12º Encontro Brasileiro sobre Adsorção

23 a 25 de abril de 2018 | Gramado - RS

Adsorption process intensification for water treatment and purification

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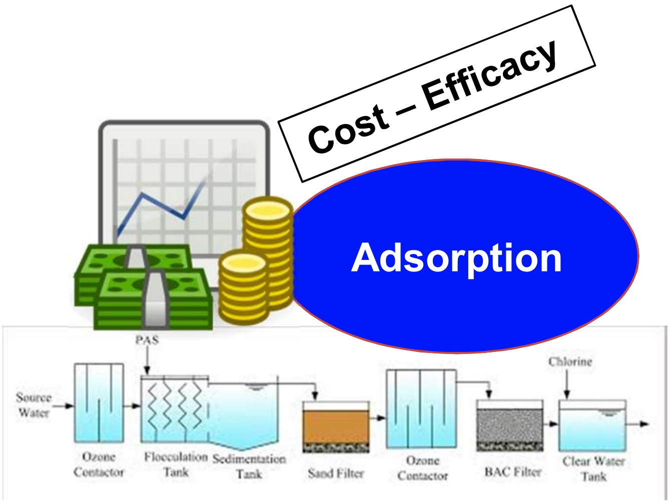
Instituto Tecnológico de Aguascalientes

1. Background - water pollution control

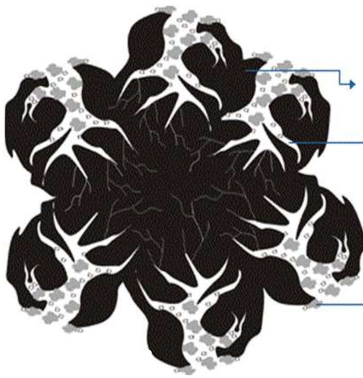
- Water pollution – environmental problem worldwide
- 30% of world population is affected by lack of drinking water
- Water pollution sources: anthropogenic and geogenic chemicals

Schwarzenbach et al. Annu Rev Environ Resour 35 (2010) 109-136.

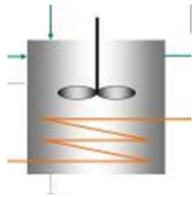


- Different technologies for water purification
- All methods have technical and economic limitations for real-life applications
- Adsorption: Cost – effective process

2. Relevant parameters of adsorption process

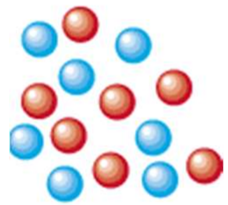


- Process configuration

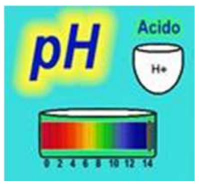


- Adsorbent type

- Fluid properties



- Operating conditions



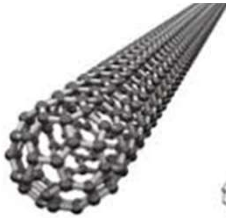
3. Adsorbents used in water treatment

- Activated carbon – main commercial product for water pollution control

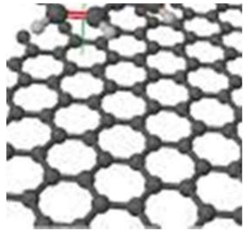
Rivera-Utrilla et al. J Hazard Mater 187 (2011) 1-23

Activated alumina

Zeolites

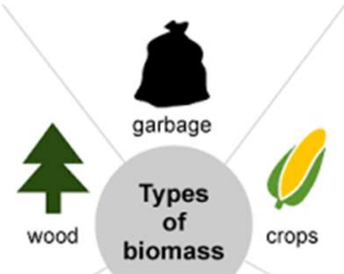


Nanomaterials

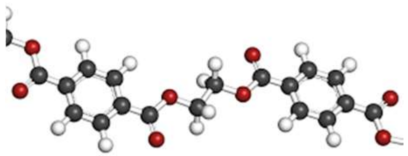


Graphene-based materials

Metal organic frameworks



Biomasses



Polymers

4. Priority pollutants for water sanitation

- Anthropogenic and geogenic inorganic and organic chemicals
- They have different properties and toxicological profiles
- Toxicity: nanogram to miligram per liter level

Heavy metals and metalloids

Emerging pollutants

Dyes

Pharmaceuticals

Pesticides

Biocides

Schwarzenbach et al. Annu Rev Environ Resour 35 (2010) 109-136.

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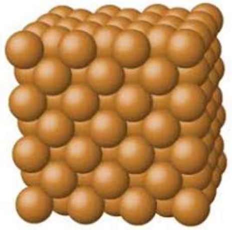
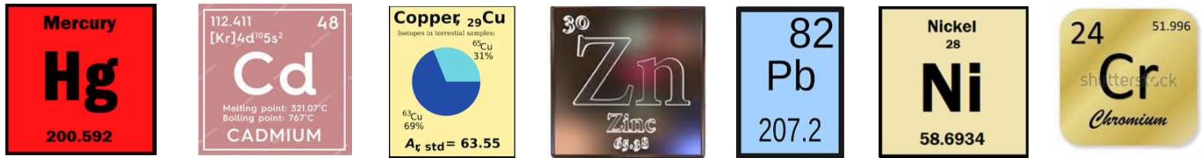
4. Priority pollutants for water sanitation



Heavy metals

- Pollutants contained in the streams of different industries
- They are toxic and non-biodegradable
- Toxicity level: mg/L



Ibrahim et al. Clin Lab Med 26 (2006) 67-97.

Pigments and dyes

- Pollutants generated by food, pharmaceutical and textile industries
- ~ 700,000 tons of dyes per year are generated worldwide due to inefficient dyeing techniques
- Acid, basic, disperse, reactive and direct dyes
- They have complex chemical structures
- Toxicity level: mg/L

Gong et al. Desalination 230 (2008) 220-228.

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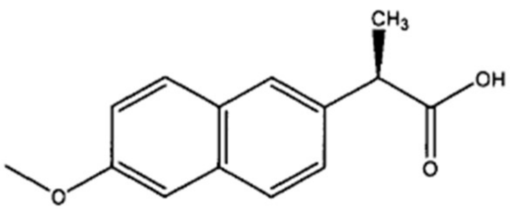
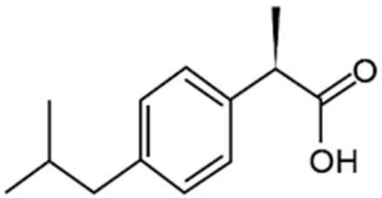
4. Priority pollutants for water sanitation

Pharmaceuticals

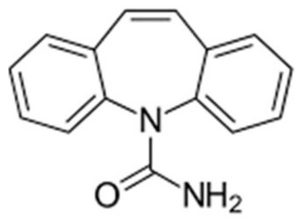
- Emerging hazardous pollutants at trace levels
- Water treatment plants are not effective to remove these chemicals
- Antibiotics, anti-inflammatories, painkillers, hormones and analgesics
- Toxicity level: ng/L and µg/L



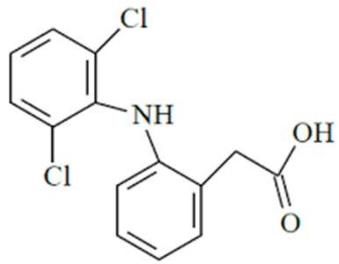
Naproxen



Ibuprofen



Carbamazepine



Diclofenac

World Health Organization (2011)
Baccar et al. Chem Eng J 211-212 (2012) 310-317.

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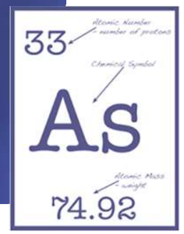
4. Priority pollutants for water sanitation

Geogenic pollutants

- Toxic chemicals recognized by WHO
- Chronic exposure via drinking water – health problems
- Examples of dilemma between public health concerns and economic feasibility of water sanitation
- Toxicity levels: Fluoride > 1.5 mg/L, Arsenic > 10 μg/L

World Health Organization



Dental and skeletal fluorosis

Keratosis and cancer

Mandal and Suzuki. Talanta 58 (2002) 201-235.
Sani et al. Sep Purif Technol 157 (2016) 241-248.
Schwarzenbach et al. Annu Rev Environ Resour 35 (2010) 109-136.

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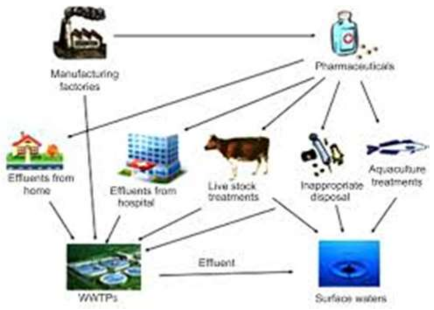
4. Priority pollutants for water sanitation



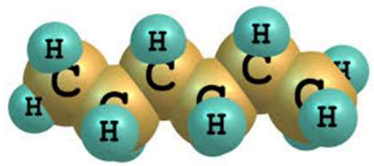
Emerging pollutants

- Analytical techniques allow the quantification of micro-pollutants
- Chemicals that are not normally quantified in water
- They are present in wastewaters of municipal, agricultural and industrial sources
- Toxicity levels: ng/L to µg/L

Personal care products

Pesticides

Disinfection byproducts



Hydrocarbons

Jeirani et al. Rev Chem Eng 27 (2016) 2-32.
Shi et al. Environ Anal Toxicology 2 (2012) 1-14.

