SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CARBON MATERIALS

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A LITTLE HISTORY...

BC 3750	Egypt, Mesopotamia
1789	element (Lavoisier)
1961	IUPAC (^{12}C atomic mass unit)
1960	W. Libby
1991	S. Iijima CNT (1952 Radushkevich) Nobel nomination
1994	G. Oláh
1996	R. F. Curl Jr. Sir H. W. Kroto R. E. Smalley
2010	A. Geim, K. Novoselov

2

http://www.nobelprize.org/

THE WINNER IS….

”**Activated carbon**, characterized by its **exceptional adsorption properties**, has been identified as an **effective solution** for air and water pollution control, which is driving its demand in both mature and emerging markets across the globe. Besides **drinking water treatment** and **air purification**, activated carbon is also actively used in controlling **mercury emissions**, caused by burning of coal in power plants. With growing use in diverse end user industries, such as **mining, food & beverage, pharmaceuticals and chemical & petrochemical**, the global market for activated carbon is expected to post strong growth over the next five years.” (Global Activated Carbon Market Forecast and Opportunities, 2019)

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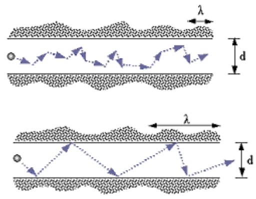
Expectations to be met

- Effective/reversible removal of molecules of different size
- Various conditions (T, conc./pressure)
- Selectivity
- Different chemical environment (humidity, pH, co-s)
- Different dynamics (static, flow)
- Different lifetime
- Regeneration



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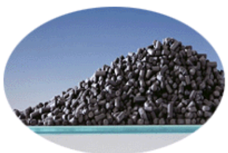
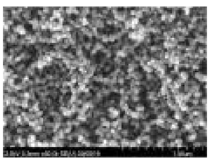
ACTIVATED/ACTIVE CARBON



Granular
0.6 - 4.0x10^{-3} m

Powder
15 - 25x10^{-6} m

Carbon fibre/cloth
10 - 30x10^{-6} m



Foam/aerogel

rigid / flexible

5 g porous carbon same area as a soccer field (500-3000 m^2/g)

Applications

Gas phase
Removal of volatile organic compounds (VOC) from air
Regeneration of organic solvents
Reduction of evaporation loss
Adsorption of landfill gas
Air conditioners
Mercury adsorption
Gasmasks
Vehicle outlet gas (SOx, NOx)
Gas storage (natural gas, hydrogen)
Gas separations (molecular sieve)
Energy storage devices (EDLC)

Catalyst support

Liquid phase
(Waste) water treatment
Food industry

Biomedical applications
haemoperfusion
detoxication

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SYNTHESIS

Precursor
Process

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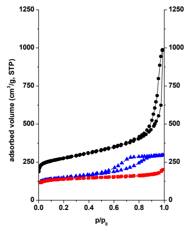
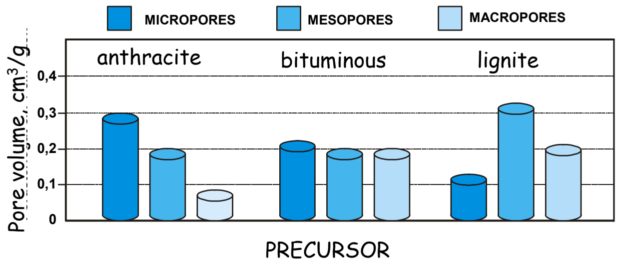
TRADITIONAL „MASS" PRECURSORS





500 000 t/year, ~ 7 %

bituminous $ 80/t (2015)

