



**Report on
Nanotechnology in the Technology Sector
Environment**

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Executive Summary

Maintaining and restoring the quality of air, water and soil is one of the great challenges of our time. Many countries face serious environmental problems such as availability of drinking water, treatment of waste and wastewater, air pollution, contamination of soil and groundwater etc. The scarcity of water, both in terms of quantity as well as quality poses a significant threat to the well-being of people - especially in developing countries. There is thus considerable commercial potential in environmental technologies. According to Boehm (Boehm, 2006) the projected world market for applications of environmental nanotechnologies by 2010 is approximately \$6 billion. Claire (Claire in (Rickerby and Morrison, 2007)) even expects the market for soil and groundwater remediation to grow to around €23.6 billion worldwide with the UK and Japan as expanding near-term markets and central and eastern Europe as important mid-term markets.

Conventional remediation technologies have so far shown only limited effectiveness in reducing the levels of pollutants - especially in soil and water (Rickerby and Morrison, 2007). Nanomaterials will be able to perform significantly more effectively than larger particles because of the much greater surface area (Rickerby and Morrison, 2007). Most effective will probably be a combination of more than one (nano)technology in a hybrid system and membrane technologies are expected to play a role in this (Rickerby and Morrison, 2007).

So far only few industrial companies consider environmental technologies as a core business, even though there is obvious potential for market applications (e.g. drinking water purification) (Morrison, 2006). A large hurdle are the initial costs for the material, pilot run and facilities (Morrison, 2006). Morrison (Morrison, 2006) suggests to link environmental issues with public health as a driver for creating markets.

Various applications have been successfully demonstrated at the laboratory scale but most of them still require verification of efficacy and safety in the field and are thus still far from market. Further research is also needed to assess the environmental impact of the nanoparticles released. There are serious concerns about the release of free nanoparticles in the environment also for remediation purposes. One way of minimizing the probability of exposure is to encapsulate the nanomaterial within an inert barrier (e.g. silicon can be used to coat quantum dots) or - as employed by the CONCORDE project - to immobilize nanostructure onto a surface (Morrison, 2006). Employing such methods can maintain the activity and functionality of the nanomaterial while minimizing the probability of nanoparticle dispersion.

Methods for environmental remediation can be divided into adsorptive vs reactive and into in situ vs. ex situ techniques, see Table 1 (Tratnyek and Johnson, 2006). Ex situ remediation is often very costly whereas in situ remediation cost less but the delivery of the treatment to the contaminated site is challenging. Further more, the NP released will stay in the environment and have thus to be nontoxic. For in situ treatment it is necessary to create either an in situ reactive zone with relatively immobile NP or a reactive NP plume that migrate to contaminated zones (NP must be mobile).

Table 1: Classification of remediation methods applying nanoparticles into in-situ and ex-situ methods and adsorptive and reactive methods.

	In situ	Ex situ
Adsorptive	Sequestration by addition of binding agents	Treatment of wash solution ex-situ with adsorbents
Reactive	Zero valent iron injection/ addition	Treatment of wash solution ex-situ with TiO ₂ photooxidation

1. Nanotechnology for Air Purification

Keywords: catalyst, photocatalysis, air pollution, air quality, degradation

1.1 Definition

This sub-sector describes the development of nanotechnologies to degrade air pollutants. Air is defined as the atmospheric layer which is within 1000m from the earth surface. In most cases though the remediation technologies address only the ambient air in the immediate surrounding assuming that the air will be mixed by the wind.

1.2 Short Description

Many European cities are facing serious problems with air quality and smog. To meet the requirements by the current European legislation new technologies have to be developed. Great hope is placed on nanoparticulate catalysts to degrade the ambient air pollutants (indoor and outdoor). Target compounds include: particulate matter, NO_x, soot, ozone, CO and VOCs.

Overview over methods, materials and target compounds:

Method	nanomaterials	Target compounds
Catalytic traps	metal oxides (LiCrO ₂ , CoCr ₂ O ₄), CeO ₂ (CeO ₂ (U)??), MnCr ₂ O	NO _x , soot, PM
Photocatalysis	TiO ₂	VOC, NO _x
Static filter	CNT	PM

1.3 State of R&D

1.3.1 Catalytic traps

It is estimated that the world-market for oxide catalysts is over €3 billion (Morrison, 2006). Due to the wide-spread use of catalysts in the synthesis of materials (some 95% of materials will have undergone catalysed steps at some point during production) the economic impact will be even two orders higher (Morrison, 2006). The understanding and control of metal oxide catalytic activities is seen as critical to the development of sustainable chemistry (Morrison, 2006). Catalysts find application not only in remediation processes, but they can also contribute to a more efficient use of energy and raw materials.

Challenges in the synthesis of nanostructured catalysts are that many reactions employ mixed catalysts consisting of different oxides or (noble) metals, and that the function of active centres is not only determined by the constituent atoms but also by the surrounding crystal or surface structures; it is thus necessary to accurately control the synthesis of nanostructured catalysts (Morrison, 2006; Rickerby and Morrison, 2007). There is also a need to understand the chemical reactivity of the catalytic active centres and how this is affected by reactor conditions (Morrison, 2006). Different material mixes, particle sizes, and operating temperatures must be tested to ensure effective catalysis and the production of the expected less hazardous compounds (and not other pollutants) (Morrison, 2006).

Noble-metal free wall-flow catalytic traps have been tested for their efficiency in eliminating soot and NO_x. It was found that catalyst crystals with a size similar to that of the particulate pollutant provide the highest number of contact points (Rickerby and Morrison, 2007). Such crystals (size range 20-50nm) can be prepared by solution combustion synthesis (Rickerby and Morrison, 2007). First applications in a pilot plant showed that the CoCr₂O₄ catalyst gave the best compromise between soot reduction and NO_x abatement compared to MnCr₂O₄, CoFe₂O₄ and currently used catalysts (Rickerby and Morrison, 2007). Also LiCrO₂ catalysed traps showed an increased efficiency (Fino et al., 2007). Additionally, the regeneration of CoCr₂O₄ and LiCrO₂ catalysts was found to be faster than the regeneration of non-catalytic ceramic filters. But in the case of CoCr₂O₄, a significant quantity of nanoparticles was generated during regeneration (Rickerby and Morrison, 2007).

Other studies investigated the oxidation of carbon monoxide by ferric hydroxide supported gold catalysts (Qiao et al., 2008) and the oxidation of naphthalene by nano-crystalline cerium oxide catalysts (Garcia et al., 2005). Garcia found that ceria synthesised by precipitation with urea was the most active catalyst for oxidation of naphthalene to carbon dioxide. The urea precipitated CeO₂ (U) demonstrated over 90% naphthalene conversion to carbon dioxide at a temperature of 175 °C. Comparing the efficiency of CeO₂ (U) with known high activity oxidation catalysts (Mn₂O₃ and 0.5% Pt/c-Al₂O₃) showed that CeO₂ (U) was a more effective catalyst for naphthalene total oxidation. The high adsorption capacity of the material provides the advantage that it can be used as a combined catalyst and adsorbent to remove PAHs from waste streams (Garcia et al., 2005).

1.3.2 Photocatalysis

Photocatalytic degradation of pollutants such as NO_x and VOCs is a very promising application. TiO₂ has shown significant efficacy as oxidising agent and has already been incorporated in paints, surface coatings, glasses and cement for construction where it is expected to develop its self cleaning and de-polluting properties (Parkin and Palgrave, 2005; Rickerby and Morrison, 2007). The reaction efficiency of TiO₂ can be increased by doping the semiconductor with noble metals. TiO₂ can also be doped with boron or nitrogen to harness visible light which is crucial for indoor application (Rickerby and Morrison, 2007). N-doped TiO₂ can make use of artificial illumination by moving the light absorbing spectrum towards longer wavelengths (In et al., 2006; ORLOV et al., 2006a).

In the frame of the PICADA project (PICADA, 2005) several laboratory scale test, macro scale tests and tests on a pilot site were conducted. The laboratory tests showed an 80% reduction in levels of NO_x (especially NO) near TiO₂ containing paints and cements. In canyon street tests, NO_x concentrations were reduced by 40-80% depending on the differences in emission sources, wind direction and orientation of the walls.

In further tests with NO and VOCs it was observed that the photocatalytic conversion of NO and toluene increased with decreasing relative humidity and toluene degradation was enhanced by the presence of NO (Leva in (Rickerby and Morrison, 2007)). The degradation rate for NO was up to 95% and 32% for toluene (Leva in (Rickerby and Morrison, 2007)).

So far the photocatalytic efficiency (percentage of incident photons used) is only around 0.01% (Rickerby and Morrison, 2007). But according to Rickerby and Morrison (Rickerby and Morrison, 2007) 10% might be possible by enhancing the photocatalytic activity with noble metals (Pt, Au, Ag), SnO₂/TiO₂ composite materials or by doping with Fe(III). It is though not clear how stable these doped materials are.

1.3.3 Static Filter

Vaseashta et al. (Vaseashta et al., 2007) tested CNT filled in a polymer composite matrix to create a static discharge to remove the PM from incoming air. According to Vaseashta et al. (Vaseashta et al., 2007) several products using static discharge are currently being commercialized.

1.4 Additional demand for research

(Photo)Catalysts

- Development of (photo)catalysts with higher photocatalytic efficiency which can use a higher percentage of the incoming photons e.g. due to doping with (noble)metals

- Development of (photo)catalysts which can use a wider spectrum of wave lengths e.g. due to doping with (noble)metals
- Investigation of pollutant conversion and release of by-products
- Understanding of dynamic mode of the photocatalysis, influence of light intensity/spectrum on the photocatalytic efficiency and the effect on multicomponent mixtures of pollutants (benzene, acetaldehyde, formaldehyde, CO and NO₂, xylenes, naphthalene, styrene, toluene, a-pinene, d-limonene)
- Prohibit the oxidation of the organic matrix in which TiO₂ is embedded and of the material which is coated by the photocatalytic material.
- Possible agglomeration of photocatalytic particles within a fixed structure and consequent change of physicochemical properties. → Functionalisation
- Immobilisation of the nanoparticles in the coating to avoid particle release over time (long term testing of nanomaterials)
- Develop standards and analytical methods for the testing of photocatalytic applications to allow a comparison of the efficiency of different products.
- Ensure that silica may not inhibit the photocatalytic activity of titanium dioxide.

