Adsorption Technology in Water treatment

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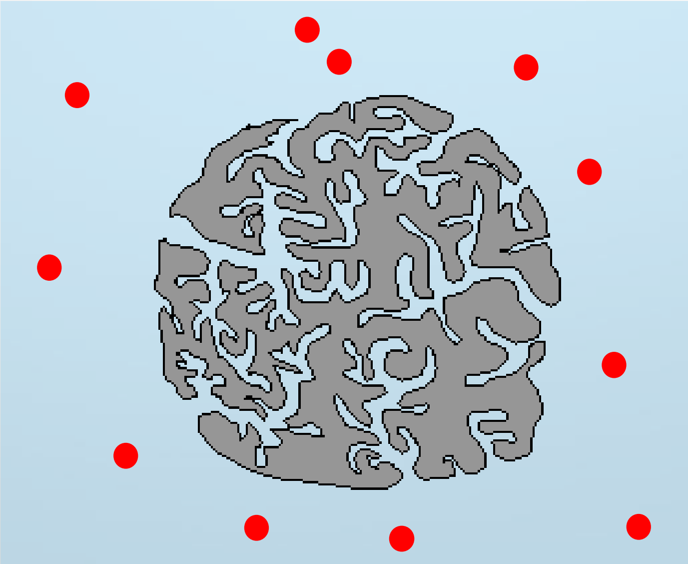
Agenda

- Terms
- Types of adsorption
- Application
- Equilibrium
- Adsorption rate
- Affecting factors
- Ion exchange
- Common adsorbents
- Activated carbon
- Low-cost adsorbents
- Examples of engineered adsorbents

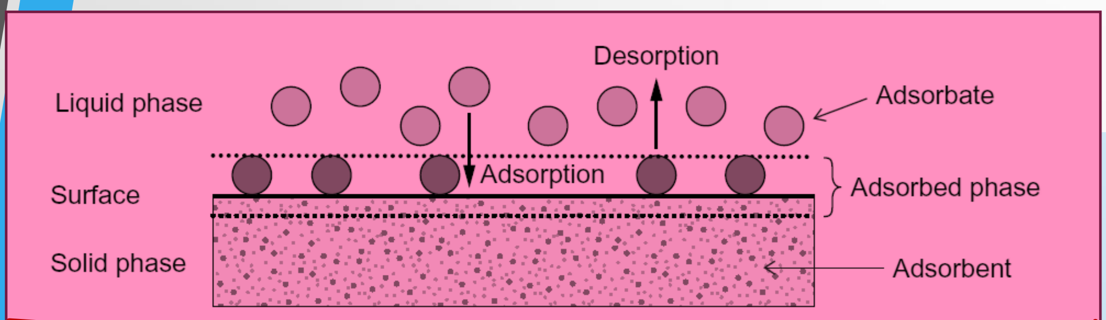
Adsorption

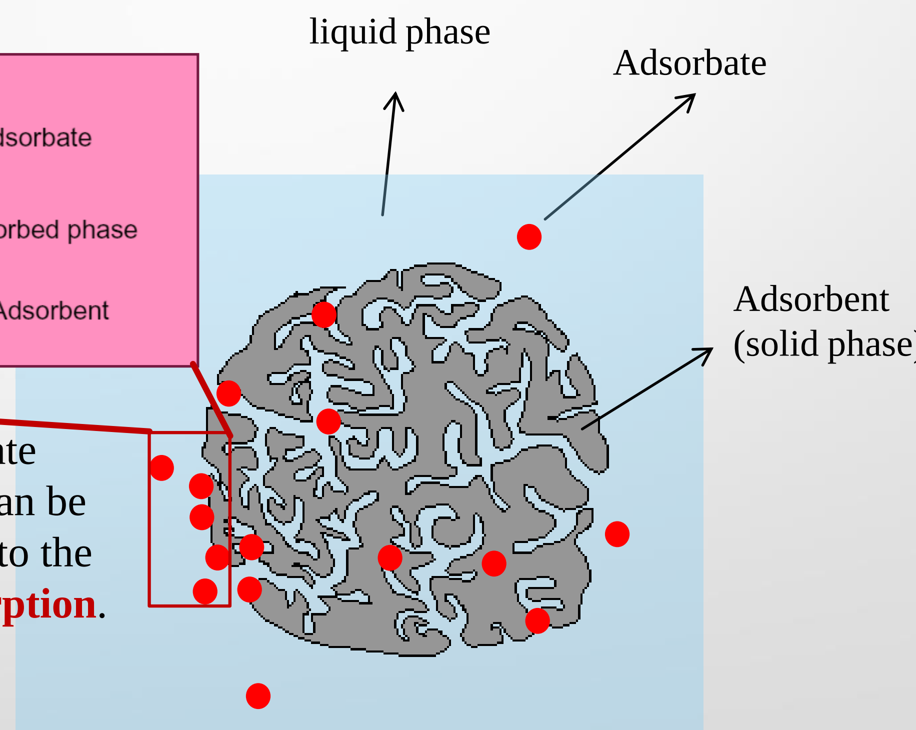
A process through which a substance, originally present in a fluid phase, is removed from that phase by *accumulation at the interface* between that phase and a separate (solid) phase



Terms

- Adsorbate or solute: the species being adsorbed
- Adsorbent: the solid material being used as the adsorbing phase





By changing liquid phase properties e.g., adsorbate concentration or temperature, adsorbed species can be released from the surface and transferred back into the liquid phase. This reverse process is called **desorption**.

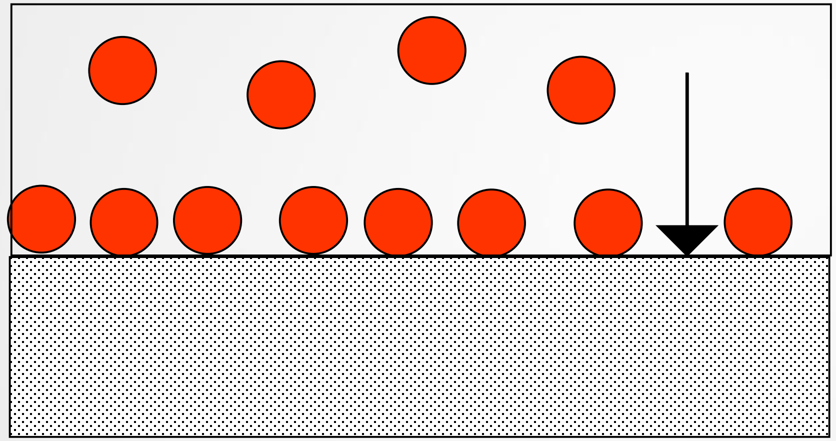
Adsorption vs. Absorption

Phase I

(fluid)

Phase II

(solid)



Adsorption

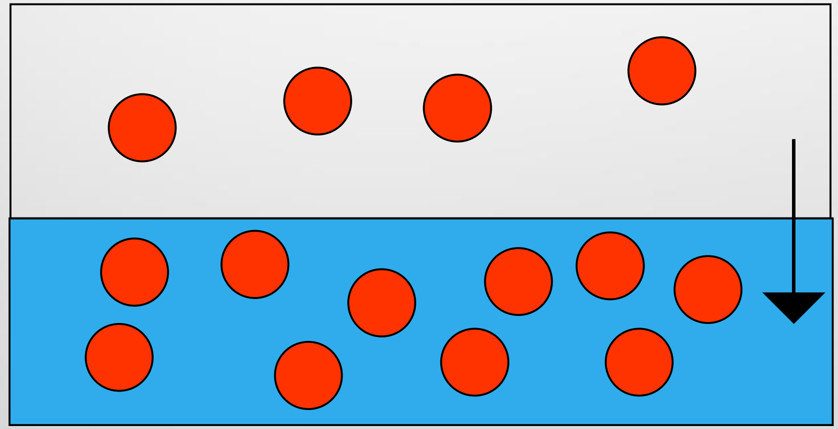
Interface (accumulation)

Phase I

(fluid)

Phase II

(fluid)



Absorption

Interface (passing trough)

Causation of Adsorption

- Lack of solvent-solute interactions (hydrophobicity –surfactants)
- Specific solid-solute interaction
  - van der Waals forces: physical attraction
  - electrostatic forces
  - chemical forces (e.g., π- and hydrogen bonding)

Types of Adsorption

- Physical adsorption (physisorption):

  Physical attractive forces (relatively weak interactions e.g., van der Waals forces)

- Chemical adsorption (chemisorption):

  The adsorbed molecules are held to the surface by covalent forces. (little application in water treatment)

Application Where/Why?

