ENVIRONMENT

PHOTOCATALYSIS FOR WATER TREATMENT

Water pollution is a concern for nearly half of the European population, as indicated by the EU25 barometer[1]. The European Union has addressed this in the EU Water Framework Directive, which sets quality objectives for water protection. The EU is also committed to the UN Millennium Development Goals (MDG), one of the targets of which is to halve the proportion of people without sustainable access to safe drinking water and basic sanitation by 2015 [2,3].

The challenges in treating waste- and drinking water are dependent on the origin of the water. Problematic substances in wastewater can include organic matter and/or different trace contaminants. Industrial wastewater may additionally contain heavy loads of metals or organic compounds. In drinking water production microbe contamination needs to be addressed especially in developing countries, but also for remote locations without access to a centralized drinking water supply.

The Report from the Workshop on Nanotechnologies for Environmental Remediation[4] identifies solar photocatalysis as the main technology breakthrough for water treatment and purification, particularly in developing regions. Initial pilot projects are now being carried out. Photocatalytic systems may also complement existing techniques in the removal of trace contaminants. Such systems are commercially available e.g. for the disinfection of swimming pools.

This briefing outlines the social and economical relevance of nano-enabled photocatalysis, provides background information on the technology, and highlights further challenges to be addressed.

Opportunities for photocatalytic water treatment

Photocatalysis based on nano-catalysts is a very promising method for the treatment of contaminated water. We can distinguish two different types of photocatalytic applications in water treatment: solar photocatalysis and photocatalytic systems equipped with artificial ultraviolet (UV)-light. Both systems can be applied at ambient temperature to degrade various chemical and microbiological pollutants in water and air.

As it makes use of sunlight, solar photocatalysis technology is inexpensive, environmentally friendly, and universally applicable. The equipment needed is minimal and also appropriate for developing countries or remote sites with no access to electricity.

In Europe, conventional technologies for wastewater treatment are in most cases able to meet the current water quality standards. The chances and potential fields of application of photocatalytic systems with artificial UV-sources are:

- New water treatment plants or plants where conventional methods need to be replaced
- For the treatment of water contaminated with trace contaminants (e.g. estrogens)
- For the treatment of (industrial) wastewater contaminated with high loads of organic compounds or metals
- Small scale systems (e.g. for swimming pool disinfection)

Photocatalysis – how does it work?

The principle of photocatalysis is very simple: A catalyst harnesses the (UV-) radiation from sunlight and uses the energy to break down different substances. Photocatalysis can be used to break down a wide variety of organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses and chlorine resistant organisms), inorganic molecules such as nitrous oxides (NOx) and, in combination with precipitation or filtration, can also remove metals (such as mercury)[4,5,6]. Due to this universal applicability, photocatalysis with nanoparticles as catalysts is used to reduce air pollution, in building materials for self-cleaning surfaces, in addition to water purification.

Titanium dioxide (TiO_2)is the most common photocatalyst (see Box 1). Comparably little research is conducted on zinc oxide (ZnO) which could be a viable alternative for some applications. A comprehensive review of photocatalytic nano-TiO_2 for environmental applications is found in Kwon et al.

ENVIRONMENT: Photocatalysis for Water Treatment

Box 1: Titanium Dioxide
The photocatalyst of choice

There are several potential photocatalysts, but the most promising and widespread substance is nano titanium dioxide (nano-TiO_2). Nanosized particles are preferred to bulk TiO_2 because they are significantly more reactive than larger particles due to their larger surface area. TiO_2 is chemically stable and has a high ability to break molecular bonds leading to degradation. Furthermore it is abundant and thus inexpensive. TiO_2 has been used for decades in commercial products; for example as pigment in white paint or as UV-absorber in sunscreens. Nanosized TiO_2 is produced by at least three companies in Europe on a commercial scale.[4]

2008.[5] This review highlights that different contaminants can be successfully degraded by nano-TiO_2 . It also includes information on the mechanism of degradation and the special properties of nano-TiO_2 compared to micro-TiO_2. The authors conclude: "Thus, TiO_2 should be treated as an emerging technology attractive in terms of photoreaction efficiency, ease of usage, and the potential for economically efficient contaminant degradation."[5] To avoid free nanoparticles in water, nano-TiO_2 particles are usually immobilised on a substrate[4] or integrated into thin-films and other materials.