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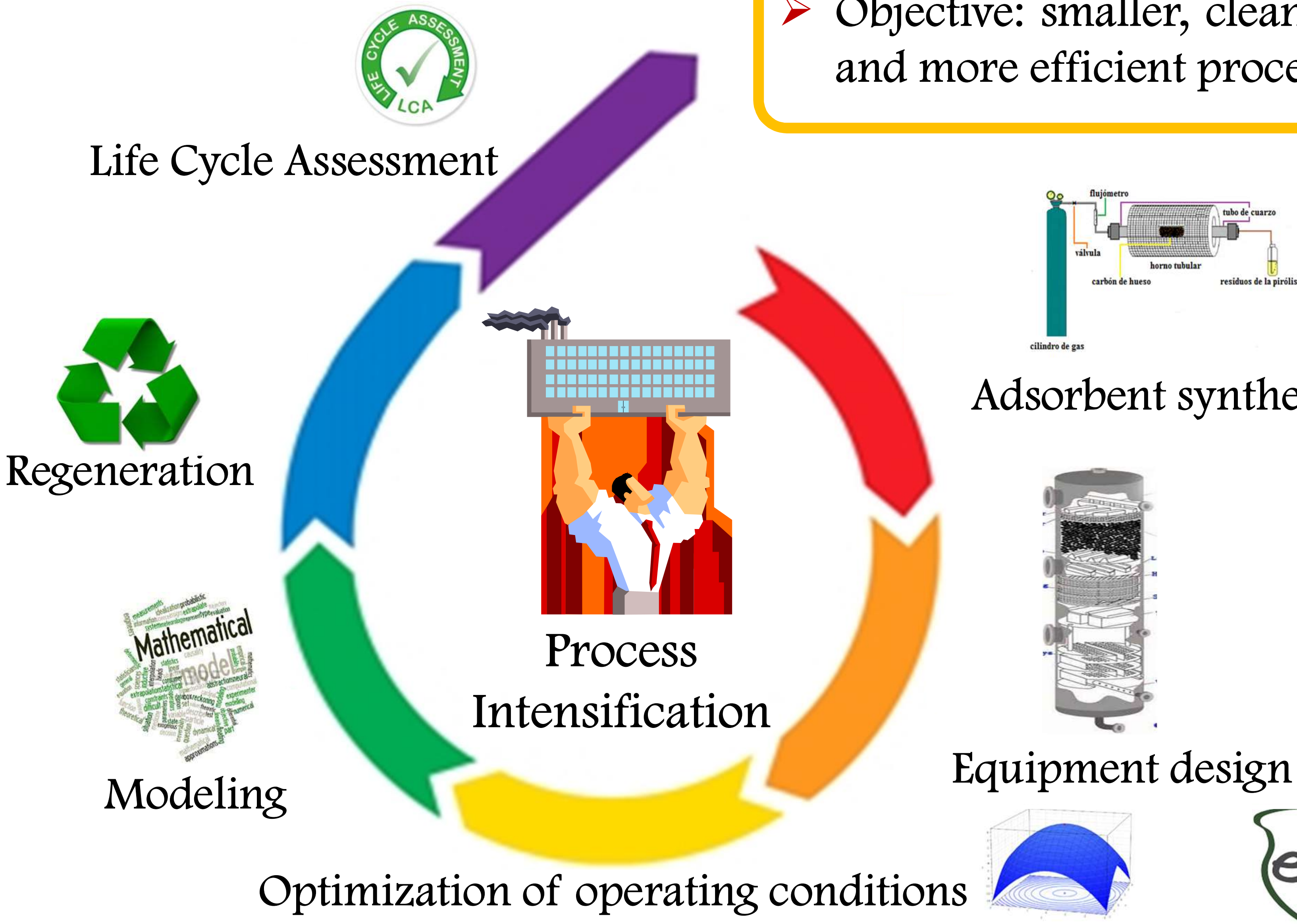
5. Adsorption process intensification and its application in water sanitation

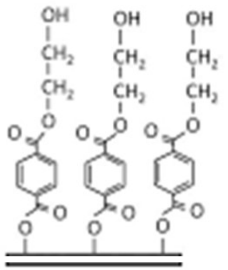
- Objective: smaller, cleaner and more efficient process



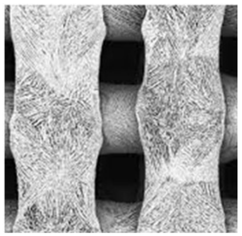
6. Adsorbent synthesis

Synthesis route

- Objective: To obtain adsorbents with outstanding properties for the removal of a specific pollutant

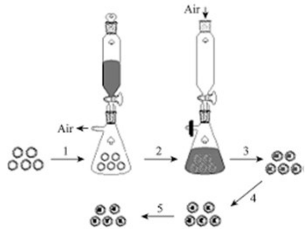


Surface chemistry



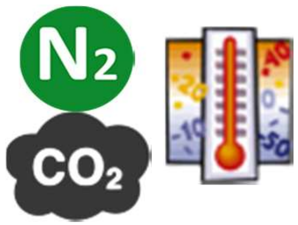
Porosity

Adsorbent performance

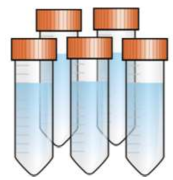


Synthesis conditions

Feedstock (precursor)



Thermal treatments



Chemical treatments

- Acids, bases, ozone, reactive gases, surfactants, organic and inorganic reagents

6. Adsorbent synthesis: Preparation of bone char for fluoride removal

Bone char synthesis route

Bone char

- Composition: 70-76% Hydroxyapatite, 9-11% carbon, 7-9% calcite
- Commercial adsorbent for fluoride removal
- Fluoride adsorption capacities from 2 – 4 mg/g
- Carbonization temperature is the main synthesis variable
- Optimization with a simple experimental design

Rojas-Mayorga et al. J Anal Appl Pyrol 104 (2013) 10-18.

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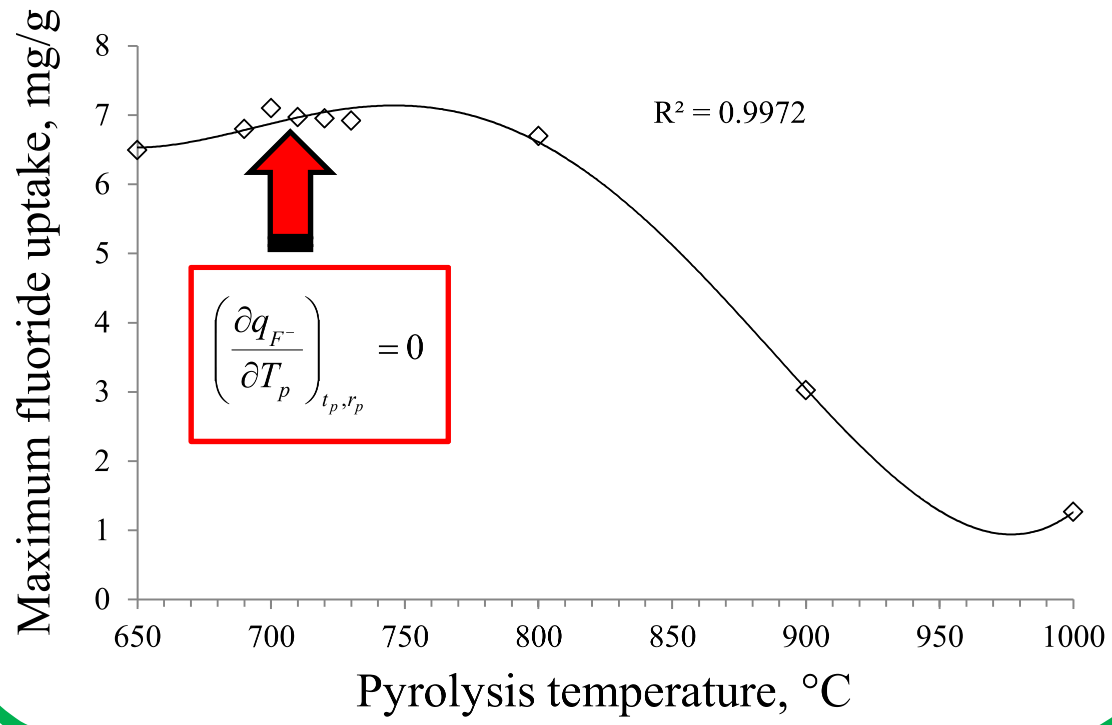
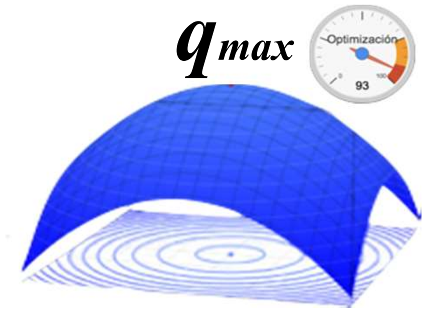
6. Adsorbent synthesis: Preparation of bone char for fluoride removal



Optimum fluoride uptake:

