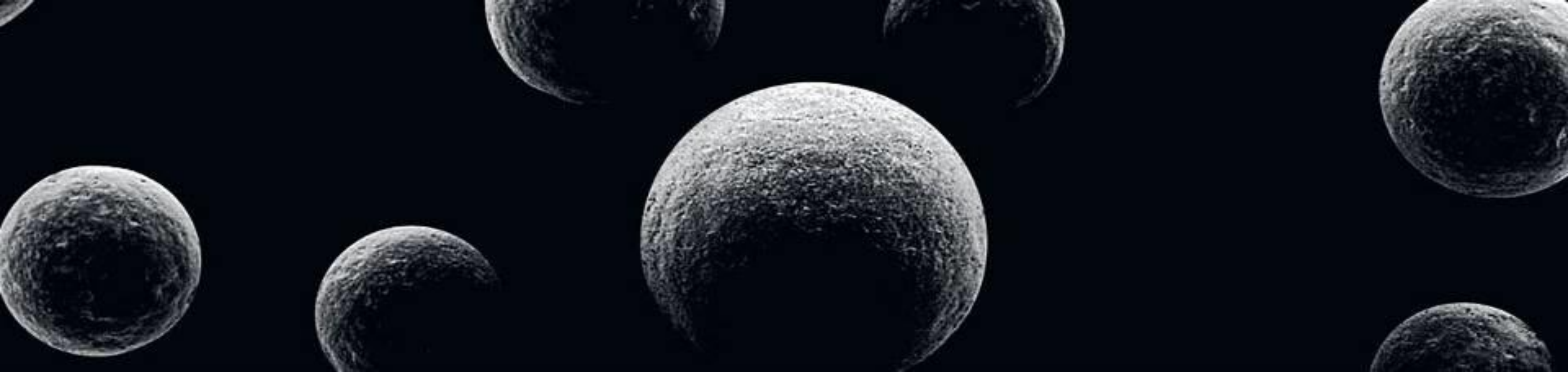


# MODIFIED ACTIVATED CARBON FOR DYNAMIC SOPRTION AND REACTION APPLICATIONS

DR. BERTRAM BÖHRINGER

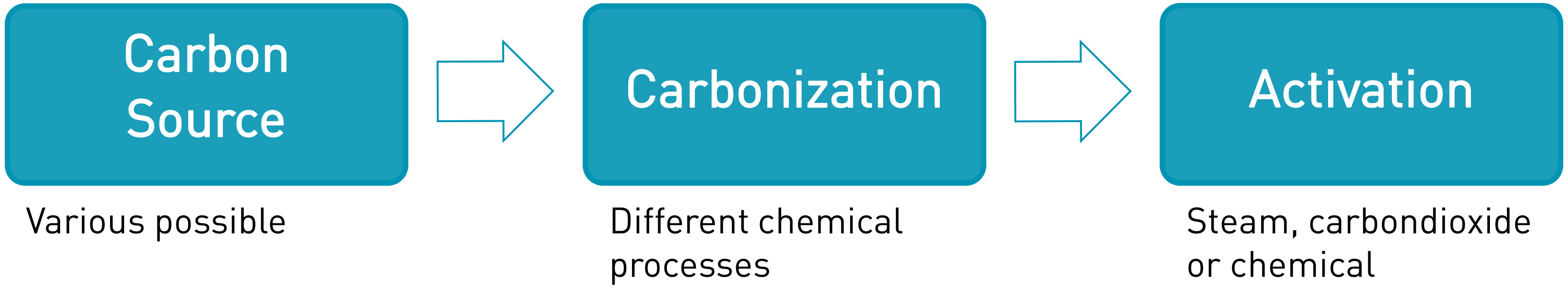
MAY 14, 2019

LEIPZIGER SYMPOSIUM "DYNAMISCHE SORPTIONSVERFAHREN“

BLÜCHER®
protects

# HOW TO MANUFACTURE AND CHARACTERIZE ACTIVATED CARBON

# SCHEMATIC SKETCH OF ACTIVATED CARBON PRODUCTION



**Carbon Source**

Various possible

**Carbonization**

Different chemical processes

**Activation**

Steam, carbondioxide or chemical

# ACTIVATED CARBONS

Raw Materials (carbon source)

- Coal
- Wood
- Nutshell
- Peat
- Polymer

Forms of AC

- Powdered
- Granular
- Pelletized
- Spherical
- Woven

Marked: Basis of SARATECH polymer based spherical activated carbon (PBSAC)

# REMOVAL OF PHARMACEUTICAL ACTIVE AGENTS FROM INDUSTRIAL WASTE WATER

# PHARMACEUTICAL WASTE WATER

| | |
|---|---|
| **Phase I** | Proof of feasibility |
| **Phase II** | On-site trials with plug and play unit (SARATECH®- Pilot plant) |
| **Phase III** | Scale-up to an industrial wastewater treatment plant |

# PHARMACEUTICAL WASTE WATER - APPROACH

## RAW WATER DATA

| | Concentration median | Concentration max. |
|---|---|---|
| **AOX** | 12 mg/l | 15 mg/l |
| **COD** | 1.542 mg/l | 3.837 mg/l |
| **Annual volume** | 340 $m^3$ | |

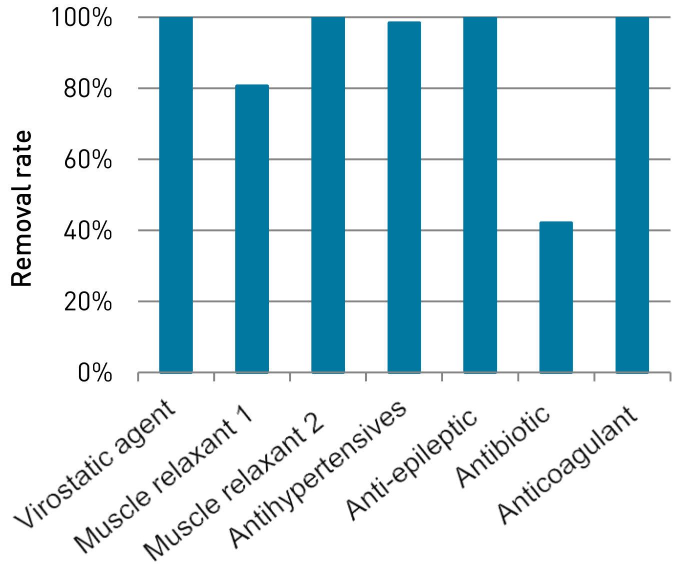
Challenges:

- High volumes of wastewater to dispose
- Variation in volume, composition and quality of waste water
- Complex mixture of substances
- Lack of data on adsorption capacities necessary for engineering