1.5 Applications and perspectives

Photocatalytic products containing nano-TiO₂ are already commercially available. In Japan around 2,000 companies in the country are undertaking research and development in this area. China is also taking a big interest in photocatalytic products. Photocatalytic products may serve several purposes. Most products are not developed for environmental remediation reasons but for selfcleaning effects or hygienic reasons. Commercially available products are thus mainly air filters (for indoor air in private households, offices etc.), tiles (for use in hospitals and bathrooms etc.), coating sprays for different materials (e.g. used in public transportation, households etc.) and water purifiers (also disinfection). It has to be noted though that there are no standardized and validated methods yet to analyse the products of the photocatalytic conversion (see previous chapter).

In Europe a number of commercial applications are currently available, mostly based on self cleaning coatings e.g. self cleaning glass, self cleaning tiles, anti-fogging glass and air purifiers. It is probably due to cultural differences that the use of nano-photocatalytic materials is not yet as widespread as in Asia. It is expected that a legal standard for indoor air quality in Europe would greatly increase investigations on the efficiency of photocatalytic systems for air purification.

A newly investigated field of application are nano-enhanced molecular sieves. Nano-enhanced molecular sieves may remove for example VOCs from air. Most interesting for environmental applications are mesoporous molecular sieves with a pore size of 2-50nm. It has been reported that titanium or manganese enhance the catalytic performance of the sieves.
<http://www.nanomagazine.co.uk/readArticle.php?id=44>

A Canadian company advertises “hygienic photocatalyst coatings” which are supposed to “transform any surface into anti-bacterial; anti-fungal; mold free surface” and “purify your surrounding air and protect your building interior and exterior from environmental contamination”. The coating incorporates “light activated Nano Titanium Dioxide (TiO₂) which assists in deactivation of bio-contamination”. They promote their product for air purification (for indoor VOCs and other air quality pollutants and for the key component of air purification equipment) as well as for the deodorization <http://www.mchnanosolutions.com/>.

1.6 Current situation within the EU

Several research projects have been or are currently financed to investigate the application of nanotechnology for air purification:

The **COST Action 540** (Photocatalytic technologies and novel nanosurfaces materials - critical issues (PHONASUM)) is a network of researchers and practitioners working in the field of photocatalysis from all around Europe. The main objective of the Action is to increase via a concerted European effort the fundamental knowledge of nanocrystalline photoactive materials and development of new products, which utilize self sterilizing and self cleaning photoactive materials in specific industrially relevant application fields such as self-cleaning and anti-microbial surfaces, water treatment, air purification and general hygienic applications. The realization of these tasks will be accomplished through the development of novel highly active photocatalytic nanomaterials and coating systems with increased sensitivity in the visible region of the solar spectrum, with high environmental stability and adaptability on the various substrate systems. The Action will also concentrate on the development of EU standards for the characterization of photocatalytic materials. The Action commenced in January 2006 and will continue for four years. (www.cost540.com)

The European **STREP** Project on Self Cleaning Glass aims at developing a European standard for self-cleaning glass (www.self-cleaning-glass.com). The consortium consists of 11 partners (industry and research) from 5 EU-countries. The standardization proposal is based on the scientific knowledge provided by :

- the study of the behavior of standard and self-cleaning glass in urban polluted atmosphere
- the understanding of the mechanisms and modeling of self-cleaning glass functionality
- the measurements of soiling methods, elements and data, essential for the setting-up of a new standardisation for self-cleaning glass

The European-Japanese Initiative on Photocatalytic Applications and Commercialisation (**EJIPAC**) 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 (www.ejipac.de). One of the main objectives of EJIPAC is to make photocatalytic technologies available to interested European industries and users, especially in the areas of self-cleaning surfaces, anti-microbial surfaces, anti-fogging, hydrophilic and architectural cooling technologies, water treatment, air purification and general hygienic applications. Moreover, the Initiative is interested in involving scientists who want to have their research results implemented and to make these technologies available to small and medium-size enterprises.

PICADA: The aim of the project was to develop a range of photocatalytically active materials and to evaluate their effect at a large scale (typically in street canyons). It started in 2002 and ended in 2005. Details on <http://www.picada-project.com/domino/SitePicada/Picada.nsf?OpenDataBase>

CONCORDE: This EU-funded project has developed nanostructured metal oxide catalysts for use in a variety of industrial applications. It had the objective of co-ordinating the R & D activities of leading European laboratories working with redoxactive, multifunctional Nanostructured metal oxides which are efficient as catalysts in chemical processes relevant for a sustainable chemistry and the protection of the environment. The project started in 2004 and ended in 2006. Details on <http://www.icp.csic.es/concorde>.

The proceedings of the final project conference are available at http://www.sciencedirect.com/science?_ob=PublicationURL&_tockey=%23TOC%235226%232007%23998719996%23670962%23FLA%23&_cdi=5226&_pubType=J&view=c&_auth=y&_acct=C000036252&_version=1&_urlVersion=0&_userid=4900406&md5=18ab9d5bcd5cb2d799b30ff5db555573

2. Nanotechnology for Wastewater Purification

Keywords: water, wastewater, treatment, households, industrial, pollutants, metals, photocatalysis, nanofiltration, adsorption, oxidation

2.1 Definition

This subchapter describes nanotechnological methods to clean wastewater and process water from households and industries. Wastewater is any water which was used for industrial processes, in households or offices and is thereafter treated in a wastewater treatment plant before released into the environment. Wastewater does not include water (e.g. groundwater, surfacewater etc.) which was unintentionally contaminated.

2.2 Short Description

The challenges in treating wastewater are manifold depending on the origin of the wastewater. Problematic substances are organic matter (POPs), estrogenic activity and nitrate. Industrial wastewater may additionally contain heavy loads of metals or dyes.

Table: Overview over methods, materials and target compounds

Method	Nanomaterials	Target compounds
Photocatalysis	TiO ₂ , ZnO	POPs, metal ions, formic acid, estrogenic activity, pesticide, dyes
Nanofiltration	Ceramic membranes, nanowire membranes, polymer membranes	Metals, anions, viruses/bacteria, organic material, dyes
Adsorption	CNT, metal (oxides), Magnetic NP	Metals, radionuclides, arsen
Electrochemical oxidation	BDD	aromatics, aliphatics and heterorganics, like phosphonates, sulfonates, pesticides, EDTA, as well as some inorganic components, like cyanides, ammonia

2.3 State of R&D

Extensive literature reviews on the diverse technologies and nanoparticles used for water treatment can be found in: Theron et al (Theron et al., 2008) and Savage and Diallo (Savage and Diallo, 2005).

2.3.1 Photocatalysis

Photocatalysis (mainly by TiO₂) is an effective method for the degradation of pollutants in water and for water disinfection. To avoid free nanoparticles in water, TiO₂ particles can be immobilised on a substrate e.g. by dip coating, spray coating or electrophoretic coating (Byrne et al., 1998). Alternatively TiO₂ thin films can be produced on FTO glass substrates and polypropylene fibres by sol-gel routes and plasma processing (Rickerby and Morrison, 2007).

McMurray et al. (McMurray et al., 2005) have tested electrochemically assisted photocatalysis (EAP) for the break down of formic acid under UVA and UVB irradiation on nanocrystalline TiO₂ films. They found that the rate of formic acid oxidation under UVB irradiation was 30% greater as compared to UVA irradiation. However, a cost analysis of the process would be required to determine the economic viability of employing UVB sources. McMurray et al. conclude that electrochemically assisted photocatalysis may prove beneficial in large-scale reactors where mass transfer limitations exist. In a further experiment, Byrne et al. (Byrne et al., 2002) added a second cathode compartment to the cell for the simultaneous photocatalytic oxidation of formic acid and the recovery of copper ions from solution. Formic acid was degraded at the TiO₂ photoanode and copper metal was recovered at the copper mesh cathode with high efficiency (Byrne et al., 2002).

McMurray et al. (McMurray et al., 2006) further investigated the photochemical degradation of the herbicide atrazine on nanocrystalline TiO₂ films under UVA and UVB-irradiation. Atrazine removal followed first order kinetics and the rate was dependent upon catalyst loading up to an optimum loading (above which a decrease in the degradation rate was observed). The maximum apparent quantum yield for the photocatalytic degradation was higher under UVB (0.59%) compared to UVA (0.34%).

TiO₂ was also tested for its efficiency in removing the estrogenic activity of several potent and environmentally relevant steroid estrogens (Coleman et al., 2004). Coleman et al. found that photocatalysis over titanium dioxide was equally effective at removing the estrogenic activity of all three steroid substrates tested in aqueous solutions with a 50% reduction in estrogenicity within 10 min. They concluded that TiO₂ photocatalysis is a promising technology for the treatment of water contaminated with endocrine disrupting chemicals.

Navagemi et al. analysed the solar photocatalytic degradation of organic compounds (Nagaveni et al., 2004a) and various dyes such as methylene blue (MB), remazol brill blue R (RBBR) and orange G (OG) (Nagaveni et al., 2004b) by combustion synthesized nano-TiO₂. The initial degradation rates with combustion synthesized nano TiO₂ was 20 times higher for RBBR, 4 times higher for MB and 1.6 times higher for OG compared to Degussa P-25 TiO₂. They attribute the enhanced photocatalytic activity of the combustion synthesized catalyst to the crystallinity, nano-size, large amount of surface hydroxyl species and reduced band-gap. The degradation of dyes (methyl-red) was also investigated by Comparelli et al. (Comparelli et al., 2004)

Modification of TiO₂ with noble metals has shown significant promise in increasing the activity of titania for a variety of catalytic processes. Orlov et al. investigated the photocatalytic performance of TiO₂ doped with gold nanoparticles (Orlov, 2006; Orlov et al., 2004). The photocatalytic degradation of methyl tert-butyl ether (MTBE) by gold-modified TiO₂ (with a gold particle size of smaller or equal to 3 nm) exhibited a threefold rate enhancement compared to unmodified TiO₂ (Orlov et al., 2007). Orlov et al. also functionalized mesoporous (pore size 2-50nm) molecular sieves with TiO₂ for the decomposition of organic pollutants in air and water (ORLOV et al., 2006b). They found that such materials exhibit a significant activity for oxidation of organic pollutants. Anandan et al. 2008 (Anandan et al., 2008) modified TiO₂ with Ag for the photocatalytic degradation of the textile dye Acid red 88.