7.2 mg/g at pH 7 and 30 °C



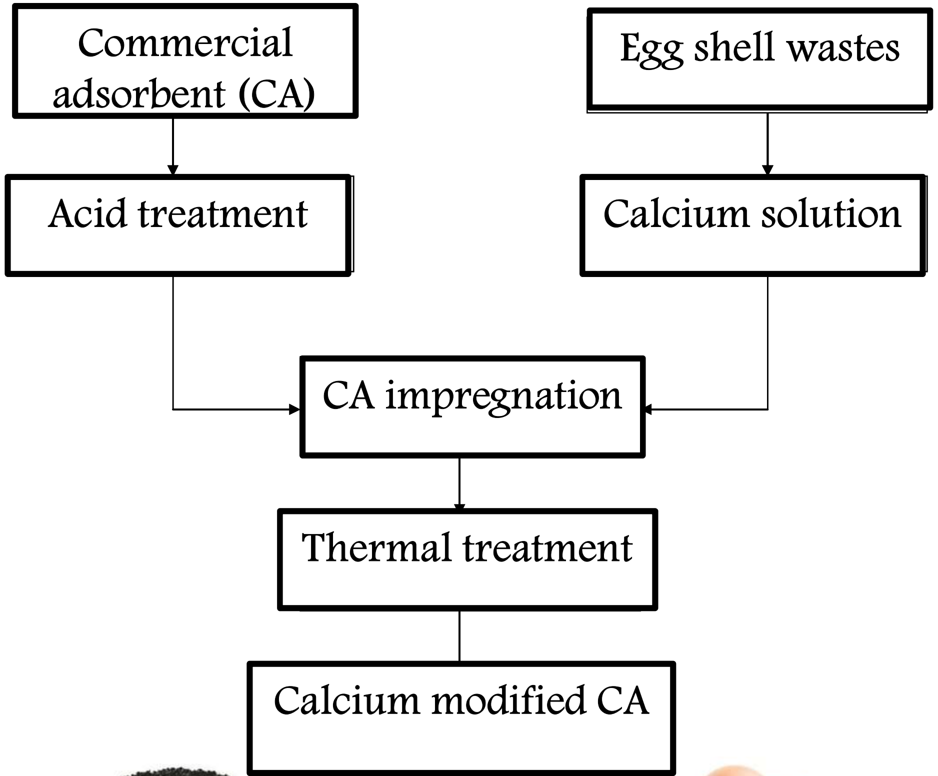
Main findings:

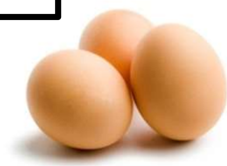
- Optimum pyrolysis temperature (i.e., 700 °C) to maximize fluoride uptake
- Pyrolysis temperatures > 700 °C cause the dehydroxylation of the hydroxyapatite of bone char reducing its fluoride adsorption capacity

Rojas-Mayorga et al. J Anal Appl Pyrol 104 (2013) 10-18.

6. Adsorbent synthesis: Intensification of metal adsorption properties of commercial activated carbons

Commercial activated carbons: Metal adsorption capacity < 1.0 mg/g





➤ **Objective:**

To increase the adsorption capacity for heavy metals of commercial activated carbons using a chemical treatment with a calcium solution obtained from egg shell

➤ **Approach:**

Taguchi experimental design

Statistical analysis is used to identify the best preparation conditions

Guijarro-Aldaco et al. Ind Eng Chem Res 50 (2011) 9354-362.

6. Example: Intensification of metal adsorption properties of commercial activated carbons

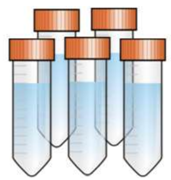
Variables used in Taguchi L9 design (9 experiments):

- Commercial activated carbon (AC): Coconut AC, Bituminous AC, Lignite AC
- Acid treatment (1 M): without treatment, HCL, H_3PO_4
- Calcium concentration (volume %): 25, 50, 100
- Temperature of thermal treatment: 200, 400, 600 °C

Response variable

$$q = \frac{(C_0 - C_t)V}{m}$$

Zinc adsorption capacity



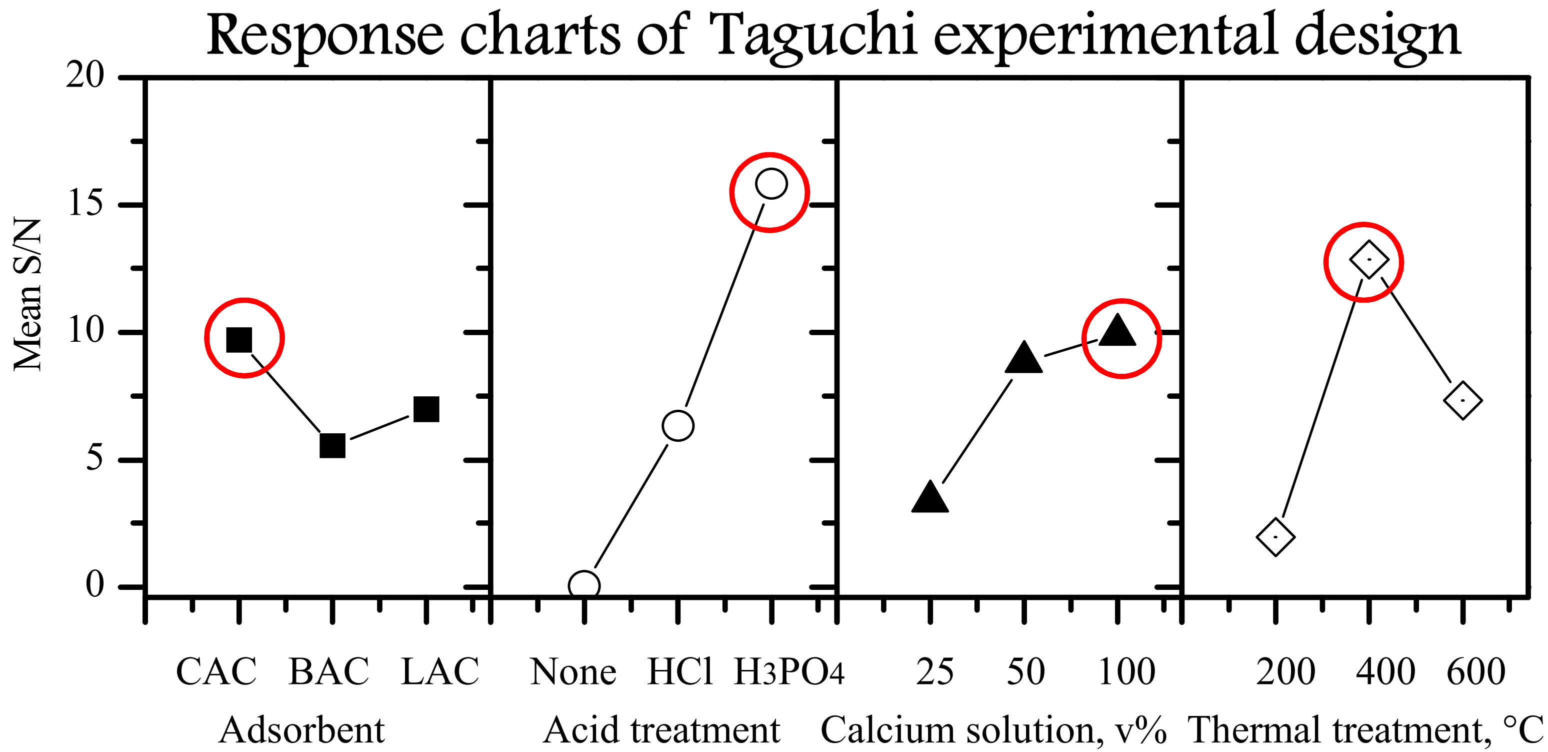
- Batch reactors
- 30 °C, pH 5
- 100 mg/L of Zinc

Signal-to-noise ratio

$$S/N = -10\, log\left(\frac{1}{n}\sum_{i=1}^{n}\left[\frac{1}{q_i^2}\right]\right)$$

Guijarro-Aldaco et al. Ind Eng Chem Res 50 (2011) 9354-362.

6. Example: Intensification of metal adsorption properties of commercial activated carbons

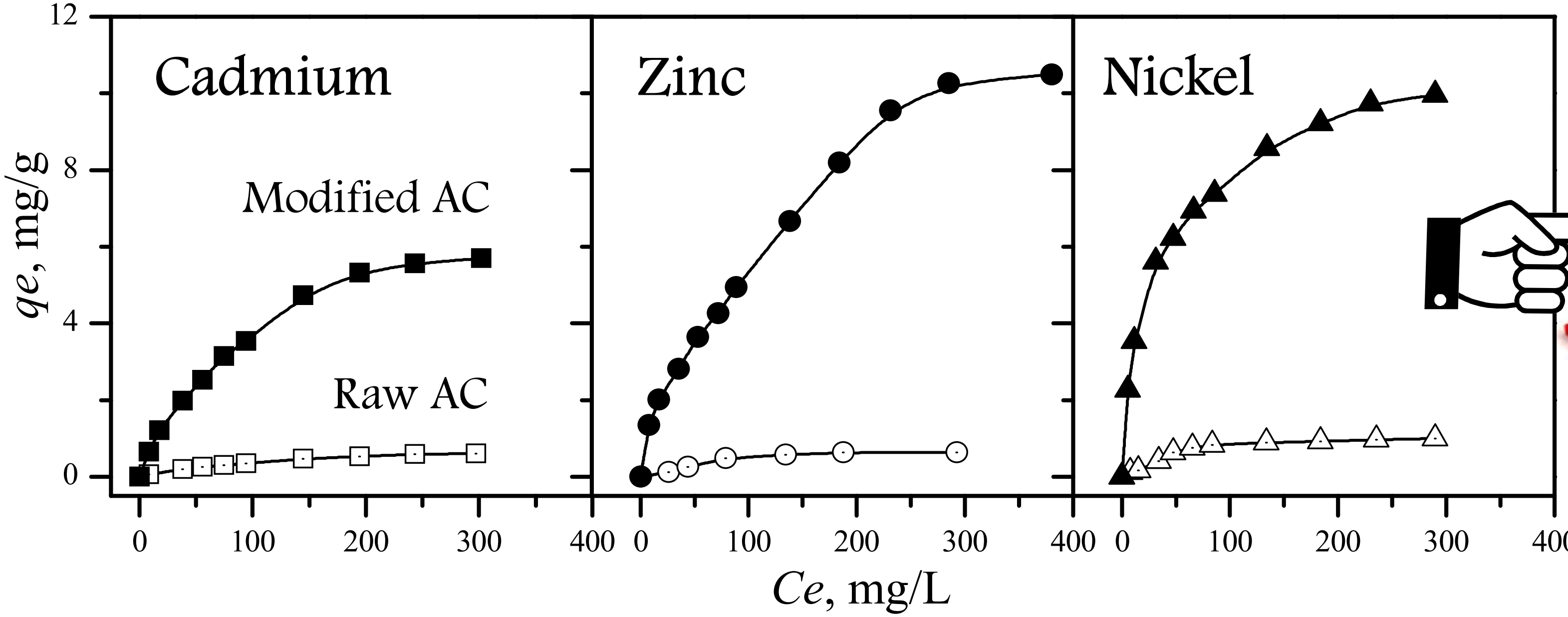


Best conditions

- H_3PO_4 treatment
- Concentration of calcium solution: 100 %
- Thermal treatment: 400 °C

Guijarro-Aldaco et al. Ind Eng Chem Res 50 (2011) 9354-362.