For the activation of TiO_2, UV irradiation from sunlight or artificial light is needed. UVB has shown to be even more efficient than UVA. To allow activation also by visible light, TiO_2 can further be modified with a second semiconductor, dyes, nitrogen, carbon or sulphur. For example, nitrogen-doped TiO_2 demonstrated superior photocatalytic activities compared to commonly-used unmodified nano-TiO_2 particles in both chemical compound degradation and bactericidal reactions.[6].

Impacts

Globally, 1 billion people lack access to safe water supplies and 2.6 billion are without access to basic sanitation[7]. This is especially true for the least developed regions of Asia, Central & South America, and Africa, innovative methods for water treatment are needed urgently. In the most developed markets such as the USA, Canada, Japan, and most of Western Europe, the success of a new water treatment method is mainly based on its ability to improve the quality of drinking water and/or to reduce water contamination[8].

The beneficial effects of clean water are obvious. Most importantly, the improvement of water supply, sanitation, hygiene, and management of water resources could prevent almost one-tenth of all diseases worldwide.[8] Nanotechnology is one of the most promising emerging technologies for efficient, economical and environmentally friendly water and waste water treatment - offering great potential for manufacturers in Europe.

Economic/Industry

Global demand for water treatment products reached \$44.6 billion in 2008 and it is predicted, by Freedonia Group Inc., to increase annually by 5.7% reaching \$59 billion by 2013. The fastest annual growth was predicted to be in large developing countries like China and India due to rapid industrialisation and increased efforts to expand access to safe water supplies and adequate sanitation facilities especially in rural areas.[7]

The worldwide turnover of nanotechnological applications in water and wastewater treatment reached \$1.6 billion in 2007 and was predicted to increase to \$6.6 billion in 2015. In 2015 the leading countries in water treatment with nanotechnological methods are proposed to be the USA, Germany, Japan, and China[9]. Disinfection is one of the fastest growing market segments with broad applications and benefits; photocatalysis with nanocatalysts is a promising method for disinfection. In addition, photocatalysts combined with filtration membranes can reduce membrane fouling and thus enhance water cleaning efficiency significantly[10].

Figure 1: *Immobilised nano-titania particle used within the SODISWATER project pilot scale solar-photocatalytic disinfection apparatus, which was developed during the EU funded project.*

ENVIRONMENT: Photocatalysis for Water Treatment

Photocatalytic water treatment applications have almost become a mature market. Small-scale photocatalytic systems with artificial UV-light have already been on the market for several years (http://www.ube.es/index.html), whereas solar photocatalytic water treatment plants are at a demonstration phase (http://www.raywox.com) and pilot projects for drinking water purification in developing countries have only just started (http://www.rcsi.ie/sodis/).

In the RayWOx solar photocatalytic water purification system (see ***Figure 2***), contaminated water with added photocatalysts flows through the glass tubes of the solar receiver and is cleaned with the help of solar radiation. This system, distributed by KACO new energy, currently uses nanoscale iron salt as a photocatalyst, but has also been successfully tested with a suspension of nano-TiO_2.

An estimation of the Technology Readiness Levels (TRL) is outlined for three selected applications in ***Figure 3***.

Societal/Impact on European Citizen

The widespread application of nano-TiO_2 has beneficial impacts on the health of the general public and thus on the quality of life. Since nano-TiO_2 particles are inexpensive and may be integrated into different materials, photocatalytic systems, and

Figure 2: *RayWOx solar receiver by Hirschmann for solar photocatalytic water purification.*

surfaces they are not limited to large-scale applications in water treatment facilities. They may also be applied in homes, hospitals, or offices for disinfection or the degradation of water pollutants.

The use of nano-TiO_2 for water treatment and disinfection is expected to have a positive effect on the environment, as it can replace more toxic substances such as organic biocides. It can also improve the quality of the water released from water treatment plants by assisting traditional treatment methods to target more substances at a higher efficiency and remove even trace contaminants such as estrogens and antibiotics.

