

# Advanced Catalysts and Nanomaterials for Industrial Water Treatment

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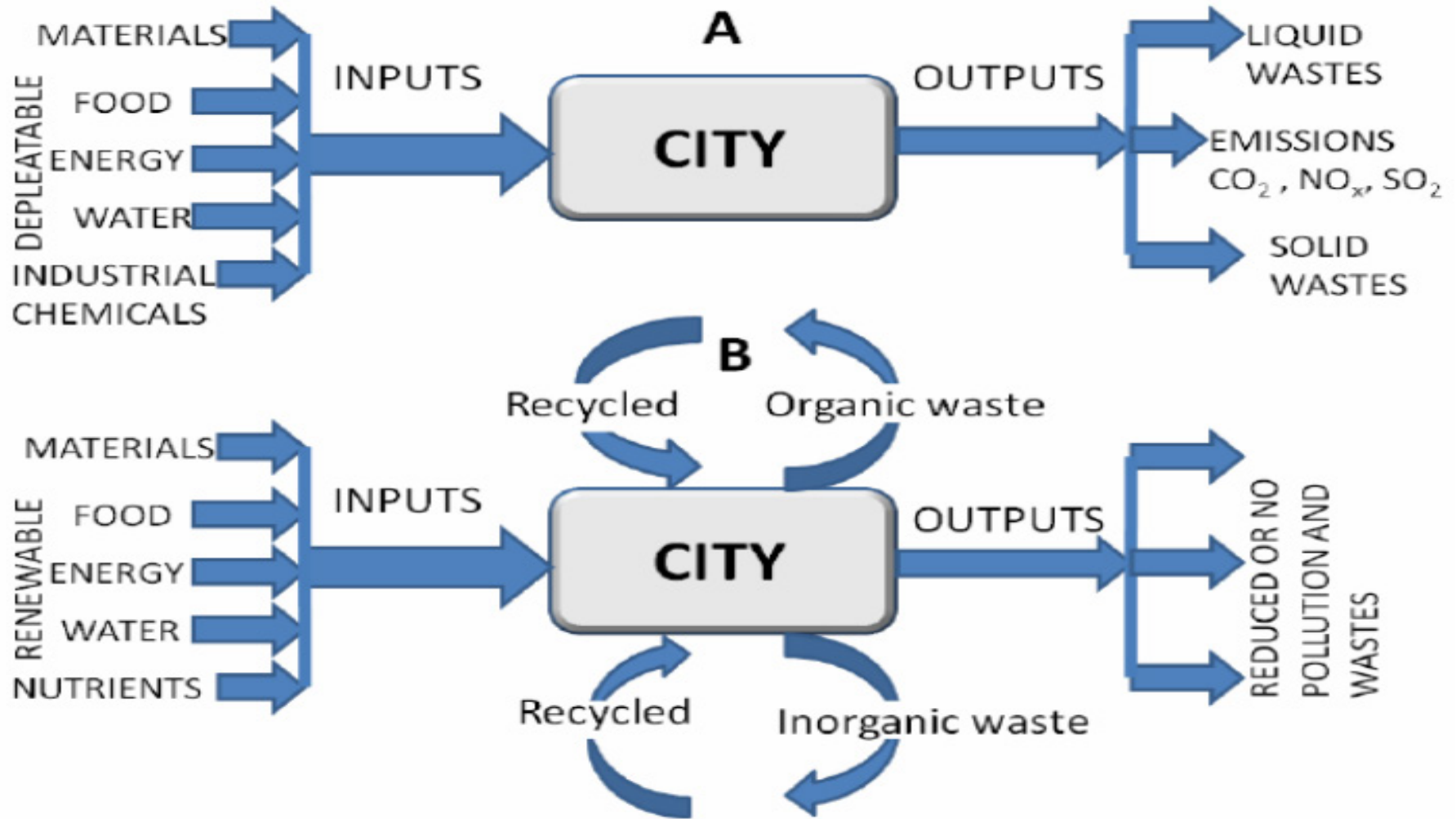


