

TECHNICAL PAPER

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Understanding Activated Carbons *Identifying the best type for the application*

Introduction

It would be fair to say that most chemical industry professionals can explain the differences between adsorption and absorption. But when asked which type of activated carbon would be best suited for a particular application, few chemists or chemical engineers would be able to identify what properties to look for.

Activated carbon is used in a wide variety of applications such as purification or recovery of chemical products, catalysis or catalyst supports, and various environmental applications such as VOC abatement and wastewater purification.

With such broad use in industry, it is critical for engineers and chemists to understand the differences between activated carbons in order to obtain the best performance from their processes.

Activated carbon definition

Activated carbon is a highly porous adsorptive medium with a complex structure composed primarily of carbon atoms. It consists of graphitic-like sheets, called "basal planes", which are joined by random cross-linking.

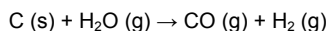
These basal planes are stacked unevenly (unlike the orderly stacking of true graphite layers) and are enveloped in a swarm of unpaired electrons. The cross-linking and randomized bonding of basal planes results in a highly porous structure with a myriad of cracks and crevices between the carbon layers. The porosity and resulting enormous internal surface area make activated carbon an effective material for catalysis or adsorbing a wide range of molecules.

Activated carbon is usually activated by steam or chemical treatment, with steam being more common.

Steam activation usually involves two steps: carbonization and activation. With certain types of carbon, an additional processing step of briquetting or extrusion is carried out prior to carbonization to increase density and hardness of the final product. Briquetting or extrusion can also be used to alter the pore size distribution.

Carbonization involves the conversion of the raw material, such as coal, into a disordered carbon structure with a very low volatile content. This is done at elevated temperatures in an oxygen-lean environment.

In activation, some carbon atoms are reacted away, leaving behind the highly porous structure. Activation is carried out with steam at high temperatures. At these conditions, carbon reacts with steam to form carbon monoxide and hydrogen gas, as denoted in the equation:



In some activation units, the carbon monoxide and hydrogen gas may be burned to produce heat to help maintain the activation temperature. The resulting pores are aligned along adjacent basal planes and are therefore slit shaped. Initially micropores are formed. Prolonged activation will result in micropores enlarging to mesopores and eventually to macropores. The activation process can be accelerated by impurities present in the char as ash, resulting in a more macroporous carbon (Fig. 1).

Chemical activation is used to produce pore structures somewhat different from steam-activated carbons. The most common process consists of mixing wood or some other cellulose-based material with a strong dehydrating agent and then heating to a predetermined temperature. A dehydrating agent such as phosphoric acid, sulfuric acid, or zinc chloride extracts the moisture and supports, as well as prevents the cellulose material from collapsing during activation. The activating agent is normally removed by extraction.

The resulting chemically activated carbon has a highly developed structure with very high pore volume, particularly in the mesopore range. The macropores result primarily from the cellulose structure present in the starting vegetative material (Fig. 2). Due to the lower activation temperatures, the micropore structure may not be as highly developed as some steam-activated carbons. However, the mesopore and macropore walls are highly convoluted,

resulting in a high surface area without a high micropore volume.

Fig 1		
IUPAC differentiation of pore sizes		
Micropore	diameter	< 2 nm
Mesopore	diameter	2-50 nm
Macropore	diameter	> 50 nm

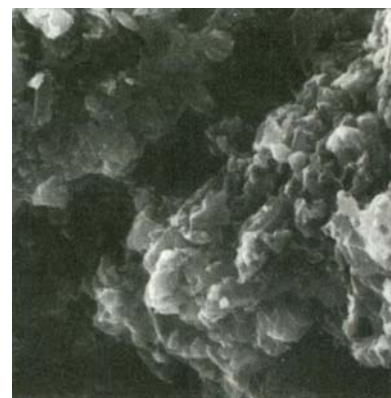
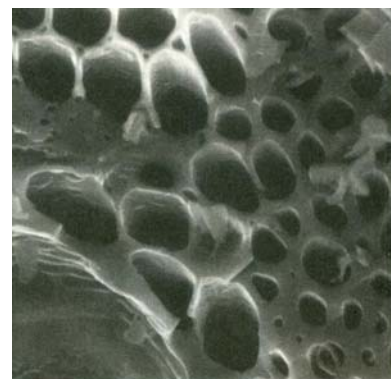


Fig. 2 Two electron microscope pictures. The top is a chemically activated carbon; the bottom is a steam activated carbon.

