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## A review on Granular activated carbons: Importance of surface Properties, their modification and investigation

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### Abstract:

The capacity for adsorption is an important factor in the management of the environment for hazardous substances. The literature indicates that surface chemistry has a significant impact on adsorption capacity. This research article has put light on the granular activated carbons and the importance of their surface modification. Various methods of investigation of surface properties such as N<sub>2</sub> physisorption SEM, XRPD, SSNMR spectroscopy, XPS spectroscopy, DRIFT spectroscopy, Raman spectroscopy, INS spectrometer, CO chemisorption were reviewed briefly.

### Introduction:

Activated carbons are microcrystalline, porous and non-graphitic form of carbons that has been processed to improve its internal porosity. Activated carbons are produced from carbonaceous source materials such as bamboo, coconut husk, willow peat, wood, coir, lignite, coal, and petroleum pitch. It can be produced (activated) by the following process: Physical activation: The source material is developed into activated carbon using hot gases. Air is then introduced to burn out the gasses, creating a graded, screened and de-dusted form of activated carbon. Chemical activation is also one of the processes used for activation of activated carbons. Activated Carbon is extensively used for the removal and recovery of hazardous metals due to its availability and high affinity towards the scavenging of metal ions

Organic matter, pesticides, odour-causing compounds and heavy metals such as lead, copper, Chromium, zinc, nickel, mercury, are the most widely found common pollutants in water wastes coming from industries. In most of the developing countries, industrial effluents are directly dumped in the nearby flow of waterbodies making them extremely dangerous for the aquatic life and also hazardous for humans to use. This leads to a serious environmental problem. When these hazardous metals are discovered in excess of the tolerance thresholds, they can induce poisoning, cancer, and brain damage.

The capacity for adsorption is an important factor in the management of the environment for hazardous substances. The literature indicates that surface chemistry has a significant impact on adsorption capacity. There are a number of ways to change the properties of the surface, which can change the properties of activated carbon. Adsorption

properties can also be affected by adsorbate properties and how they relate to surface structure. By adding some atoms to the structure of the surface and making it more acidic or basic, surface modifications can be carried out. Chemical modification, which involves the introduction of oxygen and ammonia atoms, is the primary method for making the surface more acidic and basic, respectively. However, it may also introduce chemical wastes into the environment. Chemical and physical modifications alter the surface of activated carbon, resulting in a variety of properties. The application of some brand-new physical techniques, such as plasma discharge, microwave radiation, and corona treatment, can result in surface modifications. An innovative and practical method for modifying the surface of an activated carbon surface could be corona treatment.

It is evident from practical experience in regions where granular activated carbon (GAC) is used to treat drinking water that high levels of organic matter and heavy metals in the source water significantly reduce the adsorption capacity, reducing the carbon filters' lifespan. Pesticides, odour-causing compounds, heavy metals and other industrial micropollutants have all been shown to hinder the adsorption of these molecules in drinking water [S-S], but few studies have focused on the effect of adsorbed naturally occurring material on carbon's surface properties. Since a maximum removal of approximately 60% was achieved, this high regeneration efficiency cannot be solely attributed to the removal of organic material from the carbon surface. It appears that the regeneration treatment alters the carbon's surface properties in some way to make it more appealing to organic molecules in solution.

Today, natural adsorbents and industrial or agricultural waste adsorbents serve as the foundation for activated carbon, which is an environmentally friendly and highly effective pollutant removal method. At the pilot or industrial scale, however, the activation and modification process is costly. Subsequently, this survey paper intends to sum up the change of surface properties of activated carbon by physical and synthetic enactment, process conditions, designated pollutants.

Physical adsorption is greatly influenced by pore size and volume. It is now well established that the oxidative generation of micropores of variable size and shape distribution results in the high specific surface area (up to 1500 m<sup>2</sup> g<sup>-1</sup>) that is obtained in all cases, as reported in numerous works in the literature. During carbonization, a portion of the additive is incorporated into the carbon body and removed via leaching when phosphoric acid is present; An activated carbon's local structure is typically described as consisting of significant amounts of graphite-like (or sp<sup>2</sup>) species depending on the temperature of activation. Although all of them are characterized by the same predominant structural unit, activated carbons may differ in terms of their nano-structure, which means the connectivity of the sp<sup>2</sup> domains from molecular dimensions up to a few nanometres.