If we have to remove soluble material from a solution, but the material is neither volatile nor biodegradable, we often employ adsorption.

- Simple to operate!
- Efficiency
- Reasonable capital and operating cost
- Small footprint
- Flexibility – use of different media products
- Residual disposal usually not a major issue

Adsorption Capacity

- The amount of adsorbate adsorbed per unit mass of adsorbent (q, mg/g)

$$q = V.\ (C_{initial} - C_{final})\ /m$$

m: mass of adsorbent (g)

V: solution valume (L)

C : adsorbate concentration

Adsorption Equilibrium

$$\text{Adsorbate} + \text{adsorbent} \underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

The adsorbent and adsorbate are in contact long enough

→

Equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution

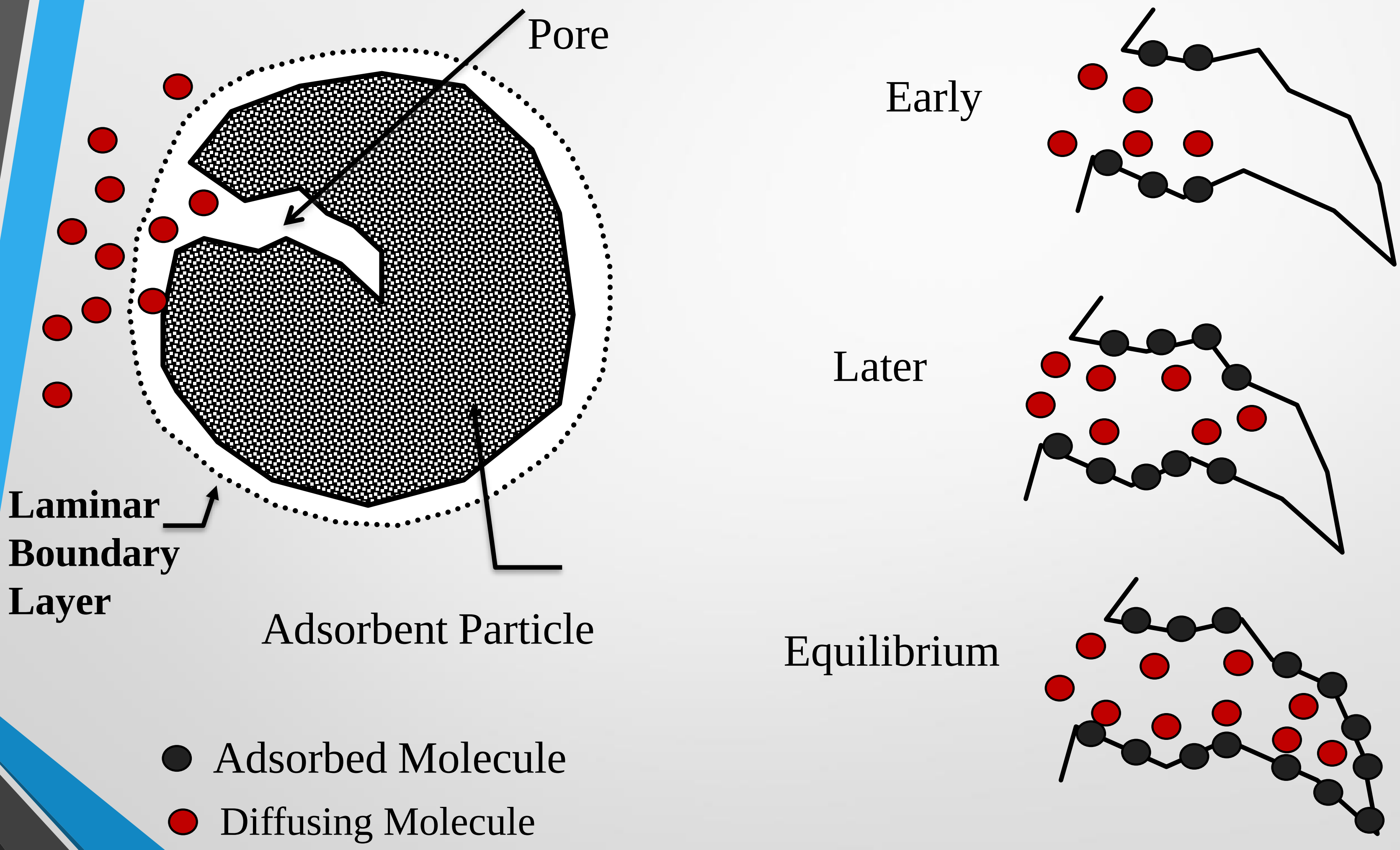
Adsorption Equilibrium

- Adsorption equilibrium data provides the basis for assessing the adsorption processes and, in particular, for adsorber design.

- Information about the equilibrium in a considered adsorbate/adsorbent system is necessary, for instance, to characterize the adsorbability of water pollutants, to select an appropriate adsorbent, and to design batch, continuous flow, or fixed-bed adsorbers.

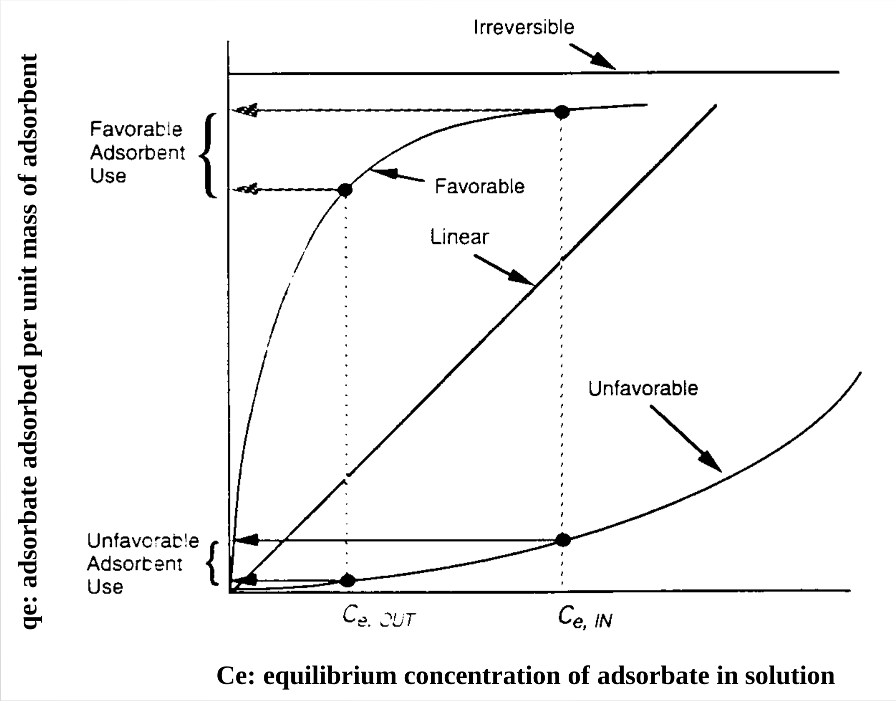
- The equilibrium stage in a considered system depends on the strength of the adsorbate/adsorbent interactions and is significantly affected by the properties of the adsorbate and the adsorbent but also by properties of the aqueous solution, such as temperature, pH value, and occurrence of competing adsorbates.

Adsorption Equilibrium



Adsorption Isotherm

Typically, the dependence of the adsorbed amount on the equilibrium concentration is determined experimentally at constant temperature, and the measured data are subsequently described by an appropriate isotherm equation.



Isotherm models

Langmuir Isotherm

assumes monolayer coverage and constant binding energy between surface and adsorbate.