Through the use of various raw materials, modification of the preparation method and selection of different activation methods, carbons of vastly different physical, adsorptive and catalytic properties are manufactured (Fig. 3).

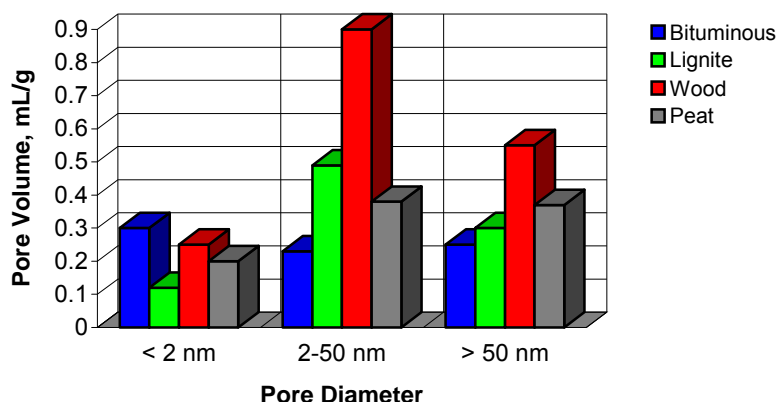
Adsorption

Activated carbon is used to remove impurities or isolate products from a process or waste stream. Impurities are removed by adsorption, which is influenced by a variety of factors such as:

- Carbon pore structure
- Surface complexes on the pore wall
- Diffusion effects
- Adsorbate type, concentration
- Carbon system design

Fig. 3 Pore Volume Distribution

Raw material	Activation	Pore Structure		
		Micro	Meso	Macro
Bituminous Coal	Steam	High	Low	Medium
Lignite	Steam	Medium	High	High
Peat	Steam	High	Medium	High
Wood	Chemical	High	Very High	High



Adsorption is a time-related phenomenon that is diffusion controlled. The adsorption process can be described in three steps. Initially, as a liquid or gas contacts activated carbon particles, the impurities in the bulk liquid come into contact with the external surface of the carbon particles. Next, the adsorbates diffuse into the internal pore structure. The final step is relatively fast and involves the attraction of the adsorbates to the surface of the pore walls, where chemical or electrostatic forces hold them.

Adsorption can be classified into two types: physical and chemisorption. In physical adsorption, the adsorbates are held on the surface of the pore walls by weak electrostatic forces of attraction (van der Waals forces). Chemisorption involves relatively strong forces of attraction, or in some cases actual chemical bonds between the adsorbates and oxygen complexes on the pore wall surface. Therefore, diffusion effects, pore size characteristics, surface complexes and accessible surface area will influence the efficiency of an activated carbon for removing impurities.

Liquid-phase adsorption

For liquid-phase applications, the first two steps of the adsorption process are relatively slow, and involve diffusion of impurities into the internal porosity of the carbon particles. As a result, adsorption rate is to some degree diffusion-controlled. In any application of activated carbon, whether powdered, granular or extruded, there is some minimum time required for adsorption to occur.

Adsorption in the liquid phase is also affected by many chemical and physical parameters, such as the species being adsorbed, its concentration, pH, and temperature. Generally, non-polar organic species are readily adsorbed by activated carbon.

Adsorption trends often follow the relative solubility of substances; the more soluble a substance, the less likely it is to be adsorbed. Therefore, variables such as temperature, concentration and pH affect both solubility and adsorptive capacity.