TiO₂ can also be modified with a second semiconductor, dyes or nitrogen which allows the semiconductor to be activated even by visible light (Liu et al., 2006; Obare and Meyer, 2004). The water purification potential of N-doped TiO₂ was evaluated by studying the photodegradation of Acid Orange 7 (AO7) and E coli (Liu et al., 2006). N-doped TiO₂ demonstrated superior photocatalytic activities compared to common Degussa P25 particles in both chemical compound degradation and bactericidal reactions (Liu et al., 2006).

A recently published study analysed the photocatalytic efficiency of quantum-sized ZnO by means of the degradation rate of reactive brilliant blue X-BR in aqueous solution (Su et al., 2008). The experimental results indicated that the photocatalytic property of the ZnO was excellent.

2.3.2 Nanofiltration

Hilal et al. (Hilal et al., 2004) summarize different applications and research on nanofiltration (NF) membranes in a comprehensive overview.

Transport processes of the solute in the pore is dominated by diffusion, although convective transport is significant for organic nitrogen compounds (Lee and Lueptow, 2001). Electromigration contributes negligibly to the overall solute transport in the membrane (Lee and Lueptow, 2001).

Diverse nanofiltration membranes are tested for their efficiency in removing different compounds and particles. Several authors have shown that NF can successfully remove viruses and bacteria (Jacangelo et al., 1997; Laurent et al., 1999; Yahya et al., 1993). Other papers discuss the removal of sulphate (Andrew, 2001), nitrate (Lee and Lueptow, 2001; Ratanatamskul et al., 1998), lead (Jakobs and Baumgarten, 2002) and chromate (Hafiane et al., 2000).

Yuan et al (Yuan et al., 2008) describe a self-assembly method for constructing thermally stable, nonwoven nanowire membranes that exhibit controlled wetting behaviour ranging from superhydrophilic to superhydrophobic. These membranes can selectively absorb oils up to 20 times the material's weight in preference to water, through a combination of very strong hydrophobicity and capillary action. They can also separate similar organic solvents such as benzene and toluene. The membranes can easily be recycled many times. Yuan et al. propose their new material for applications in the removal of organics, particularly in the field of oil spill cleanup. As the economic and toxicological arguments about the use of manganese oxide are owing, it is though not sure whether the material will find commercial applications (Lahann, 2008).

Schorr (Schorr, 2007) found that the surface area of ceramic filter materials can be greatly increased (10-50 times) by the growth of nanomaterials such as manganese oxide, iron oxide and/or copper (oxide) within the pores. These nanoenhanced membranes can effectively remove phosphates, heavy metals, lead, arsenic and other pollutants.

Visvanathan et al. (Visvanathan et al., 1998) investigated the effects of different parameters on the performance of nanofiltration for removal of trihalomethane precursors (THMPs). Higher pressure, THMP concentration and suspended solids increased the rejection only negligibly. On the other hand the presence of divalent ions reduced the rejection capacity. Generally rejection was found to be greater than 90% for a precompact membrane.

Different authors found that monovalent ions like nitrates are rejected to a lower extent (Lee and Lueptow, 2001; Molinari et al., 2001; Ratanatamskul et al., 1998). Lee and Lueptow (Lee and Lueptow, 2001) showed that urea as small organic compound has an even lower rejection than ionic compounds such as ammonium, nitrate and nitrite. They thus highlight the important role of electrostatic interaction in rejection whereas the molecular weight and chemical structure of nitrogen compounds appear to be less important.

Molinari et al. (Molinari et al., 2001) compared the performance of RO and NF concerning the separation efficiency of pollutants like silica, nitrate, manganese and humic acids (HA). The mean rejections of the NF membrane were lower than for the RO membrane, and equal to 35%, 6%, 80%, 35% respectively. Mn^{2+} rejection was the highest due to the positive charge of the NF membrane.

Molinari et al. (Molinari et al., 2001) also compared membrane washing agents and found NH_3 aqueous solution to be the best washing substance for membrane cleaning. Washing only with water was not able to remove Mn^{2+} and Cu^{2+} ions. Washing with NaOH lead to the precipitation of insoluble hydroxides, like $Mn(OH)_2$, and consequent plugging of membrane pores.

Several studies were conducted to assess the cleaning efficiency of NF membranes with industrial wastewater. Afonso and Yanez (Afonso and Yanez, 2001) investigated the performance of NF in the treatment of fish meal wastewater and found that NF reduced the organic load and partially desalinated the wastewater which made water reuse possible. Jakobs and Baumgarten (Jakobs and Baumgarten, 2002) studied the removal of lead from nitric acid solutions from the etching process. They achieved a recycling rate of up to 90% which not only reduces the need for fresh acid for the etching process, but also the alkali needed for neutralizing the waste acid stream could be drastically reduced. As an added benefit the nitrate load of the remaining wastewater was also decreased.

Tang and Chen (Tang and Chen, 2002) studied the recovery of electrolyte solution and the rejection of colour from wastewater produced by the textile industry. At low pressure of up to 500kPa, relatively high fluxes were obtained, with an average dye rejection of 98% and NaCl rejections of less than 14%. Thus, a high quality of reuse water could be recovered. Even after a number of cycles, the membrane did not foul irreversibly, with an overall mean waterflux recovery of 99%. Similar results were found by Voigt et al. (Voigt et al., 2001) with a TiO_2 -NF membrane and Weber

et al. (Weber et al., 2003) with a K-NF membrane. Voigt et al. tested their membrane in a pilot plant for its efficiency in decolouring of textile wastewater. The pilot plant tested with 30 types of different coloured wastewater over a period of 6 weeks. Depending on the composition of the dyes, decolouring rates of 70-100% were obtained with running costs around €0.25-1.4 per m³. Weber et al. (Weber et al., 2003) further compared the efficiency of different membranes regarding the treatment of textile wastewater, alkaline solutions from bottle washing machines, and pickling bath solutions. They found that the permeability rates of a ceramic membrane are clearly superior to those of polymer nanofiltration membranes.

2.3.3 Metals, Metal oxides and other metallic compounds

Nanoscale metals and metal oxides can be used for the absorbance of metals (Nowack, 2008; Rickerby and Morrison, 2007). Pacheco et al. (Pacheco et al., 2006) describe the removal of cadmium ions from simulated industrial wastewater using sol-gel structured nanoparticles of silica and alumina. The results show that it is possible to reduce the cadmium concentration from 140 ppm to less than 5 ppb using Si-Al particles. Al-Si particles were significantly less efficient. Deliyanni et al. (Deliyanni et al., 2007) conducted experiments to investigate zinc removal from diluted aqueous solutions (i.e. effluent) by sorption onto synthetic nanocrystalline akaganeite which was shown to be a promising inorganic adsorbent.

Active agents like manganese oxide can be used to change the valance state of metal ions in water (e.g. arsenic oxide from 3+ to 5+ which can then be more easisly removed (Schorr, 2007)). Iron and other metal oxides (sometimes in combination with metals) can also adsorb heavy metals and radionuclides (Schorr, 2007). Pollutants are caged in zeolite-like structures (Schorr, 2007). Iron oxide has also been used to break down organics, pesticides etc. into non-hazardous compounds (Schorr, 2007) and to effectivly remove phosphate. Reactions can often be enhanced through the addition of other nonomaterials such as copper (oxide) (Schorr, 2007).

A few studies investigate metal oxide-CNT composites for the removal of metals and anions (see also chapter on groundwater remediation). Peng et al. (Peng et al., 2005a) synthesized among others carbon nanotubes-iron oxides magnetic composites as adsorbent for removal of Pb(II) and Cu(II) from water.

2.3.4 Carbon Nanotubes

Oxidized, hydroxlated as well as modified CNTs are good adsorbents for metal ions and also for organic compounds. Yang and Xing though highlight that the adsorption of of PAHs on CNTs is reversible (Yang and Xing, 2007). Gotovac et al. found that purification of CNT improved the absorption (Gotovac et al., 2006).

Efficient absorbtion has been found for various metal ions such as Cu, Ni, Cd and Pb as well as for different organic compounds such as dioxin, PAH and DDT (Li et al., 2001; Liang et al., 2005; Nowack, 2008; Peng et al., 2005a; Peng et al., 2005b). The adsorption capacity was found to be proportional to the cylindrical external surface (Yang and Xing, 2007). In their study neither the inner cavity nor the interwall space of MWCNT contributed to the adsorption.

Fullerenes were found to be only weak sorbants for many types of organic substances (absorbtiion capactiy max. 60%) (Ballesteros et al., 2000). But they showed significant efficiency in the removal of organometallic compounds(Ballesteros et al., 2000). In general, the adsorption of organic compounds on fullerenes depends greatly on the disperion state of C60 which is insoluble in water if not modified (Nowack, 2008).

2.3.5 Nanostructured Boron Doped Diamond (BDD)

Haenni in (Rickerby and Morrison, 2007) reports that BDD has the largest electrochemical window of all known electrode materials and is considered today as a really new and very versatile electrode material. BDD can be grown artificially by Chemical Vapor Deposition (CVD) with in-situ boron doping on silicon. The nano-diamond crystal shape in these solutions is in the order of 2-10nm. Gandini et al. (Gandini et al., 2000) showed that BDD has an outstanding production capacity of very strong chemical oxidizing agents such as hydroxyl radicals which can effectively oxidize pollutants in wastewater regadless of water turbidity (some three-5 fold faster than conventiaonal chlorine dosing). BDD electrodes have the advantage of self-cleaning by reversing the current polarity.