6. Example: Intensification of metal adsorption properties of commercial activated carbons

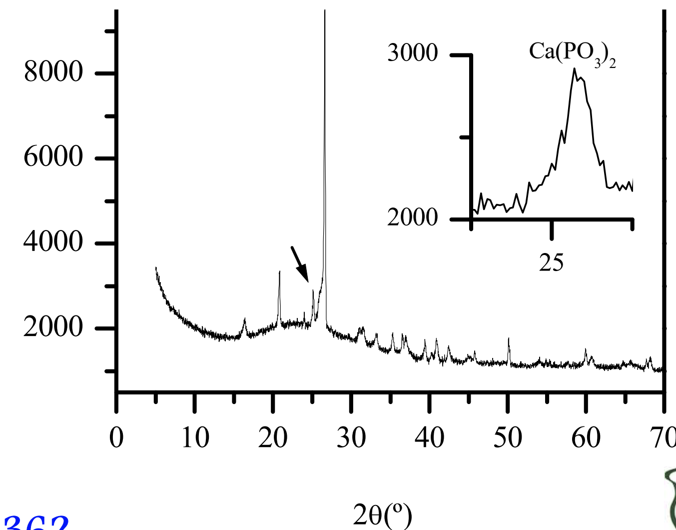


15 times !

Adsorption capacity

Main findings:

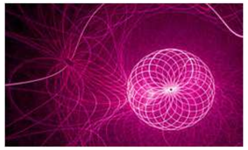
- Adsorbent performance increased due to the formation of moieties containing phosphorus and calcium that interacted with metal ions
- Surface chemistry is more important than the adsorbent porosity



Guijarro-Aldaco et al. Ind Eng Chem Res 50 (2011) 9354-362.

6. Adsorbent synthesis: alternative technologies

Microwave



Plasma

Ultrasound

Biological

TAKE THE CHALLENGE

- Several variables to be analyzed and optimized
- Optimization using experimental designs
- Hybrid routes (e.g. Microwave + Ultrasound)
- Green and energy-saving technologies for industrial production of new adsorbents
- Synthesis procedure impacts the cost of adsorption process

Bhatnagar et al. Chem Eng J 219 (2013) 499-511.
Jamshidi et al. Ultrason Sonochem 32 (2016) 119-131.

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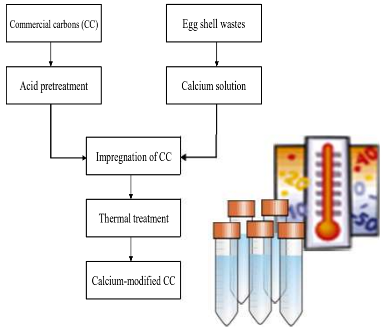
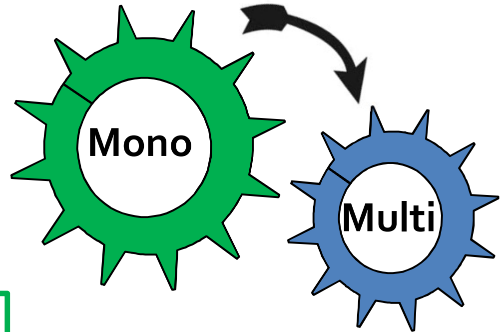
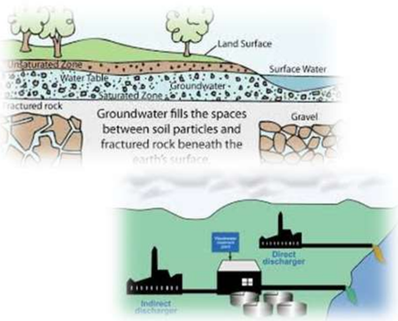
6. Adsorbent synthesis: Challenges for real life systems



Preparation protocols

- Common scenario: Synthesis of the adsorbent is carried out assuming that only one pollutant (i.e., adsorbate) is removed
- Ideal conditions !!



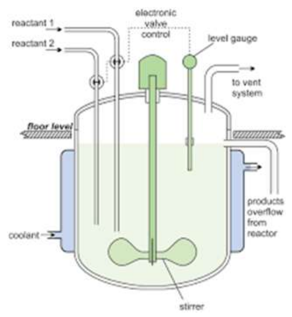


Real life systems

- Multi-component systems: groundwater and industrial streams
- Presence of several chemicals impacts the adsorbent performance
- Multi-objective optimization for the simultaneous removal of different pollutants

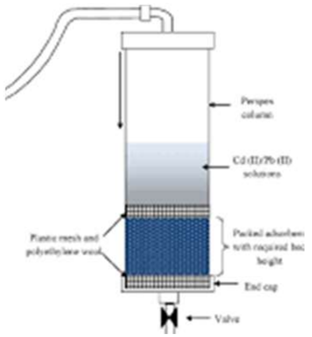
Conflicting synthesis conditions

7. Equipment design



Stirred tank

- Adsorption rates
- Maximum adsorption capacities (i.e., isotherms)
- Thermodynamic parameters
- Study of adsorbate – adsorbent interactions
- Operation at equilibrium (ideal condition)



Packed bed column

- Scale up parameters
- Breakthrough curves
- Adsorption capacities under dynamic operating conditions
- Mass transfer parameters

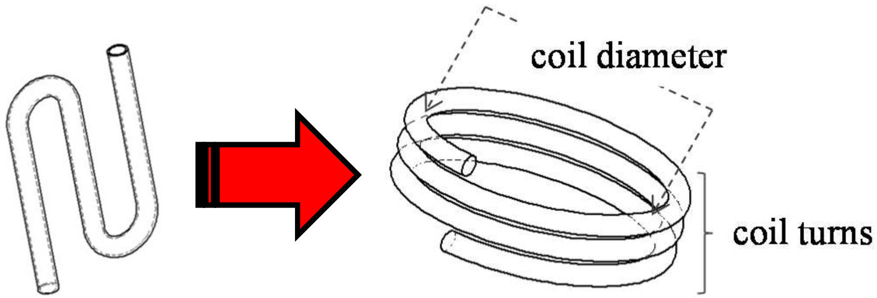
- Adsorption capacity: Packed column < Stirred tank

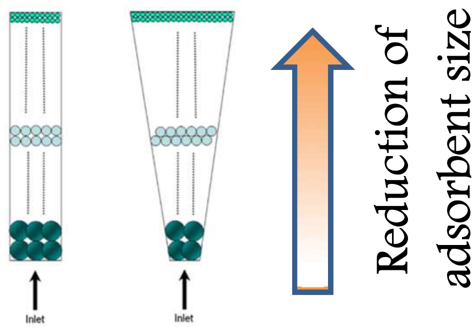
7. Equipment design

- Objective: To minimize the impact of mass transfer phenomena to improve the separation efficacy

Adsorption configuration ✗ Axial dispersion and mass transfer phenomena can reduce up to 80% the performance of adsorption columns

- Alternative: bed geometry or configuration





Helical coil packed columns

- To reduce the equipment size
- To improve mass transfer rates

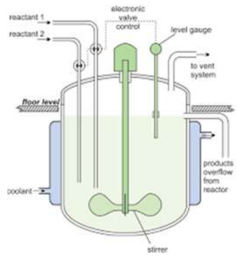
Moreno-Pérez et al. Desalination Water Treat 57 (2016) 24200-24209.

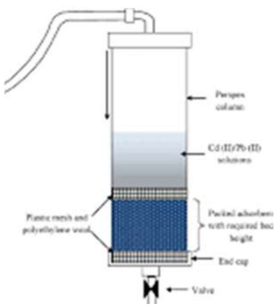
Stratified columns

- To reduce the antagonistic adsorption of heavy metals

Sze and McKay. Water Res 46 (2012) 700-710.

7. Equipment design





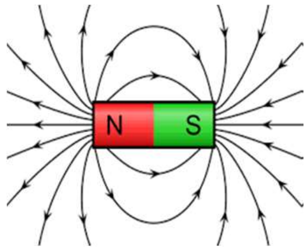
Adsorption system

+

electricity

- Fluoride adsorption with electro-activated alumina

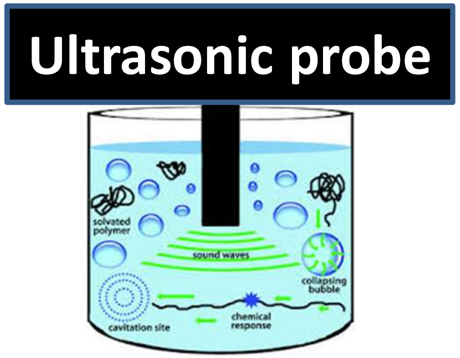
Lounici et al. Desalination 161 (2004) 287-293.



Magnetic fields

- Metal adsorption in the presence of magnetic field

González Vázquez et al. Ind Eng Chem Res 55 (2016) 9323-9331.