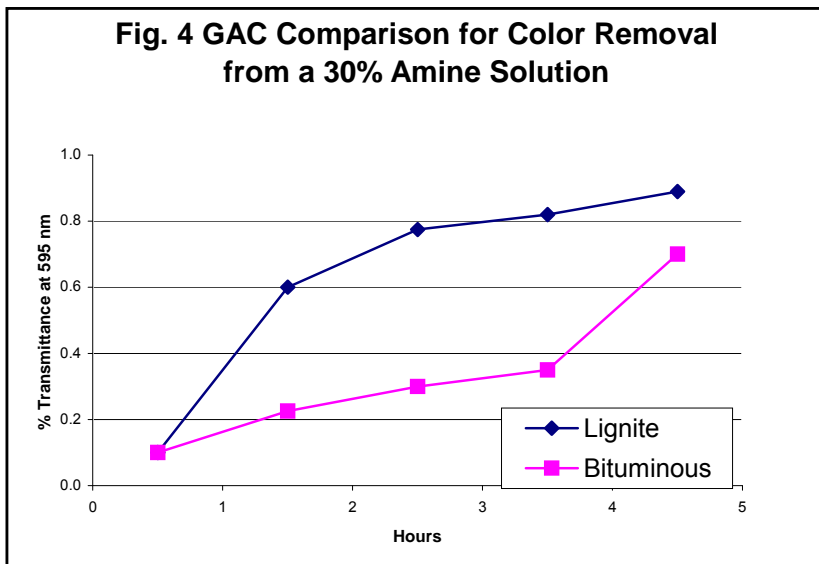
Purifying amine and glycol gas-treating solutions

Amine and glycol solutions are widely used in the chemical industry in gas-treating scrubbers. These solutions need to be purified with activated carbon to prevent foaming and fouling. Because the impurities are typically large molecules, such as oils, a macroporous carbon will usually perform better.

An international company producing anhydrous ammonia from natural gas uses MEA solution to remove acidic gases, which could foul its catalytic process downstream. Six years ago, the company switched from a bituminous coal-based carbon to a lignite coal-based activated carbon. To its surprise, the company found that it was able to extend the life of the 200-ft³ carbon beds from three months to four months. Due to lignite-activated carbon's lower density, 32% less carbon was needed. The longer service life and lower density resulted in a saving of about 50% in the amount of carbon purchased.

The graph in Fig. 4 on the next page shows the difference in performance between lignite coal-based and bituminous coal-based granular activated carbons (GAC) for amine purification.

Different carbons can also impact the relative adsorptive capacity or adsorption rate. If a solution contains many large molecules, such as color bodies or polymeric species, a carbon with a high macro and mesoporosity will perform better. With small molecules, the converse may not always be true because other factors besides microporosity, such as the surface chemistry of the pore wall, may have an overriding effect. A common misconception is that single-solute isotherms can predict carbon performance in the liquid phase. Most real-world process streams contain a number of adsorbable substances. This can lead to unexpected results due to competitive adsorption or blockage of micropores by larger molecules. Plant trials are the only true test of a carbon's performance.



Color Removal Applications

Many solutions, whether natural or synthetic, are contaminated with undesired impurities. These impurities often impart color, which can become more intense at high processing temperatures. Activated carbon can often be used to remove these residual impurities.

Because the type of impurities present will vary widely depending upon the solution, the selection of the proper activated carbon is critical. The following two examples highlight how, in two different process streams, two different carbons (lignite and bituminous) achieved the best color removal.

This emphasizes the importance of testing a variety of activated carbons for each application.

Brine purification

A brine producer of chloride-based solution deals with a high level of naturally occurring organics. They cause the material to have a brown color when crystallized.

Fig. 5 Lab-scale tests of adsorption capacities of three activated carbons

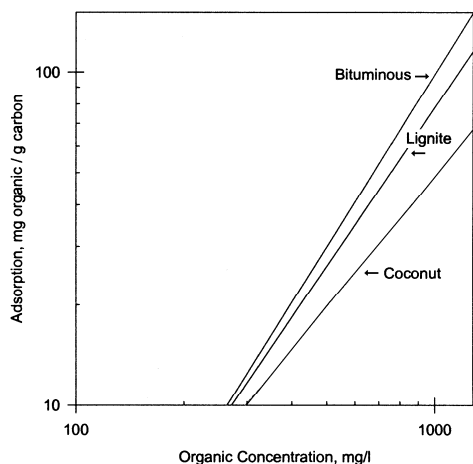


Fig. 5 displays the lab scale tests of the equilibrium adsorption capacity of three different types of activated carbon as a function of organic concentration in the brine. Generally, single solute isotherms are not a good indication as to the relative performance due to competitive adsorption. These isotherms were done on the actual brine, which was to be treated and, therefore, give a good indication of the difference in adsorptive performance between carbons.