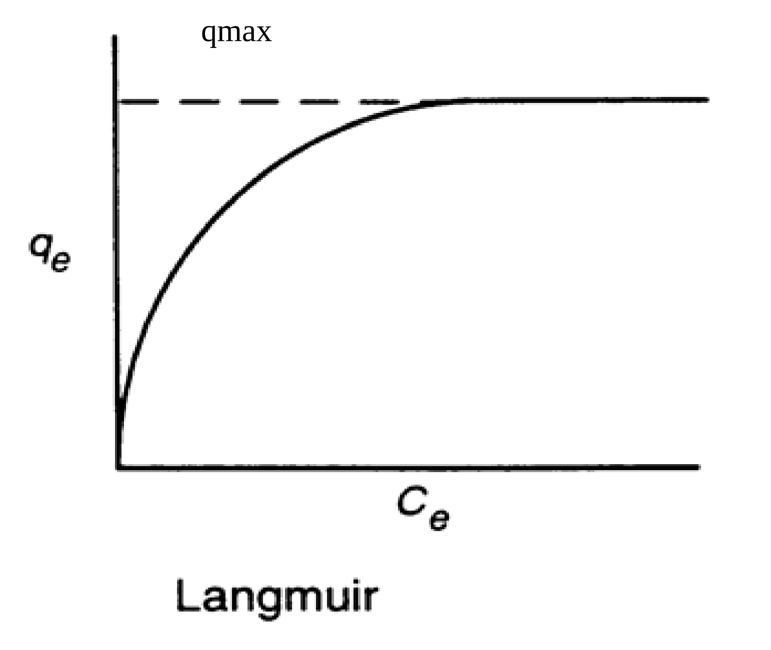
Non-linear

$$q_e = \frac{K \times q\max \times C_e}{1 + K \times C_e}$$

Linear

$$\frac{Ce}{qe} = \frac{1}{K \times q\max} + \frac{Ce}{q\max}$$

qe: mg/g
Ce: mg/L
K : Langmuir constant



Isotherm models

Non-linear

$$q_e = K_F C_e^{1/n}$$

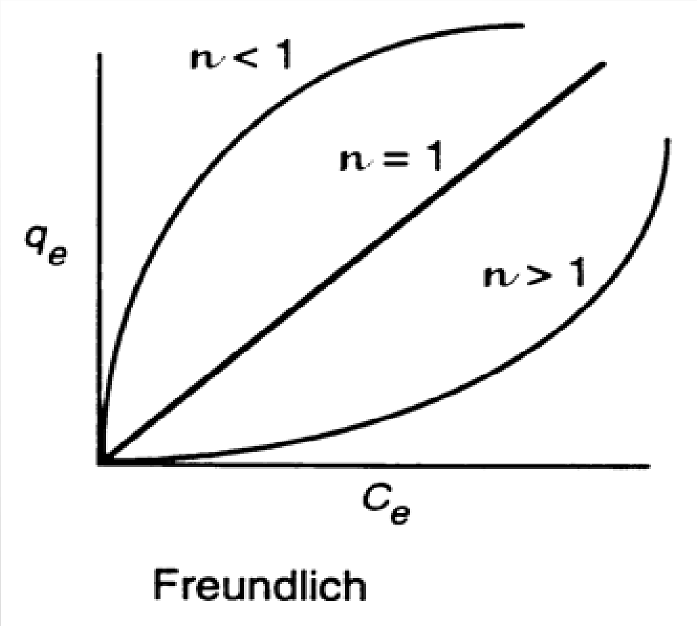
Linear

$$\log q_e = \log K_F + 1/n \log C_e$$

qe: mg/g
Ce: mg/L
K : Langmuir constant

Freundlich Isotherm:

Freundlich model is used for the special case of heterogeneous surface energies.

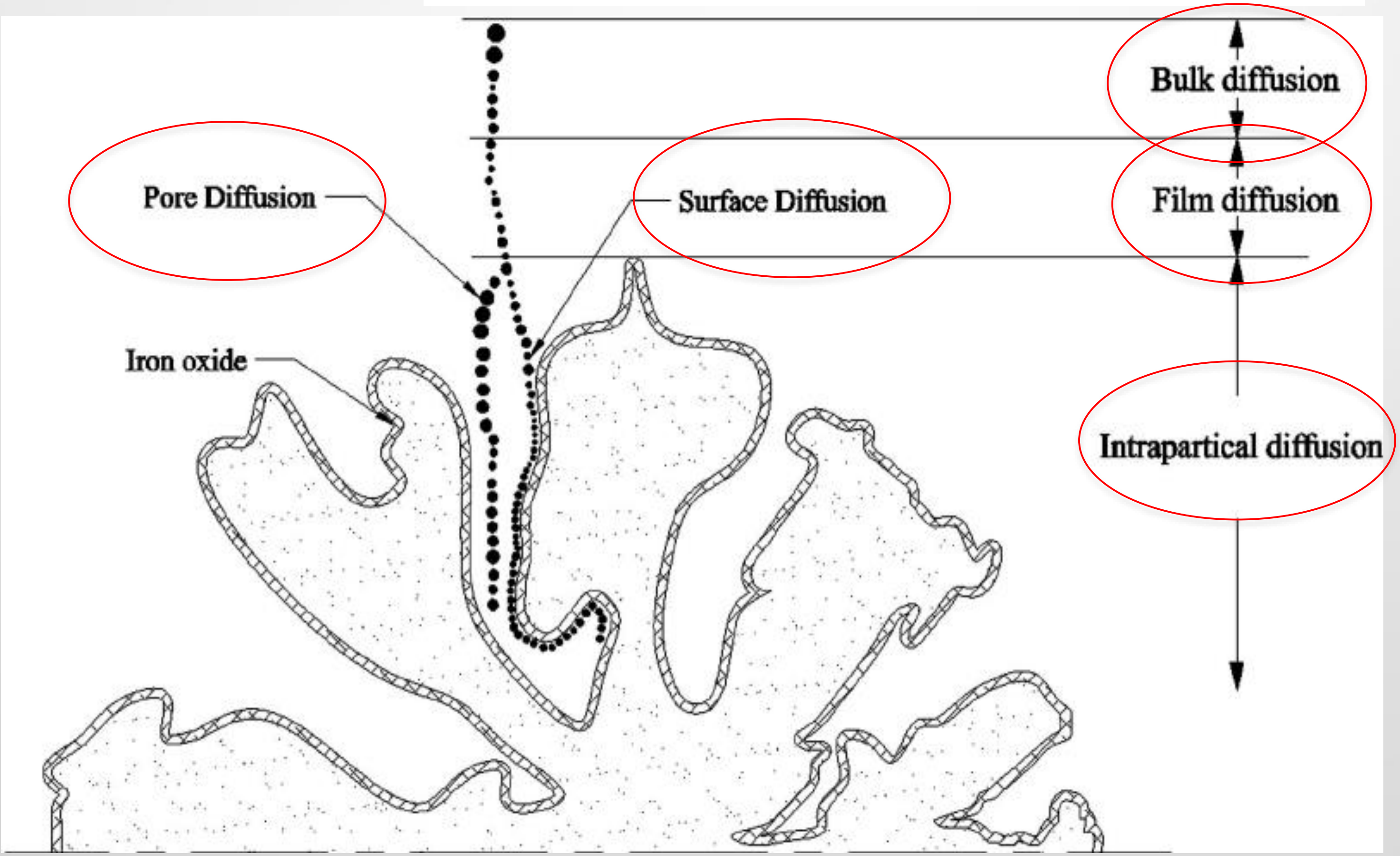


Adsorption Rate

Which step controls adsorption rate?

For most operating conditions, film diffusion is rate-limiting. if sufficient turbulence is provided, transport of the adsorbate within the porous is rate-limiting.