# Overview

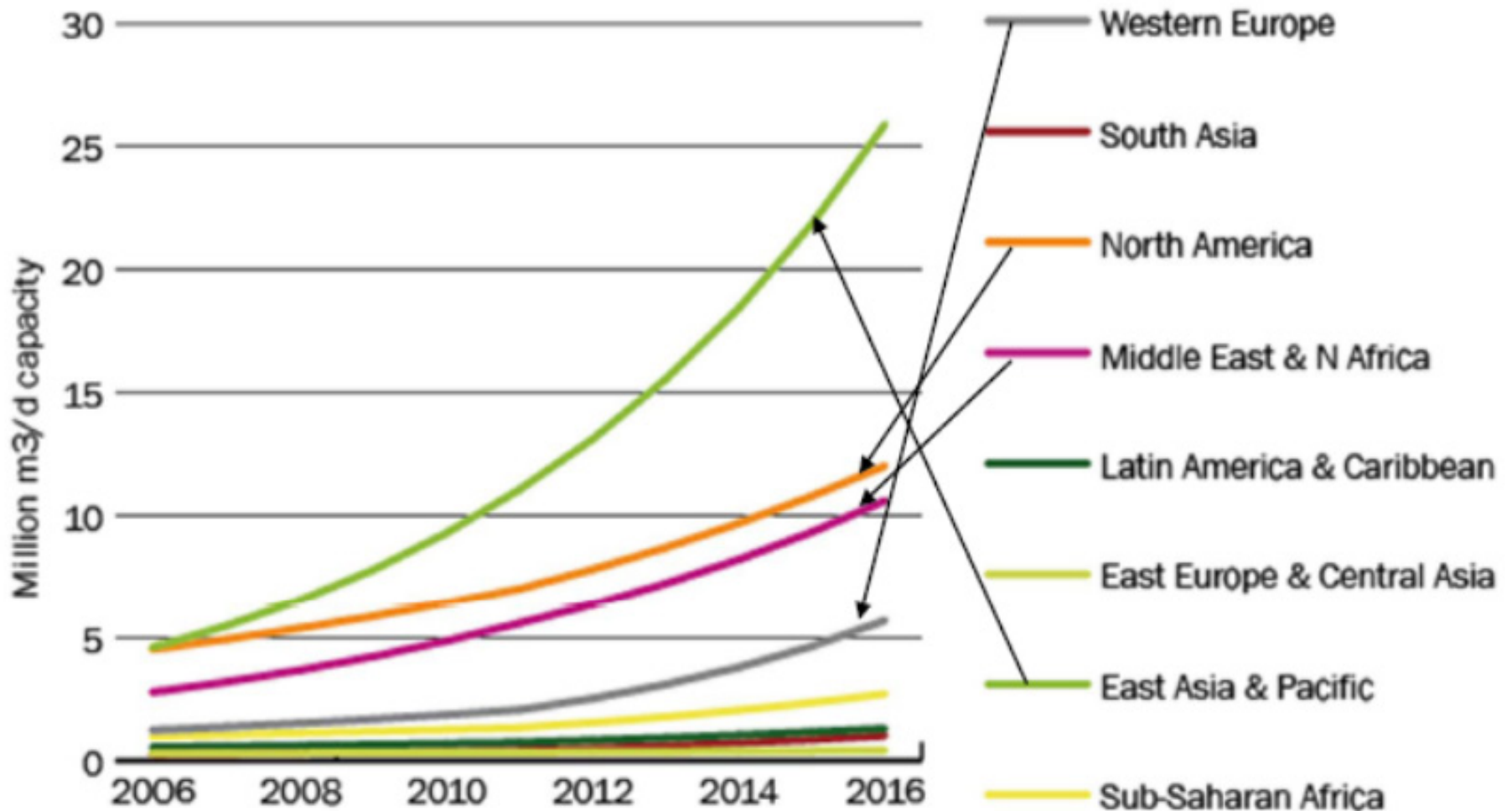
- Based on the strategic documents of the NoEs (Networks of Excellence) EMH (European Membrane House), ERIC (European Research Institute of Catalysis) and ENMIX (European Nanoporous Materials Institute of Excellence)
- Three ChemWater Vision 2050 workshops entitled: "Vision and Challenges", "Tools and Methodologies" as well as "Processes, Materials and Technologies for Water Sustainable Process Industry", held during 2012.



