Workshop Nanomaterials for Water Treatment: Opportunities and Barriers
Conclusions

1. Opening session

As much as half of the total amount of drinking water consumed in the world returns as sewage water with an incredible variety of contaminants dissolved on it. This enormous amount of wastewater forces scientists and authorities of around the world to face various solutions to water scarcity, such as water re-use, purity level of the water needed for the different uses, the sustainability of the actual model etc.

European Commission's vision

Environmental technologies in Europe should be based on three main research strategy axes: EC environmental policies, European competitiveness on the global markets and Science & Technology excellence. Based on these main research strategy axes, water issues might be among the EU priority research areas in the forthcoming years. In that sense, the EU is funding several large projects in different areas, such as NEPTUNE (Technologies for municipal wastewater treatment), NANO4WATER (nano-structured membranes for water filtration) and TECHEAU (technologies for drinking water production and distribution).

One of the EU priorities is the promotion of research that supports a smart, sustainable and inclusive growth. Actually, the EU is already investing in this topic via the WssTP (Water supply and sanitation technology platform). WssTP has started 6 water pilot programs (coasts, cities, industry, agriculture, groundwater & extreme hydroclimatic events), meanwhile Acquea (Industry driven Eureka cluster) highlights the importance of improving or developing innovative technologies in areas such as membrane technology, real time monitoring, disinfection or wastewater treatment with low energy consumption.

Emerging contaminants

Emerging contaminants were defined as "things in our water we know little about but scare us". That is why it is necessary to measure health and ecosystem risks of conventional and emerging contaminants, depending both on the exposure and on toxicity of the pollutant. In general no risks are expected for personal and pharmaceutical care products (PPCPs) since maximum finished water concentrations (usually ng/L levels) are below the expected effect concentrations. In most cases, these PPCPs residues can be quantitatively eliminated from water combining different technologies (e.g. biological treatment + oxidation + sorption). However, since there is still a lack of an integrated treatment system in many sewage treatment plants, PPCP residues have been detected in many wastewater treatment plants effluents. This means that PPCPs (and many other chemicals) are still discharged into surface waters.

2. Nano zero valent iron (nZVI) for groundwater remediation

ZVI nanoparticles react with a wide range of contaminants, and the effect of particle size on the reactivity of nZVI is as important as other effects such as particle composition, contaminant structure and solution chemistry.

It is essential to develop in-situ nanoparticle detection methods during the ground injection process, as many factors can influence the transport of surface modified nanoparticles in the soil. Some of the most important factors are the surface modifier, size, pH, velocity of flow and the type of soil and media.

The mobility of the nanoparticles can be studied using laboratory scale columns (1-D) and 2-D scale tanks. We still need nZVI with increased mobility and nZVI nanoparticles with longer reactive lifetime in order to achieve satisfactory results.

3. Photocatalysis with TiO_2

After many years of research in the field of heterogeneous photocatalysis, TiO_2 still seems to be the best photocatalyst around. In this kind of works, it is common to monitor the photocatalytic activity by means of dye decolouration tests, but attention should be paid to possible side reactions that could lead to errors (i.e: the rupture of a single bond from methylene blue molecule would decolourize the solution, but the molecule would remain almost intact). Known degradation products, ions, or gases should be used to monitor the degradation and mineralization of the target molecules to get accurate results.

Solar photocatalysis

Solar photocatalysis is also a promising process that could be used to produce potable water in semi-arid countries. The possibility of using free solar energy represents the main attractive feature of this technique, and much work is being developed in places like the Plataforma Solar de Almería (PSA). In these works, the parabolic collector configuration has been demonstrated as one of the best options for solar photocatalysis.

Water disinfection

When dealing with photocatalytic disinfection of water, it should be taken into consideration that on the contrary to molecules, microorganisms are at least two orders of magnitude larger than the catalyst particles. That is why a high contact is required between TiO_2 nanoparticles and the organisms. (This difference in size makes that degradation efficiencies observed in the inactivation of microorganisms do not always remain the same as those achieved with molecules).

Potential applications of the photocatalysis

Photocatalysis is recommended as a complementary treatment in WWTP, for specific applications such as chemical synthesis, or for odours elimination. Photocatalysis could represent a valid option as part of a treatment train which could contribute to minimize the energy requirements (lowering residence time) and chemicals consumption. Photocatalysis is not the best option to remove heavy metals. Although theoretically metals could be reduced via photocatalysis, in practice it has been shown to give poor results. Furthermore, some studies demonstrate that metal ions have a negative effect on the photocatalysis with TiO_2. The main challenges of photocatalysis are the scaling up and the treatment of high TOC content waters.