→ Pharmaceutical wastewater requires a tailor-made treatment system

# PHARMACEUTICAL WASTE WATER – LABORATORY RESULTS

- Excellent Removal of a Range of Pharmaceutical Agents

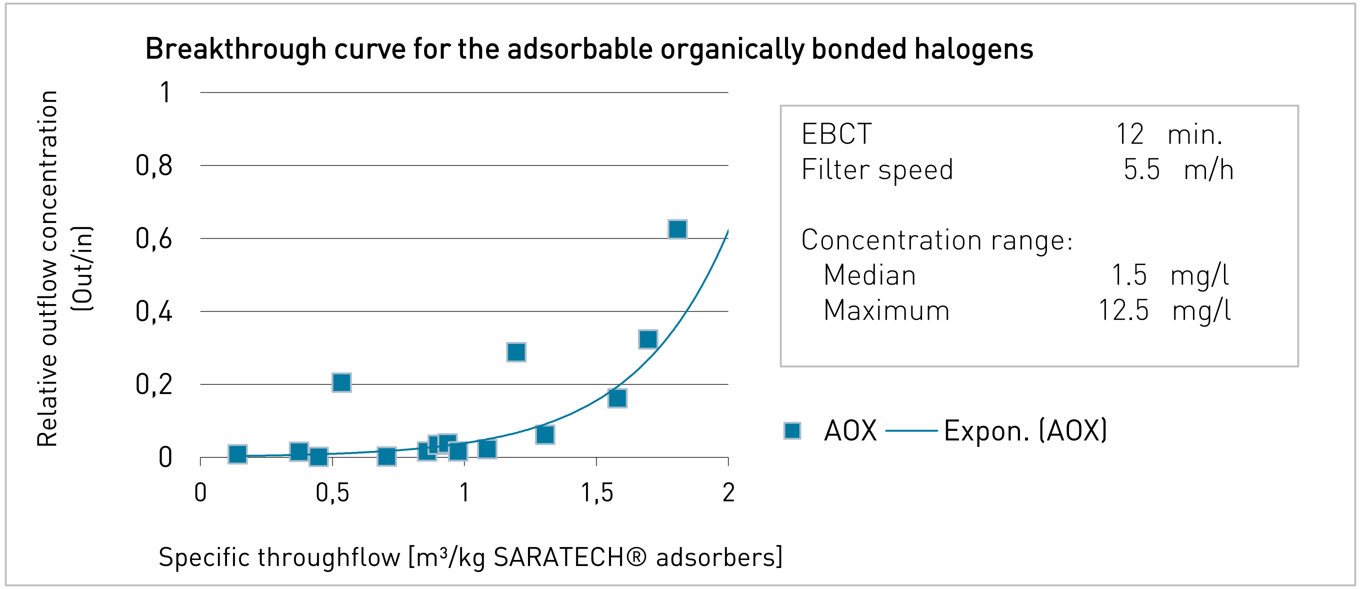


**Static trial using wastewater from a pharmaceutical manufacturer**

| | | |
|---|---|---|
| Adsorbent conc. | 250 | mg/l |
| Concentration range: | | |
| Minimum | 0.06 | mg/l |
| Maximum | 3.45 | mg/l |

Source: TZW, Karlsruhe

# PHARMACEUTICAL WASTE WATER – PILOT PLANT


Breakthrough curve for the adsorbable organically bonded halogens

Specific throughflow [m³/kg SARATECH® adsorbers]

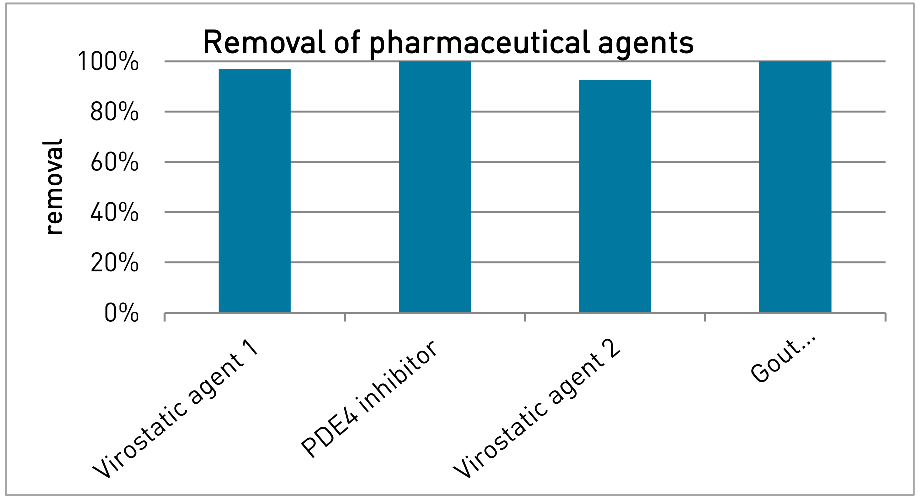
| | |
|---|---|
| EBCT | 12 min. |
| Filter speed | 5.5 m/h |
| Concentration range: | |
| Median | 1.5 mg/l |
| Maximum | 12.5 mg/l |

- Mobile plant → Determination of breakthrough curves and design parameters
- Simple to integrate without interrupting operations
- Small footprint (approx. 1 m²) and low weight (approx. 50 kg)
    - Ready to connect
    - PLC controller with optional remote access

