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Ecofriendly nanotechnologies and nanomaterials for environmental applications: Key issue and consensus recommendations for sustainable and ecosafe nanoremediation

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ABSTRACT

The use of engineered nanomaterials (ENMs) for environmental remediation, known as nanoremediation, represents a challenging and innovative solution, ensuring a quick and efficient removal of pollutants from contaminated sites. Although the growing interest in nanotechnological solutions for pollution remediation, with significant economic investment worldwide, environmental and human risk assessment associated with the use of ENMs is still a matter of debate and nanoremediation is seen yet as an emerging technology. Innovative nanotechnologies applied to water and soil remediation suffer for a proper environmental impact scenario which is limiting the development of specific regulatory measures and the exploitation at European level. The present paper summarizes the findings from the workshop: "Ecofriendly Nanotechnology: state of the art, future perspectives and ecotoxicological evaluation of nanoremediation applied to contaminated sediments and soils" convened during the Biannual ECOtoxicology Meeting 2016 (BECOME) held in Livorno (Italy). Several topics have been discussed and, starting from current state of the art of nanoremediation, which represents a breakthrough in pollution control, the following recommendations have been proposed: (i) ecosafety has to be a priority feature of ENMs intended for nanoremediation; ii) predictive safety assessment of ENMs for environmental remediation is mandatory; (iii) greener, sustainable and innovative nano-structured materials should be further supported; (iii) those ENMs that meet the highest standards of environmental safety will support industrial competitiveness, innovation and sustainability. The workshop aims to favour environmental safety and industrial competitiveness by providing tools and *modus operandi* for the valorization of public and private investments.

1. Introduction

The application of nanotechnology includes the use of engineered nanomaterials (ENMs) to clean-up polluted media as soils, water, air, groundwater and wastewaters from which the current definition of *nanoremediation* (Karn et al., 2009; Lofrano et al., 2017a). Contamination by hazardous substances in landfills, oil fields, manufacturing and industrial sites, military installation including private properties represent a global concerns need to be remediated since it poses serious risk for health and well-being of humans and the environment (USEPA,

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2004; PEN, 2015).

Compared to conventional *in situ* remediation techniques as thermal treatment, pump-and-treat, chemical oxidation including bioremediation which are almost known to be expensive, partially effective and time-consuming, nanoremediation has emerged as a new clean up method less costly, more effective as well as environmentally, socially, and economically sustainable (Otto et al., 2008; USEPA, 2013). In fact, nanotechnologies allow to treat contaminated media *in situ* and minimize the addition of further chemicals in the clean up process (Holland, 2011). Nanoremediation relies on the peculiar properties of nanoscale particles or nanomaterials *i.e.* high reactivity and high surface area, which make them able to remove a wide spectra of hazardous environmental pollutants, including organoalogenated compounds (OA), hydrocarbons and heavy metals (Karn et al., 2009; Müller and Nowack, 2010).

According to Project of Environmental Nanotechnology web site and USEPA, in the last ten years, almost 70 field scales worldwide have been successfully treated by using nanoremediation techniques, which in comparison with conventional methods have significantly reduced time frame (days *vs* months) and operational costs (up to 80%) (USEPA, 2009; PEN, 2015).

Despite such promising expectations, nanoremediation has been slowly applied in Europe (JRC, 2007) probably as a consequence of various factors as for instance the emerging societal worries on nanotechnologies and the current lack of regulatory and proper legislative supports (Nature Nanotechnology, 2007; Grieger et al., 2012).

The most applied nanoscale materials for nanoremediation are nano-scale zeolites, metal oxides, carbon nanotubes and noble metals have been demonstrated to cause several injuries in both terrestrial and aquatic organisms, thus certainly increasing governmental as well as public concerns related to their *in situ* application (Karn et al., 2009; see Table 1).

In Europe, it has been estimated that there are more than 2.5 million potentially polluted sites which need to be remediated and that 350,000 sites may cause a potential risk to humans or the environment (EEA, 2014). Here, the current debate relies on the balance between known benefits and potential risks associated to the use of nano-scale materials in terms of mobility, persistency and ecotoxicity, other than on the current technical limitations in detection and monitor nanoparticles in the environment as well as in proper risk assessment procedures (Nowack et al., 2015).

