Prospects for environmental nanotechnologies

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Introduction

There is considerable commercial interest in environmental technologies because innovative solutions to prevent and remediate pollution are essential to ensure sustainable development. The anticipated world market for applications of environmental nanotechnologies by 2010 is approximately $6000 million,[1] of which remediation is expected to be the fastest-growing sector. Potential applications include integrated clean technologies, environmental monitoring and environmental management systems, as well as end-of-pipe technologies and remediation methods; the Environmental Technologies Action Plan for the European Union (EU)[2] specifically mentions the significant impact that nanotechnologies are expected to have. Although the EU does not at present have a dedicated research programme on environmental nanotechnologies, there are a number of relevant European projects already in progress.[3]

Conventional remediation techniques have proved relatively ineffective in reducing the levels of pollutants in air, water, and soil. Filtration and purification systems for drinking water, for instance, tend to have only limited success due to the relatively low efficiency of the active materials. As a result of their greater specific surface area, nanostructured materials are significantly more reactive than micron-sized or bulk materials with the same chemical composition. Various applications of nanotechnologies for environmental remediation have been successfully demonstrated at the laboratory scale but, in the majority of cases, require verification of their efficacy and safety in the field.

This paper reviews current European research in this area and examines the opportunities that exist for the use of nanotechnologies in environmental remediation, considering the relevant phenomena from the nanoscale to the macroscale. It is based on the outcomes of a

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[1] F. Boehm, *Nanotechnology in Environmental Applications*, Report NAN039A, BCC Research, Norwalk (2006).

[2] Commission of the European Communities, *Stimulating Technologies for Sustainable Development: An Environmental Technologies Action Plan for the European Union*, Brussels, 28 January COM(2004) 38 final.

[3] D.G. Rickerby and M. Morrison, "Nanotechnology and the environment: a European perspective", *Sci. Technol. Advanced Mater.* **8** (2007) 19–24.

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recent JRC-Nanoforum workshop on nanotechnologies for environmental remediation.[4] A previous workshop[5] had already dealt with the wider issues surrounding the safe use of nanotechnologies for the benefit of the environment, including applications in pollution monitoring and resource saving as well as remediation methods.

We will address the questions of which are the most effective nanotechnologies for prevention or clean up of pollution, how dependable and close to market are remediation techniques based on nanotechnologies and what additional research is needed to exploit the full potential of nanotechnology for remediation. We will attempt to identify those environmental nanotechnologies that appear the most promising, and should be further explored, and the potential risks involved in using nanotechnologies for remediation applications. Finally we will examine whether there is a need for targeted funding for research infrastructure to support nanotechnologies for environmental remediation and what opportunities exist for setting up future EU collaborative projects in environmental nanotechnologies.

The policy context

The effects of pollution can be determined at continental, regional and local levels, together with the identification of measures required for action and specific policy issues to be addressed. In response to the Water Framework Directive,[6] for example, the HORIZON 2020 initiative[7] proposes to decrease water pollution in the Mediterranean area by 80%. Specifically targeted areas are municipal waste, effluent emissions and industrial pollution.

The priority sites for clean up differ across the EU Member States. The ones requiring most urgent action are former military sites, particularly in the new Member States. Topsoil removal is likely to remain the most important single method of choice for land remediation, in up to 90% of cases, but creates additional problems regarding the disposal of hazardous waste. The proposed Soil Directive[8] is expected to address these issues in a comprehensive way.

There are various initiatives at European level for abating atmospheric emissions and the pertinent EU legislation is embodied in the Framework Directive on Ambient Air Quality.[9] This Directive covers the revision of previously existing legislation and the introduction of new air quality standards for air pollutants.

Natural processes at the nanoscale

Full scale field trials have been carried out, supported by laboratory studies and theoretical modelling, of *in situ* environmental engineering methods for the attenuation of pollutants in soil

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4 D.G. Rickerby and M. Morrison, *Report from the Workshop on Nanotechnologies for Environmental Remediation*, Nanoforum (2007).

5 M. Morrison, *Report on the Nanotechnology and Environment Workshop*, Nanoforum (2006).

6 Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

7 Communication from the Commission to the Council and the European Parliament establishing an environment strategy for the Mediterranean, SEC(2006)1082.

8 Proposal for a Directive of the European Parliament and of the Council establishing a framework for the protection of soil, COM(2006) 232 final.

9 Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management.

and aquifers.[10, 11] Passive biotechnology is employed, using the soils and aquifers themselves as natural bioreactors. *In situ* approaches rely on naturally occurring processes to reduce environmental risk. These processes include dilution by mixing with clean recharge or groundwater to reduce contamination concentrations, adsorption to retard the transport of soluble contamination and biodegradation to destroy contaminant mass. Quantifying the extent of these processes *in situ* can demonstrate that more aggressive intervention is not necessary. This avoids excavation or pumping of contamination, which reduces the energy consumption and carbon footprint for remediation, decreases worker exposure to contaminated materials, and eliminates the need to otherwise treat contaminated water and to transport soils for disposal as hazardous waste.