SARATECH® protects

BLÜCHER® protects

# PHARMACEUTICAL WASTE WATER – TREATMENT PLANT

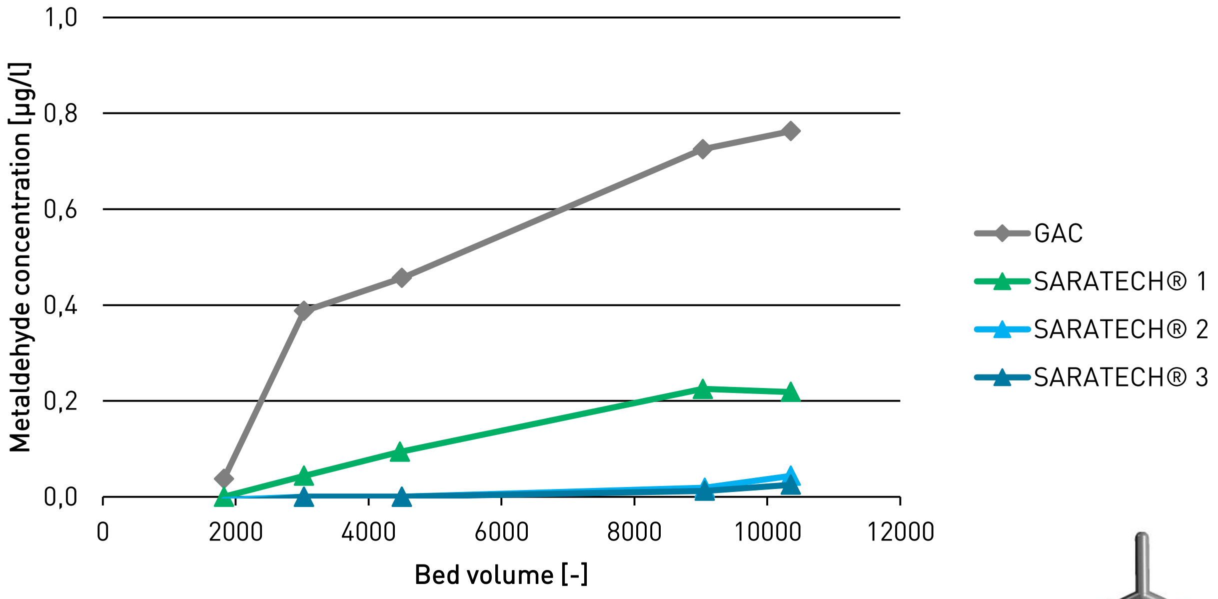


- High removal rate of pharmaceutical agents (› 90 %)
- Compliance with the regulatory limits for COD and AOX in Wastewater
- **Significant cost savings compared with other disposal alternatives**

# REMOVAL OF PESTICIDES FROM DRINKING WATER

# EFFECTIVE REMOVAL OF PESTICIDES FROM DRINKING WATER

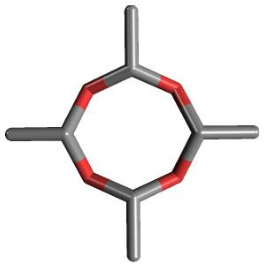
## NO BREAKTHROUGH OF PESTICIDES WITH SARATECH®

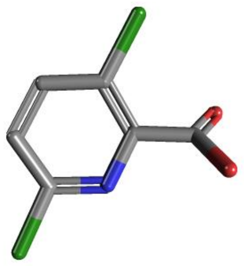


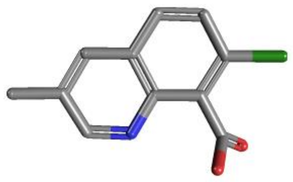
**<u>Dynamic</u> trial with drinking water (natural DOC), SARATECH® as polisher**

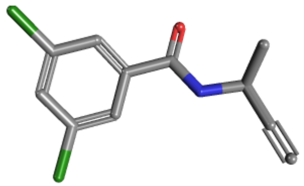
| | | |
|---|---|---|
| EBCT | 2 | min. |
| Throughput | 0.9 | l/h |
| Inlet concentration: | | |
| Median | 0.1 | µg/l |
| Maximum (peak) | 1.6 | µg/l |

Source: Water Research Centre Limited , UK (2016)


Metaldehyde

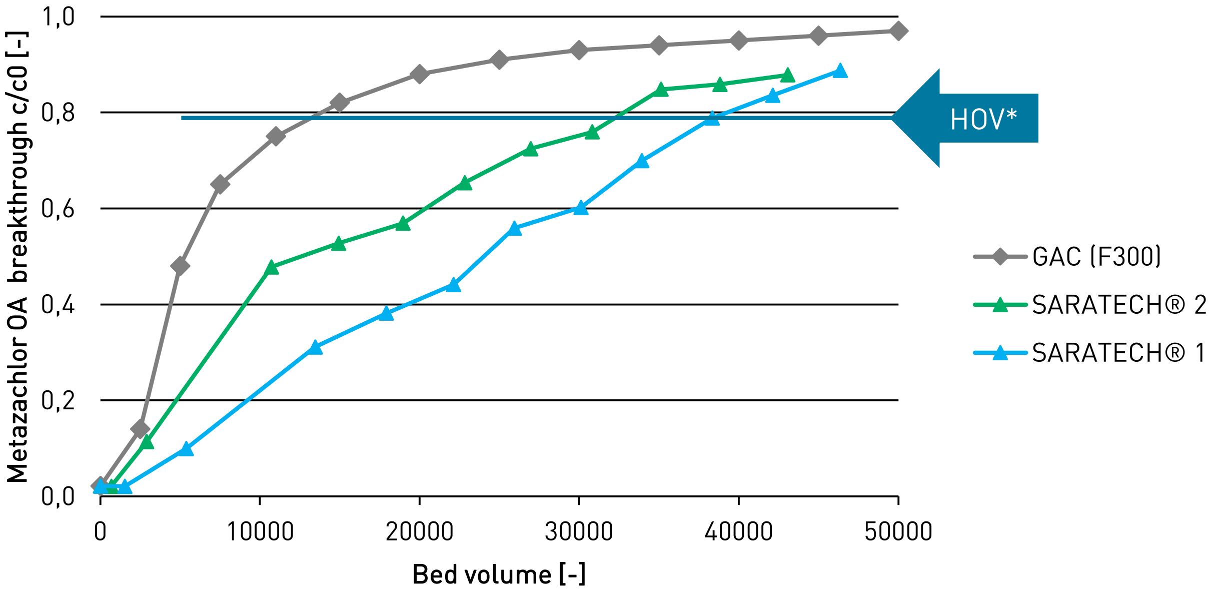

Clopyralid


Quinmerac


Propyzamide

# EFFECTIVE REMOVAL OF PESTICIDES FROM DRINKING WATER

## LONGER SERVICE LIFE WITH SARATECH®

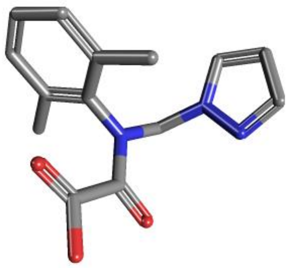


**Dynamic trial with drinking water (natural DOC), SARATECH® as polisher**

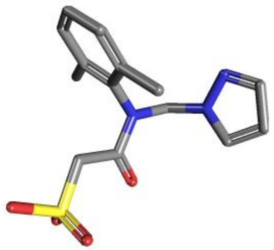
| | | |
|---|---|---|
| EBCT | 5.2 | min. |
| Filter speed | 9.8 | m/h |
| Throughput | 25 | $m^3/h$ |
| Inlet concentration: | | |
| Median | 2.2 | µg/l |

Source: VFTV e.V. (2016)