This brine producer is successfully using a bituminous carbon for decolorization. The carbon vessels are changed out every 3-4 weeks.

Decolorization of glycerin

A southwestern producer of glycerin uses granular activated carbon to decolorize its final product.

The company switched from an acid-washed bituminous coal to an acid-washed lignite carbon. As a result of the changeover to a lignite coal-based carbon, the company achieved about 8% better decolorization.

Gas-phase adsorption

Adsorption of substances out of a gaseous stream has some fundamental differences from adsorption in the liquid phase. Diffusion is much more rapid in gas-phase applications, with typical contact times on the order of 3-6 sec versus 15-30 minutes for liquid systems. This necessitates the use of larger granules to minimize the pressure drop because the flowrates across the carbon beds are so much higher. Also, gaseous impurities are typically of lower molecular weight, frequently resulting in adsorption occurring mostly in the micropores of the carbon structure where most of the surface area is present.

As the gaseous impurities diffuse down into the pore structure, they adhere to the pore wall, first in monolayer adsorption, and then in multilayer adsorption. This process can be likened to condensation on a cold surface. In fact, conditions that enhance condensation, such as low temperatures, high concentrations and high pressures, also enhance adsorption in the gas phase. Similarly, substances with a low volatility typically adsorb more readily than substances with high volatility. Gas-phase carbons are therefore highly microporous, but even gas-phase carbons can be differentiated by their micropore structure. A highly activated vapor-phase carbon will have a high micropore volume, but the average diameter of the micropores will be quite large. These carbons are well suited for the adsorption of impurities with low volatility or high concentration where the high micropore volume is needed to accommodate a greater degree of multilayer adsorption.

In the case where more volatile components need to be adsorbed, or when the impurity is present only in low concentrations, multilayer adsorption does not occur as readily. For this situation, a carbon that has undergone less activation will actually achieve a higher adsorption capacity. Low-activity carbons have smaller micropores with the pore walls close to each other. These small pores have a higher adsorption potential because more than one pore wall can exert its force on the same molecule.

The isotherms in Fig. 6 (pg 5) display the equilibrium adsorption capacity of a carbon as a function of concentration in the gas stream. Two extruded carbons are shown, both produced from the

same raw material. The degree of activation, however, varies dramatically.

The more highly activated carbon (CCl₄ No. of 78) has a very steep isotherm, achieving low adsorptive capacities at low concentrations, but increasing dramatically as the concentration increases. The lower activated carbon (CCl₄ No. of 40) has a very flat isotherm, achieving good adsorption at low concentrations. Due to the limited micropore volume, adsorption does not increase substantially as concentration increases.

However, there are exceptions. For the control of mercury and dioxin in incinerator flue gas, powdered activated carbon is routinely injected directly into the flue gas. The mercury and dioxin are adsorbed on the carbon and removed downstream by an existing particulate control device. Because the contact times are very short, often less than 1 sec, adsorption equilibrium is never reached. The removal efficiency is primarily dependent on the rate of adsorption. For this case, a finely ground, macroporous carbon is usually the most cost effective.

Carbon as a catalyst

Activated carbon is not only used as an adsorbent, but also as a catalyst and as a catalyst carrier for many processes in both the liquid and gaseous state. It has a large accessible surface area with various functional groups that act as catalytic sites for a wide variety of reactions. If the carbon does not offer sufficient activity on its own, it can be used as a support medium for metal oxide catalysts.

Once again, pore size distribution is critical to the selection of a carbon as a catalyst or catalyst carrier. Carbons of large macroporosity and mesoporosity offer better accessibility to reactants and are generally preferred for both liquid and gaseous processes. The metal oxide impregnates are thought to be adsorbed predominantly into the mesoporous structure of the carbon, rendering the micropores virtually useless. Ash constituents and surface chemistry are also important, and in some rare cases actually promote reactions. For catalyst carriers, the purest, least chemically reactive carbon is usually sought. Ash content can be reduced through acid washing, but may result in increased chloride content.