Less interventionist approaches to remediation, such as Monitored Natural Attenuation (MNA), are cheaper than other methods, but their effectiveness is uncertain, and significant monitoring costs may be required. On the other hand, far more expensive and aggressive remediation is often employed than is actually needed. Improved predictive capability is therefore required. This can be achieved by acquisition of high quality data, obtained by sampling within the polluted zone, in combination with site simulation using reactive transport models. Microbial and geochemical analysis is performed to determine the change in pollutant concentration and the underlying processes. Computer simulations of reactive transport quantify the concentration and mass flux within the *in situ* bioreactor and can be used to assess the ability of the reactor to achieve the required remediation outcomes within specified time scales. Current models employ high speed computing methods with calculation power and precision similar to that of models used for global climate change evaluation.[12]

Figure 1 shows a two-dimensional concentration map of the O_2 distribution in a model aquifer, obtained by fluorescent imaging. Biodegradation in a pollution plume emanating from a point source has caused depletion of O_2 in the core of the plume. Such models couple the microbiological ecosystem dynamics with the geochemical reactions and physical transport. Currently, the physical and chemical processes are well understood but better understanding of the microbial processes is required. One important area is identification of the basic mechanisms of biodegradation within the attached microbial colonies, and the biodegradation reactions that occur at the cell/mineral interface. This work includes quantification of rates of biodegradation in biofilms, characterization of colony dynamics, identification of organisms that degrade pollutants, elucidation of physical chemistry influencing attachment, comparison of the influence of different mineral substrata, and studying how microbes are transported in the subsurface.

An increased understanding of the processes and interactions occurring within these *in situ* bioreactors enables more effective intervention and better engineering outcomes. Advances in *in situ* engineering could allow more reliable clean up of contaminated soil and water and

[10] I.A. Watson, S.E. Oswald, S.A. Banwart, R.S. Crouch and S.F. Thornton, "Modelling the dynamics of fermentation and respiratory processes in a groundwater plume of phenolic contaminants interpreted from laboratory to field-scale", *Environ. Sci. Technol.* **39** (2005) 8829–8839.

[11] J.W. Bridge, S.A. Banwart and A.L. Heathwaite, "Noninvasive quantitative measurement of colloid transport in mesoscale porous media using Time Lapse Fluorescence Imaging", *Environ. Sci. Technol.* **40** (2006) 5930–5936.

[12] H.C. Rees, S.E. Oswald, S.A. Banwart, R.W. Pickup and D.N. Lerner, "Biodegradation processes in a laboratory-scale groundwater contaminant plume assessed through fluorescence imaging and microbial analysis", *Appl. Environ. Microbiol.* **73** (2007) 3865–3876.

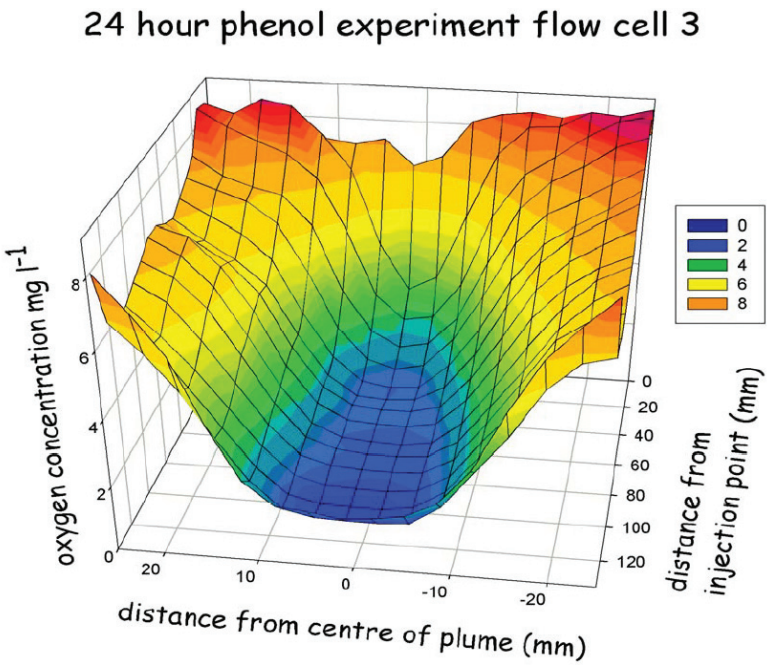

Figure 1. Two-dimensional concentration map of O_2 depletion due to biodegradation of pollution in a model aquifer quantified using a fluorescent imaging technique. (S.A. Banwart.)

treatment of waste, safeguarding aquifers, rivers and coastlines, and saving water. Other applications include carbon sequestration, and the *in situ* development of construction materials and structural platforms using soil-strengthening microbial processes. These methods exploit the indigenous microbial community and reduce the environmental impact of engineering schemes. At the same time they increase knowledge and the predictability of complex systems, and reduce the level of uncertainty for industry and regulatory acceptance.

By studying solid/fluid chemical reactions at the nanoscale scientists can discover how to better exploit natural processes. Suitable experimental techniques for nanoscale surface studies have only become available during the last 15–30 years. These techniques are now being applied to investigate nanoscale reactions in calcite and iron oxide, minerals that are abundant in nature. An important aim is to reduce contamination of and develop methods for purifying drinking water at source. As particles or structures decrease in size they acquire interesting and novel physical, chemical and electronic properties. Advantages include unique catalytic properties that can accelerate oxidation or reduction of various pollutants for particle sizes below 10 nm.

One application of this work is the removal of nickel contamination of groundwater. Contamination can arise from industrial sites, waste leakage, and by oxidation of natural pyrite (FeS_2), where it is present in trace quantities. Experiments have demonstrated the efficacy of natural chalk columns to adsorb and sequester nickel.[13] The slower the pumping rate, and the

[13] L.Z. Lakshtanov and S.L.S. Stipp, "Experimental study of nickel (II) interaction with calcite: adsorption and coprecipitation", *Geochimica Cosmochimica Acta* **71** (2007) 3686–3697.

greater the surface area, the faster and more extensive is the uptake. An effort is now under way to determine the fundamental mechanisms of biomineralization through a more detailed study of the structure of naturally occurring chalk. The long term objective of this work is to develop synthetic methods for making calcite nanoparticles to eliminate nickel from drinking water.