# Resource streams and linear (A), and cyclic (B) urbane metabolism systems



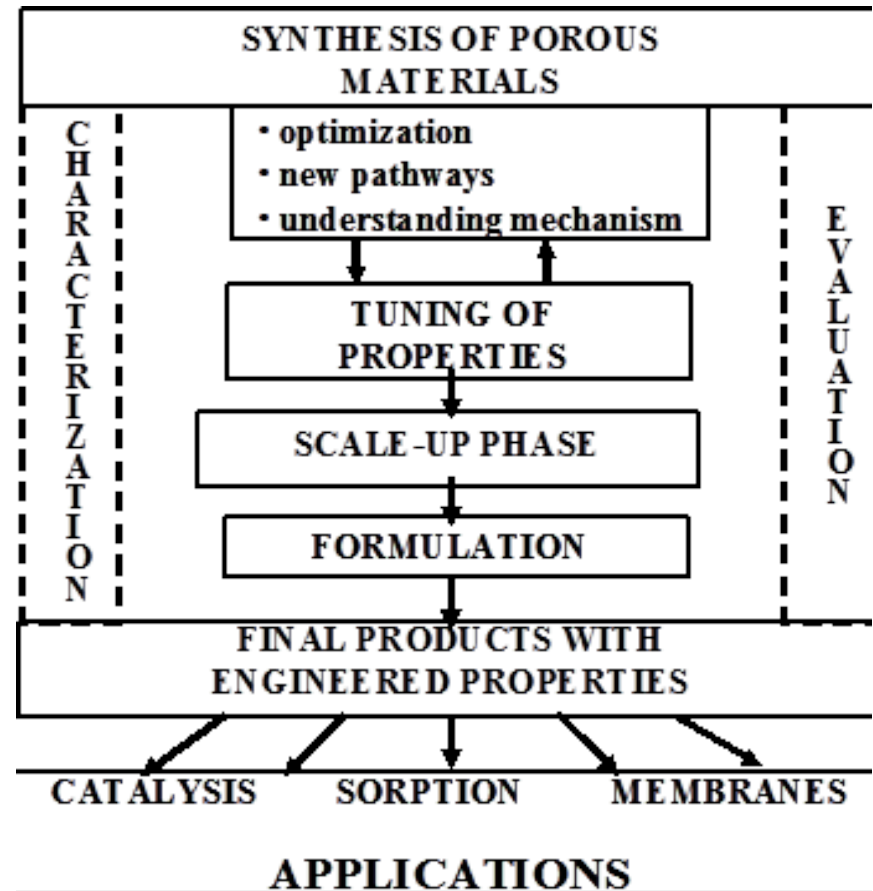
# Annual increase of installed capacities for re-use of waste water (Global Water Intelligence)



# Identification and development of nano-materials

- Nanoporous materials play an important role in chemical processing in which they can be successfully used as adsorbents, catalysts, catalyst supports and membranes and form the basis of new technologies (new, more efficient and environmentally fully acceptable processes) mainly due to their unique structural and surface properties.