Primary rate steps:



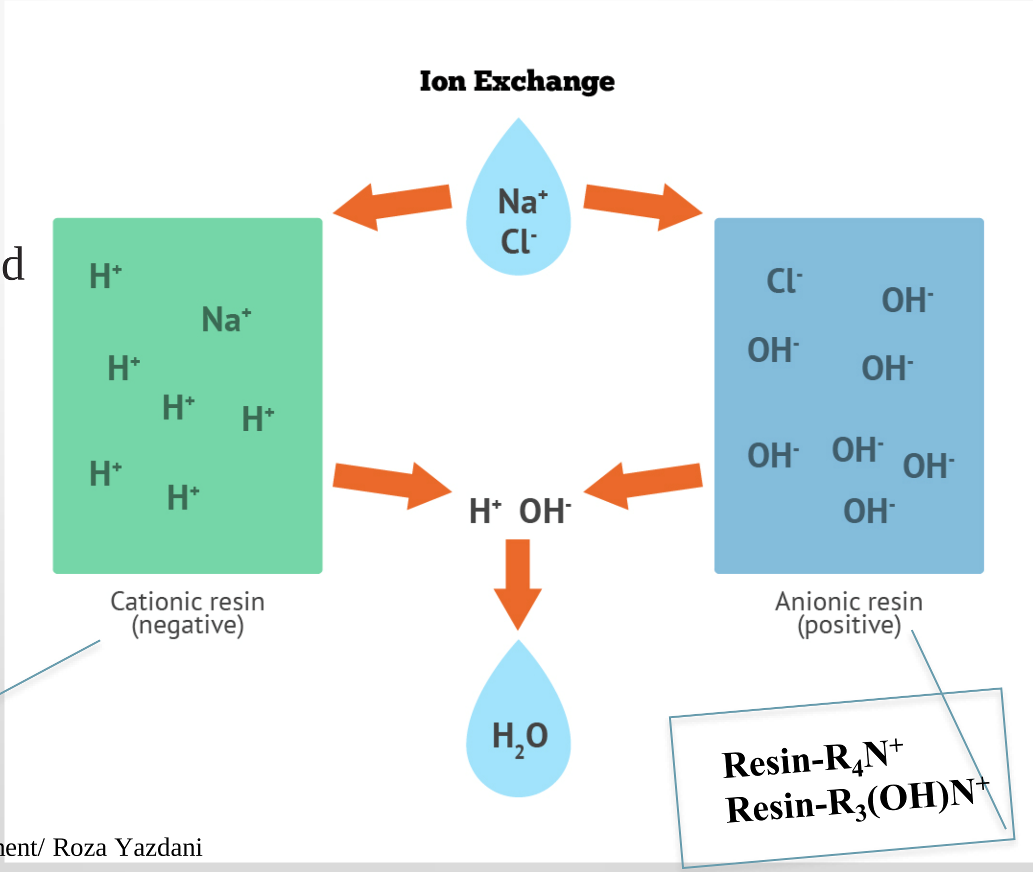
Affecting Factors

- Solubility of the adsolute (pollutant) in the liquid
- Concentration of adsorbate in the liquid phase
- Characteristics of the liquid phase (pH, temperature,…)
- Contact time
- Surface properties of adsorbent (surface area, surface charge,…)
- Particle size and pores distribution of adsorbent

Ion exchange

An exchange of ions between an electrolyte solution and a complex. The processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

In ion exchange process ions attached to a stationary functional group exchange for ions in a solution. Ions are exchanged on an equivalence basis.



Resin-SO_3^-
Resin-COO^-

Resin-R_4N^+
Resin-$R_3(OH)N^+$

Ion exchange: Terms

Counterion: Ion in solution that can exchange with an ion attached to a stationary functional group.

Presaturant ion: Ion that comes attached to the virgin resin or is exchanged onto the resin during the regeneration process.

Selectivity: Preference of one ion over another for exchange onto an ion exchange site on a resin.

Separation factor: Quantitative description of the preference of one ion over another for a given ion exchange resin.

Ion exchange: Terms

Strong acid cation resin: Ion exchange resin that will readily give up a proton over a wide pH range.

Strong base anion resin: Ion exchange resin that will readily give up a hydroxide ion if the pH is less 13.

Synthetic resins: Spherical beads that contain a network of crosslinked polymers containing functional groups.

Common Adsorbents

- **Activated carbon (chemical functional groups)**
  - Adsorbent of organics (esp. hydrophobic)

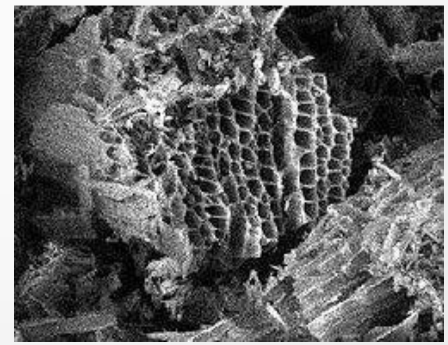
- **Metal oxides (surface charge depends on pH)**
  - Adsorbent of Natural organic matter (NOM)
  - Adsorbent of inorganics

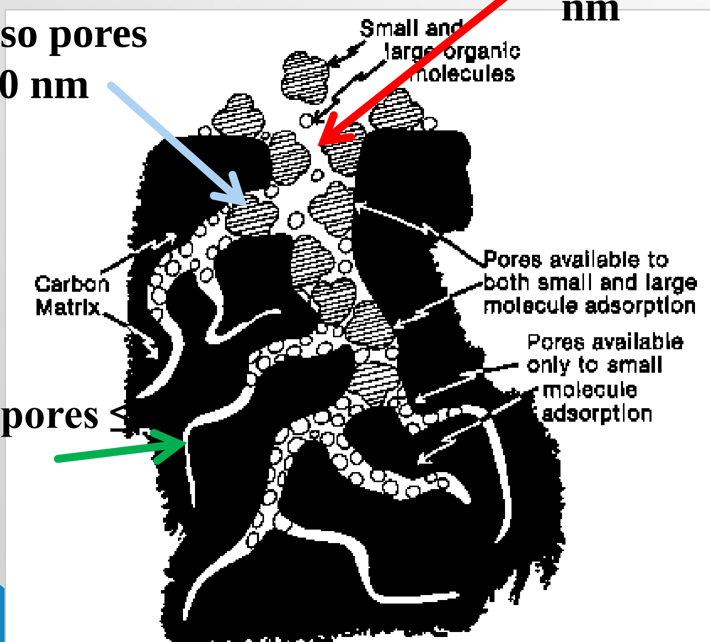
  (both cations & anions)

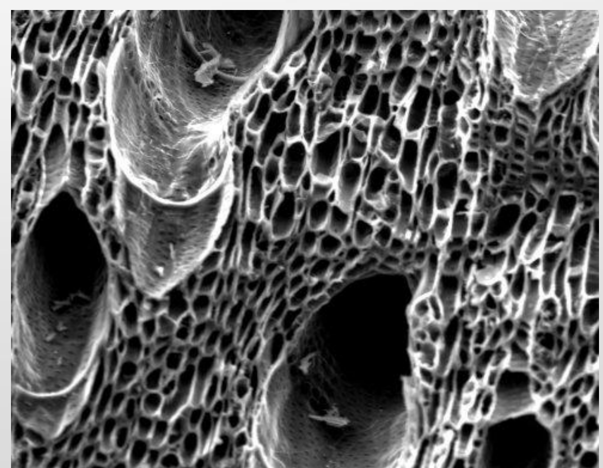
- **Ion exchange resins**
  - Cations and anions
  - Hardness removal (Ca^{2+}, Mg^{2+})
  - Arsenic