*HOV = Health Orientation Value



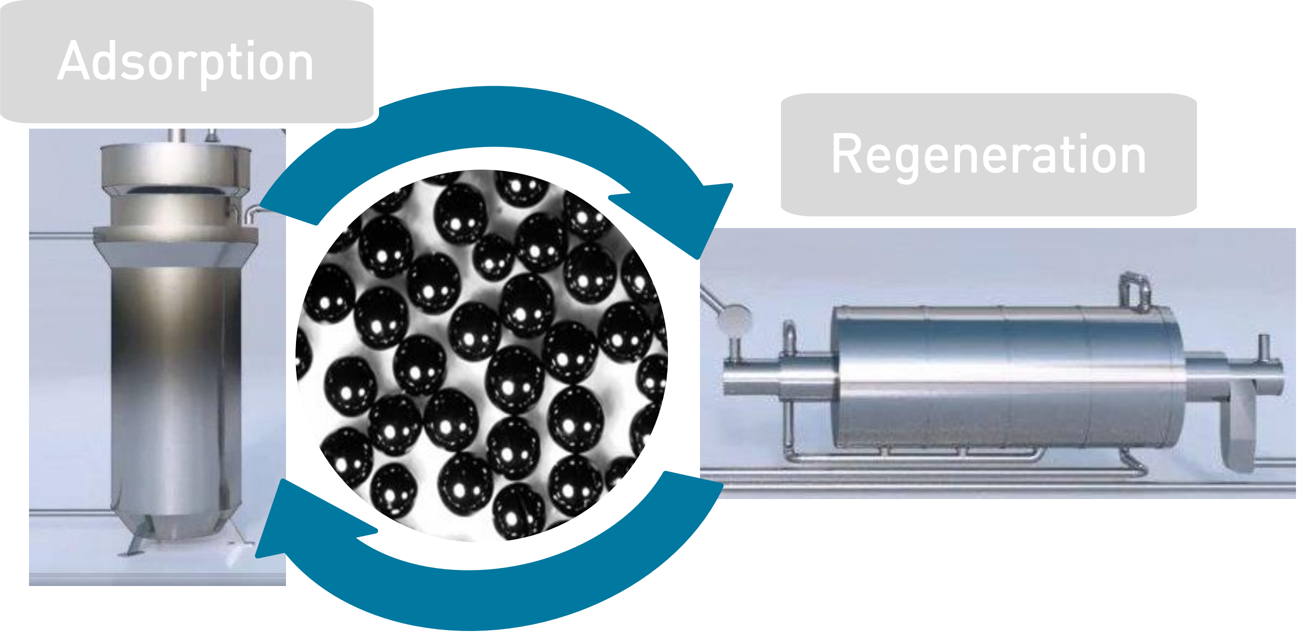
Metazachlor-OA



Metazachlor-ESA

# LONG SERVICE LIFE THANKS TO REGENERATION AND REACTIVATION

- Regeneration: Desorption of adsorbed substances from activated carbon surface:
  - Thermal treatment
  - Extraction, etc.



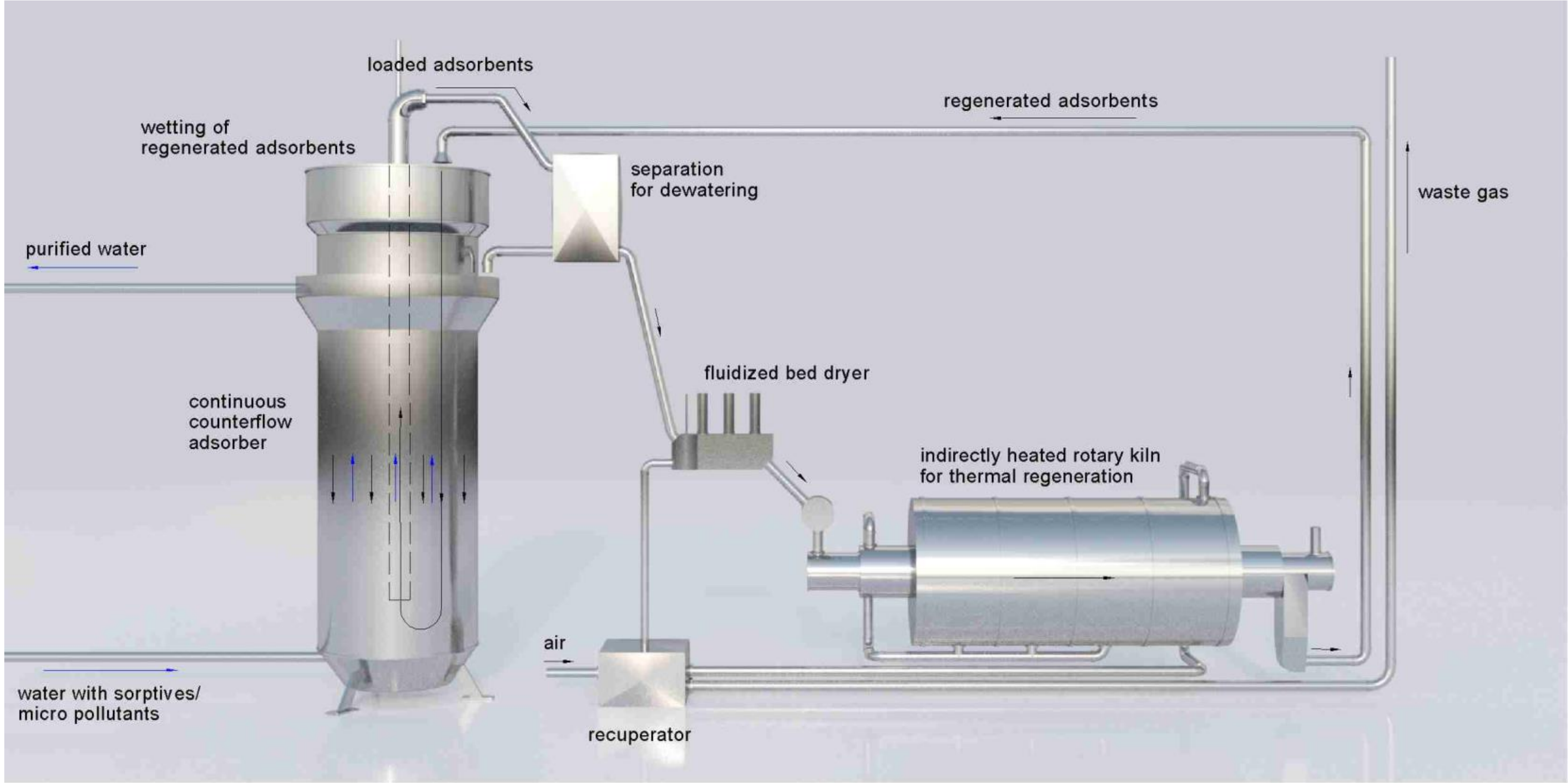
Adsorption

Regeneration

- Thermal regeneration: Desorption in an indirectly heated rotary tube kiln under an inert atmosphere
- Reactivation: Regeneration and addition of steam

# FURTHER DEVELOPMENTS

## SARATECH® CONTINUOUS COUNTERFLOW ADSORBER (CCA)



Process video available at: https://youtu.be/A9gyI4mGP2k

# NEW DYNAMIC PROCESSES

## CONTINUOUS FLOW REACTOR FOR CATALYSIS

# REQUIREMENTS FOR CATALYST SUPPORT

- Low pressure drop
- High mechanical stability
  - No dust
  - No abrasion during use
- Easy to regenerate / reuse

PBSAC

vs.