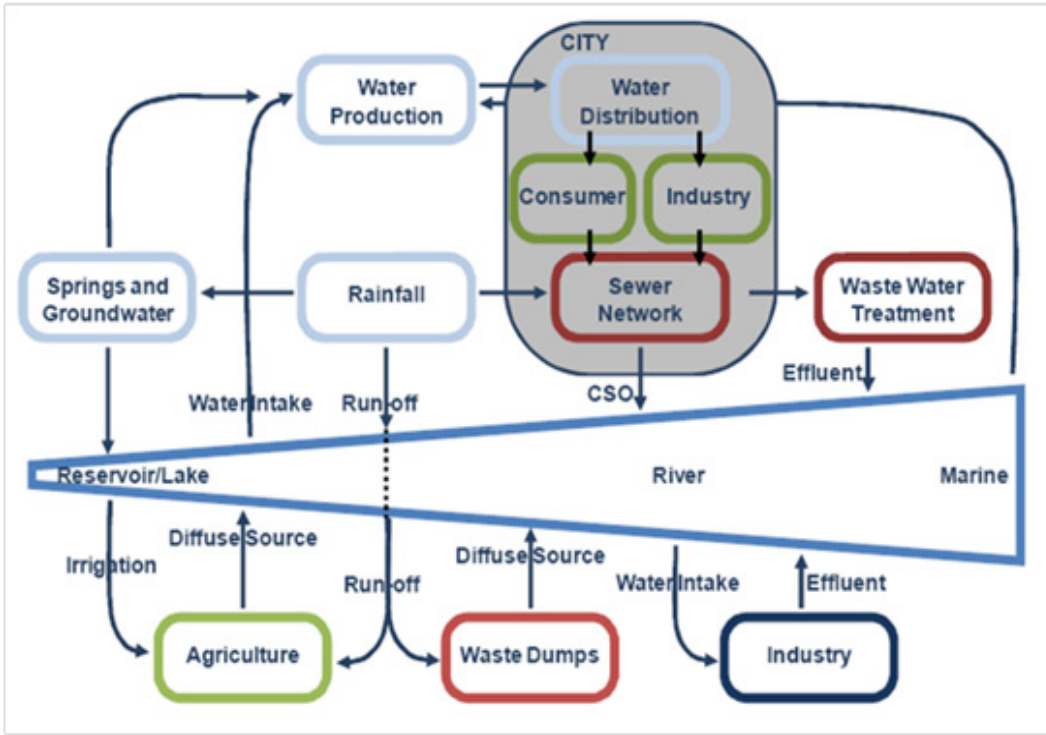
Materials with very narrow pores in the nano-scale range, i.e. from ca. 0.1 to 100 nm, are commonly referred to as **nanoporous materials**. Note that the lower end of this range, viz. from ca. 0.1 to 1 nm, coincides with the dimensions of the vast majority of molecules. The similarity of molecular dimensions and pore widths forms the basis for some unique and most striking applications of nanoporous materials in modern separation processes and heterogeneous catalysis.



# Sustainable Water Management

**Sustainable water management** requires a new thinking about water in an interdisciplinary and integrated way.

It also requires additional research and development of new materials with tailored properties and new nanotechnologies that can meet strong connections between eco-efficiency and performance, processing and manufacturing, recyclability and costs.



Most of the technologies contributing to **water management** are based on one or more of the Key Enabling Technologies (KET) (advanced materials, advanced manufacturing technologies, nanotechnology, industrial biotechnology, micro/nano-electronics, photonics).

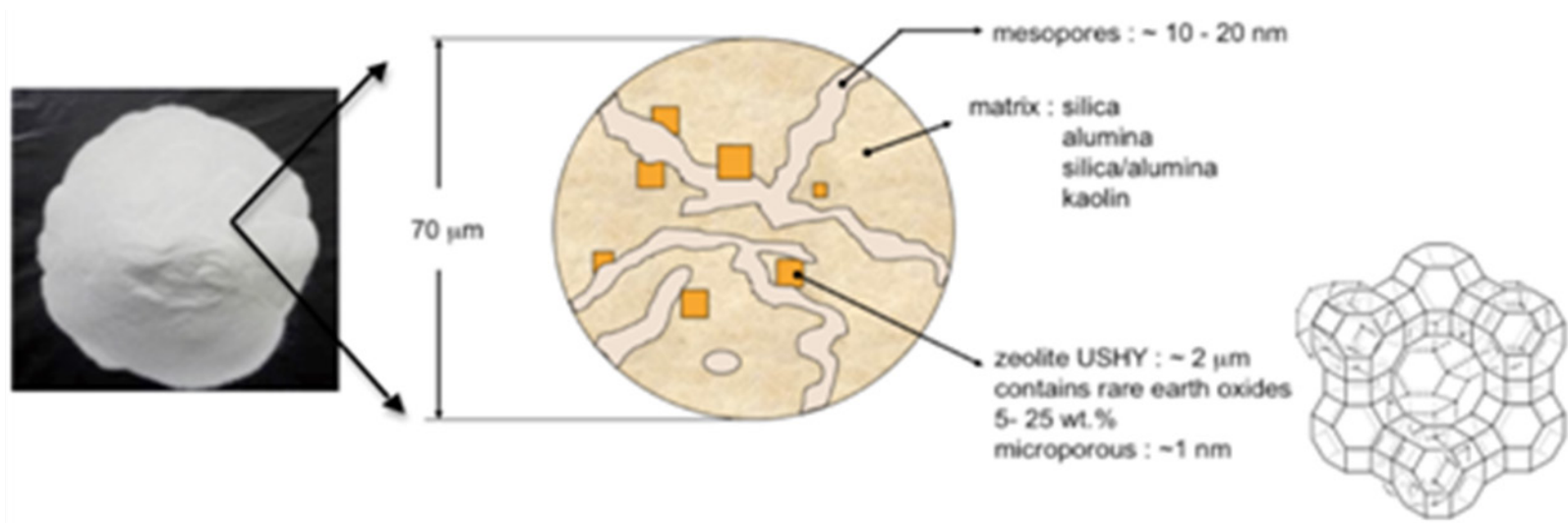
# Advanced Catalysts and Nanomaterials for Industrial Waste Water Treatment