Precursors predestinate pore size distribution

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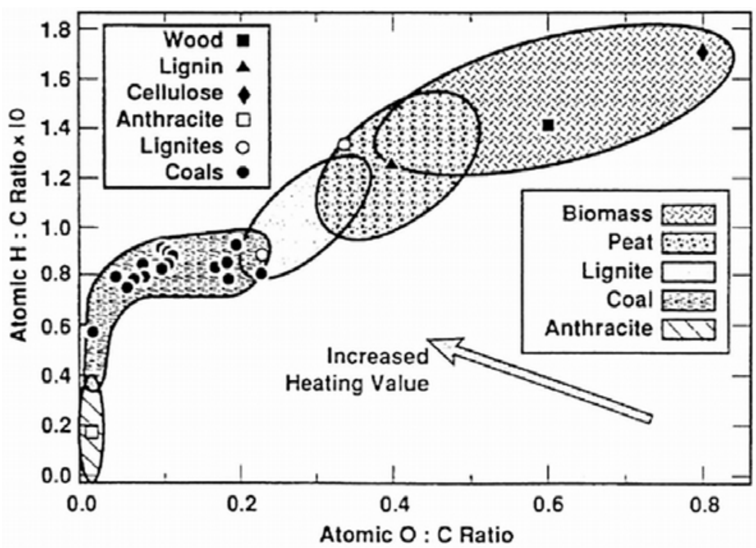
van Krevelen diagram



https://commons.wikimedia.org/wiki/File:Van_Krevelen_diagram_for_various_solid_fuels.jpg

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1. Physical activation

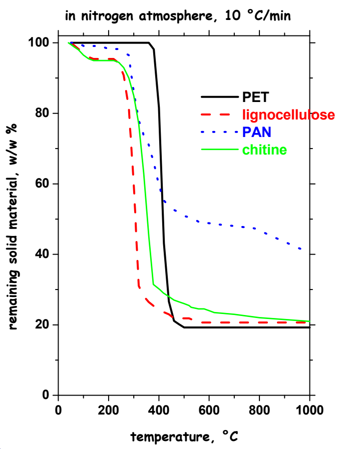
typically 2 steps

1st step: pyrolysis (inert atmosphere)

2nd step: activation (ash)

Activation agent

- Water vapor
- CO_2
- O_2
- O_3
- Air
- H_2O_2



2. Chemical

one-step (H_3PO_4, $ZnCl_2$, NaOH, KOH)

dehydration + prevention of tar formation

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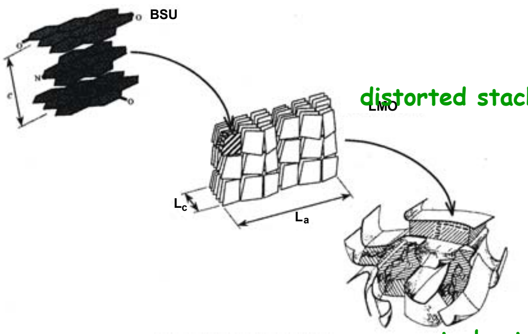
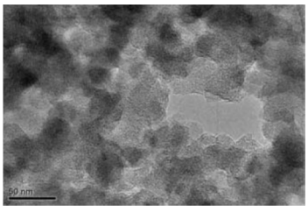
How does the porosity develop during the preparation?

small assembly of polyaromatic rings



distorted stacks

turbostratic structure



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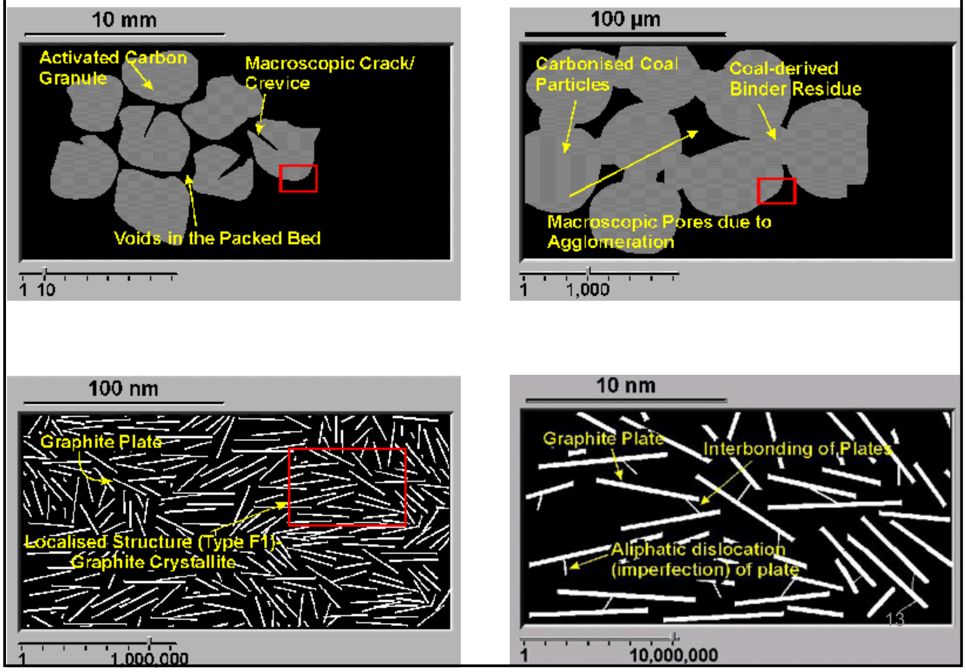
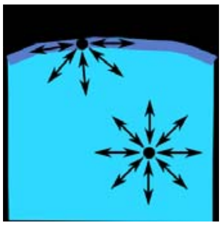
Oberlin, A. *Carbon* 1984