In this review paper studies have been done to see how the surface properties are modified and the ways through which investigation of surface area of activated carbons is done.

**Scope of literature:**

There are several physicists who have studied the surface properties and their modification using activated carbons. A. Kumar and researchers has studied Preparation and characterization of high surface area activated carbon from Fox nut (*Euryale ferox*) shell by chemical activation with  $H_3PO_4$  [1]. Studies on the efficacy of coal-based adsorbents were done by R. Bobdey and colleagues in removal of toxic metal lead from waste water by modifying the surface of activated carbons. [2,3]. A. Budianto et al has done Physical and chemical activation to produce activated carbon from empty palm oil bunches waste [4]. Gayle Newcombe and his fellow researchers have studied the importance of surface properties in the adsorption of naturally occurring organics using activated carbons [5]. H. Demiral has studied the surface properties of activated carbon prepared from wastes[6]. LotfiSellaoui and coworkers has investigated a new statistical physics model to interpret the binary adsorption isotherms of lead and zinc on activated carbon [7]. Matheus Pego and researchers studied the surface modifications of activated carbon and its impact on application [8].

**Modification of Surface properties of activated carbons:**

A certain degree of surface chemical heterogeneity, which is related to the presence of heteroatoms—atoms in the carbon structure that are not carbon—such as oxygen, nitrogen, hydrogen, sulphur, and phosphorus—is largely responsible for the chemical characteristics of activated carbons. These elements are either introduced during the activation process or derived from the nature of the starting material [9,10]. The acidic or basic nature of the surface of activated carbon is determined by surface functional groups, which are formed from these heteroatoms, and the delocalized electrons of the carbon structure [11].

The modification of process conditions, such as the raw material or adsorbent, carbonization, and activation process, with the appropriate condition, has been the primary focus of a number of studies that have been carried out to enhance the adsorption capacity of activated carbon adsorbents. Modifying the surface of activated carbon is another method that effectively demonstrates modifications in the structure of various surface functional groups. As a result of these modifications, the adsorbent's surface area increased and a new functional group was formed through the addition of atoms and texture modification. Various research has been carried out where surface modification of activated carbons has led to better adsorption effectiveness [12, 13]. The adsorption of pollutants from wastewater is effectively enhanced by altering physical and chemical activation processes, particularly when industrial dyes and heavy metal ions are removed.

## Methods of investigation of surface properties:

**N<sub>2</sub> physisorption:** N<sub>2</sub> physisorption at 77 K can be used to measure the carbons' surface area and pore volume using a Micromeritics ASAP 2020 instrument. The method that is outlined in reference was used to analyze the adsorption isotherms[14].

**SEM:** A Zeiss EVO MA10 instrument with a LaB6 filament can be used to take SEM images at a voltage of around 20 kV. The samples are placed on an Al stub that was covered with a disk with two layers of adhesive. AZtecEnergy analysis software is generally utilized for the EDX analysis which can be carried out with a x-act detector.

**XRPD:** PANalytical's PW3050/60 X'Pert PRO MPD diffractometer is used to collect X-ray powder diffraction patterns in the Debye–Scherrer geometry. The source is a Cu anode which is filtered by a Ni foil to attenuate the K line and focused by a PW3152/63 X-ray mirror (= 1.5409). In a glass capillary, the samples are measured as powders. The Scherrer equation can be used to calculate the average dimension ( $L_a$ ) of the crystalline domains:  $L_a = K\lambda/\beta\cos(\theta_{\text{Bragg}})$ , where  $\lambda$  is the wavelength of the Cu K radiation.  $K$  is the shape factor, and  $\beta$  is the FWHM (in  $2\theta$ , corrected by the instrumental broadening) of the (100) and (110) reflections.

**SSNMR spectroscopy:** For <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C nuclei, SSNMR spectra can be taken using a Bruker Avance II 400 instrument operating at 400.23, 162.02, and 100.65 MHz, respectively. At 12 kHz, cylindrical zirconia rotors with a diameter of 4 mm and a sample volume of 80µl can be used. During the acquisition phase, all CPMAS experiments utilizes the Ramp-Amplitude Cross-Polarization pulse sequence with a 75 kHz rf field. On a 2.5 mm probe, <sup>1</sup>H MAS experiments are carried out. The rotors are spun at around 30 kHz and had a volume of 12 l. The probe background signal is suppressed with a DEPTH sequence. The resonances of adamantane, glycine, and 85 percent phosphoric acid could be served as external standards for the <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P chemical shifts.