- Solid catalysts have been extensively used in various water treatment technologies from about two decades, but a number of open issues in their uses have been identified by discussion within ChemWater as constrains limiting the actual use of catalysts for water treatment technologies in process industry.
- The use of solid catalysts in water treatment technologies requires also adapting the solid characteristics with respect to those typically used in conventional catalytic applications.



## Limited attempts have been made often to tailor solid catalysts for the water treatment applications, but more attention to this issue has been given recently:

- Pore structure design (intra-particle diffusivity is usually an issue determining the catalytic performances) -> Hierarchically ordered porous nanomaterials
- Leaching (often driven from the reaction products and thus depending on the progress of the reaction)
- Stability (related, but not only depending on the possible leaching), and selectivity (typically, quite complex mixtures should be treated in practical applications)





# Advanced Catalysts and Nanomaterials for Industrial Waste Water Treatment

## Specific subtopics identified

- Advanced multiscale design of hierarchic catalysts for use in new structured photocatalytic reactors
- Optimal catalyst design for wastewater treatment of complex reaction mixtures
- Analysis of eco-toxicity and toxicological effects in the wastewater treatment using catalysts
- New micro- and nano-structured materials (fibers, nanotubes, multilayer composite materials) for a more effective catalyst design in water treatment technologies

# Examples

## Dewatering of (bio)ethanol:

- The conventional dewatering of alcohols by azeotropic, extractive or two-pressure distillations is typically more energy-intensive and requires a complex process layout.
- Especially for ethanol/water and other systems possessing azeotropes, two alternative processes are available:
  - Pressure swing adsorption employing 3A or 4A molecular sieves (LTA zeolite) and
  - steam permeation using hydrophilic organic or inorganic (4A zeolite) membranes.
- The application of membrane processes is especially beneficial for systems of low relative volatility. The hydrophilic LTA zeolite membrane layer is extremely selective in the separation of water from organic solutions by vapor permeation and pervaporation and can be used, therefore, for the production of water-free ethanol.
- Some demonstrations and industrial applications are ongoing.

# Examples

## Nanotech photocatalytic materials for water treatment using sunlight:

- Heterogeneous photocatalysis involves the use of a semi-conducting material which can be excited by the absorption of light.
- The applications of photocatalysis include water treatment and purification, air treatment and purification, and 'self-cleaning' surfaces.
- There are a wide range of materials employed in photocatalytic research and applications. The important properties of these materials include the band gap energy and hence the wavelength of light required for excitation, the chemical and photochemical stability, particle size and surface area.
- Titanium oxide is still the most used semiconductor photocatalyst, for its robustness, availability and low cost.

# Examples

## Nanotech photocatalytic materials for water treatment using sunlight:

- Photocatalysis has been reported to be effective against a wide range of chemical pollutants including persistent organic pollutants (POPs).
- Heterogeneous photocatalysis is a rapidly expanding technology for water treatment.
- Photocatalysis may be applied for a wide range of cases of industrial relevance, although limited when the concentration of pollutants is rather low:
  - Removing trace metals and other inorganic chemicals (bromate, chlorate, cyanide, azide, halide ions etc.),
  - Destruction of organics, including hardly biodegradable chemicals such as herbicides and pesticides,
  - Water disinfections
  - Seawater treatment.
  - With membranes, it can be used to protect them from (bio)fouling.