- Ultrasound-assisted adsorption of dye with activated carbon

Dashamiri et al. Ultrason Sonochem 34 (2017) 343-353.

- These technologies require additional investigation to know their technical limits for scale-up and industrial applications

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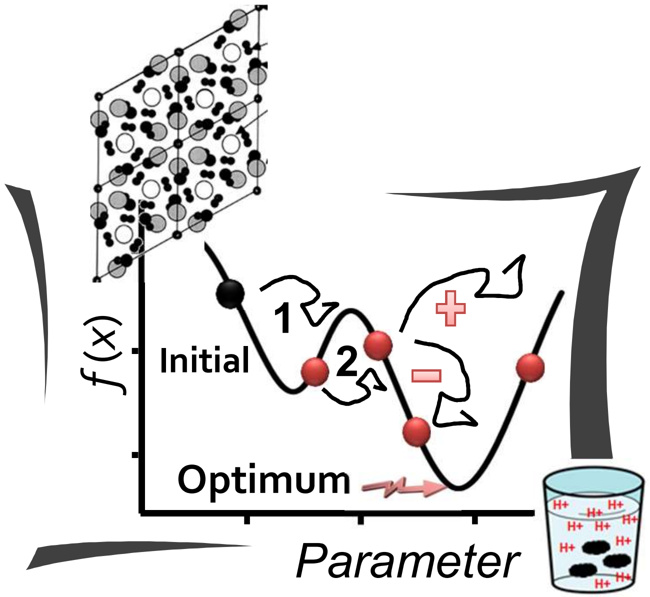
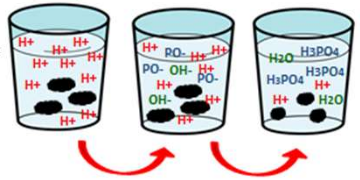
8. Optimization of adsorption conditions

Process performance

- Process configuration
- Fluid properties (e.g., pH, temperature)
- Pollutant characteristics and concentration
- Presence of other adsorbates



- Factorial experimental designs
- Taguchi experimental designs
- Response surface methodology



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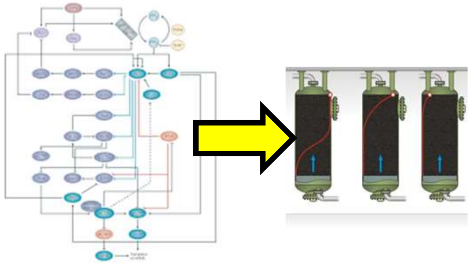
9. Adsorption modeling



Models

- Design, operation, optimization and control of water treatment process

- Theoretical: algebraic and differential equations

Isotherms

$$q_{e,L} = \frac{q_{m,L} K_L C_e}{1 + K_L C_e}$$

Kinetics

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

Mass transfer phenomena

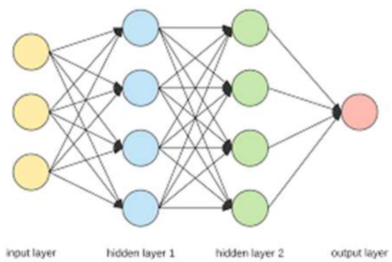
$$\varepsilon \frac{\partial c}{\partial t} + \rho_b \frac{\partial q_{bed}}{\partial t} + \nabla \cdot (cu) = \nabla \cdot (D_D \nabla c)$$

- Empirical: algebraic, artificial intelligence algorithms

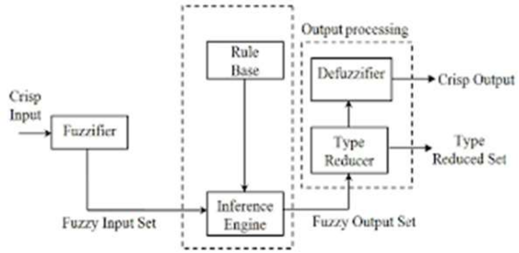
Yang breakthrough model

$$\frac{[F^-]_{outlet}}{[F^-]_{feed}} = 1 - \frac{1}{1 + \left(\frac{Q^2 t}{k_y q_{bed,Y} m_{bed}} \right)^{(k_Y [F^-]_{feed} / Q)}}$$

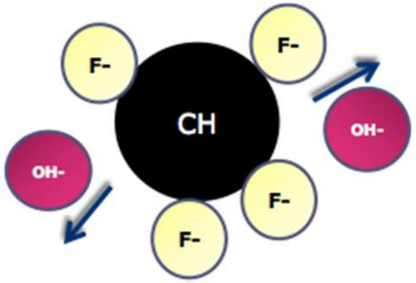
Neural networks



Fuzzy logic

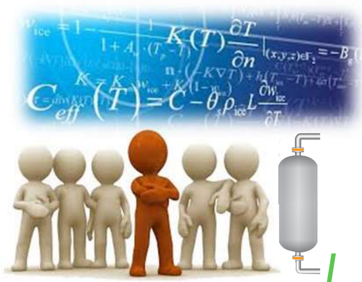


9. Adsorption modeling



$$(\varepsilon + \rho_b K_p)\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = D_D \frac{\partial^2 c}{\partial x^2}$$

- Non-linear and multivariable adsorption models especially for real systems
- Global optimization problems for the estimation of model parameters
- Adsorption modeling is challenging for real-life systems
- Numerical methods used in mass transfer models or other empirical approaches

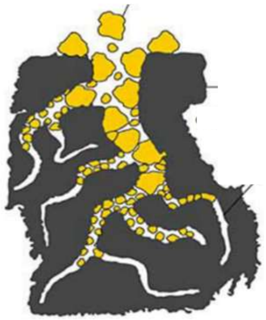


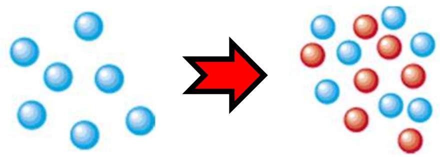
Desirable characteristics √

- Reliable estimation of process performance without requiring extensive experimental data
- Acceptable accuracy in correlation and prediction
- Model is useful to evaluate the effect of operating variables
- Balance between mathematical complexity – model accuracy
- There is no an universal model !!

Worch E. J Water Supply Res Technol 57 (2008) 171–183.

9. Adsorption modeling for real life systems



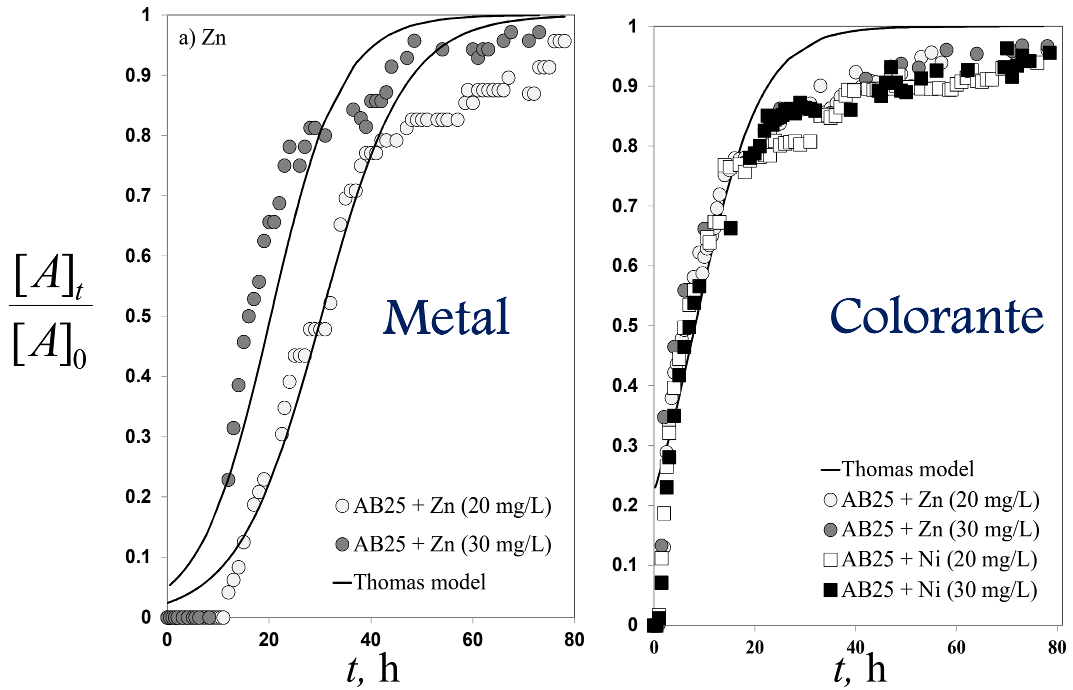


$$R_q = \frac{Adsorption\ in\ mixture}{Adsorption\ in\ single\ solution}$$

Multicomponent adsorption

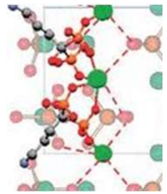
Impact of several pollutants

$R_q > 1$ Synergistic
$R_q < 1$ Antagonistic
$R_q = 1$ Non interaction



Mixture

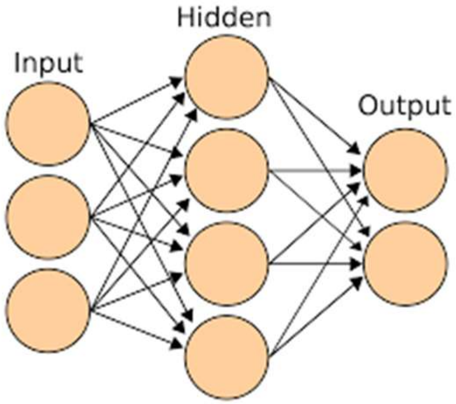
Heavy metal + Dye AB25



- Dye: Synergistic effect on heavy metal adsorption
- Metal: Non-interaction effect on dye adsorption

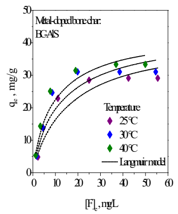
- Models with better properties for the analysis of real life systems !