**XPS spectroscopy:** An ultrahigh vacuum system with a VSW Class 100 Concentric Hemispherical Analyzer can be used for the XPS measurements. After being mounted on copper tape, the samples are appropriately degassed before being placed in the analysis chamber. Core excitation is produced by utilizing a 1486.6 eV non-monochromatic Al K X-ray source (VSW TA10). The survey spectra have an energy step of 1 eV, while the C 1s spectra has an energy step of 0.2 eV. The XPS measurements uses two different modes: high resolution for core line scans and quantitative surface composition and low for survey spectra.

In the case of carbon matrix, the XPS analysis depth is approximately 10–15 nm. The Unifit2008 software is used to analyze and process the spectra. A third-order polynomial function and the Shirley model for inelastic processes are used to approximate the background, and a convolution of Gaussian functions can be used to fit the detailed spectra.

**DRIFT spectroscopy:** In DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) a Nicolet 6700 instrument with a ThermoFisher Smart accessory and an MCT detector can be used to collect DRIFT spectra at a resolution of  $4\text{ cm}^{-1}$  for an average of 1024 scans. On powdered samples without dilution in KBr, the measurements are carried out in the air. After being collected in reflectance mode, the spectra are converted successively into Kubelka–Munk units (K.M.).

**Raman spectroscopy:** Using a Renishaw inVia Raman microscope with an excitation of 514 nm, Raman spectra is taken. After determining if the sample remains stable under the laser beam, the laser power is set at 0.5 percent of the total. An 1800 lines per mm grating monochromator disperses the sample's scattered photons before simultaneously collecting them on a CCD camera; The objective of the collection optic can be set at 20. On powdered samples, twenty 50-s acquisitions are made in order to obtain the spectra. A Renishaw Micro-Raman System 1000 with a frequency-doubled  $\text{Ar}^+$  laser operating at 244 nm is used to collect UV-Raman spectra. In order to prevent carbon degradation, the laser power is adjusted accordingly. A CCD detector simultaneously collects the photons scattered by the sample, which are dispersed by a 3600 lines per mm grating; The objective of the collection optic is set at around 15 mm. On powdered samples, ten; 30-second acquisitions are taken to obtain the spectra.

**INS spectrometer:** At the ISIS spallation neutron source (Rutherford Appleton Laboratory, UK), the TOSCA spectrometer is used to record the INS spectra.<sup>26</sup> The samples had been treated for a long time in a vacuum at  $150\text{ }^\circ\text{C}$  to get rid of the physisorbed water. They were then placed inside thin aluminum envelopes and sealed Al cells with In wires. Every one of the controls were performed inside a glove-box to forestall pollution by dampness. At 20 K, the cell was placed in a duplex CCR cryostat, and the measurements were taken. Each INS spectrum was measured with a high statistic by integrating for 1500 A of the proton current—the proton accelerator was operating at approximately 150 A per hour. Mantid software was used to extract and combine the signals from detectors in both the forward and backward directions<sup>27</sup> without affecting the resolution in any way. A representative macroscopic amount (7.706 g for CW and 7.650 g for Chemi) of samples was measured in each experiment because the beam size was 40 mm x 40 mm. The spectra were normalized based on sample mass and incoming proton current values to enable a quantitative comparison of the samples because the intensity of the INS signal is proportional to the amount of the corresponding chemical species.

**CO chemisorption:** The CO chemisorption method was used to evaluate the metal dispersion of Pd/C catalysts. CO chemisorption measurements were carried out on samples that had been pre-reduced in  $\text{H}_2$  at  $120\text{ }^\circ\text{C}$  using a dynamic pulse method at  $50\text{ }^\circ\text{C}$ .<sup>28</sup> In a typical experiment, the catalyst (200 mg) is loaded into the U-tube, heated in He to  $120\text{ }^\circ\text{C}$  (at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ ), reduced in  $\text{H}_2$  for 30 minutes, and then cooled to  $50\text{ }^\circ\text{C}$  in He (at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ ). As is well documented, a CO/metal average stoichiometry of 1 was assumed for the metal dispersion calculation.