Activated Carbon

- The most common adsorbent
- Adsorptive properties/high surface area





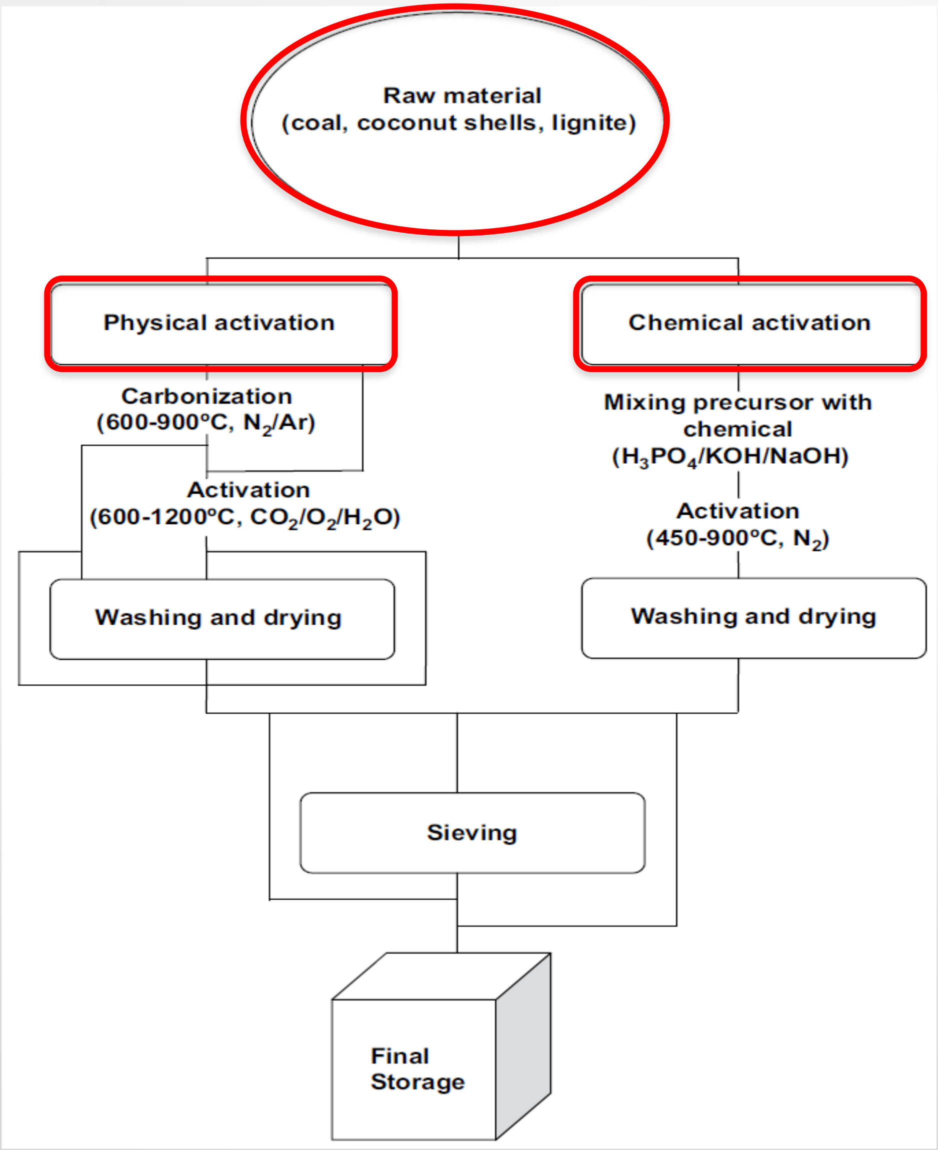


Activated Carbon

➢ **Granular Activated Carbon (GAC)**
Particle size: larger than 0.1 mm
used in *packed beds*

➢ **Powered Activated Carbon (PAC)**
Particle size: smaller than 100 µm
used by direct addition

Production of Activated Carbon



Properties of Activated Carbon

Factors Affecting Activated Carbon Properties?

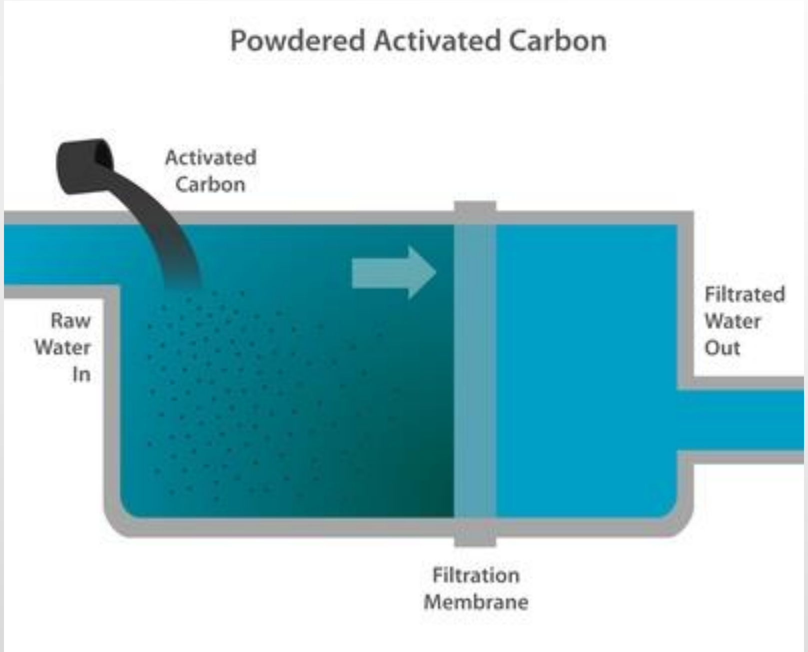
- Initial materials e.g., wood, lignin, coal, petroleum residues…
- Activation method
- Pores and pore size distributions
- Internal surface area
- Surface chemistry (esp. polarity)
- Apparent density
- Particle Size: Granular vs. Powdered

Activated Carbon Systems

generally consist of vessels in which granular carbon is placed, forming a filter bed through which influent passes.

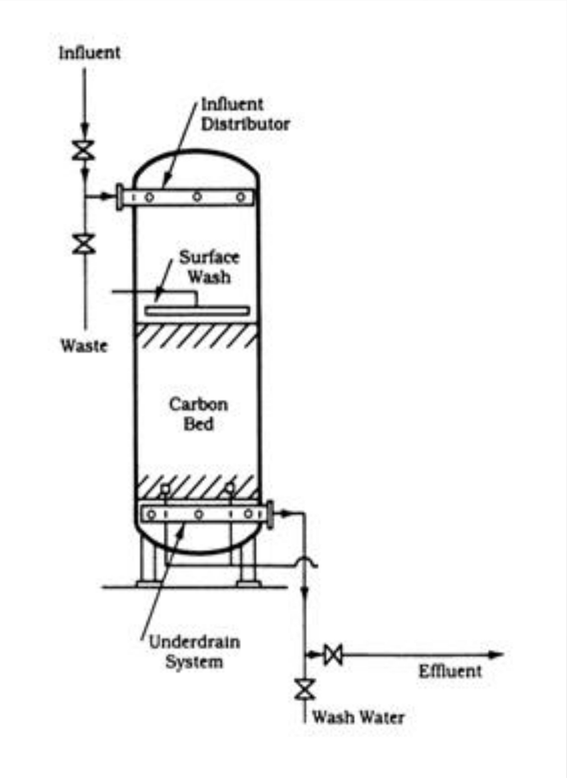
Activated Carbon Systems

Powdered activated carbon is often used when temporary quality problems arise; it can simply be added to the water.