9. Adsorption modeling: Application of artificial neural networks

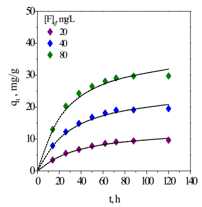


Artificial neural network (ANN)

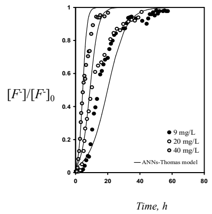
- It emulates the behavior of human brain
- ANN is a robust and flexible black box model
- Nonlinear relationships between input and output variables
- ANN can be applied for the correlation and prediction of adsorption process



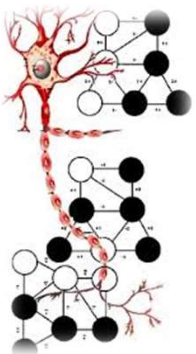
Isotherms



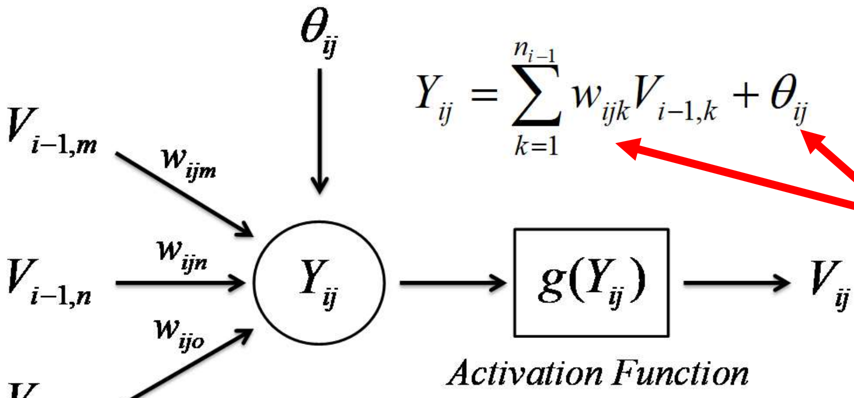
Kinetics



Breakthrough curves



ANN model



$$Y_{ij} = \sum_{k=1}^{n_{i-1}} w_{ijk} V_{i-1,k} + \theta_{ij}$$

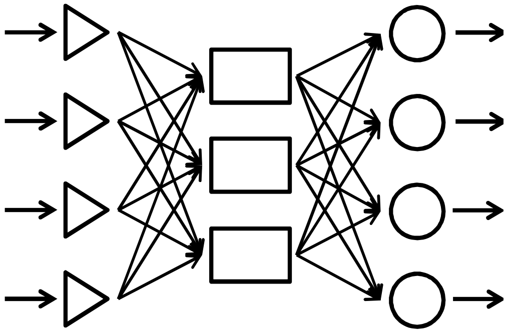
ANN parameters: weights and biases

9. Adsorption modeling: Application of artificial neural networks

Input variables

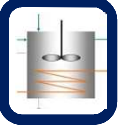
- Adsorbent properties
- Pollutants properties
- Adsorption conditions
- Process configuration

ANN model

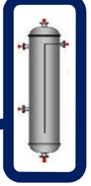


Output variables

$q_{e,i}$



$$\frac{[F^-]_{outlet}}{[F^-]_{feed}}$$



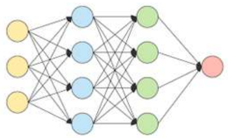
- Selection of input and output variables is paramount
- Characteristics of adsorption systems are used to predict the process performance at other scenarios
- Identification of relevant parameters of adsorption process

9. Adsorption modeling: Application of artificial neural networks

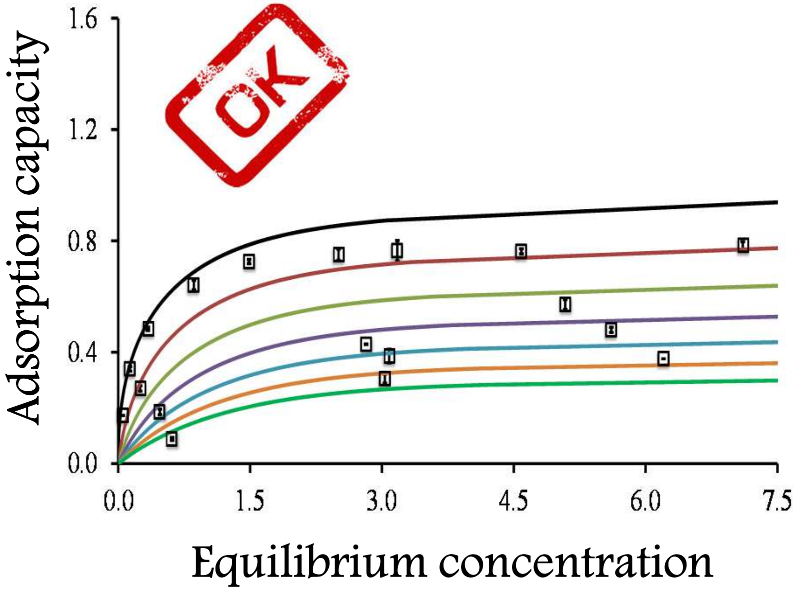
System A + B with antagonistic adsorption

Intensive output variable

Binary adsorption data

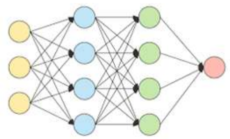


$q_{e,i}$

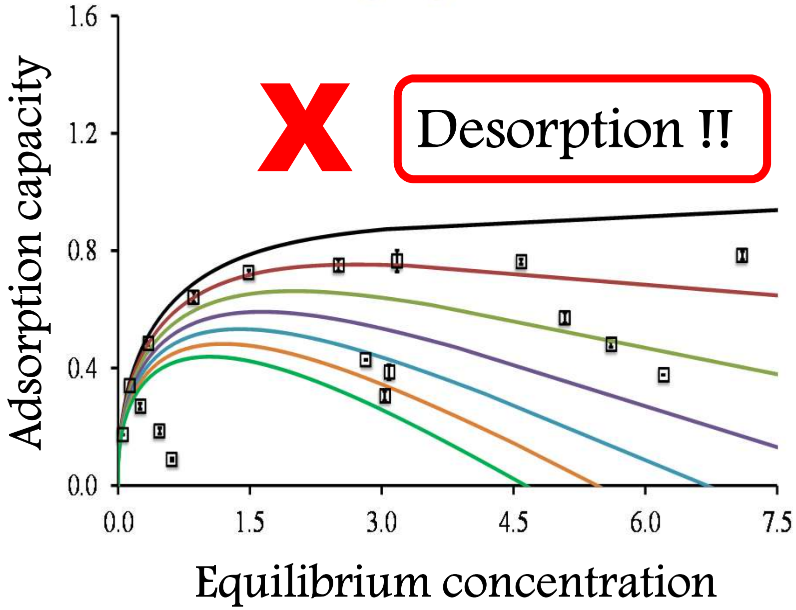


Extensive output variable

Binary adsorption data



$[M_i]_e \Rightarrow q_{e,i}$



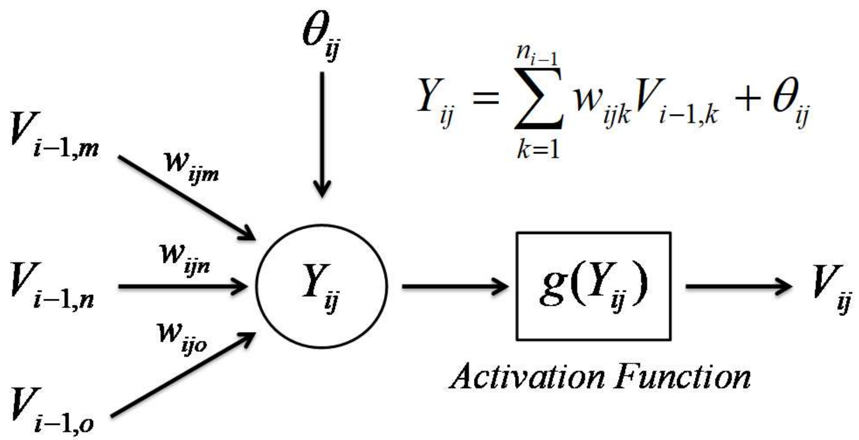
- Predictions of ANNs are proper using intensive output variables
- Not use the removal rates and equilibrium concentrations

Mendoza-Castillo et al. J Mol Liq 251 (2018) 15-27.

eba12 2018

9. Adsorption modeling: Hybrid adsorption models

ANN model



Thomas model

$$\frac{[A]_t}{[A]_0} = \frac{1}{1 + \exp\left(\frac{k_{Th}}{Q}(q_{bed,T} W_{bed} - [A]_0 V_{eff})\right)}$$

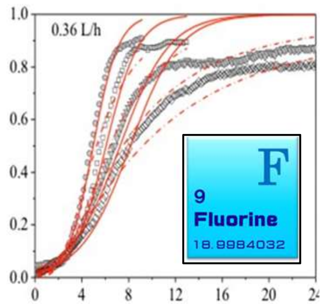
$$Min\ F_{obj} = \frac{1}{2}\sum_{m=1}^{n_n}\sum_{j=1}^{ndat}\left(\left.\frac{[F^-]_t^{\exp}}{[F^-]_0}\right|_j - \left.\frac{[F^-]_t^{calc}}{[F^-]_0}\right|_{m,j}\right)^2$$