It was discussed whether photocatalysis can really demineralise organic chemicals or not. It was concluded that in most cases the answer to this question is affirmative, but there are some exceptions (i.e. cyanuric acid) which are recalcitrant to this technology. Degradation of organic chemicals leads to CO_2 + water + (in some cases) small simple carboxylic acids, which were observed to be biodegradable. During this degradation process the toxicity of the water sample decreases with time.

Slurries' or supported photocatalysts' efficiencies cannot be compared, but both slurries and supported systems require good chemical engineering to build an efficient system. The inadequate knowledge in this area seems to be one of the limiting factors in order to commercialise photocatalysis treatments.

So far, commercial applications of photocatalysis are still scarce. Process costs may be considered another obstacle to their commercial application, but it is not the only one.

4. Photocatalysis with TiO_2 (2)

In this session three real applications of the photocatalysis were shown: degradation of cyanotoxins, degradation of a PPCP and ageing of TiO_2 coatings under realistic conditions.

Photocatalytic degradation of cyanotoxins

Cyanobacteria blooms are a serious problem worldwide, as many of these bacteria segregate cyanotoxins, such as microcystin - LR (MC - LR), which has hepatotoxic activity. The photocatalytic degradation of MC-LR results in 21 secondary metabolites. Although all of them are finally degraded via photocatalysis, the time needed to achieve these results varies from one compound to another. It is essential to determine this degradation time in order to combine photocatalysis with cheaper treatments (i.e: biological treatment). Furthermore, the toxicology of the secondary metabolites should be determined.

For urban water, it should take about one hour to eliminate hepatotoxicity caused by cyanotoxins, and 2,5 hours to reach total mineralization. Industrial water mineralization highly depends on the pollutants dissolved in the water.

Photocatalytic degradation of clofibric acid

Clofibric acid (CA) is a PPCP detected in WWTP effluents, surface water and groundwater. It is a persistent compound that is not eliminated with conventional technologies. The degradation rates of CA (working with TiO_2 coatings) under different environmental conditions were analyzed, observing that the elimination rate of clofibric acid is reduced in presence of other pharmaceuticals and enhanced in presence of humic acids and surfactants.

Ageing of TiO_2 coatings

In order to study the ageing of coatings, a new test was designed. The ageing of TiO_2 coatings was carried out under a circulating water flow in an aluminum flume for up to four weeks under different conditions. Physical damage on the coatings was observed by a tape test. Results showed that tests containing dissolved NaCl resulted in coatings with more damages in their surface. Images obtained by SEM also confirmed a drastic change in the coatings morphology when NaCl was present in the water. It is also remarkable the reduction of photocatalytic activity observed for all samples, whatever the water characteristics. This activity reduction was demonstrated to be related to aluminum contamination from the flume. Aluminum ions dissolved into the water which led to the coating Al coverage, which impeded the contact between TiO_2 and the target contaminant.

5. Photocatalysis with TiO_2 (3)

Photocatalytic degradation of pesticides

The problem of pesticide contamination in drinking water in developing countries is a reality today. Between these pesticides, organophosphates have been detected at ppm levels, which is a suitable concentration for the application of photocatalysis technology.

The photocatalytic experiments showed that organophosphate pesticides were completely decomposed in less than an hour. The degradation subproducts formed during the photocatalysis (such as phosphoric acid) have high toxicity, however, due to their strong adsorption to nanoTiO_2 surface, the removal efficiency is high, and it results in a swift detoxification.

Some real applications of solar photocatalytic reactors were also presented, such as the single family pilot reactor installed in Thailand. The reactor aims to degrade pesticides from water in a ceramic rainwater reservoir, and it consists on a simple filtration tank, a photocatalytic reactor with aluminium sheet to concentrate the light, and a water reservoir. The main advantages of the system are the low cost and that electricity is not required. This pilot reactor achieved a complete elimination of acephate (1,09 x 10^{-5} mol/L) in just one hour circulation time.

The potential of titania nanotubes

Titania nanotubes catalysts seem to be a promising alternative for water decontamination. Two different routes have been used to fabricate them; *anodic oxidation* of titanium metal in presence of fluorine anion and *hydrothermal treatment* of titanium dioxide. Although the surface area achieved in the case of dispersed nanotubes is eight times higher than P25 nanoparticles, the light does not reach the inner part of the nanotube, thereby reducing the effective surface area. Moreover, the nanotube’s inner area could even promote the pair electron-hole recombination, so that their effectiveness does not reach the conventional P25 except in specific cases.