The natural oxidation processes of iron can be exploited to clean up toxic elements in groundwater, for example heavy metals from fly ash.[14] Metallic iron oxidizes to green rust, which is rich in Fe(II), and then further to red rust, which contains Fe(III). Nanoparticles of green rust can be formed by mixing powdered iron and sand in the presence of water. Fe(II) in these nanoparticles is highly reactive and efficient at removing redox-sensitive elements such as chromium and chlorinated solvents.

The development of methods of CO_2 sequestration by capture and geological storage requires an understanding of reactions with the host rock.[15] Among the proposed methods is using CO_2 to decrease viscosity of oil and enhance oil recovery, but in this case the gas is not removed; it simply returns with the oil. Another scenario is to inject it into depleted reservoirs, but this carries the risk of catastrophic release if the cap rock fails. An alternative method is by reaction of the gas with rocks or sand, that is, to immobilize it by the formation of carbonate minerals and clay so that it is stabilized in solid form. One of the most promising methods is by reaction with basalt.[16]

The basic principles of photocatalysis are already exploited in commercial products such as self-cleaning glasses, architectural coatings and building blocks able to remove NO_x from the air. Current objectives include the development of new catalysts with significantly increased activity. Of particular interest is titanium dioxide modified with gold nanoparticles.[17, 18] At very small particle sizes (2–3 nm diameter) gold loses its metallic properties and becomes a semiconductor, which increases the photocatalytic activity of the TiO_2 (even at gold concentrations of less than 1%, activity is doubled). A laboratory scale fixed bed reactor has been constructed at the University of Cambridge to study photocatalytic groundwater remediation and field trials are now also underway.

Indoor air treatment can be carried out using titanium dioxide nanoparticles doped with nitrogen.[19, 20] This increases both light absorption and catalytic activity. Catalytic coatings based

[14] L.L. Skovbjerg, S.L.S. Stipp, S. Utsunomiya and R.C. Ewing, "The mechanisms of reduction of hexavalent chromium by sodium green rust sulphate: formation of Cr-goethite", *Geochimica et Cosmochimica Acta* **70** (2006) 3582–2592.

[15] E.H. Oelkers and J. Schott, "Geochemical aspects of CO_2 sequestration", *J. Chem. Geol*. **217** (2005) 183–186.

[16] B.P. McGrail, H.T. Schaef, A.M. Ho, Y.-J. Chien, J.J. Dooley and C.L. Davidson, "Potential for carbon dioxide sequestration in flood basalts", *J. Geophys. Res.* **111** (2006) B12201.

[17] A. Orlov, D. Jefferson, M. Tikhov and R. Lambert, "Enhancement of MTBE photocatalytic degradation by modification of TiO_2 with gold nanoparticles", *Catal. Commun*. **8** (2007) 821–824.

[18] A. Orlov, M. Chan, D.A. Jefferson, D. Zhou, R.J. Lynch and R.M. Lambert, "Photocatalytic degradation of water-soluble organic pollutants on TiO_2 modified with gold nanoparticles", *Environ. Technol.* **27** (2006) 747–752.

[19] S. In, A. Orlov, F. García, M. Tikhov, D. Wright and R.M. Lambert, "Efficient visible light-active N-doped TiO_2 photocatalysts by a reproducible and controllable synthetic route", *Chem. Commun.* **40** (2006) 4236–4238.

[20] A. Orlov, M. Tikhov and R. Lambert, "Application of surface science techniques in the study of environmental photocatalysis: nitrogen-doped TiO_2", *Comptes Rendus Chimie* **9** (2006) 2794–2799.

on these doped titania nanoparticles are currently under development for environmental and public health applications. The nanoparticle size is in the 1–30 nm range and can be selectively controlled.

Mesoporous and microporous materials are being developed for green chemistry and catalytic applications, including selective catalysis, photocatalysis, membranes and energy applications. These materials are functionalized by depositing catalysts inside their pores. Examples include silica-based mesoporous molecular sieves modified with titanium[21] for 4-chlorophenol decomposition or with manganese for gas-phase oxidation reactions with propane.

Naturally occurring atmospheric nanoparticles greatly outnumber those from anthropogenic sources. The major source of these in Europe is the North African desert. They have a major impact on the production of nitrous acid (HONO), an important atmospheric contaminant, because the mineral dust provides a large catalytic surface area. Work is being carried out to identify and quantify pathways for the formation and destruction of HONO on photocatalytic components of mineral dust,[22] starting with TiO_2, which is the most active component and the fourth highest by mass.

Water treatment

Photocatalytic treatment of water is an effective method for the degradation of pollution and the destruction of microörganisms. The basic mechanism of photocatalysis is illustrated in Figure 2. Research activities in this area include water treatment and purification, electrolysis using solar energy, self-sterilizing surfaces, and sensors. Currently more than 5000 publications exist on photocatalytic organic degradation.

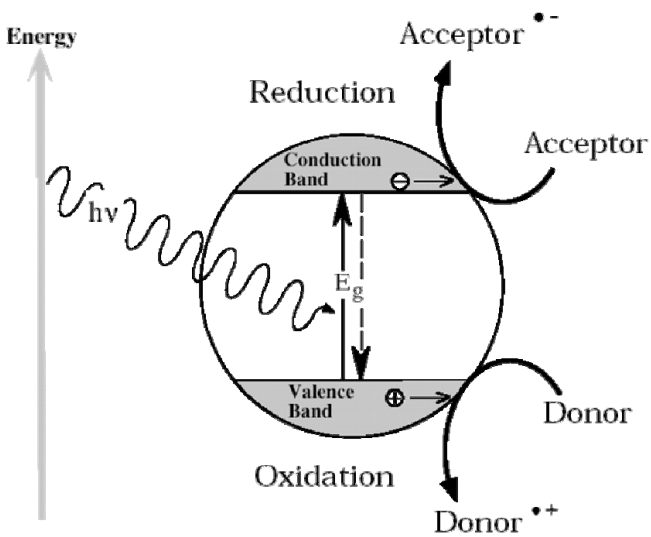

Figure 2. The principle of photocatalysis: absorbed photons create electron–hole pairs causing redox reactions that degrade compounds on the surface. (D.W. Bahnemann.)