Morphology

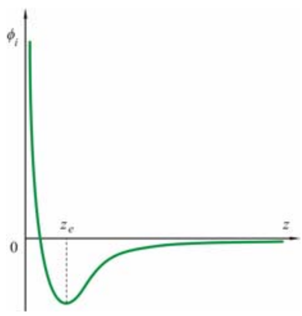


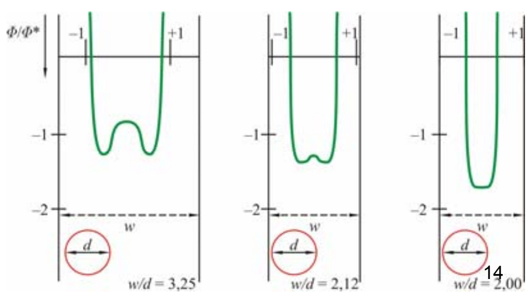
Consequences: high surface area complex porosity



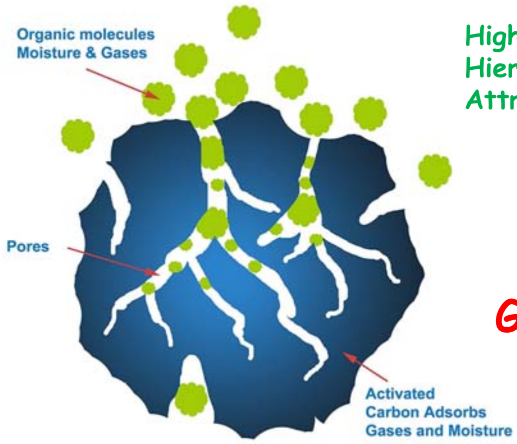
$$\gamma = \left(\frac{\partial G}{\partial A_S}\right)_{p,T}$$

Secondary forces





Morhology



High surface area
Hierarchical pore size distribution
Attraction by secondary forces

General adsorbent

https://www.amazon.co.uk/DRY-PURIFYTM-Dehumidifier-Deodorizer-Charcoal/dp/B01N2G842L

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Surface chemistry

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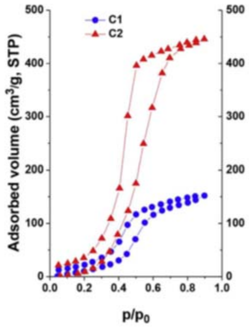
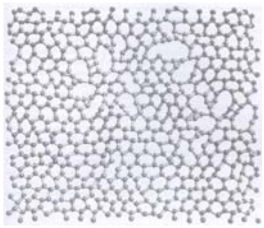
Hydrophobic (?)



1 Chemical heterogeneity of the carbon network



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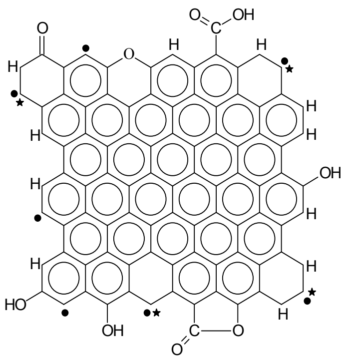
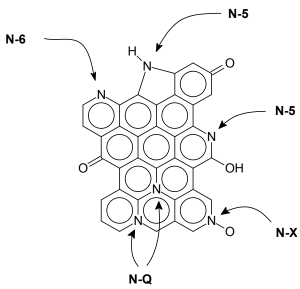
O'Malley, B. *et al*. *Phys Rev* 1998