Work has been done trying to improve the photocatalytic activity of nanotubes under visible light by non-metal doping. Although N-doping self-aligned titania nanotubes show an improvement in photocurrent response under solar radiation, doping an homogeneous surface is far more difficult, so the efficiency under visible light is not that good. It was highlighted the vital importance of taking into account the effect of light to draw conclusions and not just focus on differences in surface areas, which is a widespread practice.

In general there was a considerable controversy regarding the “nano” effect of the titania nanotubes.

6. *Potential environmental implications of nanoparticles*

“We do not want nanomaterials to be the 21st century pollutants”

Nanotechnology holds great promises in a wide range of sectors (electronics, medicine, biotechnology…) but history showed that several technologies that were initially promising could reveal catastrophic if uncontrolled: we have to steward properly nanotechnology. In the last decades the number of papers published on nanotechnology has experienced an exponential growth. However the wide majority of these papers deals with the applications of nanotechnology while those related to environmental health and safety implications of nanotechnology only account for 0,25% of this number. This shows that former mistakes could be repeated with applications coming before their risks could have been investigated seriously.

Research has been performed on the antibacterial activity of nanomaterials. The reason of focusing research on how nanoparticles affect microorganisms is that bacteria are the ground of all ecosystems, so if they are affected by nanomaterials, the release of such materials into the environment could result in a modification of the ecosystems. In addition, bacteria are sensitive organisms which could be used as indicators for nanomaterials toxicity.

Fullerenes (C_{60}) in the environment

The use of fullerenes (C_{60}) as photocatalyst and antioxidant is being widely investigated. This molecule has the drawback of being highly hydrophobic (and therefore insoluble), but can be stabilized in water through the use of transitional solvents such as toluene or long-term stirring. It then forms agglomerates called nC_{60} which are the form in which fullerenes could be found in water. However, when C_{60} swifts to nC_{60}, it loses the ability to generate reactive oxygen species (ROS) and the oxidation potential is also diminished. In addition, nC_{60} remains significantly toxic, as it has been found to hinder zebra fish larvae hatching and increase the tendency of hatched larvae to get pericardial oedema.

Bioaccumulation of nC_{60} in earthworm was shown to be inversely dependent on their concentration. This bioaccumulation does not correlate with its K_{ow} (octanol-water partition coefficient), which suggests that standard thermodynamics concepts may not apply to nanomaterials. If we focus on the effect of nC_{60} in bacteria, the nanoparticles seem to be adsorbed to the surface of bacteria but its size prevents it to penetrate them. Cell damage is supposed to come from an interruption of the electron flow between the two sides of the membrane.

Some work is being developed to avoid C_{60} nanoparticles spreading to the environment, some of them based on immobilizing C_{60} on bigger silica beads easy to separate from water, which results in an increased surface area.

Transformations of nanoparticles in the environment

Nanoparticles are likely to undergo complex transformations in the environment that may change their toxicity and transport behaviour. There is an urgent need of dynamic analytical methods to be able to characterize these changes and determine to which kind of nanoparticles will be exposed the environmental receptors. For instance nC_{60} clusters were shown to be trapped by natural organic matter (NOM), which hinders their contact with bacteria and reduces therefore their toxicity. Something similar happens with nZVI, as pure nZVI nanoparticles were found to damage some bacteria but when the nanoparticles are coated (in stabilization purposes), this genotoxicity is reduced.

Although nowadays much attention is being paid to personal and pharmaceutical care products (PPCPs), including endocrine disrupters, the interest seems to be slowly shifting to nanomaterials. Nanoparticles are being observed in wastewater and WWTP biosolids due to their inclusion in commercial products. The fate and occurrence of these nanomaterials are still uncertain and the scientific community has started to track nanomaterials thought-out the urban and natural water.

Another question was raised related to the effect of aggregation of the nanoparticles in water. Can the risk be discarded taking into account that nanomaterials always tend to aggregate and then lose their "nano- aspect"? These questions do not have any clear answers yet, but probably in the future LCA approaches will be necessary to take all theses aspects into consideration.

Nowadays, most of the nanoecotoxicology research papers consider pure nanoparticles, without having into account the modifications of the nanoparticles that are continuously happening in the natural media. There is a huge research field in more realistic situations.