[21] A. Orlov, Q.Z. Zhai and J. Klinowski, "Photocatalytic properties of the SBA-15 mesoporous silica molecular sieve modified with titanium", *J. Mater. Sci.* **41** (2006) 2187–2193.

[22] R.J. Gustafsson, A. Orlov, P.T. Griffiths, R.A. Cox and R.M. Lambert, "Reduction of NO_2 to nitrous acid on illuminated titanium dioxide aerosol surfaces: implications for photocatalysis and atmospheric chemistry", *Chem. Commun.* **37** (2006) 3936–3938.

At the University of Ulster a laboratory-scale reactor has been developed that uses electrochemically assisted photocatalysis (EAP) to break down organic molecules in water. It was used to investigate photocatalytic destruction of persistent organic pollutants such as 17-β-oestradiol,[23] p-nitrophenol (PNP)[24] and atrazine.[25] Atrazine is a herbicide widely used to control weeds in agriculture, but is now banned in the EU. It is commonly found in surface- and groundwater and its persistence in the environment is due to the presence of the s-triazine ring, which resists biodegradation.

This photocatalytic degradation system uses TiO_2 nanopowders immobilized on substrates by dip coating, spray coating, or electrophoretic coating. Sol-gel routes and plasma processing have also been used to produce TiO_2 films on FTO glass substrates. A photogalvanic system with a TiO_2 photoanode was constructed to allow photodegradation of organic pollutants and recovery of dissolved metal ions from plating waste via a galvanization process using a two-compartment cell with a copper mesh cathode and a titanium dioxide anode.

Studies have shown that the photocatalytic inactivation of bacterial spores (e.g. *cryptosporidium*) in river water samples is effective within a period of a few hours. Photocatalytic disinfection of water containing pathogenic microörganisms is an effective method for providing clean drinking water and works also for chlorine-resistant organisms such as *Clostridium perfringens,* which are an indicator of faecal pollution. These results could have implications for clean drinking water in developing countries or in emergency situations, where waterborne diseases constitute a severe threat. Tests on *E. coli* have shown significantly increased disinfection efficiencies using photocatalysis as compared to UVA irradiation alone.[26]

A noteworthy project in this field is SODIS Water[27]—solar disinfection of drinking water for use in developing countries and emergency situations. The main barrier to commercialization is the need for education of potential customers regarding the limitations of conventional treatment systems. Photocatalysis on both a laboratory and pilot scale has been shown to be an effective method for the treatment of water containing pollutants and microörganisms. Solar photocatalysis will be the primary technology breakthrough for water treatment and purification, particularly in developing regions. Further research is needed to find how to control the treatment to eliminate toxic products. The potential risks of using nanoparticles for the purification of water and air also need to be investigated.

A double skin sheet reactor[28] for water purification by photocatalysis has been designed at the University of Hannover using PMMA, a material that is transparent to UV radiation. A pilot

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[23] H.M. Coleman, M.I. Abdullah, B.R. Eggins and F.L. Palmer, "Photocatalytic degradation of 17β-oestradiol, oestriol and 17α-ethynyloestradiol in water monitored using fluorescence spectroscopy", *Appl. Catal. B: Environ.* **55** (2005) 23–30.

[24] M. Shani Sekler, Y. Levi, B. Polyak, A. Novoa, P.S.M. Dunlop, J.A. Byrne and R.S. Marks, "Monitoring genotoxicity during the photocatalytic degradation of p-nitrophenol", *Appl. Toxicol.* **24** (2004) 395–400.

[25] T.A. McMurray, P.S.M. Dunlop and J.A. Byrne, "The photocatalytic degradation of atrazine on nanoparticulate TiO_2 films", *Photochem. Photobiol. A: Chem.* **182** (2006) 43–51.

[26] P.S.M. Dunlop, J.A. Byrne, N. Manga and B.R. Eggins, "The photocatalytic removal of bacterial pollutants from drinking water", *Photochem. Photobiol. A: Chem.* **148** (2005) 355–363.

[27] http://www.sodis.ch

[28] R. Dillert, A.E. Cassano, R. Goslich and D. Bahnemann, "Large scale studies in solar catalytic wastewater treatment", *Catal. Today* **54** (1999) 267–282.

plant was subsequently constructed employing an aerated cascade photoreactor[29] to compensate for low pressure in the system. Tests showed that the total organic carbon (TOC) levels in industrial wastewater could be reduced to levels equivalent to drinking water quality. The photocatalytic activity was determined by measuring the removal rate of methylstearate adsorbed on the surface of a TiO_2 film applied by a sol-gel process.

An alternative method for the treatment of process and waste water is to apply membrane technologies for nanofiltration.[30] An example of a typical porous membrane structure is shown in Figure 3. Differential transport of components across the semipermeable membrane[31] allows their separation into a retentate, enriched in less mobile components, and a permeate, enriched in faster components. The driving force across the membrane is the applied pressure. The pressure required is lower than that for reverse osmosis because nanofiltration membranes have larger free volumes in the polymer. Both methods are effective in removing multivalent ions and small organic molecules.