# Examples

## Catalytic ozonation and reduction of nitrates/nitrites:

- Catalytic ozonation is an innovative technology for the elimination of organic compounds (oxalic acid, aniline, ...) in water and waste water.
- Activated carbon has been proved to be an efficient ozonation catalyst, but its performance can be increased when impregnated with oxides such as cerium oxide.
- Nitrate/nitrite removal in water is an important and developing area of research due to the increase of pollution in natural sources of drinking water. The catalytic removal of nitrate in water consists in the reduction of nitrate to nitrogen over bimetallic catalyst, composed by a noble metal (Pt, Pd) and a promoter metal (Cu, Sn, ...), supported on nanoporous materials, in the presence of a reducing agent.

# Examples

## Removal of arsenic in water:

- Arsenic contamination of drinking water sources has been reported in several European countries. It is a serious public health concern due to its carcinogenic effect. Arsenic can be removed by coagulation and filtration, ion exchange, membrane and adsorption technologies:
  - Ion exchange resins are effective in removing only arsenate (As(V)), but ground water usually contains arsenite (As(III)).
  - The use of membranes is quite expensive compared to other methods.
  - Arsenic removal by adsorption on activated alumina, granular ferric hydroxide and manganese greensand have been found to be effective, but some of these technologies need careful pre-treatments of the adsorbents.
- Some other promising systems to be used for arsenic removal in water are:
  - Titanium-based nano-materials
  - Ion-exchange resin impregnated with nano-scale iron hydroxide
  - Titanate nanofibers
  - Iron-oxide coated sand.

# Synergistic cooperation

**Remarkable progress may be achieved by synergistic co-operation of:**

- **Synthesis, molecular modeling of properties and applications of nanoporous materials:** The synthesis conditions have to be chosen taking into consideration the desired properties of the nanoporous materials. The ultimate objective is the ability to design sophisticated molecular building blocks that may act as carriers of structural and functional information to be expressed in a specific target material having superior properties in adsorption, catalysis and membrane applications.
- **Adsorption and catalysis:** The strong synergism between adsorption and catalysis arises from the fact that the former is always the first step in a catalytic process.
- **Catalysis and membrane technology:** There is a strong synergistic co-operation between catalysis and membrane science in the development of catalytic membrane reactors. These concepts require progress in the synthesis of the corresponding materials as well as modeling of the interaction of reaction and mass transport in porous media. Novel porous membranes like hybrid materials-based ones will become available.



## Research Needs: Concrete changes with a strategic importance are faced in the following areas (I):

- Increasing the selectivity and long term stability of nanoporous materials in order to reduce nitrates in ground water and waste water.
- Optimizing catalysts for the hydrodechlorination of chlorinated hydrocarbons.
- Development of nanoporous materials for removal of particulate matter, harmful dissolved components and salt, removal of trace contaminants (metals, etc.) used in wastewater treatment technologies.
- Expansion of the range of iron-based oxidation nanoporous materials, e.g. by incorporation in zeolites.
- Development of colloidal reagents and nanoporous materials which are suitable for in situ applications in contaminated ground water aquifers.
- Protection of nanoporous materials against being overgrown by biofilms and hence deactivated in long-term operations.

## Research Needs: Concrete changes with a strategic importance are faced in the following areas (II):

- Continue developing new materials that will support other sectors than chemical industry and help these sectors to be more water efficient and sustainable.
- Development of high surface to volume carriers for bacteria.
- Antifouling: New catalysts combined with oxidants (titania/ozone).
- The mechanism of nanoparticles removal from drinking water is still not known.
- The efficiency of existing treatment processes must be improved.
- Combination of existing water treatment processes (more effective, lower cost, lower energy consumption).
- Membrane applications: Fouling and concentrate waste water treatment and disposal must be addressed.
- Do nanoparticles affect the removal of other substances during drinking water treatment processes?



- Thank you for your attention