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 or nanoparticles (ENM/Ps) for environmental remediation, known as *nanoremediation*, represents a challenging and innovative solution, ensuring a potentially quick and efficient removal of pollutants. Although there is a growing interest for nanotechnological solutions for pollution remediation, with significant economic investment, environmental and human risk assessment associated with the use of ENM/Ps are still a matter of debate. Currently, limited *in situ* applications of nanoremediation interventions are available. The development and production of innovative nanotechnologies applied to water and soil/sediment remediation suffer for a lack of data regarding environmental impact and specific legislation, which make difficult to implement nanotechnology at European level. This paper summarizes the findings from an expert 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); discussion between institutions, research community, industry and stakeholders took place with the aim of identifying new ideas for contaminated land and sediment recovery as the potential implementation of nanoremediation. The workshop included four topics: i) risk assessment of ENM/Ps for environmental remediation; ii) current *in situ* and *ex situ* applications; iii) innovative and sustainable nano-materials; iv) business development. An overview of three projects (i.e. two still ongoing) was presented during the workshop with the aim to provide insights into the state of the art of collaborative research about nanoremediation across Europe.

1.Introduction

Environmental pollution can be significantly reduced by means of techniques able to clean up or remove pollutants from an environmental matrix from which the current definition of environmental remediation. Different remediation techniques aim to reduce any risk for the environment and/or human health associated with the presence of pollutants in environmental matrices. However, there are several limitations, which stimulated the development of new solutions able to better, faster, and cheaper perform pollution remediation.

Nanotechnology is an innovative scientific and economic field leading to develop further remediation approaches (Lofrano et al., 2017a). Engineered nanomaterials or nanoparticles (ENM/Ps) have several physico-chemical properties that make them particularly attractive, *inter alia*, for water and soil remediation. The use of ENM/Ps for environmental remediation, known as *nanoremediation*, represents a challenging and innovative solution, potentially supporting pollutants removal reducing time and costs of cleanup operations (Karn et al., 2009; Corsi et al., 2014; Lofrano et al., 2016). Currently, critical factors as financial and lack of proper legislative supports, limit the development of nanoremediation at European level. 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). Such emerging needs and new research achievements in nanoremediation have been discussed during the 7th BECOME (Biannual ECOtoxicology Meeting) workshop held in November 2016 in Livorno (Italy). Specific attention was focused on wastewater treatment (i.e. including industrial effluents), *in situ* remediation of soil and sludge to be recovered and reused, and ecofriendly ENM/Ps or nanostructured products from renewable sources. The need to provide further knowledge in terms of ENM/Ps stability in *in situ* applications, of mobility assessment and ultimate fate models, have been also underlined.

Based on ecotoxicological data, the best workflow for ENM/Ps design have been discussed to develop new ecosafe ENM/Ps for environmental remediation. The role of Academia and other research institutions in technology transfer has been addressed providing tools and *modus operandi* for the valorization of public investments with clear outcomes on productivity. The workshop included four main topics: i) ecotoxicological risk assessment of ENM/Ps used for environmental remediation; ii) current *in situ* and *ex situ* applications of ENM/Ps; iii) innovative and sustainable nano-materials for remediation; iv) business development.

An overview of three projects (i.e. two still ongoing) was presented as case studies to provide insights into the state of the art of collaborative research across Europe on nanoremediation.

Future perspectives regarding the development of ENM/Ps for environmental remediation were discussed and summarized in this position paper in order to suggest the potential direction to follow about nanoremediation, in the near future, at the international level.

2. Risk assessment of ENM/Ps for environmental remediation

The exponential production of ENM/Ps, due to their inclusion in many applications, induced the European Parliament in 2009, to call on the Commission to review waste legislation, emission limit values and environmental quality standards in air and water. More recently, the Commission evaluated the need to review Registration and Authorisation of Chemicals (REACH) directive for nanomaterials (COM, 2012) and to suggest recommendations on how REACH can adequately be adapted to ENMs (Schwirn et al., 2014). In order to ensure an efficient assessment of the environmental effects due to the release of ENMs, the OECD promoted an international cooperation program and developed a series of recommendations, identifying alternative testing strategies to be used in risk analysis context (ENV/JM/MONO, 2016).

To date, effective concentration of ENM/Ps released in the environment remains uncertain and is mainly based on information regarding the life cycle of ENM-based products (Gottschalk et al., 2009). A realistic scenario predicted concentrations in water ranging from 0.03 μg/L for nanosilver to 0.5 ng/L for carbon nanotubes (Muller and Nowack, 2008).