2.3.6 Magnetic Particles

Magnetic nanoparticles can easily be separated from water by applying a magnetic field. Pollutants adsorbed to magnetic nanoparticles can so be easily removed from water and the nanoparticles are recovered. Examples of magnetic NP are magnetite Fe_3O_4 , maghemite ($\gamma\text{-Fe}_2\text{O}_3$) jacobite (MnFe_2O_4) which can be used for the removal of chromium(VI) (Hu et al., 2005a; Hu et al., 2006; Hu et al., 2004; Hu et al., 2005b). Hu et al. (Hu et al., 2004) found the adsorption process of Cr(VI) to magnetite to be pH and temperature dependent. The adsorption capacity increased with rising temperature. In a later work with jacobite nanoparticles, Hu et al. (Hu et al., 2005b) showed that the equilibrium time for Cr(VI) adsorption onto modified MnFe_2O_4 nanoparticles was as short as 5 min. They further found that EDTA and SO_4^{2-} inhibited the adsorption of Cr(VI) over a pH range from 2-10, whereas NH_4^+ enhanced the uptake of Cr(VI) at pH greater than 6.5. Regeneration of the jacobite and Cr(VI) was possible without compromising on the adsorption capacity or changing the valence respectively. Also maghemite was shown to be an effective adsorbant of Cr(VI) (Hu et al., 2005a). The adsorption reached the equilibrium within 15 min and was independent of the initial Cr-concentration. The maximum adsorption occurred at pH 2.5. Competition with other ions such as Na^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , NO_3^- , and Cl^- was ignorable, which illustrated the selective adsorption of Cr(VI) from wastewater. Regeneration studies verified that the maghemite nanoparticles, which underwent six successive adsorption-desorption processes, still retained the original metal removal capacity.

Hu et al. (Hu et al., 2006) further investigated the adsorption effectivity of maghemite nanoparticles (10nm) for the selective removal of toxic heavy metals (Cr(VI), Cu(II), and Ni(II)) from electroplating wastewater. The adsorption process was found to be highly pH dependent. The adsorption of heavy metals reached equilibrium within 10 min. Regeneration studies indicated that the maghemite nanoparticles undergoing successive adsorption-desorption processes retained original metal removal capacity. The authors suggest that the adsorption of Cr(VI) and Cu(II) could be due to electrostatic attraction and ion exchange, and the adsorption of Ni(II) could be as a result of electrostatic attraction only.

Magnetic NP can also be coupled with other substances such as CNT. Jin et al. (Jin et al., 2007) functionalized water-soluble multiwalled carbon nanotubes (MWNTs) with magnetic Fe nanoparticle and studied the removal of aromatic compounds in water and subsequent recovery.

2.4 Additional demand for research

Photocatalytic applications are promising but industrialized countries already have elaborated water treatment systems in operation that meet the current legislation. These systems will not be replaced unless photocatalytic systems prove to be cheaper or yield a significantly improved water quality. It is though not yet possible to analyse all side and end products of photocatalytic conversion which depend not only on the substances present in the water, but also on temperature, pH and other factors. It is thus necessary to develop the according analytical methods to determine side and end products.

Future objectives in the water treatment with oxidative nanomaterials are to further reduce COD (chemical oxygen demand) and to find an alternative cathode material to BDD in order to lower costs, reduce energy through the use of a low overpotential cathode, reduce N-organics and NH_4 content, and optimise the efficiency by increasing the process temperature. Another target (according to Haenni) is to decrease phenol in wastewater below 100 ppm.

In the field of nanofiltration, further research is needed to avoid membrane fouling e.g. by the use of hydrophilic low-fouling membranes or the control of the membrane charge. It will also be necessary to find materials that can be produced in larger quantities for commercial application.

2.5 Applications and perspectives

As mentioned in the previous chapter, industrialized countries already have elaborated water treatment systems in operation which will not be replaced unless the new system is significantly less costly or more efficient. Of the methods described in this subsector, photocatalysis and nanofiltration are the closest to the market and may find possible applications - probably not as mass products but maybe for the treatment of certain industrial wastewater. Applications of photocatalytic systems for the treatment of wastewater may be introduced in situations in which no effective or only very expensive systems exist today. But large scale testing is still needed before commercialisation.

Research on nZVI is more focused on application in the ground. If advertised to wastewater or surface water it has to be recovered. The same problem applies also to other nanomaterials that would be released as free particles into the water. Recovery systems would need to be developed (e.g. magnetic particles, centrifugation) which may be expensive and not practical for large scale applications.


Still one product for wastewater treatment can be found on the market: AC Environmental has developed a product called AC Nano (a JNJ Smart-Sorb product) which is supposed to remove heavy metals (lead, cadmium, nickel, zinc, copper, manganese and cobalt) from contaminated soils, groundwater and industrial wastewater. A similar product also addresses arsenic contamination and they are working on a AC Nano-product that will remove mercury. AC Nano is claimed to be non-toxic. Currently, they are working on developing AC Nano that will also remove mercury. Unfortunately, the product is not specified. It could not be found out what kind of nanomaterial is used. One possibility could be nZVI. (<http://www.ac-environmental.com/products/acnano/removing-heavy-metals>)

The EU project MEMBAQ is developing biotechnological membranes for water purification by incorporating recombinant aquaporin molecules into industrial membranes. Aquaporins are natural protein channels that transport water through cell membrane. They have unique selectivity and transport only pure water molecules due to their narrow pore diameter that prevents salt and other ions from passing while allowing high permeation rates for water with theoretically up to fifty times greater efficiency than conventional industrial membranes. Potential applications of this technology include water purification and industrial wastewater reclamation and reuse. <http://www.membaq.eu> (Nielsen, C.H.: Vandrensning med aquaporiner. Kvant, July (2008) pp. 27-31)

2.6 Current situation within the EU

The **COST Action 540** (Photocatalytic technologies and novel nanosurfaces materials - critical issues (PHONASUM)) is a network of researchers and practitioners working in the field of photocatalysis from all around Europe. The main objective of the Action is to increase via a concerted European effort the fundamental knowledge of nanocrystalline photoactive materials and development of new products, which utilize self sterilizing and self cleaning photoactive materials in specific industrially relevant application fields such as self-cleaning and anti-microbial surfaces, water treatment, air purification and general hygienic applications. The realization of these tasks will be accomplished through the development of novel highly active photocatalytic nanomaterials and coating systems with increased sensitivity in the visible region of the solar spectrum, with high environmental stability and adaptability on the various substrate systems. The Action will also concentrate on the development of EU standards for the characterization of photocatalytic materials. The Action commenced in January 2006 and will continue for four years. (www.cost540.com)

The European-Japanese Initiative on Photocatalytic Applications and Commercialisation (**EJIPAC**) 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 (www.ejipac.de). One of the main objectives of EJIPAC is to make photocatalytic technologies available to interested European industries and users, especially in the areas of self-cleaning surfaces, anti-microbial surfaces, anti-fogging, hydrophilic and architectural cooling technologies, water treatment, air purification and general hygienic applications. Moreover, the Initiative is interested in involving scientists who want to have their research results implemented and to make these technologies available to small and medium-size enterprises.



There are further four new EU FP7 projects on the remediation of (waste) water with nanotechnology:

- MONOCAT - Monolithic reactors structured at the nano and micro levels for catalytic water purification
- WATERMIM - Water Treatment by Molecularly Imprinted Materials
- Nametech - Development of intensified water treatment concepts by integrating nano- and membrane technologies
- NEW ED - Advanced bipolar membrane processes for remediation of highly saline waste water streams
- Clean Water - Water Detoxification Using Innovative vi-Nanocatalysts

The short description of these projects can be found at:

http://circa.europa.eu/Public/irc/rtd/eesdwatkeact/library?l=/projects_information/catalogue_projects/pdf_1/_EN_1.0_&a=d

3. Nanotechnology for the Treatment of Drinking Water

Keywords: drinking water, treatment, pollutant, arsenic, desalination, photocatalysis, nanofiltration, oxidation, degradation

3.1 Definition

This subchapter describes methods to purify drinking water. Drinking water denotes water used for drinking by humans independent of its source. The sources for drinking water are very different depending on the geographic region. In industrial countries it is mainly groundwater (see also chapter on groundwater). In developing countries many people depend on surface water such as lakes and rivers and sometimes rain as sources for drinking water.

3.2 Short Description

Depending of the source, the challenges for drinking water production are divers. Different nanotechnological approaches should now target the needs of the drinking water supply. In developing countries microbes are the major challenges. Desalination of seawater is discussed in industrialized regions with water scarcity (e.g. Saudi Arabia). In some countries also contamination with arsenic is problematic. The removal of hardness is a further topic addressed for reasons of comfort. The following table gives an overview over the methods addressing the different target compounds which may contaminate drinking water.

Table: Overview over methods, materials and target compounds

Method	Nanomaterials	Target compounds
Photocatalysis	TiO ₂	Microbes
Nanofiltration	Ceramic membranes	Hardness, organic matter, microbes, desalination, arsenic
Adsorption	CNT, metal (oxides), Magnetic NP	Metals, arsenate
Electrochemical oxidation	BDD	microbes
Redox-reactions	Iron oxide (Fe(II))	Metals, arsen, chlorinated solvents

3.3 State of R&D

3.3.1 Metal oxide - CNT Complex

Experiments showed that ceria supported on carbon nanotubes (CeO₂-CNTs) is an effective adsorbent for arsenate, and that the adsorption is pH-dependent (PENG et al., 2005b). Ca²⁺ and Mg²⁺ significantly enhanced its adsorption capacity suggesting that it is a promising adsorbent for drinking water purification. The loaded adsorbent could be efficiently regenerated by diluted NaOH, and achieved a regeneration efficiency of 94%. Di et al (Di et al., 2006) corroborate these results. They prepared ceria nanoparticles supported on aligned carbon nanotubes (CeO₂/ACNTs) as a novel adsorbent for Cr(VI) from drinking water. The best Cr(VI) adsorption occurred at a pH range of 3.0-7.4.

Li et al. (Li et al., 2001) investigated amorphous aluminiumoxide (Al₂O₃) supported on carbon nanotubes (Al₂O₃/CNTs) as adsorbant for fluoride from water. They found that its adsorption capacity is significantly higher than that of the reference materials (AC-300 carbon and c- Al₂O₃).

3.3.2 Photocatalysis

There are many studies on the efficacy of photocatalytic degradation by nanomaterials (mostly TiO₂) and they show that photocatalytic materials are effective against a wide variety of contaminants. The main focus for the use of photocatalysis in drinking water treatment is though clearly disinfection.