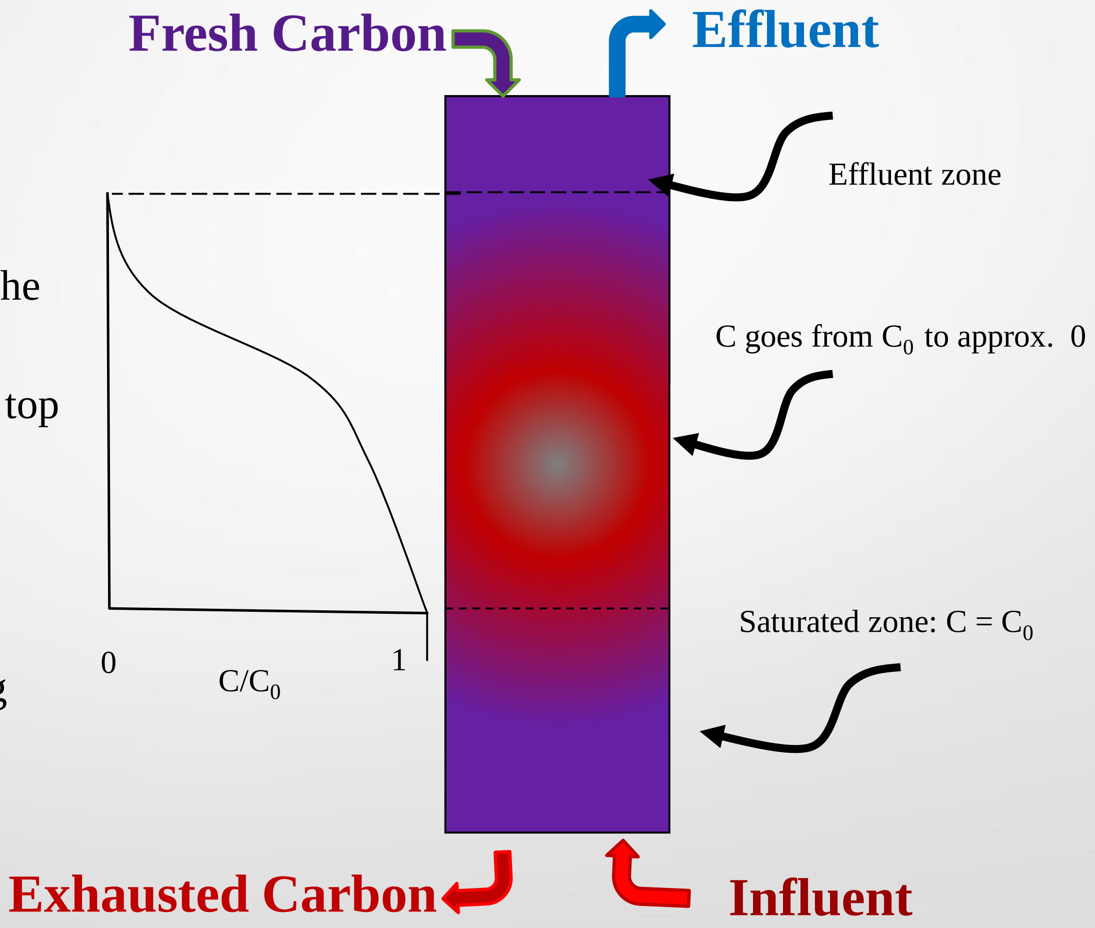
Fixed carbon bed contactors

- provide filtration and adsorption.
- have to be periodically backwashed or cleaned.

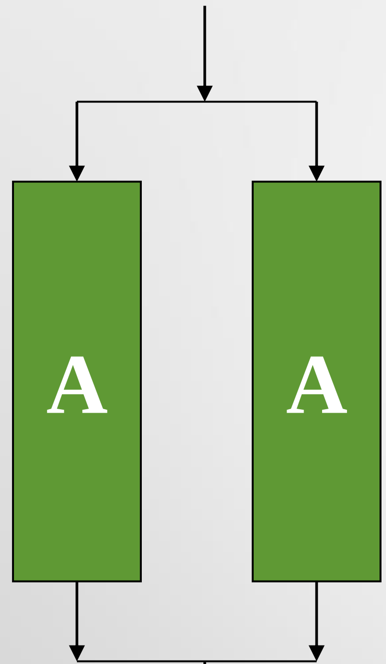


Fluidized bed mode (up-flow)

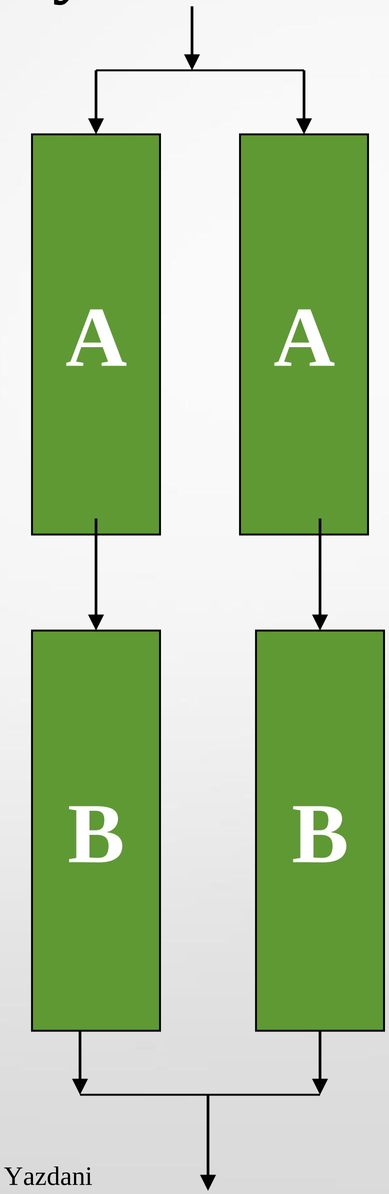
- Fluidized beds do not filter.
- Exhausted carbon is continuously removed from the bottom.
- Fresh carbon is added to the top at the same rate.
- This eliminates the need to shutdown the contactor after exhaustion occurs.
- Up-flow minimizes clogging and unintentional filtration.



Carbon Contactors System Configuration



Simple Parallel Design

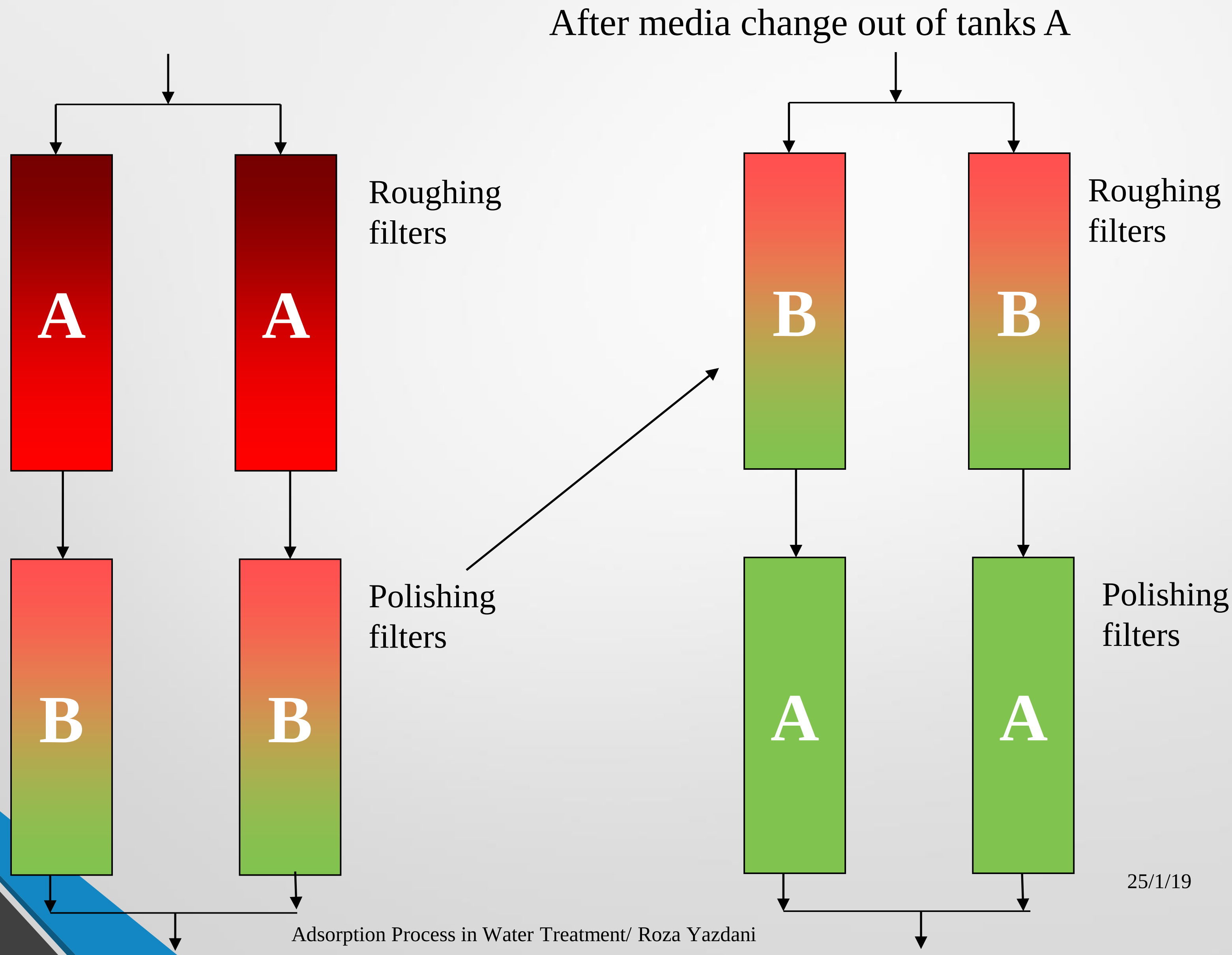


Roughing filters

Polishing filters

Series Design

System Configuration



System Configuration

Series - Advantages

- More conservative – added safety
- Maximum use of media

Series – Disadvantages

- Higher capital cost – more tanks
- Higher pressure drop
- Problems in backwashing

Difficulties in full scale application

In full scale application AC usually behaves differently than controlled lab tests, why?