Ecotoxicology can be also used to verify the eco-sustainability of ENM/Ps in the environment and to support decision of policy-makers to define risk levels. The risk level depends upon the mobility of ENM/Ps in the matrix, with lower risk associated to solid materials and higher risks in case of dry, dispersible ENM/Ps (Pal et al., 2007).

Among the most important topics discussed during the workshop was the lack of ecotoxicological standardized protocols to test ENM/Ps in terms of differences in the species tested, in techniques for particle preparation, in means of dispersions, in dose/concentrations tested and in the duration of exposure. All these variables strongly influenced the results limiting the comparison of the observed effects (Zhou et al., 2016; Petersen 2015, Corsi et al., 2014; Kühnel and Nickel, 2014). As reported by Savolainen and co-authors (2013) it is extremely important to develop a common, strategic vision of future researches in ENM/Ps at European and global level. In particular, the need to found common, appropriate and valid ecotoxicology protocols, in order to compare the results and to support environmental policies, becomes urgent. Regulators are expected to take decisions on level of ENM/Ps to be safely released in the environment, as strongly required by stakeholders and industries. Greener growth requires stringent, but also flexible environmental policies, in order to minimize the barriers of economic growth and competition (OECD, 2014). Only strengthening the knowledge about the environmental risk of ENM/Ps, awareness can be increased like as the adoption of safer products and techniques (Botta & Kozluk, 2014). Thus, validation of ecotoxicological procedures for testing ENM/Ps should be the next European target that will promote their eco-friendly application in remediation strategies.

Marine environment has been historically recognized an important source of goods in terms of fishery and services (e.g. maritime activities), but also of vital importance for human health and well-being. An increasing number of ENM-based products are being developed specifically for marine applications such as *in situ* nanoremediation (i.e. absorbent nanowires for oil spills, desalination using reverse osmosis, etc.), which have been significantly increased the benefit of nanotechnologies in reducing marine environment threats. Nevertheless, current uncertainties related to potential adverse effects of ENM/Ps on marine organisms, and the overall ecosystem, urgently require their ecosafety assessment (Corsi et al., 2014; Lofrano et al., 2017b).

Marine nano-ecotoxicology can provide tools able to discriminate nanotechnologies that do pose any risk on marine wildlife promoting, at the same time, those practices which will increase benefits to the marine ecosystem as a whole.

The risk associated with the release and accumulation of contaminants into the marine environment has been strongly faced with the development of an environmental risk assessment (ERA) framework. Past, but also recent, accidental marine pollution events have been handled by the application of ERA approaches and solved with a certain level of accuracy by linking the ecological effects to the physico-chemical nature of the stressor in terms of concentration-time-response relationship. A similar approach can be applied to the ENM/Ps (Klaine et al., 2012) even though it needs to be tuned to “nano-specific” features as exposure and effect scenarios.

Exposure scenarios, as well as patterns of uptake and toxicity, are substantially still unknown for natural marine environment (Koelmans et al., 2015) and represent a major challenge for marine nano-ecotoxicologists. Bridging current knowledge acquired from lab-controlled experimental conditions to environmental realistic scenarios resembling natural ecosystems is therefore their featured mission (Gottschalk et al., 2013). This is further complicated by the general lack of appropriate methodologies able to detect and quantify ENM/Ps in environmental matrices though some advancements are available for specific ENPs (Proulx et al., 2014; Nowack et al., 2016).

The many peculiar features of ENM/Ps as chemical core, size, shape and surface energy have been shown to substantially affect their final properties once released in complex natural environmental media as for instance sea waters. In this context, marine waters are even more diverse since physico-chemical parameters, and inorganic and organic composition substantially differ from surface, column and deep waters as well as in lagoon, estuaries, coastal areas and deep oceans (Nowack et al., 2012). The ENM/Ps fate in terms of dispersion might be triggered by parameters as pH, osmolarity and natural organic matter (NOM) mainly based on colloids and proteins, which are able to interact with the specific properties of the ENM/P itself thus affecting uptake and toxicity in exposed organisms (Corsi et al., 2014). The final outcome of such interactions is also affected by the biological status of the organism itself as for instance its ability to face and react to such exposure. Further effects could also be seen at higher level from organism, to population and community and the entire ecosystem (Matranga and Corsi, 2012).

Therefore, the main issue for marine nano-ecotoxicologists is whether current findings are or not representative of real natural scenarios where several interactions/transformations between ENM/Ps and natural marine waters and populating organisms could occur. In addition, ENM/Ps final fate, although not fully predicted by models, has been hypothesised to be type-specific (e.g. metal-oxide, carbon based) so that the ability to reach specific target ecosystems urgently need be further investigated (Nowack 2009).