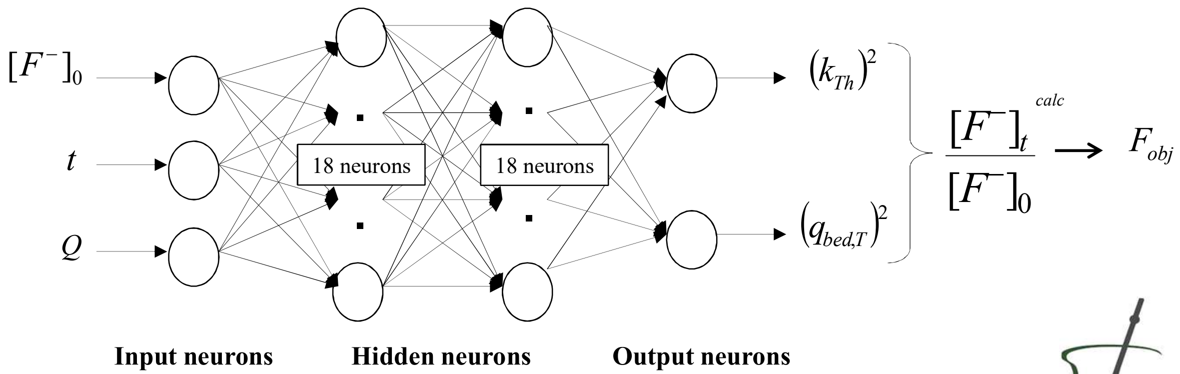
subject to:

$k_{Th} > 0$

$q_{bed,T} > 0$

Fluoride adsorption with bone char packed bed column

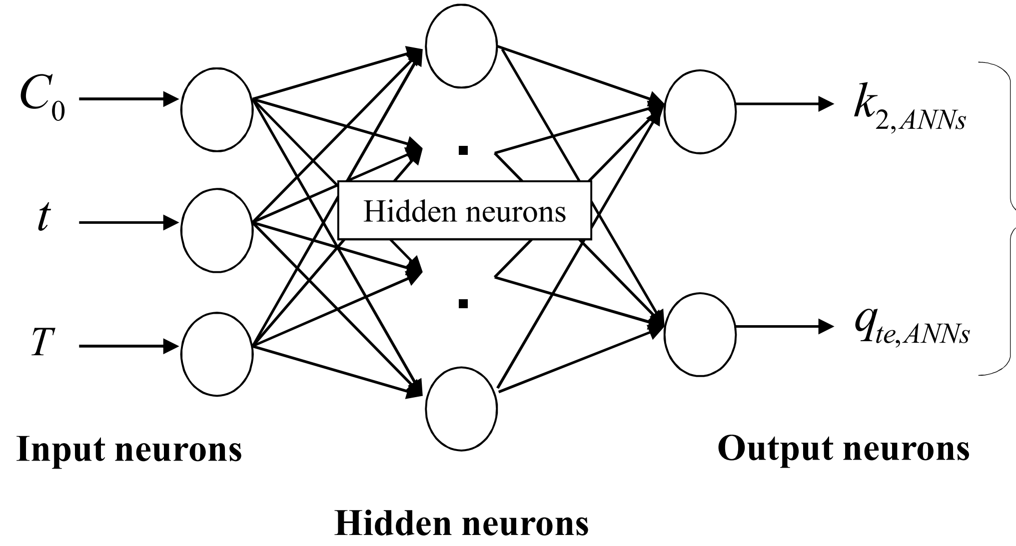




Tovar-Gómez et al. Chem Eng J 228 (2013) 1098-1109.

9. Adsorption modeling: Hybrid adsorption models

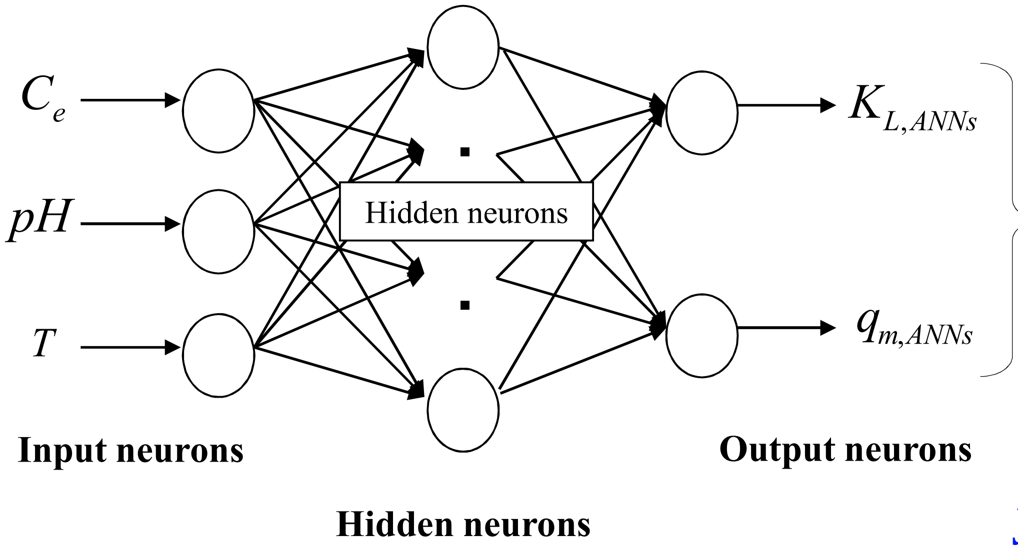
Adsorption kinetics: ANN-Pseudo second order model



$$q_{t,ANNs} = \frac{q_{te,ANNs}^2 k_{2,ANNs}}{1 + q_{te,ANNs} k_{2,ANNs} t} \longrightarrow F_{obj}$$

Modeling of fluoride adsorption on modified zeolite

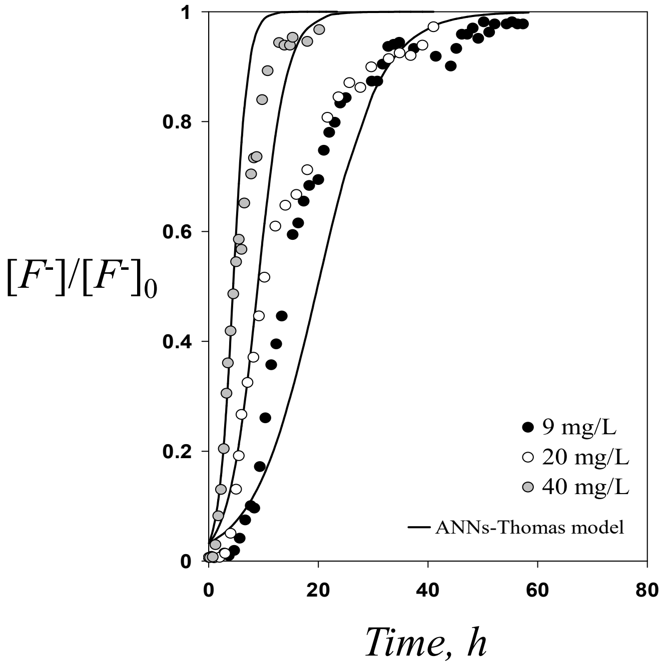
Adsorption isotherms: ANN-Langmuir model



$$q_{e,ANNs} = \frac{q_{m,ANNs} K_{L,ANNs} C_e}{1 + K_{L,ANNs} C_e} \longrightarrow F_{obj}$$

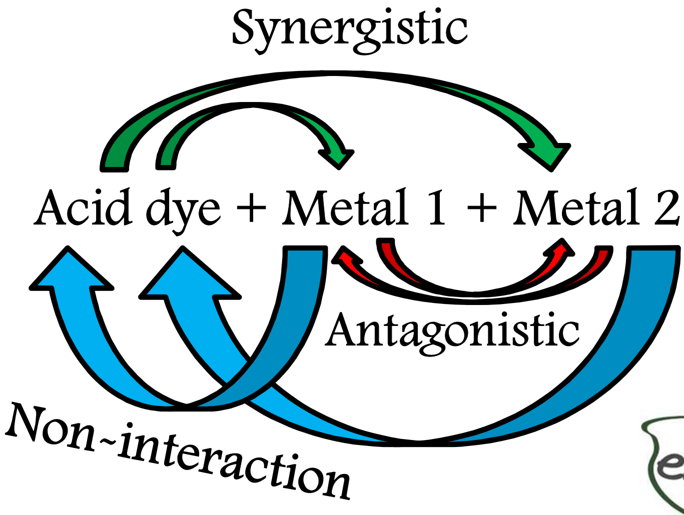
Saucedo-Delgado et al.
J Fluorine Chem 204 (2017) 98-106.

9. Adsorption modeling: Application of artificial neural networks

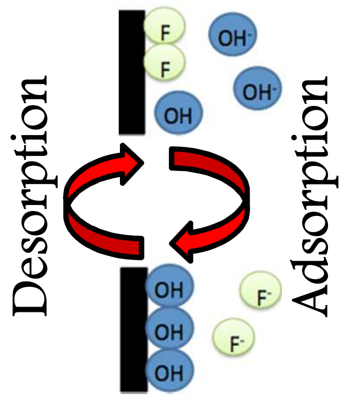


- ANN can improve the performance of theoretical models
- Characteristics of the adsorption system can be incorporated in the model
- Robust model with better correlation and prediction abilities

- New adsorption models for groundwater, wastewaters and industrial streams
- Modeling of complex adsorption behaviors



10. Regeneration



- Fundamental stage to estimate the cost of water treatment
- It allows to remove the pollutants loaded on the surface and to recover the adsorbent capacity
- The objective is to maximize the recovery of adsorbent performance

Regeneration	Regeneration agent	Mechanism
Thermal	Physical waves	Extraction
Chemical	Electrical currents	pH changes
Microbiological	Chemical reagents	Thermal desorption
	Microorganisms	Reaction/Degradation

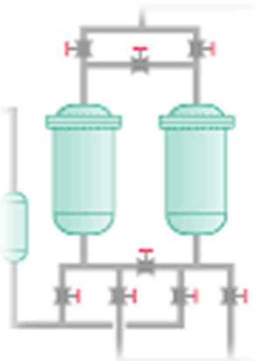
Salvador et al. Microporous Mater 202 (2015) 259-296.