NOM

Bio-film

Carbon Regeneration

Removing the previously adsorbed materials from the carbon pore structure

- Thermal
- Steam
- Solvent extraction
- Acid / base treatment
- Chemical Oxidation

Problems associated with Activated Carbon

higher cost

after use → **exhausted** → no adsorption capacity

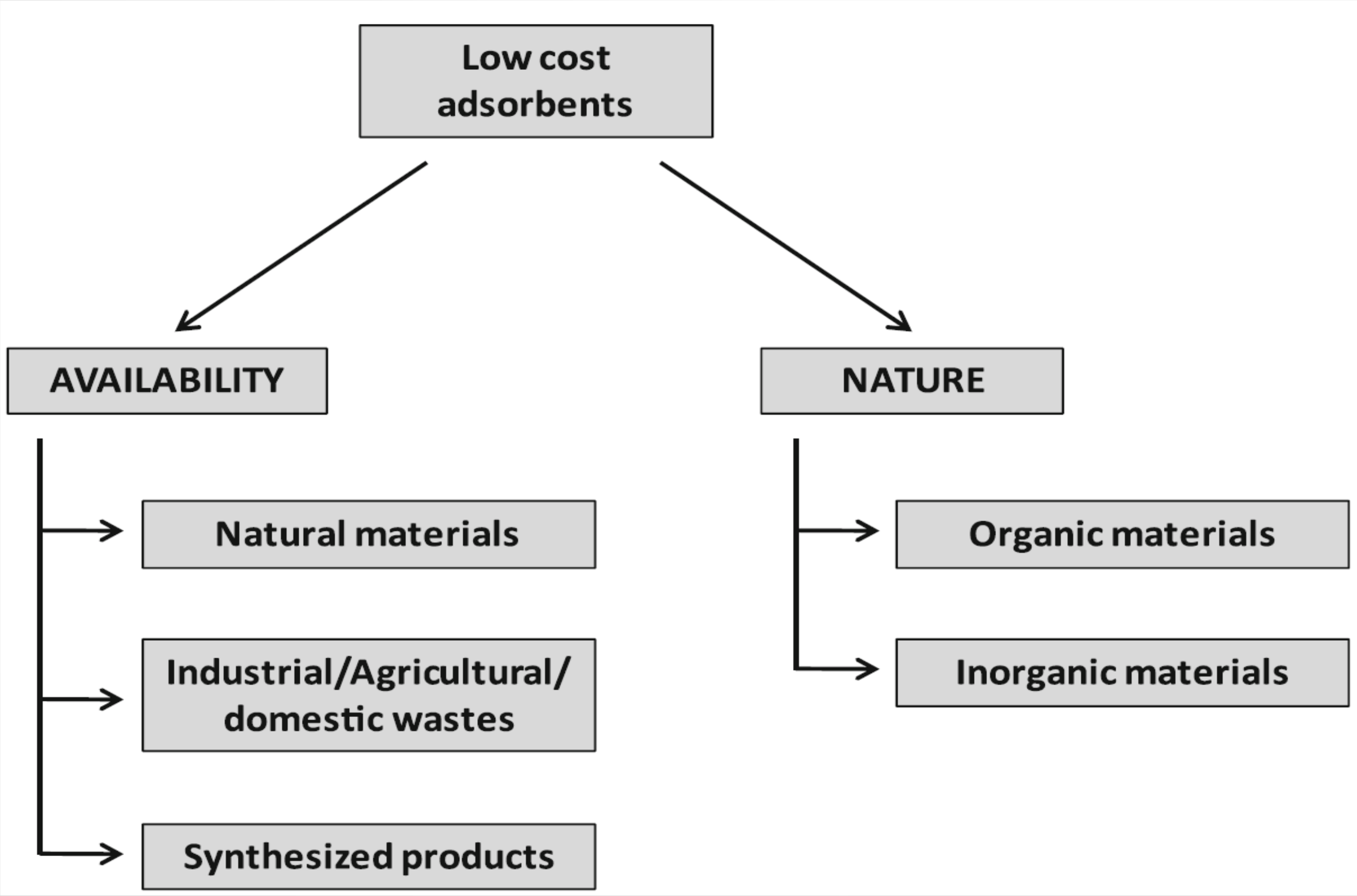
be **regenerated** → for further use

regeneration → **additional cost**

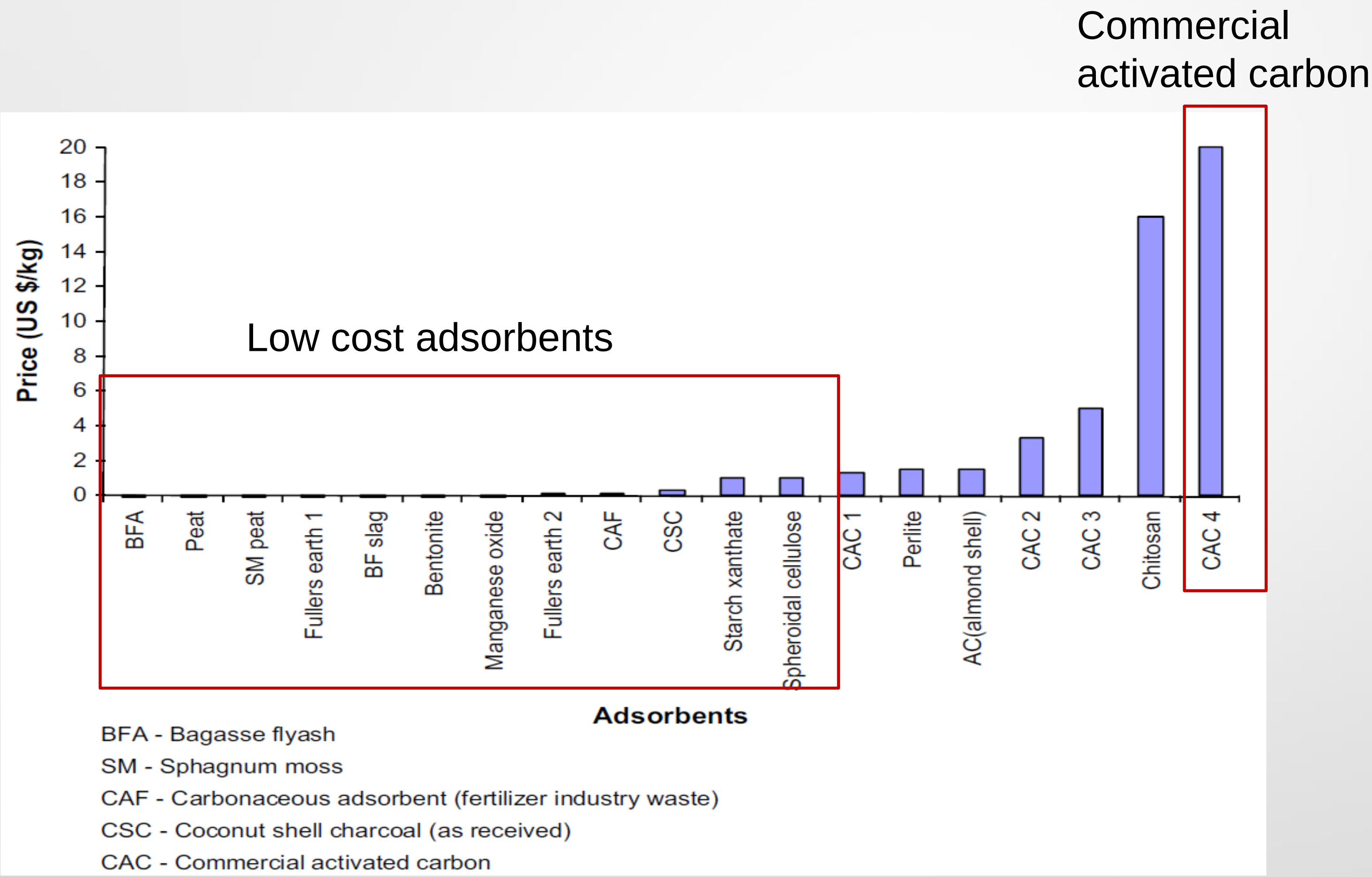
Regeneration → **carbon loss** → lower adsorption capacity