Treatment technologies, based on new ecofriendly ENM/Ps, should be developed considering the safe-by-design approach in order to significantly decrease any environmental risk associated to their application within nanoremediation.

To implement the effective application of nanotechnology in this field, a thorough ecosafety assessment of ENM/Ps should be performed addressing the following key aspects: (1) understanding the behavior of ENM/Ps in natural complex media, with particular focus on the physico/chemical modifications by environmental factors, which might affect their reactivity and fate; (2) identify possible toxicological targets of ENM/Ps and provide a mechanism-based evaluation of ecotoxicity in different species; (3) assess the risk of the (sub)-products generated in the environmental matrix during and after the remediation treatment, for example the “complex” ENM/Ps + contaminant as well as the generation of potential harmful by-products, as active metabolites produced during oxidation processes.

Investigations of the most common used ENM/Ps for remediation, nanoscale zero valent iron (nZVI) showed that it might cause hazardous effects to organisms in the environment, especially microorganisms (Kumar et al., 2014). A review of the recent published literature showed that although nZVI is a reactive substance with toxic properties, it could also stimulate microbiota through its influence on environmental parameters (Semerad and Cajthaml, 2016). Results show clearly that there is a need for further investigations to achieve a deeper understanding on how nZVI, as well as other ENM/Ps applied for remediation, affect organisms in areas surrounding their applications. However, it should be considered that the purpose of *in-situ* nanoremediation is to reduce the toxic pollutants in a contaminated area and that the application of ENM/Ps may reduce the overall toxicity of the contaminated site even if it has properties which could cause toxic effects on biota (Semerad and Cajthaml, 2016).

When ENM/Ps enter the environment, they are subject to a variety of processes (Stone et al., 2010; Nowack et al., 2012; Tangaa et al., 2016). NPs may homoaggregate to each other or heteroaggregate to other particles in the environment and subsequently in the sediment. They may also dissolve, transform chemically and react with environmental ligands. In order to optimize a remediation process we must be able to predict what happens to the ENM/Ps introduced to a polluted site during and after the elimination of the target pollutants.

The tendency of ENM/Ps to rapidly agglomerate and aggregate when released to the environment may hinder effective remediation (Karn et al., 2009). Different approaches have been used for describing the aggregation processes, which typical fall into two categories, one based on particle number (e.g. Praetorius et al., 2014) and another based on mass (Dale et al., 2015; Markus et al., 2015). The particle number based approach describes the aggregation kinetics using an attachment efficiency, a collision frequency and the particles concentrations whereas in the mass based approach the attachment efficiency and collision frequency is replaced with a mass based rate of aggregation (Dale et al., 2015). The development of these models has primarily been driven by the need to understand the fate of ENMs in the environment and their possible environmental risk.

Despite lack of methods for *in-situ* assessment of ENM/P speciation, ageing and agglomeration state (Peijnenburg et al., 2016), predictive fate and transport models for ENM/Ps are useful tools in the design and selection of a nanoremediation strategy for a specific contaminated area.

A concept which integrates modeling of the fate of both the ENM/P and the pollutant in a contaminated layer of sediment have been recently developed. The concept consists of a hydraulic model which is coupled to a fate modeling module enabling a combined description of transport and fate as function of time and position. State variables-concentration of pollutants and ENM/Ps are mutually coupled and the transformation processes expressed as differentials with respect to time. In the first version of the concept, processes for the pollutants include adsorption to Solid Particular Matter (SPM), adsorption to ENM/P being dependent of the state of the ENM/P, i.e. the degree of homo- and heteroaggregation, and of sedimentation. Degradation and evaporation of the pollutants were not included in this initial version, but these processes can readily be added. The mathematical mass based equations presented by Markus et al. (2015) can be used for the ENM/P homo- and heteroaggregation. The modeling results are given as the concentrations of pollutants, as a function of time after a simulated treatment with ENM/P, in a contaminated area of sediment within a selected period. Another output of the conceptual model is the distribution of the degree of ENM/P aggregation at a certain time (with respect to homo- and heteroaggregation).

Although deep insight on the environmental effect and fate of ENM/Ps is still in its infancy, the model is able to compare and screen the impact of different ENM/Ps when injected or dosed in a contaminated sediment layer. It is possible to apply the proposed concept to assess ENM/Ps properties, which are crucial for their fate and transport. It can be used to explore the consequences of different input values such as pollutants, ENM/Ps, salinity and sediment properties. The concept provides the basic for ecosafe design of the ENM/P and choice of strategy for remediation.