The Report from the Workshop on Nanotechnologies for Environmental Remediation (Rickerby and Morrison, 2007) names solar photocatalysis to be the main technology breakthrough for water treatment and purification, particularly in developing regions. Photocatalytic disinfection is an effective method to provide clean drinking water and works also for chlorine resistant organisms and even organic pollutants such as herbicides and pesticides (Rickerby and Morrison, 2007). Photocatalytic applications have been tested on laboratory and pilot scale and commercial systems are already available. The main barrier to widespread commercialisation (e.g. in developing countries) is the need for education of potential customers (Rickerby and Morrison, 2007).

Dunlop et al. (Dunlop et al., 2002) prepared TiO₂ electrodes by the electrophoretic immobilisation of TiO₂ powder (Aldrich and Degussa P25). They found that the application of an electrical bias to the working electrode increased the rate of disinfection by 40% to 80%. They further studied the photocatalytic inactivation of *Clostridium perfringens* spores on TiO₂ electrodes (Dunlop et al., 2008).

Sichel et al. (Sichel et al., 2007) studied the dependence of photocatalytic water disinfection on solar irradiation conditions under natural sunlight. This dependency was evaluated for solar photocatalysis with TiO₂ and solar-only disinfection with three microorganisms. It was shown that once the threshold solar dose is given, the photocatalytic disinfection efficacy is not enhanced by any further increase in irradiation.

Lindstrom et al. (2007) have developed a miniaturised photocatalytic reactor with an immobilised, highly porous film of anatase titania nanoparticles with a high specific surface area on the walls of the 100 µm wide channels of a glass microfluidic device. Microfluidic reactors are excellent for photocatalysis since a large density of UV photons can be concentrated in the immobilised photoactive layer within a small volume efficiently coupled to the light source (LINDSTROM et al., 2007).

3.3.3 Nanostructured Boron Doped Diamond (BDD)

Haenni in (Rickerby and Morrison, 2007) describes the BDD/Si electrodes to allow a very high anodic potential which may be used to produce very efficient oxidants for water treatment and disinfection. Disinfection is achieved without chlorine, independently of water turbidity, and with low by-product potential. For viruses and bacteria (E.Coli, Legionella) inactivation is 3-5 times faster than with conventional chlorine dosing. Destruction of algae, fungi and protozoan is also assured. COD (chemical oxygen demand)/TOC (total organic carbon) is reduced by the production of hydroxyl radicals for the destruction and increased biodegradability of organic pollutants (pesticides, phenols, solvents, PCBs). Based on electrodes from BDD by Gandini et al. (Gandini D et al., 2000), the DiaCell®-Systems were developed and are today installed for water disinfection and conservation e.g. in spas and swimming pools as well as for electro-oxidation of industrial wastewater, hazardous effluents and landfill leachates.

3.3.4 Metals, Metal oxides, Magnetic particles

Stipp et al. in (Rickerby and Morrison, 2007) describe the removal of nickel from drinking water by calcite nanoparticles. They also studied iron oxide (Fe(II)) as effective substance to degrade redox sensitive elements such as chromium and chlorinated solvents.

Sorption on iron (III) oxides such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous ferric oxide (ferrihydrite) and goethite (α-FeOOH) have been found to be effective in removing both As(V) and As(III) (Rave et al., 1998; Sun and Doner, 1998; Wilkie and Hering, 1996; Zeng, 2003).

3.3.5 Nanofiltration

Hilal (Hilal et al., 2004) summarizes different applications and research on nanofiltration (NF) membranes in a comprehensive overview.

Transport processes of the solute in the pore is dominated by diffusion, although convective transport is significant for organic nitrogen compounds (Lee and Lueptow, 2001). Electromigration contributes negligibly to the overall solute transport in the membrane (Lee and Lueptow, 2001).

Diverse nanofiltration membranes are tested for their efficiency in removing different compounds and particles. Several authors have shown that NF can successfully remove viruses and bacteria (Jacangelo et al., 1997; Laurent et al., 1999; Otaki et al., 1998; Urase et al., 1996; Yahya et al., 1993). Other papers discuss the removal of sulphate (Andrew, 2001; Redondo and Lanari, 1997) and nitrate (Lee and Lueptow, 2001; Ratanatamskul et al., 1998; Redondo and Lanari, 1997).

Monovalent ions like nitrates found to have lower extent of rejection (Lee and Lueptow, 2001; Ratanatamskul et al., 1998). Redondo and Lanari (Redondo and Lanari, 1997) further investigated the removal of hardness and organic matter on several pilot plants.

Molinari et al. (Molinari et al., 2001) compared the performance of RO and NF concerning the separation efficiency of pollutants like silica, nitrate, manganese and humic acids (HA). The mean rejections of the NF membrane were lower than for the RO membrane, and equal to 35%, 6%, 80%, 35% respectively. Mn^{2+} rejection was the highest due to the positive charge of the NF membrane.

Several studies investigated the combination of NF with other treatment methods such as (SW)RO and multistage flash. Hassan et al. (Hassan et al., 1998) found that (at a pressure of 22 bars) the NF unit reduced turbidity and microorganisms and removed Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^- by 89.6%, 94.0%, 97.8% and 76.6%, respectively. Monovalent ions (Cl, Na, K) were rejected by ca. 40% (Hassan et al., 1998). Mohesn et al (Mohesn et al., 2003) showed that NF is efficient for reducing the organic and inorganic substances and allows for a high water recovery of up to 95%. In an integrated system with NF, RO and membrane crystallizer (MC), NF increased the water recovery of the RO unit up to 50% leading to a total recovery of 100%.

In total, the combination of NF with other methods allows producing fresh water from seawater at a 30% lower cost (Al-Sofi, 2001). Hilal et al. (Hilal et al., 2004) highlights the advantages of a NF pretreatment of seawater in desalination: NF pretreatment prevents membrane fouling by removal of turbidity and bacteria, prevents scaling by removal of hardness ions and lowers the requested pressure to operate SWRO. These results were confirmed in a pilot plant study (Hassan et al., 2000).

The removal of arsenic from water has been studied by different authors. Seidel et al. (Seidel et al., 2001) and Brandhuber and Amy (Brandhuber and Amy, 1998) found that the rejection of the uncharged As(III) species was significantly lower compared to As(V). Waypa et al. (Waypa et al., 1997) found the rejection of both species to be equally effective. The rejection of As(V) decreased sharply when the pH was lowered (Seidel et al., 2001) (Vrijenhoek and Waypa, 2000). The separation of the uncharged As(III) was independent of pH over the studied pH range (Seidel et al., 2001). Vrijenhoek and Waypa (Vrijenhoek and Waypa, 2000) found arsenic (V) was removed by 60-90% from synthetic feed waters while Brandhuber and Amy (Brandhuber and Amy, 1998) found out that the rejection of As(III) was only about 40%.

3.4 Additional Demand for Research

Photocatalytic applications are promising but industrialized countries already have elaborated water treatment systems in operation that meet the current legislation. They will thus not be replaced unless photocatalytic systems prove to be cheaper or yield a significantly improved water quality. It is though not yet possible to analyse all side and end products of photocatalytic conversion which depend not only on the substances present in the water, but also on temperature, pH and other factors. It is thus necessary to develop the according analytical methods to determine side and end products.

Future objectives in the water treatment with oxidative nanomaterials are to further reduce COD (chemical oxygen demand) and to find an alternative cathode material to BDD in order to lower costs, reduce energy through the use of a low overpotential cathode, reduce N-organics and NH_4 content, and optimise the efficiency by increasing the process temperature.

In the field of nanofiltration, further research is needed to avoid membrane fouling e.g. by the use of hydrophilic low-fouling membranes or the control of the membrane charge. It will also be necessary to find materials that can be produced in larger quantities for commercial application.

3.5 Applications and Perspectives

As mentioned in the chapter before, the lack of knowledge on the efficiency and effectiveness of photocatalytic reactions limit the application currently to disinfection. Systems for water disinfection are already on the market (e.g. tubes coated with nano-TiO₂) and should have a significant market potential in developing countries. This application is not yet common, but the use is expected to increase significantly in the next years. Applications for photocatalytic systems are also seen in the treatment of contaminated water for which no effective or only very expensive systems exist today.

The same can be stated for water treatment with metals, metal oxides, BDD and other materials. At the time, there is no need to replace current systems in most cases and therefore the application of nanotechnological materials will be restricted to niche markets or applications where no conventional treatment exists so far.

With nanofiltration the situation is different. Nanofiltration has further fields of application such as removal of hardness and desalination which makes it to be a promising technology especially in combination with other techniques. In addition, there is no risk associated with nanofiltration as no particulate material is involved and because filtration is a physical process (not based on chemical reactions where potentially unknown sideproducts could be produced).

Even though there is extensive research on nanofiltration and great hope is placed on new discoveries (e.g. <http://www.technologyreview.com/nanotech/16977/>), nanofiltration is not yet ready for largescale application among others due to problems with membrane fouling. But it can be expected that in around 10 years, the applications will be commercially available. On www.freepatentsonline.com already a few applications of nanofiltration membranes are found e.g. for drinking water treatment (<http://www.freepatentsonline.com/EP1359124.html>) or for water softening (<http://www.freepatentsonline.com/5152901.html>)

A google-websearch revealed only a few products advertised as nano-enhanced drinking water purification systems. At the University of South Australia (UniSA) scientists have developed a purification system which uses silica particles coated with an active nano-material. Its "active" nanomaterial is though not further specified (www.unisa.edu.au/news/2008/110808.asp).

At Rice University, a method is being developed which removes arsenic from water with iron oxide nanoparticles. The nanoparticle production should be possible by using only fatty acids (e.g. oil) and rust. The simple production process should allow the application of this method in developing countries and countries in transition (e.g. India and Bangladesh).