## Conclusion:

1. An activated carbon's local structure can typically be described as consisting of significant amounts of graphite-like (or sp<sup>2</sup>) species depending on the temperature of activation.
2. It is now well established that the oxidative generation of micropores of variable size and shape distribution results in the high specific surface area.
3. Surface properties can be investigated by various techniques such as N<sub>2</sub> physisorption, SEM, XRPD, SSNMR spectroscopy, XPS spectroscopy, DRIFT spectroscopy, Raman spectroscopy, INS spectrometer, CO chemisorption, etc.

## References:

1. Arvind Kumar, Hara Mohan Jena, *Preparation and characterization of high surface area activated carbon from Fox nut (Euryale ferox) shell by chemical activation with H<sub>3</sub>PO<sub>4</sub>*, Results in Physics, 6 (2016), 651-658, ISSN 2211-3797, <https://doi.org/10.1016/j.rinp.2016.09.012>.
2. Bobdey Radhesh Atul, Dr. Neeta Gupta, Prof. Dr. Ramdas U. Khope “Studies on the Efficacy of Coal-Based Adsorbent in Removal of Toxic Metal Lead from Waste Water”, published by Corrosion and Protection Journal, Vol-50, Issue 11, Page 182-187, 2022.
3. Bobdey Radhesh Atul, Dr. Neeta Gupta, Prof. Dr. Ramdas U. Khope “Adsorption studies of lead from waste water using porous coal-based adsorbent in conjunction with organic chelating agent, Guaiacol”, published by NeuroQuantology Journal, Vol-20, Issue 22, Page 1167-1172, 2022.
4. Budianto, Agus & Kusdarini, Esthi & Amrullah, N & Ningsih, Erlinda & Udyani, K & Aidawiyah, A. (2021). Physics and chemical activation to produce activated carbon from empty palm oil bunches waste. IOP Conference Series: Materials Science and Engineering. 1010. 012016. 10.1088/1757-899X/1010/1/012016.
5. Gayle Newcombe, Rob Hayes, Mary Drikas, *Granular activated carbon: Importance of surface properties in the adsorption of naturally occurring organics*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 78, 1993, Pages 65-71, ISSN 0927-7757, [https://doi.org/10.1016/0927-7757\(93\)80311-2](https://doi.org/10.1016/0927-7757(93)80311-2).
6. Demiral, H., & Demiral, İ. (2008). *Surface properties of activated carbon prepared from wastes*. *Surface and Interface Analysis*, 40(3-4), 612–615. doi:10.1002/sia.2716
7. Sellaoui, L., Depci, T., Kul, A. R., Knani, S., & Ben Lamine, A. (2016). A new statistical physics model to interpret the binary adsorption isotherms of lead and zinc on activated carbon. *Journal of Molecular Liquids*, 214, 220–230. doi:10.1016/j.molliq.2015.12.080
8. Pego, m., carvalho, j., & guedes, d. (2017). *Surface modifications of activated carbon and its impact on application*. *Surface review and letters*, 1830006. Doi:10.1142/s0218625x1830006x
9. V.L. Snoeyink, W.J. Weber Jr., *Environ. Sci. Technol.* 1 (1967) 228–234.
10. Y. El-Sayed, T.J. Bandosz, *J. Colloid Interface Sci.* 273 (2004) 64–72.



11. K. László, A. Szucs, Carbon 39 (2001) 1945–1953.
12. Cheol Hwan Kwak, Chaehun Lim, Seokjin Kim, Young-Seak Lee, Surface modification of carbon materials and its application as adsorbents, Journal of Industrial and Engineering Chemistry, Volume 116, 2022, Pages 21-31, ISSN 1226-086X, <https://doi.org/10.1016/j.jiec.2022.08.043>.
13. R. A. Bobdey and R. U. Khope, Analysing 4- Methyl Catechol for Surface Modification of Granular Activated Carbons in Order to Change Its Adsorptive Properties Towards Toxic Metal Lead from Aqueous Solution, Asian Journal of Organic & Medicinal Chemistry, Vol. 7, No. 2, 2022, Pages 256-260.
14. R. Pellegrini, G. Leofanti, G. Agostini, E. Groppo, M. Rivallan and C. Lamberti, *Langmuir*, 2009, **25**, 6476