Risk assessments

As traditional risk assessment states, there is a clear relationship between risk, toxicity and exposure: if there is toxicity but no exposure, risk is equal to zero. It is feasible to play on both parameters (exposure and toxicity) to control the risk by reducing exposure or by employing nanoparticles designed to avoid toxicity. In this context, a big question emerges: is it possible to eliminate the features that make a nanoparticle toxic without compromising its effectiveness in the applications? Would the risk be higher if we have a lower toxicity but a higher exposure?

Pedro Alvarez stated that the EU recently defined nano TiO_2 dust as a potential human carcinogenic substance when inhaled.

OECD and nanomaterials (Organisation for Economic Co-operation and Development)

OECD's work on Nanotechnology is divided in two committees: Working Party on Nanotechnology (WPN), focused on the development of the technology, and the Working Party on Manufactured Nanomaterials (WPMN), focused on safety of nanotechnology. The objective of the WPMN is to coordinate the scientific research at an international level to try and fill knowledge gaps on the effects, exposure and risk of nanomaterials and finally release internationally harmonized standards to evaluate manufactured nanomaterials safety.

The activities of the WPMN at present are distributed over three main projects: the Database on Research into the Safety of Manufactured Nanomaterials (gathers research projects that investigate the environmental and human health and safety of manufactured nanomaterials in order to identify knowledge gaps and promote the collaboration between research groups), the Manufactured Nanomaterials and Test Guidelines project (aims at reviewing current OECD test guidelines for chemicals and evaluate their applicability to manufactured nanomaterials in order to finally develop guidance for an appropriate testing of these compounds) and the Safety Testing of a Representative Set of Manufactured Nanomaterials (13 classes of manufactured nanomaterials will be tested with the objective of generating some knowledge on the safety characteristics of manufactured nanomaterials).

The work of the WPMN will lead to the development of internationally harmonized standards for testing environmental and health safety of manufactured nanomaterials and may serve as an input for governments to build up regulations for these materials.

US EPA's vision

US Environmental Protection Agency has been working on nanotechnology for the last years. EPA's work focuses on fate, transport, characterization and toxicity (ecotoxicity & human health) of nanomaterials (mainly Ag, TiO_2 and ZnO), but their environmental applications are also investigated.

Characterization and detection of nanoparticles in water

Characterization is crucial to ensure that the system tested corresponds as close as possible to reality. In that sense, particular attention should be paid to nominal concentrations, as nanoparticles get adsorbed on a wide range of surfaces and the real concentration of dispersion may be much lower than its nominal concentration. Aggregation of nanoparticles is another important phenomenon, influenced by numerous parameters such as concentration, aqueous matrix, capping agents, or the stability of the dispersion. A reliable evaluation of size is also difficult, as microscopy and Dynamic Light Scattering techniques usually lead to different results. In that sense, there is an open discussion about the relevance of actual dose metrics for nanomaterials, as mass concentration units do not allow to discriminate between a big number of small particles and a small number of big particles, although both situations may lead to different exposure scenarios.

Some questions arise regarding the detection and characterization problems related to the study of engineered nanoparticles (ENP) in natural media. How to assess the risk of ENP in natural media? How to distinguish their toxicity with respect to natural nanoparticles, naturally occurring at much higher concentrations (10^8 natural NP/ml versus 1, $5x10^3$ ENP/ml)?

Based on Substance Flow Analysis a Particle Flow Analysis model can be developed in which a three phase flow is considered: production, use phase and waste handling. Emissions are calculated in each phase both for the present situation and in explorative scenarios. While some models are already available to estimate emissions of nanoparticles to the environment, the prediction of their fate in the environment remains very complex and cannot be done until we determine what parameters are relevant.

But particle size related phenomena are not the only problems to face when studying ecotoxicity of nanoparticles. Nanoparticles, as chemicals, may experience chemical speciation that should be taken into account to evaluate their toxicity. The kind of speciation experienced will highly depend on the chemical nature of the material and on the media composition.

It is essential to study not only acute toxicity effects, but also chronic effects. That is why standard toxicity test should be complemented by ecotoxicogenomic studies, in order to watch not only death but also stress experienced by the organism.

Finally, it was stated that although nowadays the main sources of nano TiO_2 at present are sunscreens, the market for self-cleaning cement and coatings is foreseen to develop in the near future. These emissions, which nowadays are negligible, should also become more relevant.