Carbon Black

# PRESSURE DROP

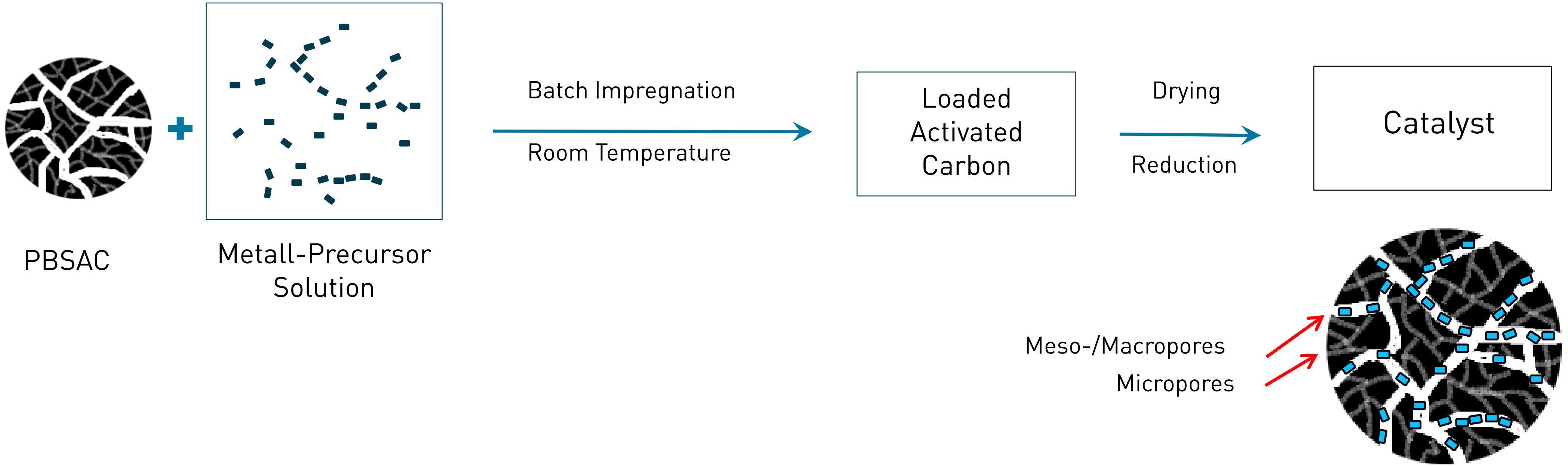
- Ergun equation

$$\Delta p = \underbrace{\frac{150\mu\, L}{D_p^2}\,\frac{(1-\epsilon)^2}{\epsilon^3}}_{\text{Laminar Flow}} v_s + \underbrace{\frac{1.75\, L\, \rho}{D_p}\,\frac{(1-\epsilon)}{\epsilon^3}}_{\text{Turbulent Flow}} v_s|v_s|$$

Definitions

| | |
|---|---|
| $\Delta p$ | is the pressure drop across the bed, |
| $L$ | is the length of the bed (not the column) |
| $D_p$ | is the equivalent spherical diameter of the packing |
| $\rho$ | is the density of fluid, |
| $\mu$ | is the dynamic viscosity of the fluid |
| $v_s$ | is the superficial velocity (i.e. the velocity that the fluid would have through the empty tube at the same volumetric flow rate) |
| $\epsilon$ | is the void fraction of the bed (bed porosity at any time) |

