ObservatoryNANO
BRIEFING No.22
ENVIRONMENT
SEVENTH FRAMEWORK PROGRAMME

NANOSORBENTS FOR ENVIRONMENTAL APPLICATIONS

Nanosorbents are nanoscale particles from organic or inorganic materials that have a high affinity to absorb substances. Nanosorbents have applications in air or water purification, and also in remediation of groundwater or wastewater treatment processes. One of the most prominent examples of a conventional sorbent for environmental application is activated carbon. This conventional material is cost-effective in application and thus widespread in the European drinking water industry for water purification. However, nanostructured sorbents offer the opportunity of an even greater sorption capacity and may be designed to target specific contaminants. Different carbon-based materials and metal oxides are under investigation to address a variety of contaminants. However, most potential nanosorbents are in the state of research; very few applications are market-ready and will require both translation from lab to field scale plus appropriate safety testing. This BRIEFING will describe the technologies, look at their potential impact, and highlight a number of challenges being faced in their route to market.

Superior sorbents for multiple applications

Most environmental applications of nanosorbents are in the field of drinking water production and wastewater treatment, with other applications targeting soil and groundwater contamination or air pollutants. The intention in creating and evaluating nanosorbents is to develop sorbents with an even better sorption capacity than conventional sorbents based on the large surface area of nanoparticles, an increased substance specificity (e.g. by surface functionalization of the nanoparticles), ability to integrate multiple reactive agents together, and to engineer mass transport limiting conditions. Hence, nanosorbents have a high capacity to rapidly and specifically recover or remove target contaminants. The most promising applications at the time are:

- Soil/groundwater remediation by carbo-iron;
- Nanoclays for the adsorption of organic contaminants and phosphorus;
- Nano-aerogels for the removal of uranium from groundwater;
- Nano-iron oxides to adsorb pharmaceuticals and hormones from wastewater; and
- Nano-metal oxides, dendrimers and polymer nanofibres for the removal of arsenic and heavy metals.

Background

Sorption is a process where a substance (sorbate) attaches (adsorbs) to another substance (called sorbent) by physical or chemical interactions. Sorbates must diffuse from a water or gas phase onto the sorbent surface, and frequently into the internal pores of a sorbent. Since nanoparticles have a very high surface area, the sorption potential of nanosorbents is significantly increased compared to conventional materials. Furthermore, the bottom-up approach in nanoatechnology allows a tailored design of the nanosorbents to meet specific needs. Nanosorbents can be engineered to have multiple reactive nanoparticles or nano-structured components (e.g., metal impregnated activated carbon; palladium-gold nanocomposites).

For example; researchers from different universities in the USA and Asia have invented a nanostructured sorbent, Captymer™, which consists of branched macromolecules with physically and/or chemically tunable sites that are put together to form globular microparticles. Due to the high density of the adsorbing sites, the product is advertised to have a twice as high sorption capacity as conventional materials. According to the company AquaNano[1], the product can be configured to be regenerable or disposable and is available as powder or beads. It may be applied for the selective removal of contaminants (such as perchlorate, nitrate, bromide and uranium) from potable groundwater sources, to recover nutrients (such as nitrate and phosphates) or to remove boron/borate from wastewater streams. The company claims that *"future versions of Captymer media will be designed to address the separation needs of the mining, chemical, oil/gas, biofuel, food, pharmaceutical and nuclear industries*."

Hong Kong Polytechnic University has developed a polymeric nanosorbent, which is successfully applied in wastewater treatment by the Dunwell Group[2]. It is promoted as effective adsorbent for many organic and inorganic contaminants in wastewater. The saturated nanoparticles containing the adsorbed contaminants can be separated from the wastewater by a membrane system and then regenerated. In a different approach the Idaho National Laboratory[3] uses metal oxides embedded in a polymer matrix for the adsorption of arsenic.

Another category of sorbents are nanoclays, nanometre-thick clay platelets usually having montmorillonite as main constituent. The platelets can be modified with different organic compounds to improve their properties (organoclays or polymer-

-clay nanocomposites (PCN))[4]. Studies showed that the adsorption capacity of the investigated organoclay was significantly higher than of the unmodified clay. The organoclay was able to adsorb hydrocarbons up to 10 times of its own weight within one hour[5, 6]. Different nanoclays have also been investigated as sorbents for dyes[7] and phosphorus[8]. In both studies the organoclays were found to have an extremely high contaminant affinity indicating that nanoclays may become superior sorbents for dye and phosphorus removal from wastewater.

Another promising opportunity is to combine nanosorbents with a catalyst for the combined sorption and degradation of contaminants. The adsorbing part of the particle is responsible for the concentration of the contaminant at the particle surface which facilitates the decomposition of the contaminant by the catalyst. For example, magnetic nanoparticles can be dotted with reductive materials or photo catalysts.

Another example is Carbo-Iron by the German Helmholtz Center[9] consisting of elementary iron attached to an activated carbon particle. The activated carbon is responsible for the sorption while the elementary iron is reactive and can reduce different contaminants. Furthermore, the Carbo-Iron is easily suspended in the phase of the organic contaminant while regular nano-iron stays at the edge of the organic phase (***Figure 1***).