3. Current in situ and ex situ applications

3.1 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 (i.e. Deep Water Horizon, USA), industrial and military activities, relevant accidents and incorrect or illegal waste management are the main responsible of sediment and soil contamination (Libralato et al., 2008; 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). 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 (Libralato et al., 2016).

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 where the amount of pros and cons are almost the same, at least at the beginning when unexplored aspects are still present, and contradictory results exist considering both human health and environmental effects (Lofrano et al., 2017b). Certainly, some concerns occur regarding the use of ENMs in contaminated soil/sediment: once dispersed in a contaminated site would ENM/Ps be mobile to a point that they could be taken up by plants or animals at the site or further away, and adversely affect them? How to consider the environmental benefits and risks of ENM/Ps for *in situ* applications? Does their use and behavior pose questions regarding environmental fate and impact? Do they provide easier and better results than the relative MPs? Moreover, a remediation technology must attend to cost-benefit approaches considering practical immediate issues and long-term expectancies. For example, nano-iron has an average cost of about 100 €/kg compared to 10 €/kg of iron MPs (SiCon, 2016), mainly due to the relative economies of scale. The very high reactivity of iron NPs makes its *in situ* application sometimes difficult and the remediation activity could present a limited long-lasting ability (Libralato et al., 2016). Thus, a case-by-case analysis must be undertaken to assess the potential real applicability and need for nanoremediation.

3.2 Wastewater

The pursuit of sustainable technologies for environmental remediation has become the priority over the past few years, due to the impact of the unprecedented increase in human population and its adverse effects on natural ecosystems. In particular, the lack of water resources is ever growing due to land degradation, pollution, urbanization, and global economic development. In this situation, the concept of wastewater treatment should be explored with a different goal, in which wastewater is transformed toward sustainability, assuring a safe citizens' quality of life and boosting the economy production chain, through the reuse of effluents in irrigation, water supply and water storage in rural and urban environments. In this context, nanotechnology would represent a major breakthrough in the potential sustainable water management.

Due to the tunable properties and outstanding features of ENM/Ps, nanotechnology emerged as a robust and efficient technology that overcomes the limits of existing processes in wastewater treatment (Qu et al., 2013). The main advances of nanotechnology rely in the ability to degrade almost completely several types of recalcitrant compounds (Shao et al., 2013; Lofrano et al., 2016), the antimicrobial properties for disinfection, the possibility of regeneration and reuse and the low energy consumption (Pouretedal and Sadegh, 2014).

A wide range of ENM/Ps have been tested for the removal of inorganic and/or organic contaminants (see the reviews by Hua et al., 2012; Shantosh et al., 2016; Anjum et al., 2016 and citations therein). The three main applications are: i) Nano-adsorbents: made of either carbon-based or metal-based NMs. Such application has high efficiency on adsorption of organic pollutants and also for metal removal, due to extremely high specific surface area, more accessible sorption sites and lower intraparticle diffusion (Lofrano et al., 2016). ii) Membrane systems based on nanofibers or nanocomposites, which offer a great opportunity to improve the membrane permeability, fouling resistance, mechanical and thermal stability, and to provide new functions for contaminant degradation (Liu et al., 2015). iii) Nano catalysts: with particular focus on photocatalyst such as TiO_2 (Carotenuto et al., 2014; Lofrano et al., 2016). This application for the wastewater treatment allows fast and efficient removal of metals, and several types of organic pollutants such as for instance hydrocarbons, perfluorooctanoic acid, pharmaceuticals and personal care products as well as of antibiotic resistance bacteria and genes (Shao et al., 2013; Bethi et al., 2016).

Based on the achievements obtained so far, nanotechnology holds great potential as a tool for sustainable wastewater treatment and remediation. Nevertheless most of the applications are still at laboratory scale, and some drawbacks for full scale application must be overcome, such as technical challenges related to the production of huge quantity of ENM/Ps, cost-effectiveness and environmental concerns related to their potential release (Lofrano et al., 2017a).