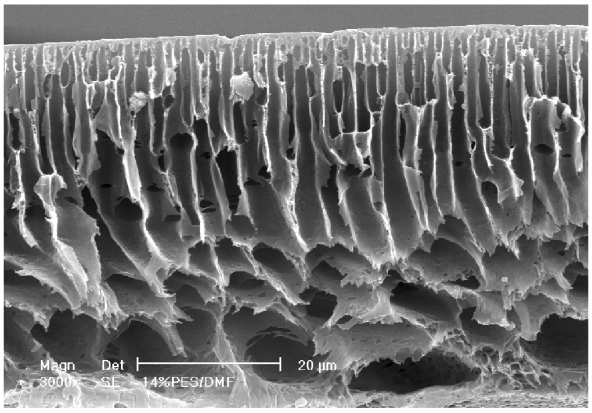

Figure 3. Cross section of a Poly(ethersulfon) nanofiltration membrane with pore sizes decreasing from the upper skin layer towards the support. Skin layer pores have a typical size around 1 nm. (B. van der Bruggen.)

Among the factors that have to be considered when developing membrane systems are rejection, flux and yield. Membranes have inherent problems associated with concentration (typically 10–20% of material ends up in the concentrate). Membrane pores are of the order of 1 nm diameter and new polymeric structures are under development incorporating charged surfaces. Nanofiltration lies between reverse osmosis and ultrafiltration techniques in terms of the size of the molecules removed. The pore size is similar to that of pesticide molecules and other chemicals found in water. It has potential uses in water softening, removal of natural organic

[29] G. Sagawe, R.J. Brandi, D. Bahnemann and A.E. Cassano, "Photocatalytic reactors for treating water pollution with solar illumination: A simplified analysis for *n*-steps flow reactors with recirculation", *Solar Energy* **79** (2005) 262–269.

[30] B. van der Bruggen and C. Vandecasteele, "Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry", *Environ. Pollut.* **122** (2003) 435–445.

[31] B. van der Bruggen, J.C. Jansen, A. Figoli, J. Geens, K. Boussu and E. Drioli, "Characteristics and performance of a 'universal' membrane suitable for gas separation, pervaporation and nanofiltration applications", *J. Phys. Chem. B* **110** (2006) 13799–13808.

matter (NOM), micropollutants and heavy metals, disinfection, desalination, and ion separation. Applications include safe discharge and reuse of wastewater, high quality drinking water, groundwater treatment, removal of organic and inorganic pollutants from surface water, and the recycling of process water.

Nanofiltration membranes consist of a multilayer structure,[32] in which separation occurs in an ultrathin top layer that is mechanically supported by a series of asymmetric layers. The synthesis parameters determining the structure of the membrane are the percentage weight of polymer, solvent type, temperature, air humidity and additives. Modification of the structure is possible by grafting a polymeric membrane to obtain a hydrophilic surface to reduce fouling of the membrane and allow stable operation. Membrane fouling depends on the interplay between solute parameters and membrane parameters. Modelling of rejection is carried out by using transport equations and approximate expressions can be derived assuming a pure filtration process. The more hydrophobic a compound is, the lower the retention, so pore size is not the only factor.

Other membrane types being studied include ceramic membranes consisting of a colloidal interlayer with an anatase top layer on an alumina support. New process designs are being developed using membrane cascades that allow the recycling of permeate or concentrate for better separation between ions and organic solutes or between different organic solutes. The quality of the permeate can be thus controlled; however this aspect will require more fundamental investigation before practical applications can be realized.

Nanofiltration is an effective method for production of high-quality water, but there are problems related to further treatment of concentrates, membrane fouling, the difficulty of obtaining a complete separation, development of suitable membrane structures, and improvement of process design. It is cheaper than reverse osmosis because lower pressures are needed. Membrane lifetime may be up to 5 years but this varies. The concentrate or retentate can contain high levels of heavy metals and toxins.

Colloids and surfaces play the principal roles in naturally occurring processes. Colloidal and interface chemistry studies the forces between colloids, the charges on them, and particle size and morphology. Interest is focused on the interface between the particles and their surroundings. Colloids are typically 1 nm–2 μm in diameter while nanoparticles are 1 nm–100 nm. Both are currently studied to characterize them at the nanoscale. The materials of interest include aqueous ions, complexes and clusters, colloidal particles such as clay and humic substances, oxides, hydroxides, oxyhydroxides, bacteria, exopolymers, enzymes, crystallites, gels and amorphous materials, and soils.

A system has been developed that utilizes iron-precipitating bacteria to immobilize organic and inorganic pollutants[33] such as arsenic, which affects more than 100 wells in Denmark. Using X-ray microscopy it has been demonstrated, in laboratory tests, that the presence of bacterial exopolymers enhances the precipitation of arsenic. Exopolymers consist mainly of

[32] B. van der Bruggen, K. Delafonteyne and L. Braeken, "Improved separation efficiency in nanofiltration by using a membrane stack", *Desalination* **199** (2006) 302–304.

[33] E.G. Søgaard, R. Aruna, J. Abraham-Peskir and C.B.Koch, "Conditons for biological precipitation of iron by *Gallionella Ferruginea* in a slightly polluted ground water", *Appl. Geochem.* **16** (2001) 1129–1137.

carbohydrates that, in combination with iron oxides, can coprecipitate arsenic and other pollutants. One of the research objectives is to investigate the differences between the kinetics of catalytic chemical and biological elimination of iron compounds in drinking water. Another is to understand and optimize applications of co-precipitation activity between iron oxides and pollutants in water. The kinetics of biological iron oxidation are about 1000 times faster than for uncatalysed oxidation and precipitation. Chemical catalytic iron oxidation and precipitation is slower than the biological process. The particle size for biological oxidation and precipitation is larger than for chemical catalytic oxidation and precipitation.