The present paper summarizes the findings from the workshop: "Ecofriendly Nanotechnology: state of the art, future perspectives and ecotoxicological evaluation of nanoremediation applied to contaminated sediments and soils" convened during the Biannual ECOtoxicology Meeting 2016 (BECOME) held in Livorno (Italy). Several topics have been discussed and, starting from current state of the art of nanoremediation, which represents a breakthrough in pollution control, the following recommendations have been proposed: (i) ecosafety has to be a priority feature of ENMs intended for nanoremediation; ii) predictive safety assessment of ENMs for environmental remediation is mandatory; (iii) greener, sustainable and innovative nano-structured materials should be further supported; (iii) those ENMs that meet the highest standards of environmental safety will support industrial competitiveness, innovation and sustainability. The workshop aims to favour environmental safety and industrial competitiveness by providing tools and *modus operandi* for the valorization of public and private investments. An overview of three European nanoremediation projects (*i.e.* two still ongoing) was presented with the aim to provide insights into the state of the art of collaborative research across Europe.

2. State of the art of nanoremediation

2.1. Sediment/soil

The quality of sediment and soil is an essential asset, being their remediation in case of pollution events, of extreme urgency. Oil spills, industrial and military activities, relevant accidents and incorrect or illegal waste management are the main responsible of sediment and soil contamination (Hurel et al., 2017). Their *ex situ* cleaning by mechanical removal of contaminated material or active *in situ* methods are often costly (Lofrano et al., 2017b; Libralato et al., 2018). Passive *in situ* approaches utilising engineered materials (EMs) (from the micro- to the nano-scale), which are deliberately introduced into the sediment/soil or delivered to surface water (*e.g.* oil spill), have shown to be potentially effective as catalytic agents, transforming contaminants into less harmful or harmless substances. However, *safe-by-design* is frequently unattended and environmental risk assessment about nanoremediation is further away to be completed, even though some countries are already at the field scale (PEN, 2015).

Several papers, since the beginning of the nano-era, focused on the dichotomy of the effects of micro- (MP) and nano-sized particles (NP). Are NPs better than MPs? Of course, as usual, it depends. Costs and benefits are not always easy to define especially for emerging materials

Table 1
List of the most commonly successfully used ENMs for groundwater, water and wastewater remediation for which ecotoxicity[a] has been reported (List of ENMs and their applications adapted from Patil et al. (2016)).

ENMs	Contaminants in environmental media			Ecotoxicity	References
	Groundwater	Water	Wastewater		
nZVI	Chlorinated compounds (PCE, TCE, DCE) Heavy metals (Pd, Cr, Cu, As, Cr, Zn)	As Phenol	Organic pollutants (PCP, 2,4 DCP) Heavy metals (U, Cr, Ni, Cu, Pb)	Marine organisms (bacteria, algae, invertebrates)	Kadar et al., 2012
TiO_2		Organic pollutants (TCP, 2,4-DCP, benzene) Nitrates, NOM, biological contaminants, Cr		Marine and freshwater organisms (bacteria, algae, invertebrates, marine mammals)	Baun et al., 2008 Minetto et al., 2016 Ma et al., 2012
ZnO		Explosive compounds Phenanthrene			
Ag/Fe **Ni/Fe** **Cu/Fe**	Hexachlorobenzene				
Carbon nanotubes		NOM, toxins and pathogens	Organic pollutants (pesticides, pharmaceuticals)	Marine and freshwater organisms (bacteria, invertebrates, fish)	Baun et al., 2008 Minetto et al., 2016

PCE (Tetrachloroethylene); TCE (Trichloroethylene); DCE (1,2-dichloroethane); TCP (tetrachlorophenol); 2,4 DCP (2,4-diclorophenol); NOM (natural organic matter)
[a] Ecotoxicity data are referred to bare particles and cannot be generalized to the diversity of specific particles used in remediation.