# CATALYST SYNTHESIS ON ACTIVATED CARBON



PBSAC

Metall-Precursor
Solution

Batch Impregnation

Room Temperature

Loaded
Activated
Carbon

Drying

Reduction

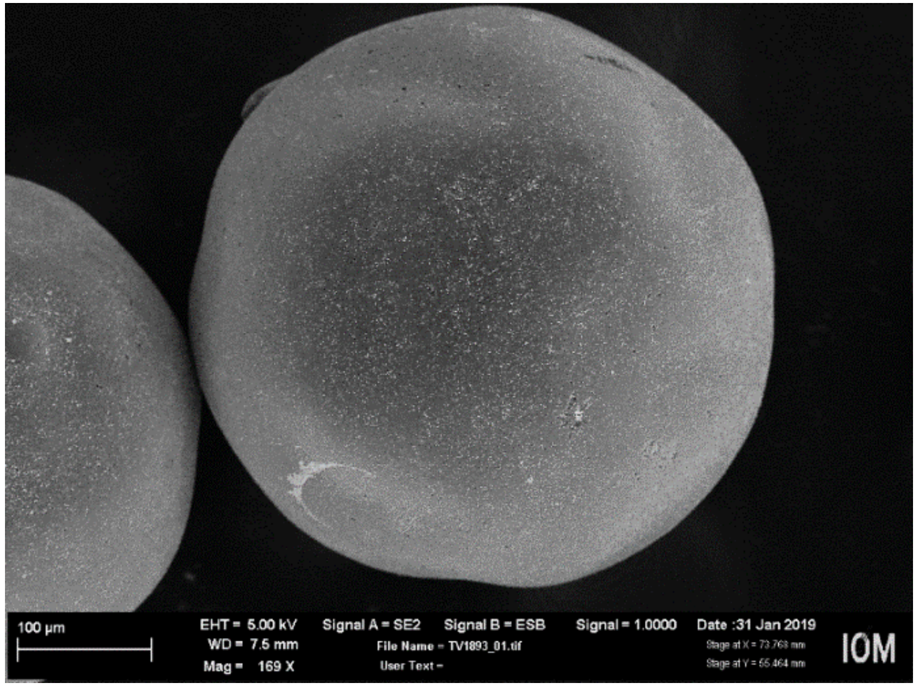
Catalyst

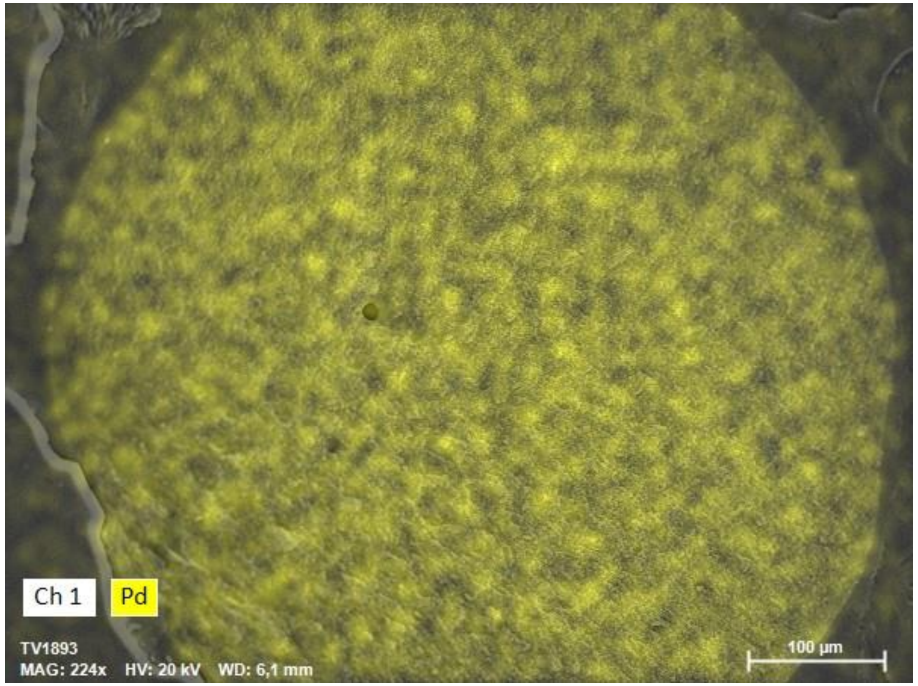
Meso-/Macropores

Micropores

# DISPERSION OF METAL (PD)

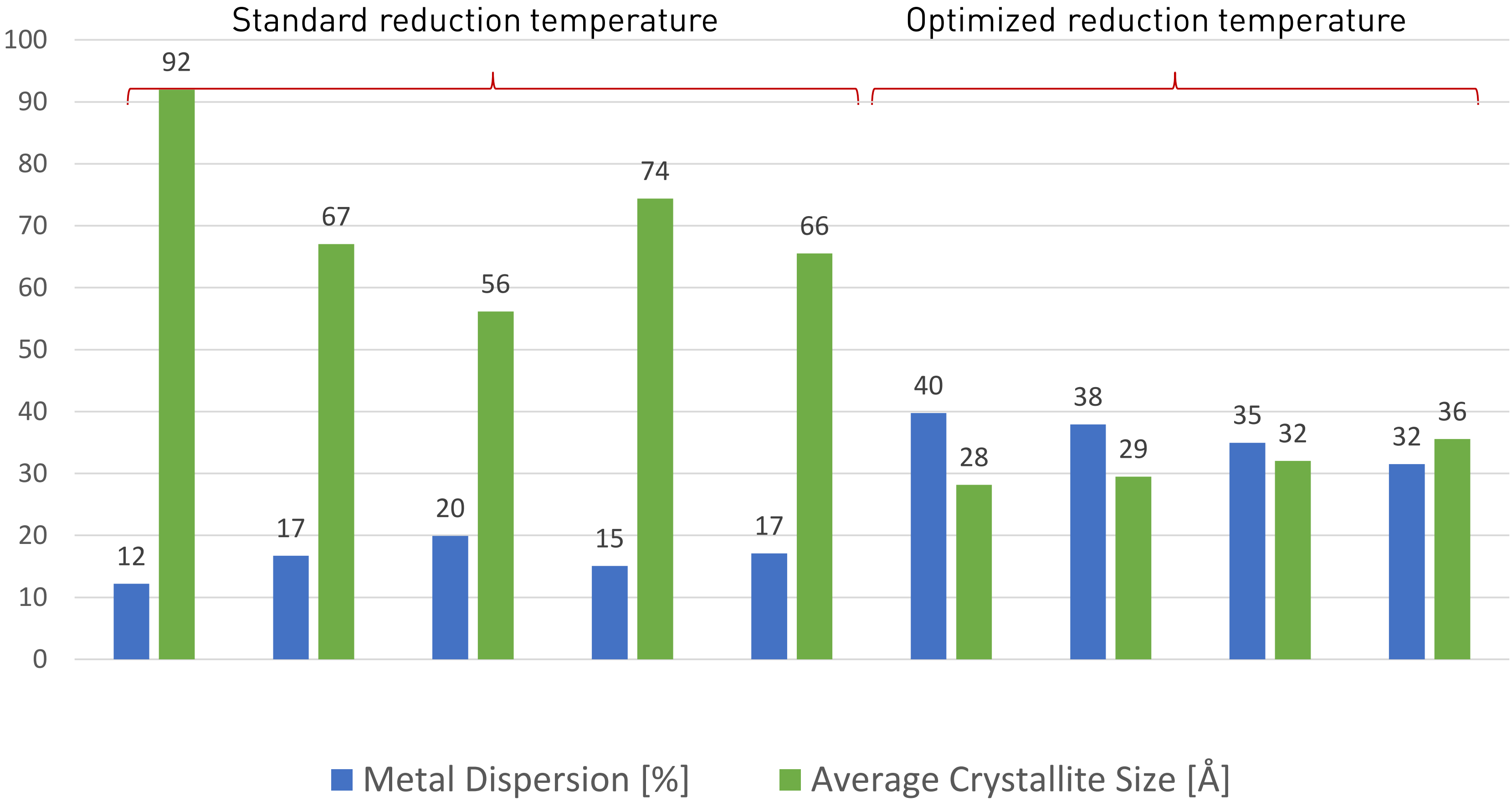
- Metal is Highly Dispersed in Carbon Matrix





# INFLUENCE OF REDUCTION TEMPERATURE ON METAL DISPERSION

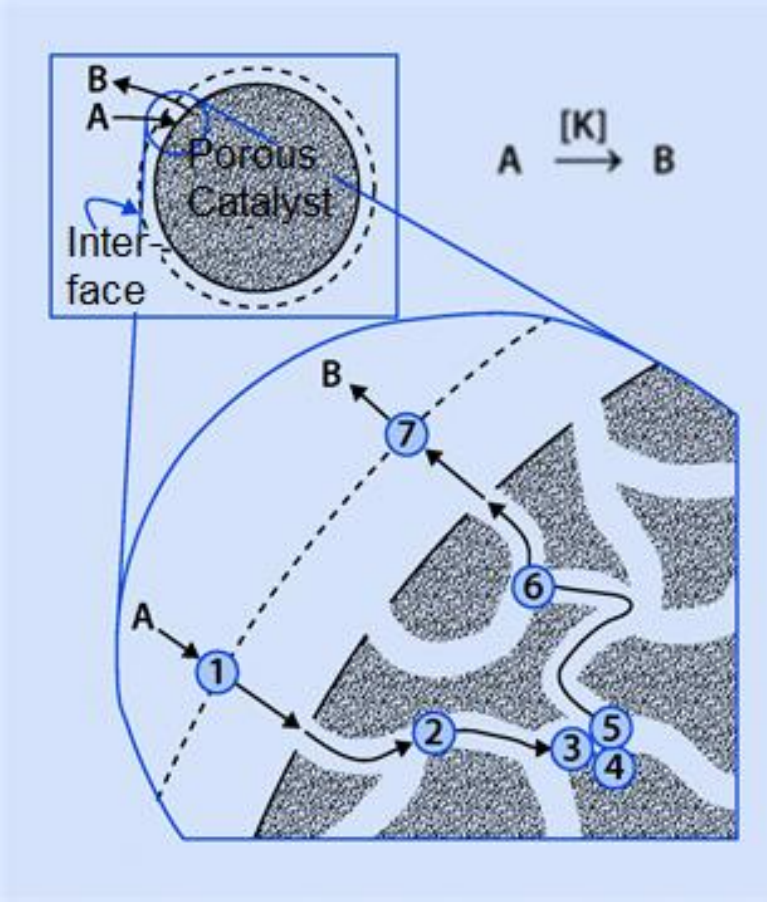
- Reduction Conditions: 5 Vol.-% $H_2$ in $N_2$