Polypropylene fibres are used as a substrate for sol-gel deposition of TiO_2 nanoparticles for photocatalytic degradation of organic pollutants. The reaction was studied at room temperature and atmospheric pressure and in supercritical CO_2 at elevated pressure.[34] The processing temperature has to be closely controlled to produce nanoparticles with a crystalline rather than amorphous structure. The primary cluster, which is ~1 nm diameter, grows to the secondary particle diameter of 4–6 nm by reaction-limited aggregation, then to the primary aggregate stage of 20 nm before reaching a final size of 400–500 nm.

Nanocrystalline diamond-like coatings are the basis of an electrochemical water purification method. Diamond is non-toxic, biocompatible, erosion-resistant, corrosion-resistant against all chemicals, and is electrically conducting if it contains boron. It has the largest electrochemical window of any material, can be used as an anode as well as a cathode,[35] and is resistant to fouling. Homogeneous polycrystalline 0.1–5 mm thick boron-doped diamond (BDD) films are deposited[36] on silicon substrates of up to 0.5 m^2 in area. The use of BDD/Si electrodes allows a high anodic potential to be applied to produce very efficient oxidants for water treatment and disinfection. Disinfecting agents are generated from water and mineral salts and disinfection takes place without chlorine. This allows wastewater oxidation without sludge generation; reduction of COD (chemical oxygen demand), TOC (total organic carbon), N-organics and ammonia; and biodegradability. A mixture of very strong oxidants is generated, which is more efficient than chlorine and no chemicals need to be added.

For viruses and bacteria (*E. coli, legionella*), inactivation is 3–5 times faster than with conventional chlorine dosing. Destruction of algae, fungi and protozoa is also ensured. COD and TOC are reduced by production of hydroxyl radicals that destroy and increase the biodegradability of organic pollutants. Future objectives are to further reduce COD and find an alternative cathode material to lower costs, to reduce energy requirements through the use of a low overpotential cathode, to reduce the N-organics and ammonia content, and to optimize the efficiency by increasing the process temperature. The current target is to decrease phenol levels in wastewater below 100 ppm.

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[34] H. Jensen, M. Bremholm, R.P. Nielsen, K.D. Joensen, J. Skov Pedersen, H. Birkedal, Y. Sheng Chen, J. Almer, E.G. Søgaard, S.B. Iversen and B.B. Iversen "*In situ* high-energy synchrotron radiation study of sol-gel nanoparticle formation in supercritical fluids", *Angew. Chem. Int. Ed.* **46** (2007) 1113–1116.

[35] Y.V. Pleskov, A.Y. Sakharova, M.D. Krotova, L.L. Bouilov and B.V. Spitsyn, "Photoelectrochemical properties of semiconductor diamond", *J. Electroanal. Chem.* **344** (1987) 401–404.

[36] D. Gandini, E. Mahé, P.-A. Michaud, W. Haenni, A. Perret and Ch. Comninellis, "Oxidation of carboxylic acids on boron doped diamond electrodes for wastewater treatment", *J. Appl. Electrochem.* **30** (2000) 1345–1350.

Effective monitoring methods are needed to determine the presence of pollutants in water. A lab on a microchip device has been developed for analysing highly radioactive solutions using an absorbimetric technique.[37] Potential applications of this device include environmental sampling and detection of clandestine reprocessing activities. Reduction of the sample volume for analysis of nuclear waste solutions has the advantages of dose reduction, faster and simplified analysis with no sample preparation or dilution, smaller uncertainty in the analysis results and reduced risk of cross contamination. Modelling of the microfluidic laminar flow shows that the small volume helps reduce the radioactive decay heating effect so no cooling element is necessary. The dose reduction is very nearly proportional to the volume reduction.

The flow in microchannels differs strongly from classical flow in macrochannels. The surface charge on the walls induces an altered ion concentration within the microlayer, which causes a significant increase in surface energy. Flow is determined by fluid properties such as density and dynamic viscosity, and their variation with concentration, which is a function of temperature. Decay heating of the solution might affect the analysis because temperature influences absorption spectra and could distort the microchannel, which could also influence the absorption measurements. However, the microvolume of radioactive solution generates a minimal heating effect, for which the maximum temperature difference is less than 0.2 °C. Concentration measurements by spectrophotometry of light absorption peaks are therefore highly reproducible.

Air purification

Current European legislation (EURO V) fixes vehicle engine emission levels at < 0.005 g/km for particulate matter. To meet this standard requires the development of catalytic trap technology and advanced systems such as the noble metal-free wall-flow catalytic trap. These new types of catalysts should be much less expensive than the noble metal-supported catalysts currently employed.

Catalyst crystals with a size similar to that of the particulate provide the highest number of contact points. A novel catalyst preparation method called solution combustion synthesis is being used experimentally to produce crystals in the size range 20–50 nm. A new type of mixed oxide catalyst was compared with several reference catalysts and found to give the best compromise between soot reduction and NO_x abatement. Results for loading and regeneration runs using a $CoCr_2O_4$-catalysed trap prepared by this method,[38] compared with a commercial catalysed and a non-catalysed trap showed that the commercial catalyst performed worse than the new catalyst but better than the non-catalytic SiC monolith.

The regeneration of the $CoCr_2O_4$-catalysed traps was faster than that of the non-catalytic ceramic filter, resulting in a reduction in the regeneration time. Almost no nanoparticles were released during regeneration by the reference catalyst and non-catalytic traps but they were

[37] G. Janssens-Maenhout and S. Nucifora, "Feasibility study of a microsystem to analyse radioactive solutions", *Nucl. Eng. Des*. **237** (2007) 1209–1219; G. Janssens-Maenhout [reference to her article in this issue].