A different combination of sorption and catalysis with nanomaterials is described by NanoAqua[10]. They use 10nm thick protein layers (S-layers) produced by the self assembly of bacterial surface proteins and enhance these layers with catalytic nanoparticles (TiO_2, ZnO) to concentrate contaminants on the surface and degrade them simultaneously (***Figure 2***).

In most cases water treatment systems making use of nanosorbents must ensure that the nanosorbent is retained and not released into the environ-

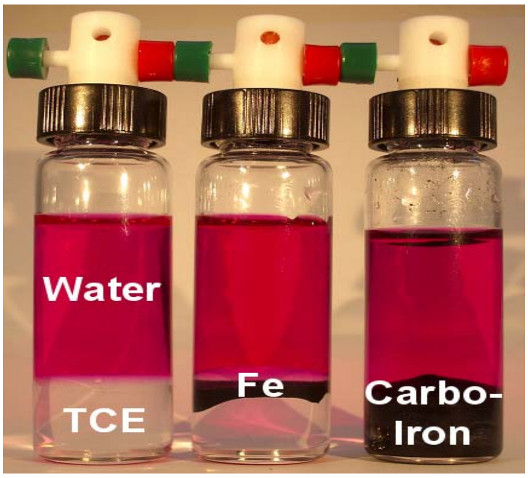

***Figure 1**: Comparison of the suspension of nano-iron versus carbo-iron in the organic phase of the contaminant (TCE: Perchloroethylene)*[9]

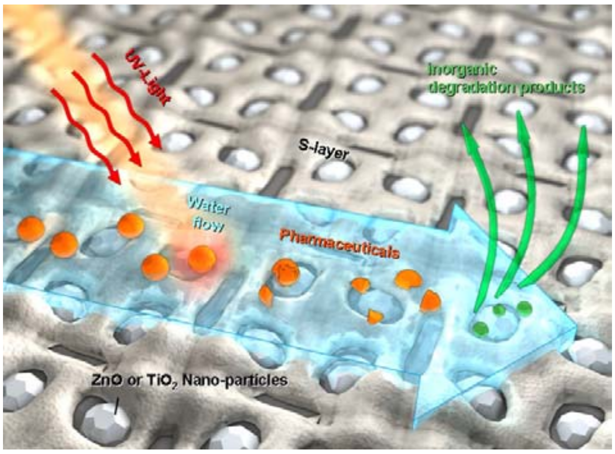

***Figure 2**: Concept of photocatalytical layers with S-layer and photocatalytical nano particles*[10]

ment or drinking water. This can be achieved by encapsulating the nanosorbents in larger particles, by filtration, or by fixing the sorbent on a support material. It is also possible to remove magnetic nanosorbents, together with the adsorbed contaminants, using magnetic forces. Generally, for a cost-effective application of the nanosorbents, they must be regenerated. This means that the contaminants are desorbed from the nanosorbent by rinsing with a cleaning agent (e.g. with a different pH). For example, ion exchange (IX) beads have been used to support nano-scale iron (hydr)oxide to remove arsenic from drinking water. The IX beads serve as a support media, and alkaline regeneration removes arsenic from the iron (not the IX resin).

Impacts

Societal/Impact on European Citizen

Clean water is a basic need for all life and since fresh water sources are scarce in many countries, there is a large societal benefit (especially also in developing countries) from new solutions to produce drinking water and to clean wastewater.

Nanosorbents can contribute to improve the drinking water quality, to recover heavy metals and other materials from wastewater streams and to remove trace contaminants from wastewater streams. However, it must be ensured that the nanosorbent itself does not pose any threat to human health or the environment and that the material is available at a reasonable price – ideally even less expensive than existing water treatment systems. In addition the system should be easy to use and not require large/extensive additional infrastructure so that it can be used also in developing countries.

Economic/Industry

The economic impacts of nanosorbents are based on three characteristics:

- The nanosorbents may become so effective that they render some sections of the existing solutions obsolete;

- The engineered selectivity of the particles may open new revenue streams for the existing processes; and
- Nanosorbents may prove useful in solving challenges that are currently very expensive and very demanding to solve.

According to a market study by BCC Research in 2009[11], the total market for all nanotechnology enabled environmental applications will be worth some €15 billion globally by 2014. This covers all environmental applications from enhancement of the environment to remediation and protection. Nanosorbents present only a small sub-section of this whole market. BCC research has concluded, in a report from 2011[12], that the total market for emerging nanotechnology products used in water treatment, including nanosorbents, will be only around €80 million in 2015. One can see that the large scale commercialisation of nanosorbents is to be expected only after some additional 10 years of applied research.

For comparison, according to a market study by Freedonia[13], the global markets for activated carbon was around €1.5 billion in 2009 and was expected to grow to reach over €3 billion by the end of 2014. Activated carbon sells currently for some €1.5/kg. Activated carbon is a good comparison material as it is used in similar application areas to where nanosorbents are expected to add efficiency and functionality. Another suitable material for comparisons could be Zeolite, which is also widely accepted in similar use cases, especially in industrial scale water treatment. A very promising material that is anticipated to have a very large market potential are nanoclays. However, the main application area of nanoclays is in the packaging industry to improve materials properties (such as structural reinforcement and mechanical strength, gas permeability barrier, flame retardancy), while adsorbing nanoclays account for only a small part of the industry.