3.6 Current Situation within the EU

There are currently four EU FP7 projects carried out on the remediation of (drinking) water with nanotechnology:

- MONOCAT - Monolithic reactors structured at the nano and micro levels for catalytic water purification
- WATERMIM - Water Treatment by Molecularly Imprinted Materials
- Nametech - Development of intensified water treatment concepts by integrating nano- and membrane technologies
- Clean Water - Water Detoxification Using Innovative vi-Nanocatalysts

The short description of these projects can be found at:

http://circa.europa.eu/Public/irc/rtd/eesdwatkeact/library?l=/projects_information/catalogue_projects/pdf_1/_EN_1.0_&a=d

4. Nanotechnology for Groundwater Remediation

Keywords: groundwater, remediation, in situ, pollution, metals, treatment, adsorption, zero valent iron, halogenated pollutants

4.1 Definition

This sub-sector describes the methods and nanotechniques investigated and applied for the remediation and decontamination of the groundwater compartment. The treatment of groundwater destined for immediate use as drinking water is discussed in the sub-sector “drinking water treatment”. Groundwater is subsurface water located in soil pores, spaces in the soil/rock formation and aquifers. The treatment of groundwater with immobile materials takes place in aquifers where a larger amount of water is located. Mobile particles can also target pore water.

4.2 Short description

In many parts of Europe groundwater is the main source for drinking water. It is therefore crucial to assure clean groundwater. Polluted groundwater may also affect the soil ecosystem and/or other water compartments such as lakes and rivers.

Groundwater sources are frequently contaminated with pesticides and sometimes with heavy metals or halogenated compounds. According to Van der Bruggen et al. nitrate concentrations in groundwater are increasing and often close to or above the legal standard (Van der Bruggen et al., 2001). Landfill leakage, agriculture and chemical accidents are the main sources of groundwater pollutants.

Overview over methods, materials and target compounds:

Method	Nanomaterials	Target compounds
Redox-reaction/adsorption (Injection of mobile or immobile particles)	nZVI	Halogenated hydrocarbons, heavy metals, nitrate, arsenate
Adsorption/redox-reaction	Iron oxide	Heavy metals, arsenic contaminants
Nanofiltration	Nanoporous membranes	Pesticides, hardness, (nitrate)
Photocatalysis	nTiO ₂	Organic pollutants

4.3 State of R&D

4.3.1 nZVI (Nano Zero Valent Iron)

The use of nZVI for groundwater remediation is the most widely investigated environmental nanotechnological technique (Nowack, 2008) and has considerable potential benefits (Tratnyek and Johnson, 2006). According to several authors (ELLIOTT and ZHANG, 2001; QUINN et al., 2005; TRATNYEK and JOHNSON, 2006) nZVI has already gone to successful pilotscale demonstrations and fieldscale commercial applications of nZVI are quickly becoming common (Li et al., 2006). There are already competitive markets among purveyors of nZVI materials (Tratnyek and Johnson, 2006). Iron NP can be produced by top-down (milling) or bottom-up (chemical synthesis) processes (Li et al., 2006).

Granular ZVI has been used in form of reactive barriers (figure a) at numerous sites all over the world for the removal of organic and inorganic contaminants (Nowack, 2008). But the smaller size of nZVI promises new advantages compared with granular ZVI (Tratnyek and Johnson, 2006):

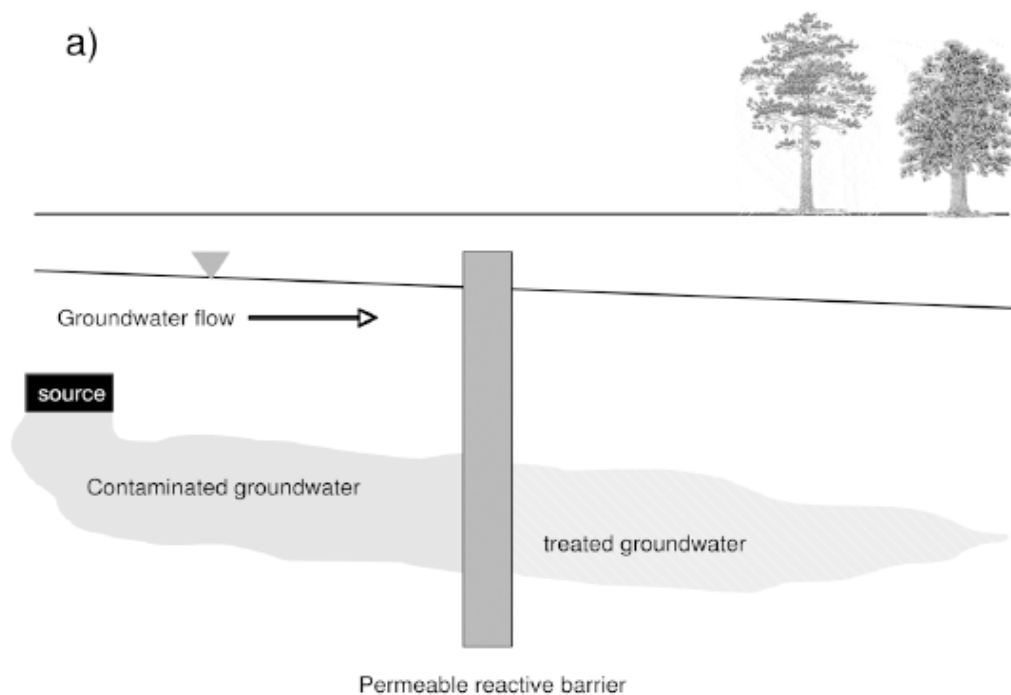
- Degradation of contaminants that do not react detectably with larger particles of similar material (eg polychlorinated biphenyls (Lowry and Johnson, 2004));

- More rapid degradation of contaminants (25-30 times faster) (eg chlorinated ethylenes (Song and Carraway, 2005)).
- More favourable products from contaminants (eg carbon tetrachloride (Nurmi et al., 2005)).

Of these three advantages the second type is the most important (Tratnyek and Johnson, 2006).

There are two possibilities for groundwater remediation with nZVI (Nowack, 2008) (Tratnyek and Johnson, 2006):

- Immobile nZVI are injected to form a zone of iron particles adsorbed on aquifer solids (figure b).
- Mobile nZVI are injected to form a plume of reactive iron to destroy any organic contaminants that dissolve from a dense non-aqueous phase liquid in aquifer (figure c).



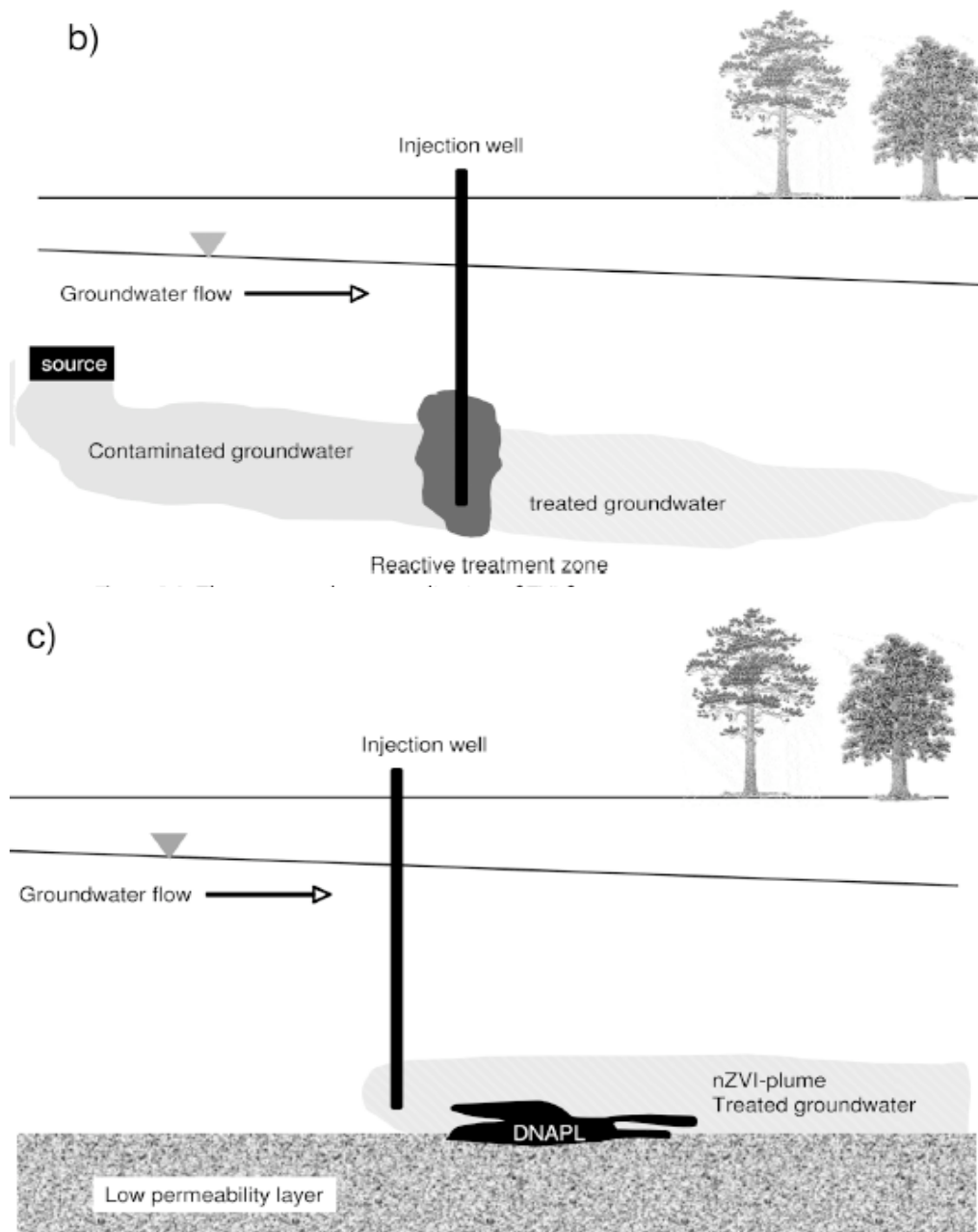


Figure 2 (Nowack, 2008): Possibilities for the treatment of contaminated groundwater with iron fillings (a) or nZVI (b+c)

Several studies have shown that nZVI (as a controlled barrier) is very effective for the degradation of halogenated solvents such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethenes, chlorinated benzenes and other polychlorinated hydrocarbons in groundwater (Schorr, 2007; Zhang, 2003). nZVI was also shown to be effective against pesticides and dyes (Zhang, 2003). The degradation is based on redox reactions, where iron donates electrons to the contaminants which are consequently reduced to less toxic compounds. Fe(0) can also reduce nitrate to ammonia, perchlorate to chloride, selenate, arsenate, arsenite and chromate (Nowack, 2008).

nZVI can also remove dissolved metals from solution (Pb, Ni). A study by Dries et al. (Dries et al., 2005) has investigated the combined removal of chlorinated ethenes and heavy metals from a simulated groundwater matrix by zerovalent iron. nZVI has also been used to immobilize Cr(VI) in chromium ore processing residue (Cao and Zhang, 2006).