10. Regeneration

$$Desorption\ efficiency = \frac{Amount\ of\ pollutant\ recovered\ from\ exhausted\ adsorbent}{Amount\ of\ pollutant\ loaded\ on\ the\ exhausted\ adsorbent}$$

$$Regeneration\ efficiency = \frac{Adsorption\ capacity\ after\ regeneration}{Adsorption\ capacity\ before\ regeneration}$$

Adsorption-desorption cycles



Regeneration process

- Regeneration agent
- Properties of adsorbent
- Properties of pollutants
- Operating conditions

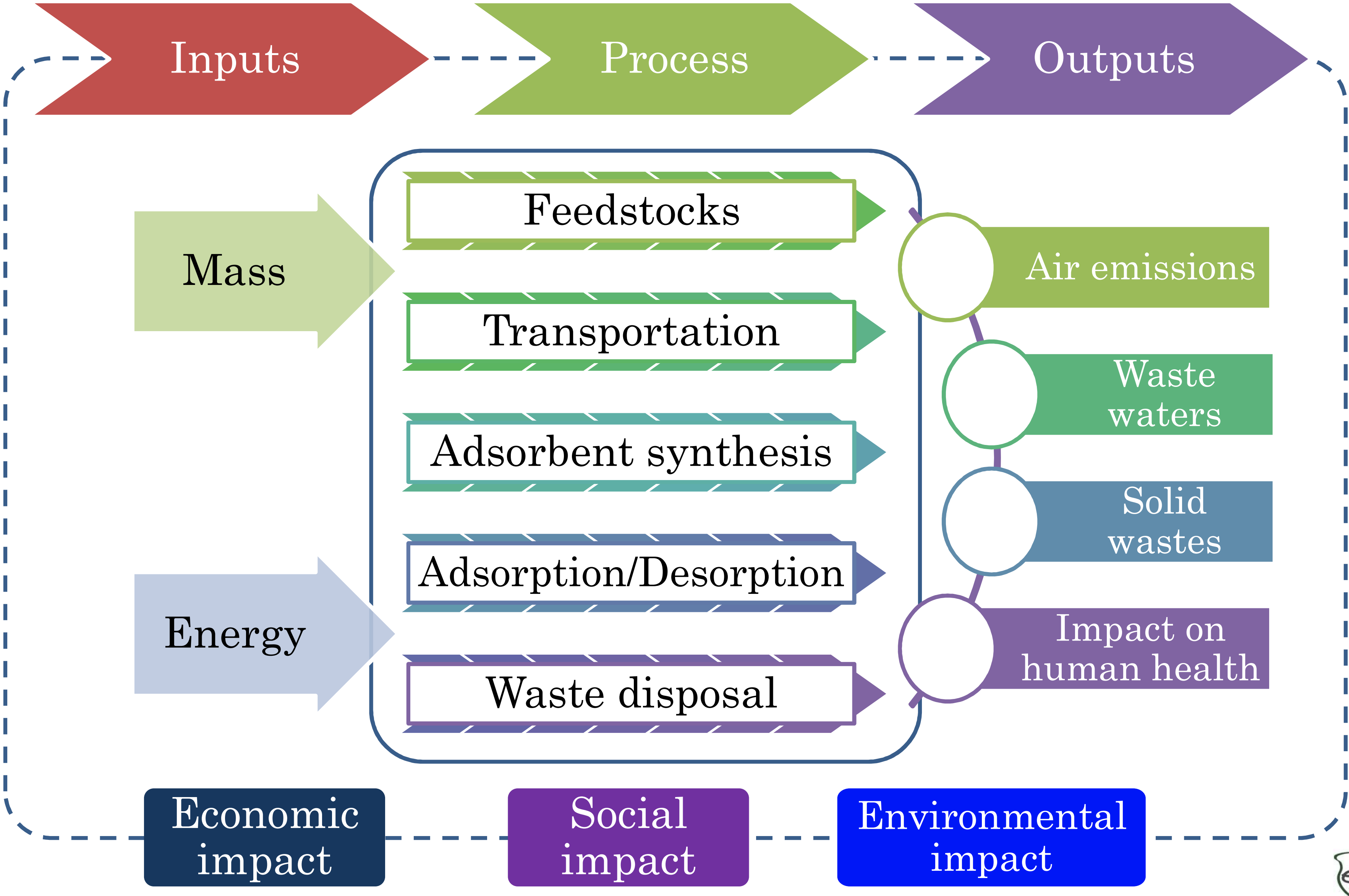
Adsorbent life time

Waste disposal

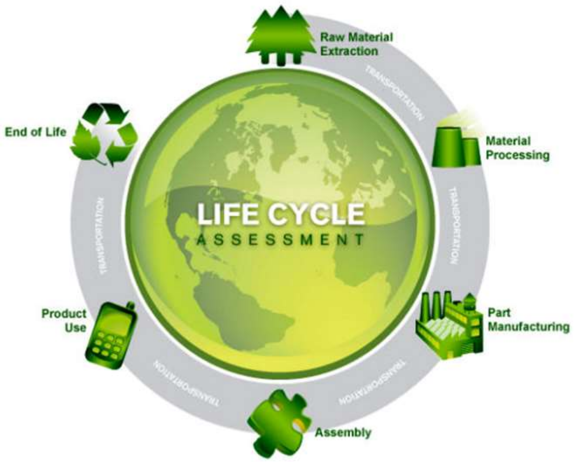
- Key aspect for reducing environmental impact
- Traditional approach: Incineration, landfill
- Options for reusing and disposing

11. Life cycle assessment of adsorption process

- Objective: evaluation of environmental interactions of life cycle of the adsorbent



11. Life cycle assessment of adsorption process

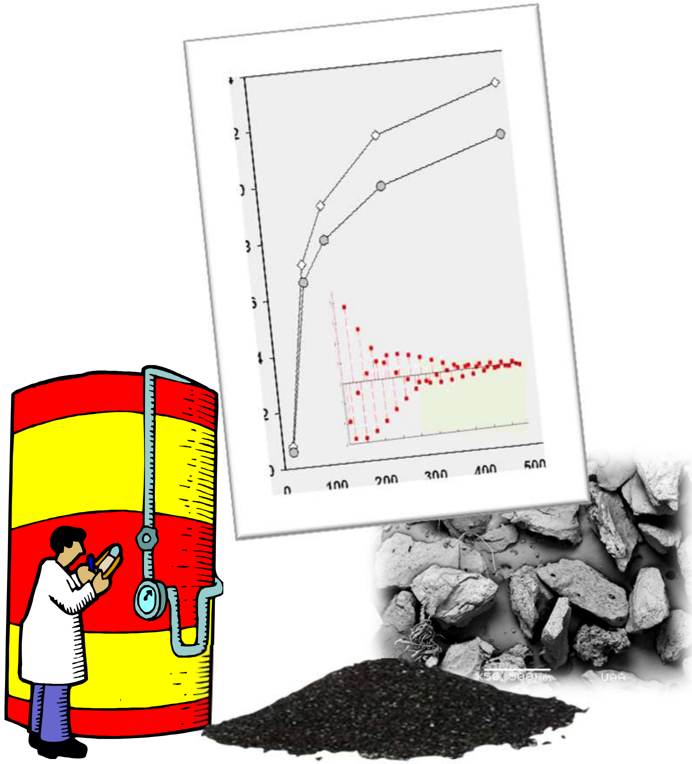


- Valuable tool to identify technical limitations of different adsorbents
- Global analysis of the water purification process

- LCA can be used to analyze the environmental impacts involved in the manufacturing chain of new adsorbents
- Guidelines for adsorbent selection and comparison
- Identification of sustainable processes for the industrial production of new adsorbents

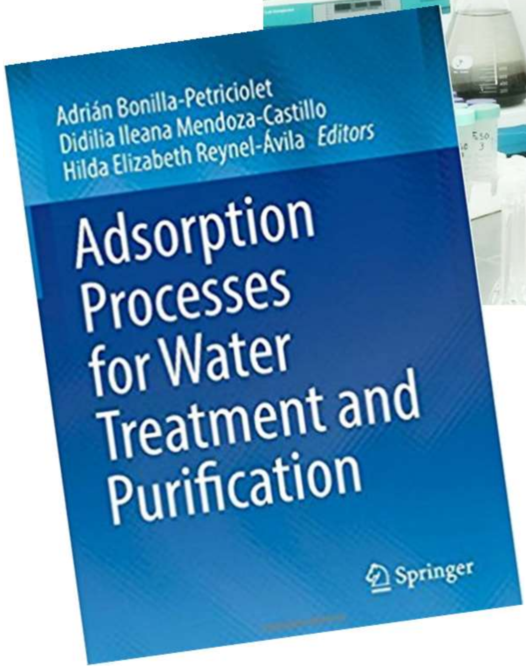
Arena et al. J Clean Prod 125 (2016) 68-77.

12. Conclusions



- Synthesis of new adsorbents for multi-component adsorption of water pollutants
- Intensification of adsorption equipment design for water treatment
- Application of green and effective regeneration procedures
- Life cycle analysis of new adsorbents with outstanding properties for water treatment
- Adsorption engineering is relevant for obtaining a robust and low cost water treatment process

13. Our research group



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Thank you