According to the expert interviews the most likely commercialization track for nanosorbents is through substituting existing sorbents and treatment chemicals with nanosorbents in the existing processes. Thus the expected economic impacts for the existing industries, in the form of required additional investments, are expected to remain modest. However, if the engineered selectivity of contaminant removal leads to new value creation from recovery of valuables, additional process steps and thus additional investments will be required.

One key driver for a more wide spread acceptation for nanosorbents comes from stricter requirements for contaminant levels in drinking water. For example, the development of nanosorbents for arsenic removal gained momentum after the US Environmental Protection Agency reduced the acceptable level of arsenic to 10 parts per billion (ppb) from the previous 50 ppb. According to Idaho National Laboratory[3], this change in regulation created a direct improvement need for nearly 4000 municipalities and affected the life of 14 million homeowners in the USA in 2002. Similar regulation can be expected for trace contaminants in drinking water in Europe.

Technology readiness levels (TRL)

There are very few applications in the state of pilot projects and even less have entered the market. Most nanosorbents are still under investigation in applied or even in basic research. The most mature projects are nanosorbents based on iron oxides since this material is abundant in the environment and can be removed by magnetic forces. Inorganic carbon-based materials such as carbon nanotubes are far from the market while there are several projects with organic macromolecules/dendrimers. The AquaNano company anticipates that their Captymer™ technology will "quickly become the industry standard by providing customers with higher performance exchange media at a cost comparable to that of existing commercially available." Generally the TRL of nanosorbents is about 2 while few projects are already at the stage of pilot projects or even entering the market.

Challenges

Technological

The technical challenges are still quite fundamental on one hand regarding the development of the nanosorbent and on the other hand regarding the system setup:

- Novel nanosorbents must fulfil a variety of requirements at the same time to be economically and societally beneficial: specificity, high sorption capacity and cost level;
- Scaling up the production is challenging especially for carbon-based materials;
- Since the water industry is very conservative, new nanosorbents systems should ideally be compatible with existing systems meaning that it must be possible to integrate the nanosorbents cost-effectively into existing systems;
- The system setup must ensure that the nanosorbent is removed entirely (for example by magnetic forces or by filtration) to avoid the release of nanoparticles to the environment and to drinking water as well as to safe costs by regenerating the nanosorbents.

Environment, Health & Safety

Nanosorbents as free nanosized objects must also comply with the stringent water regulations to ensure the safety of human health and the environment. It is understandable that European society, including decision makers and drinking water consumers, are very cautious with regard to drinking water quality. Hence, water company managers are reluctant to invest in new methods as long as their harmfulness has not been proven. This is especially true for the European society. The workshop on nanosorbents for water treatment (held on the Monte Verita, Switzerland, May 2011) has revealed significant differences between the U.S. American and European perspective on the use of new substances. The strong precautionary attitude in Europe slows down the introduction of new substances especially in the environmental sector.

To fabricate safer nanomaterials, several practical concepts are emerging for the selection of materials: no use of metals with known toxicity to humans or the environment; use of compounds already applied in water treatment (iron, titanium, carbon); research on detection and quantification of the nanomaterial in water; and engineering of systems that support the nanomaterial recovery without undesirable leaching into drinking water or rivers.

Currently there are only a couple of different nanosorbents that can be produced in commercial quantities, thus development work is still needed to get the price down to comparable levels. In the case of zero-valent iron, the experts said that the price level of the nano-material was acceptable when it was some 10-times more expensive as the micro-grade material.

Regulations & Standards

In nanosorbents, the acceptable price is highly dependent on the application – if the regulation requires performance only achievable by nanosorbents, the price is not such an important issue; if the nanosorbent is merely used in place of existing materials, the operators are very interested in the cost-competitiveness of the new materials, requiring the total cost to be lower than with the conventional substances. According to the experts the price constraint might be pretty severe as they commented that the only way the engineered nanosorbents might be able to compete against the existing technologies is by regenerating the material to allow for multiple uses.

EU Competitive Position

In the field of nanosorbents, there is significantly more research and applications activity in the US and Asia in comparison with Europe. In Europe there is little research ativity and even fewer companies who are investing in nanosorbents. The only European product in the field of nanosorbents that has passed the stage of applied research is Carbo-iron by the Helmholtz Center in Germany.

Summary

- Nanosorbents eventually present a potent alternative to conventional treatment methods. Special features are increased adsorption capacity and substance specificity.
- However, most applications are not yet ready for the market due to technical challenges (e.g. scale up, system set up), environmental concerns and cost-effectiveness.
- Few products are on the market mainly from the U.S. and Asia.
- Preconditions for an accelerated/successful market entry are: system compatibility with existing facilities, stricter environmental regulations and cost-effectiveness.

Further information

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