Particle size more often than not has a dramatic affect on the activity of a

catalyst; the smaller the particle, the more active the catalyst. This can primarily be attributed to diffusion effects and, in the case of impregnated metal oxide catalysts, a more homogenous impregnation throughout the accessible mesopores. For pharmaceutical batch processes using powdered activated carbon catalysts, a carbon with a tight particle size distribution will result in better filterability, reducing production time.

Activated carbon catalyst support

Activated carbon is widely used as a catalyst support in granular, extruded and powdered form.

Because of the many different factors affecting catalytic activity, all catalyst manufacturers prepare a catalyst using a representative activated carbon sample and test its catalytic activity. Differing carbon supports can result in catalytic activities varying by as much as 2-5 times. For this reason numerous carbon substrates are usually tested.

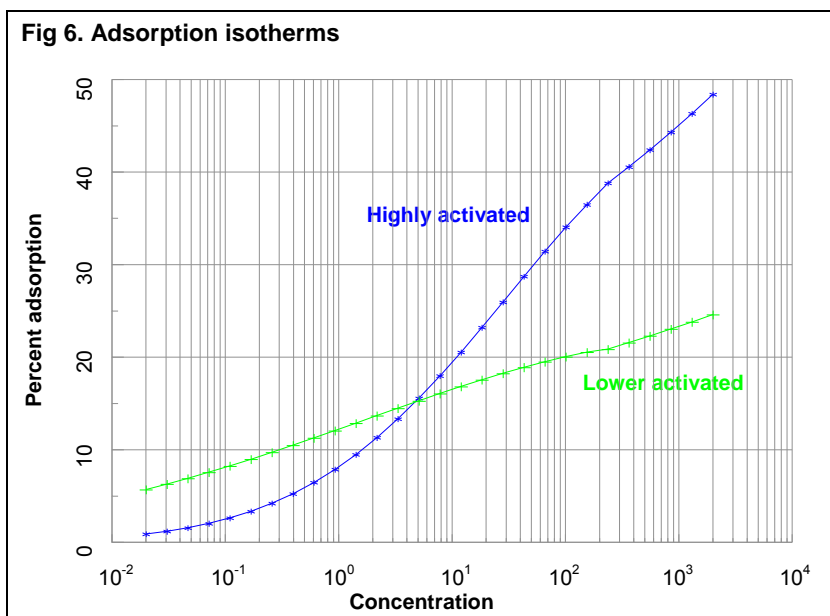
In one such case, a catalyst supplier evaluated more than five different powdered activated carbons for use as a precious metal catalyst carrier in pharmaceutical applications. It found that a highly porous, acid-washed, carbon provided the required purity and catalyst activity. It also found that particle size distribution of the carbon was critical to the catalyst performance.

Production of phosgene

For the production of phosgene, chlorine and carbon monoxide are reacted at elevated temperatures and pressures over an activated carbon catalyst. For this, a carbon of high mesoporosity usually offers the best conversion because the usefulness of the micropore surface area is limited by the rate of diffusion into and out of the pores.

Besides obtaining good conversion to phosgene, a hard carbon that will not break down and cause excessive pressure drop is required. For this reason, extruded carbons are most often employed.

A chemical manufacturer in the Midwest has successfully used a 4 mm extruded carbon of medium activity for phosgene production. The carbon reactors are typically changed out every three months because of loss of reaction efficiency.



Hardness is also important for granular carbon catalysts, as the catalyst is often used under extreme process conditions such as high pressure and temperatures.

Conclusion

Well over 150 different types of activated carbons are currently commercially available from Norit Americas Inc. Some carbons will be interchangeable for some applications with little or no effect to the process. In most cases, however, there will be an optimum carbon type that will be the most effective for certain processes.

Understanding the process stream and selecting an activated carbon with suitable properties is key to getting the most out of the process at minimum cost.

To receive more information on activated carbons and their applications call +1 800 641 9245 or visit our website at www.norit-americas.com.