metals (*i.e.* Pb^{2+} and Cu^{2+}) from waste water of refineries (Eloka-Eboka *et al.*, 2013).

Fe^{3+} and Co^{2+} loaded AC are used as lightweight and efficient microwave absorbent as well as transformed into magnetic CoFe_2O_4 and Co_3Fe_7 particles on heat treatment under an argon atmosphere due to high specific surface area ($800 \text{ m}^2\text{g}^{-1}$) and abundant pores, including micropores and macropores (Li *et al.*, 2014).

3. Influence of Acid and Base Activation

The acid and base activation is equally important, since, the precursors for producing activated carbon are biomass, they should essentially be made so that percentage of carbon content increases leading to high percentage yield (Karagöz *et al.*, 2009). The process of preparation of AC involve base leaching, activation and acid washing in subsequent order (Fig. 1)

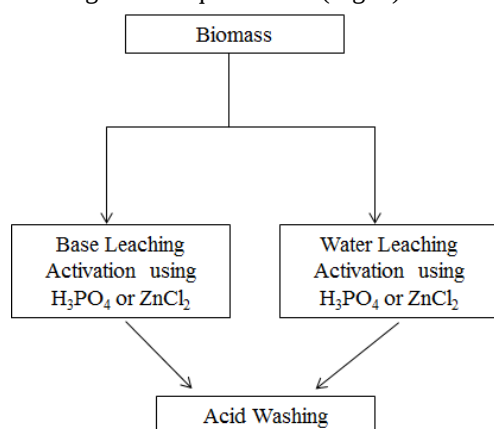


Fig. 1: Acid and base leaching

The mesoporous carbon materials whose pore size range from 2 nm-50 nm have found appreciable application in molecular adsorption (Hegazi, 2013), as catalytic support material (Skubiszewska-Zi *et al.*, 1998), in biomedical engineering (Kelley *et al.*, 1988) and as scavengers for adsorbing bulky pollutants (Anisuzzaman *et al.*, 2013). Their ability to store gas molecules can be well explored for storing fuel gases like hydrogen gas and natural gas in

vehicles (Myers *et al.*, 1992). AC has significant contribution in reducing carbon emissions from automobiles as they play important role in adsorption of carbon dioxide (Mazlee *et al.*, 2015). Thus, the high surface area of AC and its rational distribution of pore size ranging from micro porous to mesoporous, provide suitable medium for energy storage (Frackowiak, 2001).

The inorganic components in the ash obtained after heat treatment contains mainly silica and metal impurities. After leaching the precursor biomass with NaOH, the ash content decreases due to removal of SiO₂ in the form of sodium silicate with NaOH. After getting activated H₃PO₄ and ZnCl₂ there is further reduction in ash content. The base leached samples have shown to remove the ash and generate a large number of tiny pores, thereby increasing the surface area of carbon precursors. Vapourization of organic matter during the activation process creates the porous surface which has large surface area when treated by either acid or base. The adsorption capacities are substantially affected by base and acid leaching of the samples. The experimental findings have made evident the following advantages of base-leaching:

1. Reduction in ash content
2. Facilitating the formation of pore, both micropores and mesopores
3. Increases the contact area between the carbon precursor and the activating reagents
4. The organic matter in the raw material is softened by the base.

These benefits are bound to generate high surface area of activated carbon which further enhance on heat treatment till ~500 °C.

4. Influence of Acid and Base Activation

Impregnating the precursors with chemicals in variable ratio and variation in activating temperatures, greatly influence the surface characteristics of the AC. An optimum ratio of the precursor to chemical is required as increase in impregnation ratio may not always enhance the adsorption capacity in the same ratio.

Effect of H₃PO₄ activation: Chemical activation by H₃PO₄ has been studied using sugar cane bagasse (SCB) and sunflower seed hull (SSH) samples in the past by Liou (2010). On increasing impregnation ratio from 1 to 2 at ~500 °C, the adsorption capacity increases but increasing this ratio further to 4 decreases the adsorption capacity owing to the thermal breakdown at high ratio of activating chemical. Increasing the temperature beyond 500 °C however, decreases the surface capacity because of shrinkage of pores at that high temperature. It was also reported that similar temperature and impregnation ratio give different surface area for SCB and SSH samples emphasizing the fact that the nature of precursor also play an effective role in deciding surface characteristics.

Effect of ZnCl₂ activation: ZnCl₂ activation follow paulownia wood was studied by Yorgun *et al.* (2009) and observed that using ZnCl₂ resulting in carbonization and removal of moisture content which thereby resulted in charring and formation of porous carbon with high yield. It was also observed that samples activated by ZnCl₂ possess the higher volume of mesopore and its high surface than the samples activated by H₃PO₄. The reason lies in the fact that acid washing in the final stage easily washes off ZnCl₂ than H₃PO₄ and is thus prevented from getting collected on the surface. The morphology of pores developed by ZnCl₂ activation was found to be almost similar to those developed by H₃PO₄ activation, although, a faster activation is achieved by ZnCl₂ than by H₃PO₄. Also, it was found that at low and high ZnCl₂ concentrations, activated carbon with microporous and mesoporous porosity, respectively, are obtained.

Concluding Remarks:-

In this review article, we underwent the utility of agricultural wastes to produce activated carbon. The differences in the ultimate and elemental analysis of activated carbons produced from different raw materials, under the same conditions, indicate the dominant influences of the composition and structure of the precursors on their reactivity in the pyrolysis or activation reactions. The Pyrolysis of agricultural residues, including wheat, straw, olive husks, grape residue, rice husks, *etc.*, produce approximately double char than that of wood. Both H₃PO₄ and ZnCl₂ serve as chemical activating agents for the preparation of activated carbon with high mesoporous surface area as they are more effective and less expensive activating agents.

Acknowledgement:-

The authors greatly acknowledge University of Delhi for supporting and funding the innovation project.

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