2 Heteroatoms: H, O, S, N, B, P, Si, Me^{n+}, etc. (ash)

precursor/(chemical) treatment/impregnation/doping



O-containing functional groups at the edges
•:unpaired σ electron
•*: in-plane σ pair
*: localized π electron
Radovic, L. R. in *Surfaces of Nanoparticles and Porous Materials*. Marcel Dekker 1999



N-containing functional groups on carbon surfaces
N-6: pyridinic,
N-5: pyrrolic/pyridone,
N-Q: quaternary,
N-X: N-oxide
Kapteijn, F. *Carbon* 1999

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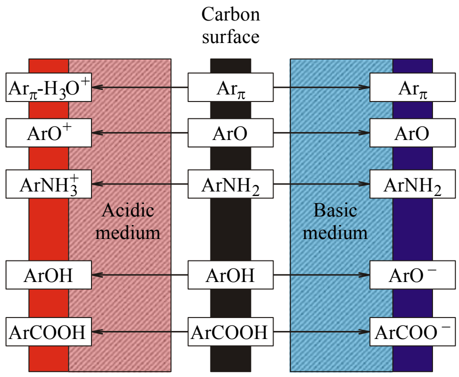
AMPHOTERIC CHARACTER



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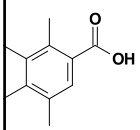
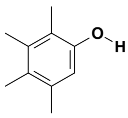
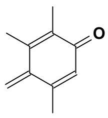
Acid/base - Brønsted & Lewis



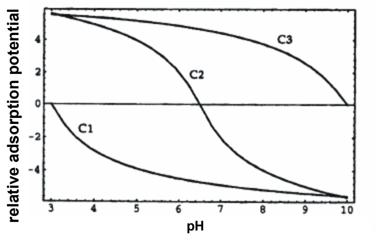
carboxyl

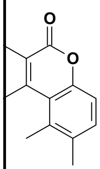


phenol

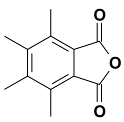


quinone

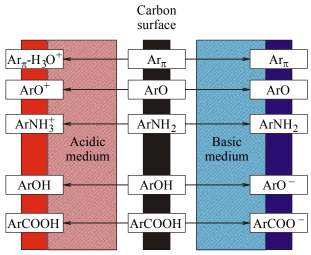


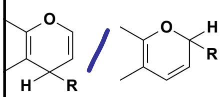


lactonic

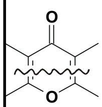


anhydrid





chromene



pyrone

$NaHCO_3$ pK_a= 6,37
Na_2CO_3 pK_a= 10,25
NaOH pK_a=15,74
HCl

carboxyl
+ lactonic
++ phenol
basic groups

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$$C_\pi + H_2O \rightarrow C_\pi H_3O^+ + OH^-$$

Böhm, H. P. *et al. Angew. Chem. Int. Ed. Engl.* 1964

POTENTIAL FAILINGS OF THE APPLICATION

*sensitivity to erosion
*susceptibility to oxidation
*catalyst
…

B $sp^2 \rightarrow sp^3$

(i) graphitization enhancement,
(ii) boron oxide-oxygen diffusion barrier, site blocking film
(iii) complex disruption of the delocalized π-electrons and a possible redistribution of the electrons

P **C-P-O** or **C-O-P** at graphene edges → blocking active sites
¿ **P** in the aromatic system?

Si **C-SiO_2** or **SiC** (T > 1400 - 1450 °C)

Impregnation: Sensitize for a limited number of target chemicals (vs catalyst support)

iodine
silver
Al, Mn, Zn, Fe, Li, Ca
transient metals: Cu, Mo, etc.

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COMPLEX CHARACTERIZATION IS REQUIRED

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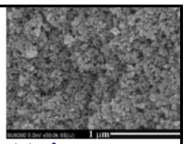
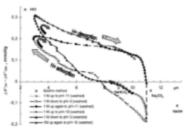
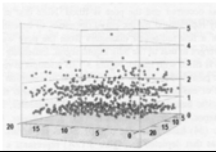


morphology:
- microscopies
- gas adsorption (N2/Ar, CO2)
- particle size
- small and wide angle scattering (SAXS, SANS, WAXS)
- NMR (cryoporosimetry)

surface chemistry:
- H2O
- „dry” methods (methods and information obtained):
  - elemental analysis, EDX, XPS, FTIR, Raman, IGC, TPD, NMR
- „wet” methods:
  - calorimetry (immersion, flow, etc.),
  - pH, point of zero charge, surface charge
  - titration methods (Böhm, potentiometric titration),
  - adsorption (organics, dyes, ions)



modelling:
- MC, DFT, engineering



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HOW TO SELECT A CARBON?