[38] D. Fino, E. Cauda, D. Mescia, G. Saracco and V. Specchia, "$LiCrO_2$ catalyst for diesel particulate abatement", *Catal. Today* **119** (2007) 257–261.

emitted during the fast regeneration required by the $CoCr_2O$ trap. This catalyst had a higher activity during regeneration and generated a significant quantity of nanoparticles (< 30 nm) during fast regeneration. Formation of these secondary particles is thought to be a result of oxidative fragmentation of soot aggregates, formation of sulphuric acid droplets, or condensation of hydrocarbons during the fast oxidation process.

Indoor as well as outdoor air pollutants must be taken into account when considering health effects. The indoor pollutants are often at ppb levels, whereas outdoor pollutant concentrations are typically in the ppm range. Photocatalysis reactions at near ambient temperature can be used to degrade air pollutants. The major areas of research in this field concern self cleaning, anti-fogging, water treatment, antibacterial, and air cleaning applications. However, improved knowledge of the mechanisms of photodegradation and the photocatalytic efficiency of the materials is also needed, together with testing at the laboratory scale and the macroscopic real world scale.

Incorporation of TiO_2 in building materials or surface coatings imparts to them self cleaning and de-polluting properties.[39] When exposed to solar radiation it acts as a catalyst for photodecomposition of pollutant molecules adsorbed on the surface and their transformation into non-toxic compounds. A consistent reduction in levels of NO_x by approximately 80% was observed for paints and cements containing TiO_2 nanoparticles tested in an environmental chamber with controlled temperature, relative humidity, air quality, and air exchange rate.[40, 41] In canyon street tests NO_x concentrations were reduced by 40 to 80% depending on variations in emission sources, wind direction and orientation of the walls.

Pollutants are consumed by the sink effect on the walls of the test chamber, absorption on the surface of the sample, photolysis by UV, and photocatalysis by TiO_2 and UV. Measurements can give information on the TiO_2 activity provided these effects are taken into account. The photocatalytic conversion of NO and toluene increases with decreasing relative humidity and toluene degradation is enhanced by the presence of NO. An inhibition effect on NO conversion occurs only at high concentrations of toluene.

Nitrates are the transformation products due to photocatalysis of NO and their level increases with the photocatalytic activity of the material. Aldehydes are the main transformation products for photocatalysis of organic pollutants. Carbonyls (formaldehyde, acetaldehyde, propanal) were detected in photocatalytic tests with the TiO_2-containing paints. The amount produced depends on environmental conditions and photocatalytic efficiency of the materials.

The next steps will be to investigate in dynamic mode, the efficiency of pollutant conversion and release of by-products, the influence of light intensity, and the effect of multicomponent mixtures of pollutants (benzene, acetaldehyde, formaldehyde, CO and NO_2, xylenes, naphthalene, styrene, toluene, α-pinene, d-limonene).

Typically only 0.01% of the incident photons are actually used for photocatalysis (e.g. by self cleaning glass) but 10% might ultimately be achievable. Photocatalytic activity can be

[39] http://www.picada-project.com

[40] T. Maggos, J.G. Bartzis, P. Leva and D. Kotzias, "Application of photocatalytic technology for NO_x removal", 1st International Symposium on Transparent Conducting Oxides, Crete (2006).

[41] T. Maggos, D. Kotzias, J. Bartzis, P. Leva, A. Bellintani and Ch. Vasilakos, "Investigations of TiO_2-containing construction materials for the decomposition of NO_x in environmental chambers", Proc. 5th International Conf. on Urban Air Quality, Valencia (2005).

enhanced by using noble metal (Pt, Au, Ag) nanocontacts, SnO_2/TiO_2 composite materials, or by doping with Fe(III).[42] Nanoparticles of TiO_2 in colloidal suspensions form chain-like structures, which can act as antennae that assist the transport of electron-hole pairs. This mechanism explains the high quantum yields for formaldehyde formation during oxidation of methanol at TiO_2/Fe(III) colloids.

International standards are required for the commercialization of photocatalytic coatings. The COST Action PHONASUM,[43] deals with novel highly reactive photocatalytic materials sensitive to visible light and used for coating systems. It aims to achieve characterization of the properties of photocatalytic materials and the design of standard test methods, and industrially relevant applications of new photocatalytic materials. A European STREP Project on self-cleaning glass[44] is developing modelling methods and laboratory tests for thin film coatings in support of a European standard for self-cleaning glass. Lastly, the European-Japanese Initiative on Photocatalytic Applications and Commercialization (EJIPAC)[45] aims at establishing collaboration between Japanese and European companies and institutions in the field of self-cleaning surface coatings and air and water purification methods.

Potential risks

One of the potential dangers of environmental remediation is that the products might be more toxic than the original pollutants. Other risks are represented by the entry of toxic by-products into the food chain, plant pathology and soil degradation. The most urgent problems for remediation are old and abandoned contaminated industrial and military sites. Some of the more hazardous contaminants of particular interest are TCE, TNT, Cr(VI), and As(III).

The application of nanoparticles for soil remediation is currently under investigation. Materials under consideration are zerovalent iron and iron oxides, catalysed by noble metals such as palladium. Permeable barriers with iron filings are already used to remediate groundwater. Iron nanoparticles could represent a more cost-effective solution as they have a much higher reactivity per unit mass but further studies of their agglomeration/aggregation are needed. There are also serious concerns regarding the effect of nanoparticle release on soil ecosystems. This is a major research challenge as there are relatively few data available.

Among fundamental requirements are physico-chemical equilibrium and kinetic data, information on effects on living organisms and development of modelling methods on a case by case basis. Alternatives to nanoparticle remediation involve the use of microörganisms and phytoremediation methods. The complexity of the systems involved means that there are many unknowns. It is therefore necessary to establish reliable methods for determining acceptable and unacceptable risks.