Alternative adsorbents

Possible classification of low-cost adsorbents



Low-cost adsorbents cost comparison

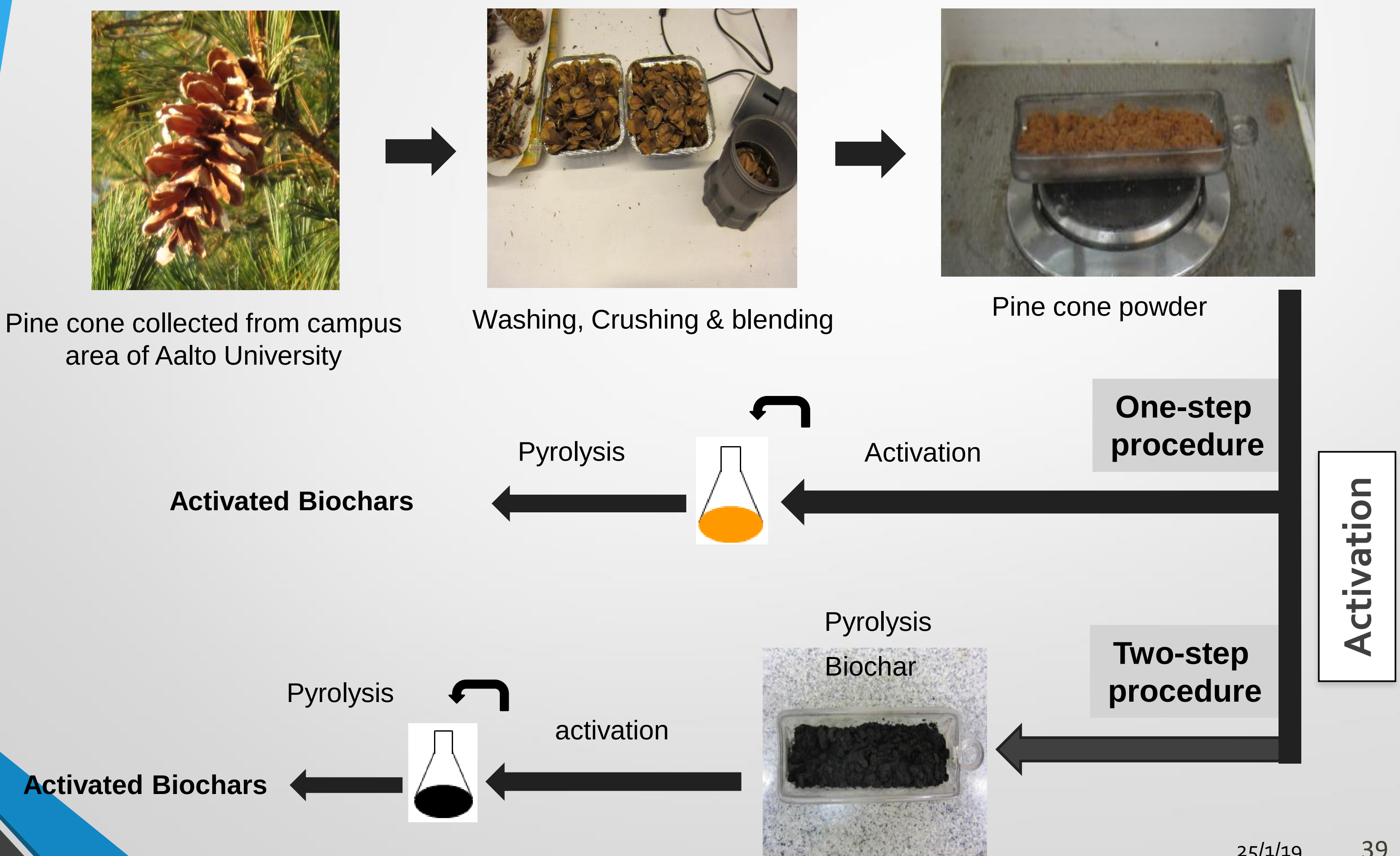


Masters Thesis Example

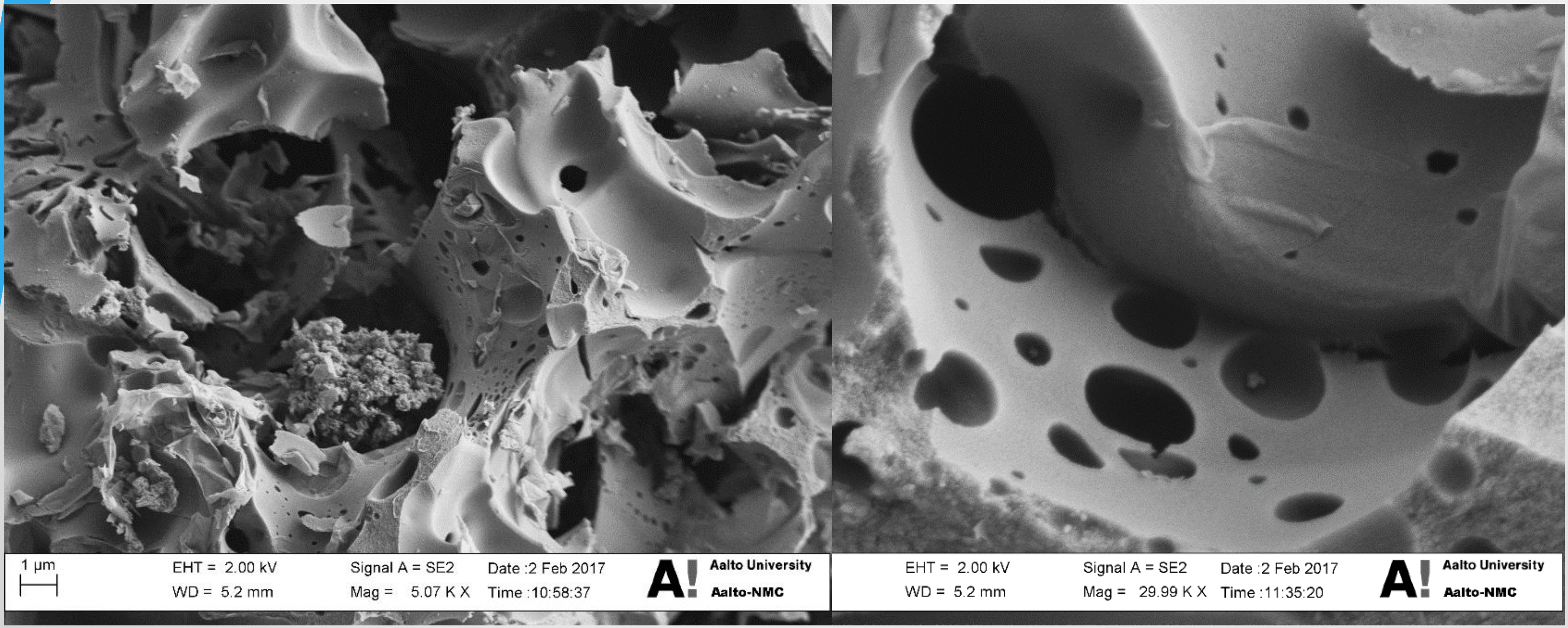
Enhanced NOM removal from lake water samples using Pine-cone activated carbon (biochar)

- **Phase (I)**: Biochar production, activation and characterization
- **Phase (II)**: NOM removal from lake water samples via adsorption batch mode

Pine-cone biochar production & activation



Pine-cone biochar characterization:
Scanning electron microscopy



Batch adsorption tests

Enhanced NOM Removal with Pine-cone Biochar