# REACTION STEPS IN HETEROGENOUS CATALYSIS

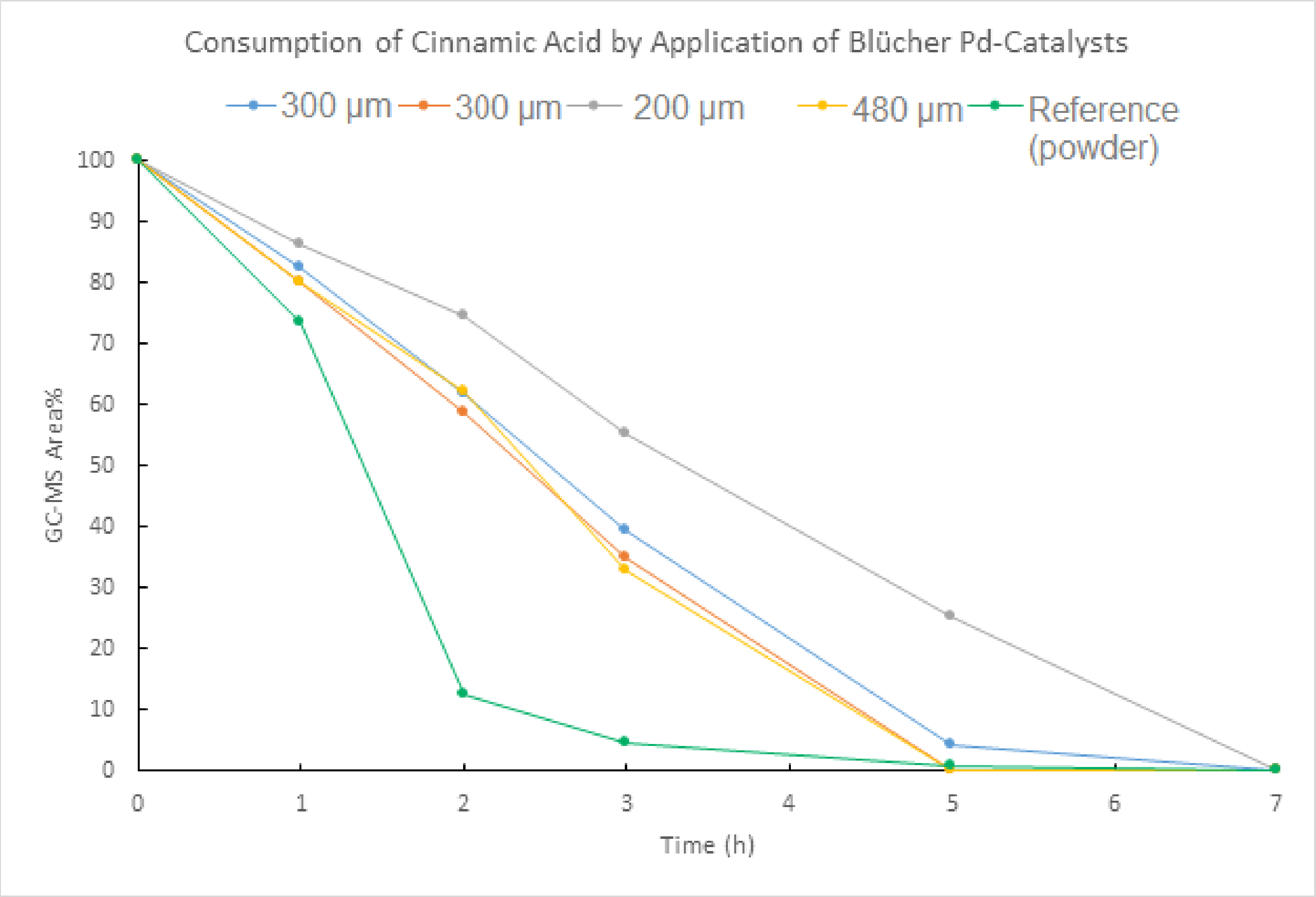
## Reaction Determining Steps

- Diffusion of reaktant (A) to catalysts (filmdiffusion)
- Transport of reaktant in the pores
- Adsorption of reaktant at active centre
- Reaction
- Desorption of prodcut (B) from active centre
- Transport of product off the pores
- Diffusion of product from catalyst to solution