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[42] Q. Chen, R. Goslich and D.W. Bahnemann, "Photocatalytic oxidation of methyl stearate on ferric-doped ultrafine TiO_2 thin films coated on glass", in "Photons, Glasses and Coatings", *Topical Issues Glasses* **3** (1999) 40–47.
[43] http://www.cost540.com
[44] http://www.self-cleaning-glass.com
[45] http://www.ejipac.de

Discussion and conclusions

Nanotechnology offers the possibility for the development of new materials and processes for environmental remediation. A better understanding of fundamental phenomena at the nanoscale and their relation to macroscale processes is essential. The application of modelling and simulation methods will allow a deeper understanding of the fundamental principles involved and provide ways to overcome problems and improve performance. Existing knowledge within the chemical industry could also contribute to prevention and remediation of pollution. It is necessary to find more effective methods to deal with the problem of transport of pollutants, for example immobilizing molecules *in situ* by chemical binding.

Fundamental research is critical for driving innovation 10 to 20 years in the future. Some of the new knowledge acquired using nanoscience techniques has already been disseminated but a great deal more information about the basic processes of nature remains to be discovered. This new knowledge is critical to environmental protection and clean up as well as to general scientific and technological development. Fundamental investigations will reveal the underlying physical and chemical processes, and this knowledge can then be applied to improve the inherent ability of soil, sediments and dust nanoparticles to remove or attenuate contaminants. New materials that exploit natural processes to make more efficient, sustainable filters for removing contamination, and selective sequestration techniques for immobilizing it, can be developed only if this fundamental research is carried out.

Several new products resulting from the application of these new technologies are already on the market. Examples include calcite nanoparticles for making paper white without bleach, and techniques for filtering groundwater through reduced iron "reactive barriers" that effectively remove toxic elements such as chromium and chlorinated solvents. Many other products remain to be developed. Some of the necessary fundamental knowledge for these developments already exists. However, a host of other very useful and effective sustainable products should evolve from the results of fundamental research. The instruments developed as a result of the nanotechnological revolution have vastly increased the length scale available for exploration. It is now possible for us to "see" at the sub-nanometre level (10^{-10} m) whereas in the past, the limit was the micrometre scale (10^{-6} m). As a result, whole new vistas of nature have become accessible for the first time, allowing us to discover and understand the fundamental physical/chemical processes at work.

Gas phase remediation of sulfur dioxide and nitrogen dioxide is the area with probably the most potential applications. The technical challenges are greater for water purification than for air purification, for which there are already effective systems on the market. Commercial systems, however, are already available that employ photocatalytic methods for water purification and nanosized titanium dioxide is being produced by at least three companies in Europe on a commercial scale. Photocatalysis uses sunlight, which is free, so that running costs are low. The most effective new methods for water treatment are likely to consist of a combination of more than one technology in hybrid systems. Some technologies, such as nanofiltration using membrane technologies, are already quite close to market but additional research and development, in particular to obtain a better understanding of membrane fouling, are needed to improve efficiency.

Additional research is needed on methods to demonstrate the effectiveness of products. Life cycle analysis is an essential tool for assessing the environmental consequences of implementing new technological approaches. A proper evaluation of the risks is required, particularly with respect to the release of nanoparticles and their fate in the environment. Risk assessment is essential and should be carried out by developers of new materials, before products are placed on the market. Furthermore, before a product is used or marketed, it must be tested for safety. This is a general rule, which applies equally to nanoproducts and -processes, and industry has an incentive to guarantee the safety of its products in order to maintain public confidence. Funding opportunities for risk assessment exist in nanotechnology programmes as well as for health, medicine and safety in the workplace.

There is a need to develop monitoring devices that can determine whether a remediation process has worked correctly or not. Design of microsensors for specific environmental monitoring requirements may sometimes be necessary but, in many cases, sensors developed for medicine and food applications could be adapted, with relatively minor modifications, for environmental monitoring. Some sensor development is already funded through existing nanotechnology research budgets. There are opportunities for setting up European collaborative projects through the EU Framework Programme, which already provides funding for work on nanosensors. Numerous research centres are carrying out work in this area and an excellent pool of European knowledge already exists.

Greater support for European level research networks in environmental technologies and field sites to demonstrate proof of concept is vital. A great deal could be learned from the U.S. experience in setting up field tests. The establishment of a European Technology Platform for Environmental Technologies, including but not limited to nanoscale technologies, might be one way to stimulate progress by encouraging interaction between scientists and technologists from relevant fields. Traditionally, environmental scientists have had no training in nanoscience so usually they do not have the expertise required to apply the instrumentation. Nanotechnologists, on the other hand, have tended to focus on producing materials for industry and do not have sufficient background in the natural sciences: especially Earth science, soil science, geochemistry, and geology. This lack of overlap between different scientific disciplines has slowed the adoption of nanoscale-sensitive instruments and the information they can provide. Targeted funding might help overcome this situation.

Discovering the mechanisms governing natural processes and applying them to improve the environment is important even though there is very little work done in this area. While there is great potential for making important discoveries, unfortunately there is not much funding available for this type of work. Application of nanoscience techniques to natural materials and processes is a topic that falls outside the scope of nanotechnology programmes because it is environmentally-related while nearly all environmental research funding is invested in monitoring and large (field) scale studies. Industrial participation is not easy to obtain because of the fundamental nature of the research. There are few researchers with expertise in the chemistry and physics of natural systems *as well as* in the techniques of nanotechnology and nanoscience. Consequently there are relatively few active research groups worldwide. Many of these are in the EU, which has the potential to leap ahead of the competition in the field if sufficient support is available.