According to Tratnyek and Johnson (Tratnyek and Johnson, 2006) nZVI used in groundwater remediation is larger than particles that exhibit true nanosize effects. They also state that the mobility of nZVI will be less than a few meters under almost all relevant conditions as nZVI tends to aggregate producing clusters that may approach microns in size and thus behave more like colloids. Tratnyek and Johnson further state that high reactivity tends to correlate with low selectivity. For this reason, remediation with nZVI may be inefficient because nZVI-particles may react with non-target substances including dissolved oxygen and water. This also implies that nZVI will have a limited lifetime in porous media. Potentially reinjections of nZVI will be necessary which makes the treatment more costly. On the other side the short lifetime of nZVI in situ may also be beneficial by not allowing unwanted exposure of the environment and humans. They conclude that human exposure is likely to be minimal.

4.3.2 Iron oxide

Iron oxide minerals can be used to remove heavy metals and arsenic contaminants (Rickerby and Morrison, 2007). The increased surface area of minerals through nanostructuring results in a greater take up of pollutants.

At the Nano&Environment workshops in Brussels (Morrison, 2006; Rickerby and Morrison, 2007) the application of magnetic iron oxide for removing arsenic from groundwater was presented. Arsenic has both natural and anthropogenic sources. Arsenic levels above the guidelines of WHO are a serious problem in several countries (e.g. Bangladesh). So far there are no existing methods that effectively remove arsenic from groundwater. Iron oxide NP may bind arsenic irreversibly (5-10 times more effectively than larger particles). The supraparamagnetic nature of the iron oxide nanoparticles allows them to be easily separated from water by the application of a magnetic field. In laboratory tests more than 99% of the arsenic in water could be bound by 12nm diameter iron oxide nanoparticles. This represents some 2500 to 25,000 fold higher efficiency than current systems. Also in the US several thousand of communities exceed the recommended level of arsenic (Schorr, 2007). Schorr (Schorr, 2007) writes that As (III and V) (and lead) can be most effectively removed by a combination of nano manganese oxide fibers and nano iron oxide.

Schorr (Schorr, 2007) further found that iron and other metal oxides (sometimes in combination with metals) can also adsorb heavy metals and radionuclides (Schorr, 2007). Pollutants are caged in zeolite-like structures. A combination of iron/iron oxide was also shown to be effective in phosphate removal - even more effective than higher cost products such as activated alumina while being active for even longer periods (Schorr, 2007).

Green rust - a very reactive iron oxide - can be used to reduce Cr(VI) to Cr(III) which is not soluble and unlike the mutagenic Cr(VI), it is an essential trace element (Stipp in (Rickerby and Morrison, 2007)). Cr(III) is incorporated within the goethite structure which makes the complex even less soluble (Stipp in (Rickerby and Morrison, 2007)).

4.3.3 Nanofiltration (NF)

Nanofiltration (NF) allows to simultaneously remove pesticides, hardness and nitrates (Van der Bruggen et al., 2001). It was shown that pesticide rejections (Van der Bruggen et al., 1998) and removal of hardness (Schaep et al., 1998; WATSON and HORNBERG, 1989) are effective, whereas only a small fraction of nitrate is removed by most membranes (Van der Bruggen et al., 2001). Schaep et al. (Schaep et al., 1998) found that generally the retention of multivalent ions is higher (up to 90%) than the retention of monovalent ions (about 60-70%). NF is also reported to be very effective (95%) in the removal of dissolved uranium (Raff and Wilken, 1999).

The removal of arsenic from water has been studied by different authors. Seidel et al. (Seidel et al., 2001) and Brandhuber and Amy (Brandhuber and Amy, 1998) found that the rejection of the uncharged As(III) species was significantly lower compared to As(V), whereas Waypa et al. (Waypa et al., 1997) found the rejection of both species to be equally effective. The rejection of As(V) decreased sharply when the pH was lowered (Seidel et al., 2001) (Vrijenhoek and Waypa, 2000). The separation of the uncharged As(III) was independent of pH over the pH range studied (Seidel et al., 2001). Vrijenhoek and Waypa (Vrijenhoek and Waypa, 2000) found arsenic (V) to be removed by 60-90% from synthetic feed waters while Brandhuber and Amy (Brandhuber and Amy, 1998) state that the rejection of As(III) was only about 40%.

Van der Bruggen et al. (Van der Bruggen et al., 2001) analysed the economical side of the implementation of nanofiltration and concluded that nanofiltration is a valuable option for groundwater treatment. The environmental impact of nanofiltration was assessed by Sombekke et al. (Sombekke et al., 1997).

4.3.4 Photocatalysis

Mattigod et al. (Mattigod et al., 2005) studied functionalized TiO₂-nanoparticles for their binding affinity for pertechnetate anions from a groundwater matrix. They also investigated their injectability into a porous medium for possible application as a subsurface semipermeable reactive barrier.

Modification of TiO₂ with noble metals has shown significant promise in increasing the activity of titania for a variety of catalytic processes. Orlov et al. investigated the photocatalytic performance of TiO₂ doped with gold nanoparticles (Orlov, 2006; Orlov et al., 2004). Compared to unmodified TiO₂, the photocatalytic degradation of methyl-tert-butyl-ether (MTBE) and 4-chlorophenol by gold-modified TiO₂ (with a gold particle size of 2-3 nm) exhibited a 50% and 100% improvement in the reaction rate for 4-chlorophenol and MTBE respectively - even if the gold concentration is less than 1%. (Orlov et al., 2007). It was also found that effective removal of both pollutants could be achieved at water flow rates that are relevant to field applications which suggests successful photocatalytic clean-up of contaminated groundwater (Orlov et al., 2007). Due to their very small Au content, the cost of these materials is compatible with large scale use (Orlov et al., 2007).

4.4 Additional demand for research

Field tests of nZVI and iron oxide are being carried out successfully in different places. Monitoring systems are now needed to assess the behaviour of the released particles in the environment and study the longterm effect of the particle release. In addition to free nanoparticles, nanostructured surfaces can make excellent remediators. More research is needed in this area.

In the field of nanofiltration, research on the most capable material is still ongoing. Challenges are also membrane fouling and the large scale application of filtration membranes in the case of groundwater remediation. At the time research on nanofiltration is more focussed on the application for drinking water and wastewater treatment.

The application of TiO₂ for remediation of groundwater is still far from the market. First results from the lab are promising. But no large-scale field trials have been carried out yet. Pilot plants have however been set up for treatment and recycling of industrial process water (Bahnemann, 2004). More research is needed on the dispersion of the material after the release and its behaviour in the environment (such as reaction with non-target materials).

4.5 Applications and perspectives

At the time the following applications are the most promising:

- in-situ remediation of chlorinated solvents in groundwater with nano iron
- on-site removal of metals, especially As, from groundwater with iron oxides
- on-site removal of pollutants (e.g. pesticides, nitrate) by nanofiltration
- on-site destruction of organic pollutants using nano TiO₂-photocatalysis

As the following paragraphs illustrate, it is confirmed that there is mass production of nZVI particles and that nZVI is applied in field trials in different places in Europe. On commercial applications of nanofiltration and TiO₂-photocatalysis, there are now information so far. It is thus to be assumed that these techniques are not yet ready for large scale applications.

A product called AC Nano (a JNJ Smart-Sorb product) which is supposed to remove heavy metals (lead, cadmium, nickel, zinc, copper, manganese and cobalt) from contaminated soils, groundwater and industrial wastewater was developed by AC Environmental. The composition of the remediation material though is not public. A similar product also addresses arsenic contamination and the company is working on a AC Nano-product that will remove mercury. AC Nano is claimed to be non-toxic (<http://www.ac-environmental.com/products/acnano/removing-heavy-metals>).

nZVI: According to Richard Mach (Naval Facilities Engineering Command) nanoscale iron was not commercially available until 2003. But within the first year, the costs for the material dropped two times (Federal Remedial Technology Roundtable http://www.frtr.gov/pdf/meetings/l--mach_09jun04.pdf). The Czech company “Nanoiron” (www.nanoiron.cz) has informed in January 2009 that they have started the mass production of nZVI particles. They offer three products:

- NANOFER 25* - Aqueous dispersion of Fe(0) nanoparticles stabilized solely by an inorganic modifier. The product exhibits an extremely high reactivity with preservation of long- term stability but is characterized by a higher degree of agglomeration and faster sedimentation.
- NANOFER 25S* - Aqueous dispersion of Fe(0) nanoparticles with special patented surface modification which is based on combination of a biodegradable organic and inorganic stabilizer. The product exhibits not only a high reactivity with a large scale of pollutants, but also very low degree of agglomeration, which implies for excellent migration and sedimentation properties. It is destined especially for the application in the reduction technologies of treatments of contaminated underground waters.
- NANOFER 25N* - Nanopowder, consisting of Fe(0) nanoparticles without surface modification, preserved in the inert nitrogen atmosphere. The product exhibits extremely high reactivity and is usable for any secondary stabilization in dependence on particular application of nanoparticles.


Verutek and the USEPA (U.S. Environmental Protection Agency) have developed a green synthesis method of nanometals using plant extracts (provisional patent obtained) (<http://www.verutek.com/Nano%20Zero%20Valent%20Iron.htm>) which is used for the treatment of soils and groundwater (<http://www.verutek.com/Role%20of%20Nanomaterials%20.htm>).