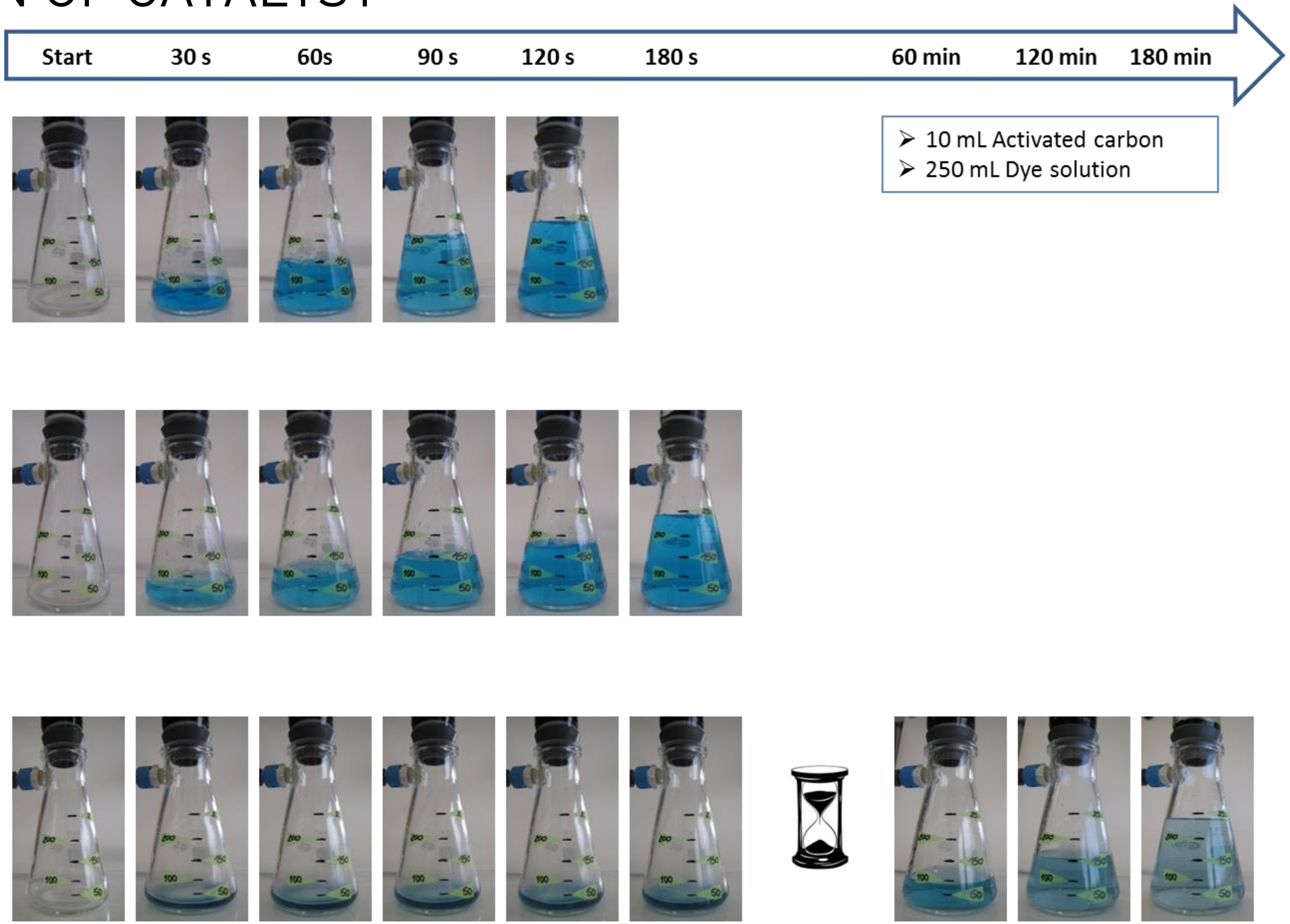


# EXAMPLE FOR CATALYST TEST IN BATCH

## HYDROGENATION OF CINNAMIC ACID: OPTIMIZATION OF PORE STRUCTURE AND SYNTHESIS PARAMETERS LEAD TO BETTER PERFORMANCE



# SEPARATION OF CATALYST



- 10 mL Activated carbon
- 250 mL Dye solution

Spherical particles show faster separation compared to powder catalysts.

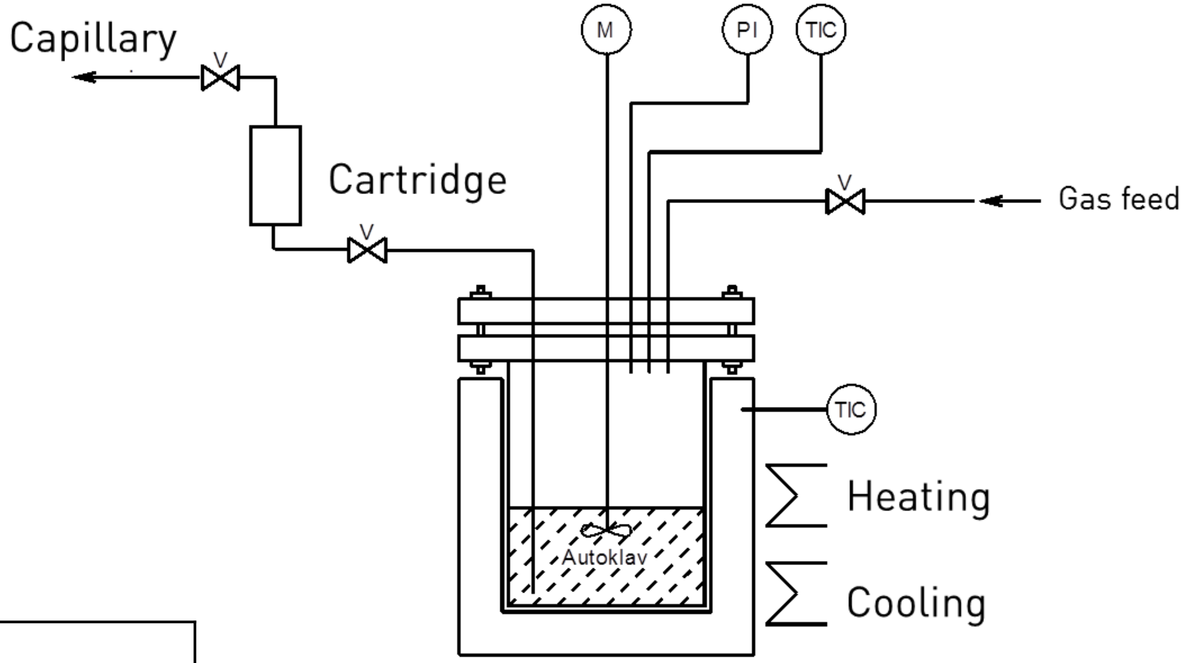
# HYDROGENATION OF ALPHA PINENE

## Reaction Condition

| Test | Rate of flow / mL min$^{-1}$ | Bed volume / min$^{-1}$ | Contact time at catalst / min |
|---|---|---|---|
| 1 | 1,2 | 0,56 | 1,8 |
| 2 | 10,3 | 4,94 | 0,2 |

## Results

| Test | alpha-Pinene / mass-% | beta-Pinene / mass-% | Pinane1 / mass-% | Pinane2 / mass-% | Conversion |
|---|---|---|---|---|---|
| Educt (test 1 + 2) | 49,0 | 51,0 | 0,0 | 0,0 | |
| Product (Test 1) | 0,0 | 0,0 | 16,9 | 83,1 | 100,0 |
| Product (Test 2) | 12,1 | 0,3 | 14,6 | 72,9 | 87,6 |
| Without catalyst | 90,2 | 6,8 | 0,5 | 2,5 | 3,0 |



# SUMMARY FLOW REACTORS

- Polmer based spherical activated carbon as catalyst support shows advantages in flow reactors
  - Low pressure drop
  - High mechanical stability
  - High purity (= low contamination)

THANK YOU FOR YOUR ATTENTION.