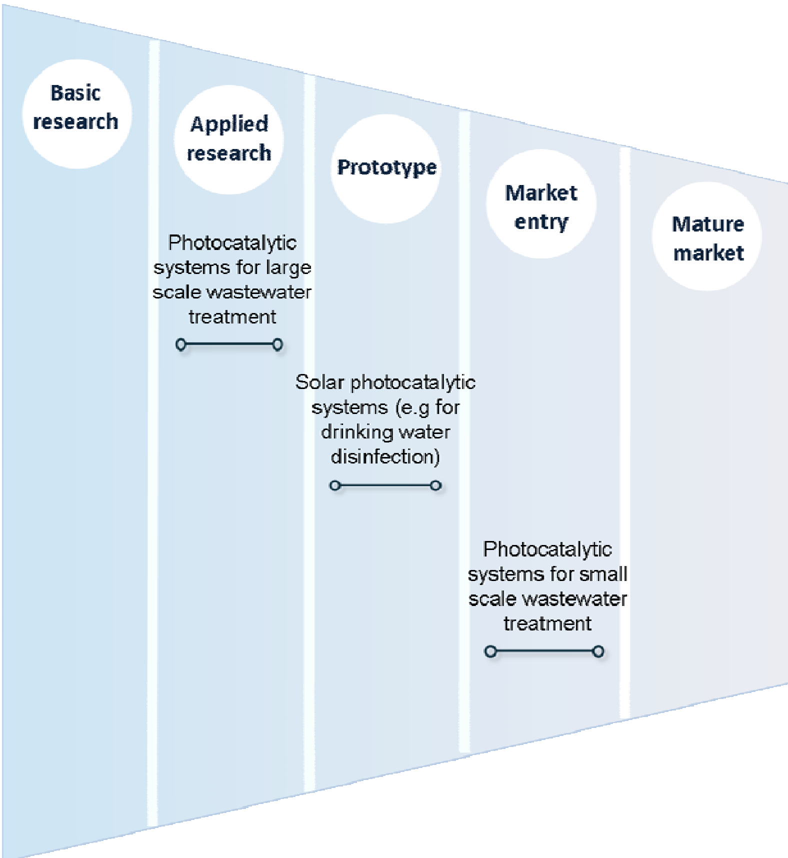

Figure 3: *Technology Readiness Levels for photocatalytic applications for water treatment.*

ENVIRONMENT: Photocatalysis for Water Treatment

Challenges

As mentioned previously, pure nano-TiO_2 is only activated by UV-light. For indoor applications it is therefore crucial to develop a catalyst that can absorb visible wavelengths. Furthermore the most efficient system set-up and substrate materials have to be determined for different applications in private and public facilities to assure maximal longevity, efficiency, and functionality of the photocatalyst. One of the major challenges is that nano-TiO_2 can destroy all organic materials and thus also any organic matrix in which the nanoparticles are embedded; nano-TiO_2 can thus only be applied in an inorganic environment.

Health & Safety

TiO_2 is inert and has been used in bulk form for many years in various materials in everyday use without negative impacts. Nanoscale TiO_2 is also expected to have little negative impact on human health and the environment, since it is usually immobilized in/on a substrate material (e.g. metals, tiles, or glass). Once integrated in a material, nano-TiO_2 is not likely to be released in an amount that would cause a risk to humans or the environment. However, nano-TiO_2 could accumulate if its use is widespread and could potentially have health impacts for workers exposed to nano-TiO_2 dust. Comparable to other nanomaterials, the environmental and human health implications of nano-TiO_2 are still uncertain and remain under intense investigation.

Regulations & Standards

There are currently no regulations related to the use of nano-TiO_2 for water treatment, but standards on test methods for photocatalytic water purification are under development (www.iso.org). Stricter water treatments standards would require new treatment methods and could thus further the application of photocatalytic systems with nanomaterials.

Summary

- Photocatalytic application of nano-TiO_2 promises to be an inexpensive, viable alternative or complimentary method for water and wastewater treatment.
- Stricter regulations and laws are the main driver for the widespread application of new technologies such as photocatalysis with nano-TiO_2 in the environmental sector.
- Disinfection of drinking water by solar photocatalysis especially in developing countries is a very promising application with pilot projects on the way.
- First small-scale photocatalytic systems with artificial UV-light for wastewater purification are commercially available.
- Studies on the (eco-) toxicity of nano-TiO_2 are not yet conclusive. However, there is only little concern as mostly immobilized nano-TiO_2 is used.
- There are still major technical challenges such as the optimum system setup and therefore predictions for the long-term success of photocatalytic systems cannot yet be made.

Contact information

Technology aspects
Empa-Materials Sciences & Technology: Nicole Müller, nicole.mueller@empa.ch *or* Bernd Nowack, nowack@empa.ch

Economic aspects
Spinverse Oy, Johanna Saari,
johanna.saari@spinverse.com

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