Meisol Ltd., a company set up in February 2008, is developing a new composite material for the remediation of contaminated groundwater, soil and wastewater. The composite material is formed by bonding nano-sized zero-valent iron (nZVI) particles with metalloporphyrin catalysts onto a diatomite matrix that shows catalytic activity toward different contaminants, especially to halogenated organic compounds, that are common soil and groundwater pollutants. <http://www.incubators.org.il/26064.htm>

Golder Associates (www.golder.com), an international company specialized in environmental engineering, is working with nZVI and bimetallic nanoparticles for groundwater remediation. In Europe the company is present with about 25 offices in 13 countries. More than 40 projects with nZVI are managed. In Europe, pilot tests and field applications for remediation in the Czech Republic, Italy and Germany are carried out since 2004. The company describes remediation with nZVI to be very effective (within a short time period), less costly and easily ajustable to site-specific requirements. Further applications of nZVI in wastewater and drinking water treatment are planned.

Alenco Environmental Consult GmbH, a German company with 7 offices in Germany and Hungary, is also advertising nano iron for remedation. A project description of the first full-scale remediation with nano iron in Europe can be found on their website: <http://www.fe4u.de>

A report published by Lloyd’s in 2007 (http://www.nanet.nu/upload/centre/nanet/nyheder/lloydsemergingrisksteamreport_nanotechnology_report.pdf) claims that it is very unlikely that any companies are using nanotechnology for remediation in the UK, even though there is no ban on using nanoparticles for environmental use.



A field test at a CHC contaminated site in Germany by the Federal Institute for Geosciences and Natural Resources (BGR) (HOUBEN et al., 2006) indicated that injection of nZVI particles caused significant changes in redox chemistry while other physico-chemical and hydrochemical parameters of the groundwater were not negatively affected. The limited penetration depth and lateral dispersion prevented the clean-up of a larger part of the test site.

Information on different case studies (supervised by governmental bodies) and background information on nZVI is found in the report of the U.S. EPA Workshop on Nanotechnology for Site Remediation (http://es.epa.gov/ncer/publications/workshop/pdf/10_20_05_nanosummary.pdf)

as well as in the presentation of the Naval Facilities Engineering Command at the Federal Remedial Technology Roundtable (http://www.frtr.gov/pdf/meetings/l--mach_09jun04.pdf)

4.6 Current situation within the EU

Unlike with soils, groundwater is always public property and thus orders for remediation come from governmental bodies. Field trials and first full-scale projects in different countries are thus mostly supervised by a state body. Still the release of nanoparticles into the environment is not regulated. Anyone could buy and release for example nZVI in any quantity.

The Perebar-Project (<http://www.perebar.bam.de>) investigated the Long-term Performance of Permeable Reactive Barriers used for the Remediation of Contaminated Groundwater. It focuses on conventional materials but the treatment method is comparable to the methods used for the application of nZVI.

There are four EU-research projects focussing on water:

- MONOCAT - Monolithic reactors structured at the nano and micro levels for catalytic water purification
- WATERMIM - Water Treatment by Molecularly Imprinted Materials
- Nametech - Development of intensified water treatment concepts by integrating nano- and membrane technologies
- Clean Water - Water Detoxification Using Innovative vi-Nanocatalysts

The short description of these projects can be found at:

http://circa.europa.eu/Public/irc/rtd/eesdwatkeact/library?l=/projects_information/catalogue_projects/pdf_1/_EN_1.0_&a=d

In the US, the Center for Groundwater research is investigating the use of nZVI for the groundwater remediation. More information on their research is found at: <http://cgr.ese.ogi.edu/iron/>

5. Nanotechnology for Soil Remediation

Keywords: soil, remediation, pollutants, metals, soil washing, in situ, zero valent iron, removal, adsorption, degradation

5.1 Definition

This sub-sector contains an overview over the few studies found on soil remediation with nano-techniques. Soil is understood as the top layer of the earth crust (lithosphere) which encompasses the A and B horizons over the bedrock.

5.2 Short description

Soil contamination with carcinogenic organic substances and/or heavy metals is found in all countries. Conventional technologies include soil washing (ex situ) or fillings with iron scap (in situ). Soil remediation is generally very expensive and the conventional methods are not always successful. New applications are therefore needed.

Overview over methods, materials and target compounds:

Method	Nanomaterials	Target compounds
Redox reactions	nZVI	Organic compounds
Sorption	Iron oxide, dendrimers/polycarbons	Heavy metals, organic compounds

5.3 State of R&D

Unlike with groundwater, only little research has been published in the field of soil remediation. The studies on soil remediation with nanoparticles focuss mainly but not exclusively on nZVI and iron oxides (possibly catalysed by noble metals such as Pd) (Rickerby and Morrison, 2007). Challenges are the lack of data on the behavior of nanoparticles in soil, the heterogeneity of the system and concerns regarding the effect of NP-release in soil ecosystems.

5.3.1 nZVI

Efficient removal of polycyclic aromatic hydrocarbons (PAHs) by nZVI has been reported (Chang et al., 2007; Chang et al., 2005) while at room temperature only about 38% of the polychlorinated biphenyls (PCBs) could be reduced because of the very strong sorption of PCBs to the soil matrix (Varanasi et al., 2007). The solubility of hydrophobic organic contaminants can though be increased by polymeric nano-network particles (Tungittiplakorn et al., 2005). Satapanajaru et al. investigated the remediation of atrazine contaminated soil and found nZVI to be an effective substance for the reductive dechlorination of the pesticide (Satapanajaru et al., 2008).

nZVI was also tested as catalyst in the microbial reduction of nitrate (Shin and Cha, 2008). The authors found the combination of nZVI and biological treatment to be twice as successful as the nZVI treatment only.

5.3.2 Other iron compounds

Ramsden in (Rickerby and Morrison, 2007) reports that iron oxide nanoparticles in the form of iron fillings are strong adsorbants for heavy metals in the soil. The nanoparticles with the adsorbed pollutant can then be collected using a magnetic field, and thereby eliminated from the ecosystem. These methods are yet untested on a large-scale and Ramsden doubts that iron fillings will be more effective than conventional iron scrap treatment due to the following reasons (Ramsden in (Rickerby and Morrison, 2007)): 1. The expense and environmental burden of preparing the nanoparticles; 2. Iron can be oxidized by oxygen and/or water before it has had a chance to react with the target compound and 3. The nanoparticles may in practice be agglomerated or aggregated. He further mentions the risk of introducing nanoparticles to the soil as smaller particles are much harder to confine than iron scrap.

Experiments were also conducted with nanoscale iron phosphate for the in situ immobilisation of Cu(II) (Liu and Zhao, 2007). It was shown that the bioaccessibility of Cu was reduced by 54-69% through the formation of different copper phosphate compounds.

5.3.3 Carbon based nanomaterials: Dendrimers, Biopolymers and Polycarbons

Dendrimers and polymers are explored for the removal of metals and organics. Xu and Zhao (Xu and Zhao, 2006) investigated the feasibility of using selected dendrimers for the removal of lead (Pb^{2+}) from three contaminated soils. They found that lower pH increased the removal rate and that the decontamination was more effective for sandy soil than for clay soil. Around 82% of the carbonate-bound Pb^{2+} cations could be removed and the dendrimers as well as the Pb^{2+} could be recovered to a high percentage.

Xu and Zhao (Xu and Zhao, 2006) further synthesized amphiphilic crosslinked polyurethane (ACPU) nanoparticles to wash sorbed phenanthrene from soil. They found the ACPU nanoparticles to be more effective sorbents than SDS solutions.

By recombinant DNA techniques, it is now possible to create artificial nanoscale protein polymers that can be controlled precisely in terms of size, composition and thus the function. Such biopolymers are being tested as metal-binding materials for the remediation of heavy metal contaminated soil (Kostal et al., 2005).

5.4 Additional demand for research

The behaviour of the released nanoparticles in soils is still unclear. Monitoring systems are needed to investigate the mobility, reaction with soil components and effects on soil ecosystems. The application of nanoparticles to soils is closely linked to the groundwater compartment.

5.5 Applications and perspectives

Many companies that have developed nanoproducts for groundwater remediation, advertise this product also for the remediation of contaminated soils. As mentioned above, the two compartments are closely linked.

Continental Remediation LLC (www.continentalremediation.com) is using nanosized calcium peroxide for the remediation of soils with different organic contaminants such as gasoline, heating oil, MTBE, ethylene glycol and solvents. Calcium peroxide is claimed to be highly efficient in removing especially aromatics. A full scale case study has been successfully completed.

Verutek and the USEPA (U.S. Environmental Protection Agency) have developed a green synthesis of nanometals using plant extracts (provisional patent obtained) (<http://www.verutek.com/Nano%20Zero%20Valent%20Iron.htm>) which is used for the treatment of soils and groundwater (<http://www.verutek.com/Role%20of%20Nanomaterials%20.htm>)

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5.6 Current situation within the EU

At the time there is no EU-project focussing on the use of nanoparticles for environmental remediation.

In European countries as well as in the U.S., the release of nanoparticles into the environment is not yet regulated. In principle, anyone can hire a company (listed above) to decontaminate one's backyard. It seems that in Europe, most remediation projects (e.g. in Germany) are carried out as collaboration between industry and local government. But based on advertisements of the companies mentioned above, target audience of companies located in the U.S. are also private persons.

The USEPA (U.S. Environmental Protection Agency) has contracted the University of Cincinnati for a research project on the fate and transport of nanoparticles in soil systems and how the presence of these nano-particles influence contaminant transports and soil remediation technologies. EPA will focus this research on comparing nano-particles occurring naturally with engineered ones based on their mobility in soil systems, aggregation and dissolution to increase the understanding on the fate of nano-particles. EPA intends to use materials such as silica as a model for naturally occurring nano-materials, whereas titania and iron oxide for engineered particles having varying reactive properties. The mobility of nano-particles through porous media and their tendency to aggregate or agglomerate to form larger macro-scale particles will be evaluated under different conditions. EPA will study the influence of accumulated nano-materials on contaminants mobility and soil remediation technologies such as encapsulation techniques.

<https://www.fbo.gov/index?tab=core&s=opportunity&mode=form&id=3d666d4532ddfc69e8479e0c1060084b&cck=1&au=&ck=>

The USEPA investigated the application of bimetallic nanoiron into the environment in a research program from 2001 till 2006. The final report can be accessed at: http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/2365/report/0

The USEPA also commissioned a report by the University of Arizona on "Nanotechnology for Site Remediation: Fate and Transport of Nanoparticles in Soil and Water Systems" (B. Latif, 2006) http://www.clu-in.org/download/studentpapers/B_Latif_Nanotechology.pdf



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