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Application oriented standardized test methods
AS CLOSE AS POSSIBLE TO APPLICATION CONDITIONS

BET surface area, PSD
Iodine number
Molasses number
Phenol uptake
Methylene blue
Dechlorination
Apparent density
Hardness/abrasion number
Ash content
Carbon tetrachloride activity
Particle size distribution

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IS IT WORTHWHILE TO WORK IN CARBON DEVELOPMENT?

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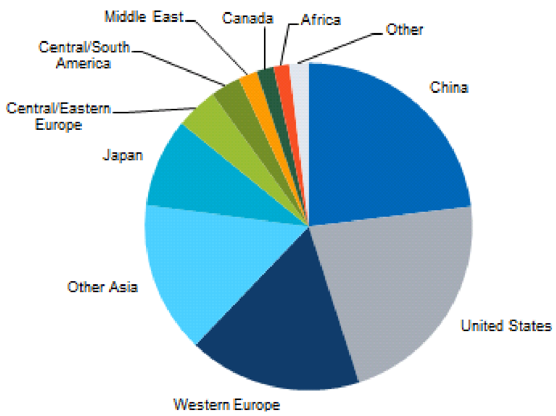
Global activated carbon (AC) consumption 2016



- total world capacity has grown by ~ 400,000 metric tons since 2012
- forecast global average annual growth rate for AC will be ca 3.5% through 2021
- water treatment 41%;
- air and gas purification 30%;
- food processing applications 14%

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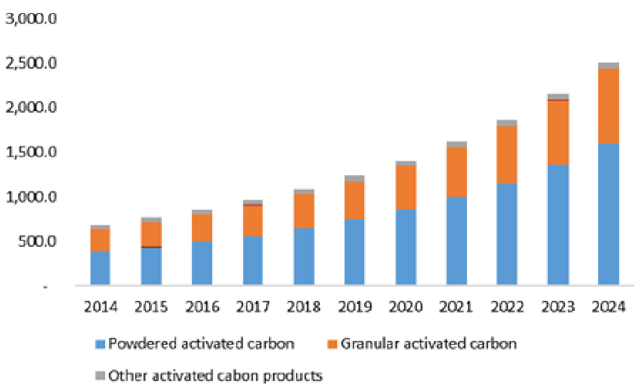
https://ihsmarkit.com/products/activated-carbon-chemical-economics-handbook.html

U.S. activated carbon market revenue by product, 2014 - 2024 (USD Million)



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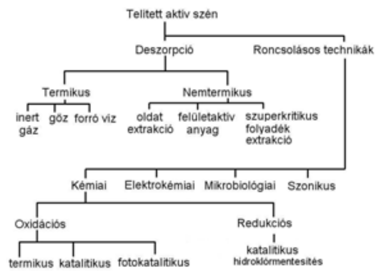
https://www.grandviewresearch.com/industry-analysis/activated-carbon-market

Regeneration of activated carbon (vs. hazardous waste)

Thermal regeneration
about 800 °C, controlled atmosphere
widely used
disadvantages: high cost
energy intensive
high carbon losses

Further regeneration techniques
Chemical and solvent regeneration
Microbial regeneration
Electrochemical regeneration
Ultrasonic regeneration
Wet air oxidation



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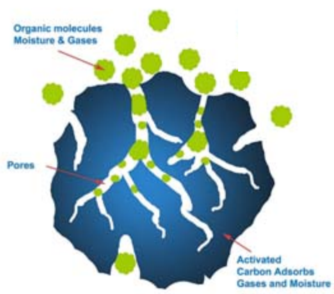
ACTIVATED CARBON: A GENERAL ADSORBENT

The „activity" of activated carbons stems from
*high surface area 500-3000 m^2/g
*complex and hierarchical porosity
(micro, meso, macro and beyond)
*chemical heterogeneity
*secondary interaction forces



TUNABLE

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