Future studies need to be done to assess the applicability and efficacy of different nanotechnologies under more realistic conditions. For instance, most of the studies were based on relatively short time exposure periods, while the long-term performance of these nanotechnologies is largely unknown. Moreover avoiding of unintended consequences on natural environments is the main issue for the effective adoption of this technology. In fact, the application of nanotechnology will inevitably lead to the release of ENM/Ps in water and in sludge, from where they will likely enter into natural ecosystems (Nogueira et al., 2015a). Therefore the removal of ENMs from these media might represents a crucial aspect for safe application of nanotechnology. Currently several methods are available, mostly involving the exploitation of magnetic properties of some inorganic material, cross-flow filtration, and centrifugation. Recently great effort has been devolved to develop treatment systems with immobilized ENPs (Delnavaz et al., 2015). Another pivotal challenge is to develop ENM/Ps which do not pose toxicity for natural ecosystems, but this aspect is more easy to achieve by choosing eco-compatible chemical compositions of the material than for the shape and the size of the ENM/Ps. Up to now few studies investigated the harmful effects of ENM/Ps occurring in wastewater and sludge, highlighting a potential risk for wildlife, related to the application of ENM/Ps in wastewater processes (Carotenuto et al., 2014; Nogueira et al., 2015b). Nevertheless a proper ecotoxicological evaluation of ENM/Ps, intended for wastewater treatment, is still lacking. Overall, the generation of ENM/Ps that meet the highest standards of environmental safety will therefore support industrial competitiveness, innovation and sustainability.

3.3 Groundwater

In situ techniques are often employed for groundwater remediation in order to avoid excavating soil and dumping it off site, or using Pump&Treat approaches, which may often be ineffective and/or excessively costly. Groundwater (or aquifer) nanoremediation, which exploits ENPs for the treatment of contaminated groundwater, broadens the range and increases the effectiveness of *in situ* remediation options. Several ENPs have been studied in the last years for groundwater remediation purposes. Even if the use of other materials has been explored, most of the particles which are currently being tested and show a good performance for groundwater remediation are iron-based NPs, both in the form of iron particles alone, and as composite materials. Iron particles include, eg., nanoscale and microscale Zerovalent Iron (nZVI and mZVI) (Wang and Zhang, 1997), and nanosized iron oxides, such as goethite for heavy metals sorption, and ferrihydrite for improved microbial-assisted degradation of organic contaminants (Bosch et al., 2010). Examples of iron-based composite nanomaterials include CARBO-IRON®, where NZVI is embedded in a carbon matrix to promote mobility and contaminant targeting (Mackenzie et al., 2012), bimetallic particles, and emulsified zero valent iron (EZVI).

Granular, millimetric zero-valent iron (ZVI) is one of the most successful reagents for groundwater remediation deployed in Permeable Reactive Barriers (PRBs). A PRB is a passive technology for *in situ* treatment of contaminated groundwater plumes (Di Molfetta and Sethi, 2006). Due to its capability of degrading a wide range of organic contaminants, and of reducing and immobilizing metal ions, ZVI has been employed in hundreds of PRBs worldwide. However, installation and construction limitations restrain the application of this technology, making the treatment of deep contaminations impracticable, for instance. Moreover, PRBs target only the dissolved plume and cannot be used for direct treatment of the source of contamination. Wang and Zhang (1997) proposed the use of nanoscale zerovalent iron (nZVI) as an alternative to granular iron. Owing to its small particle size (less than 100 nm), nZVI is characterized by a high specific surface area (10-50 m^2/g) and consequently exhibits a significantly faster contaminant degradation rate (Tosco et al., 2014b). Furthermore, nZVI aqueous suspensions can be directly injected in the subsurface, directly targeting the plume close to the source of contamination and attaining higher depths than with PRBs. nZVI's small size and high reactivity alone, however, are not sufficient to ensure an effective remediation. In recent years, several laboratories worldwide have been seeking solutions to some of nZVI's main limitations, that must be addressed in regard to the effectiveness and feasibility in field-scale applications. They include in particular stability against aggregation, short and long term mobility in aquifer systems, and longevity under subsurface conditions.

The particles' strong tendency to aggregate can be contrasted by the use of organic and inorganic stabilizers (Wang et al., 2013). Biopolymers were found to have a high applicability potential due to their stabilizing effectiveness, wide availability, low cost and environmental compatibility.

In the framework of the FP7 UE project AQUAREHAB (G.A. n. 226565), guar gum (Gastone et al., 2014), xanthan gum (Dalla Vecchia et al., 2009) and mixtures of the two (Xue and Sethi, 2012) proved to be suitable for particle stabilization and delivery (Aquarehab, 2014). The shear thinning rheological behaviour of these biopolymers (Comba et al., 2011) ensures stability against particle aggregation at low shear rates, when they are characterized by high viscosity, and facilitates transport in subsurface porous media during injection, when viscosity is significantly reduced.

NANOREM (Taking Nanotechnological Remediation Processes from the Lab Scale to End User Applications for the Restoration of a Clean Environment, G.A. n. 309517) was a FP7 EU funded project focused on facilitating practical, safe, economical and exploitable groundwater nanoremediation. In 2011, tens of sites were identified in US, and 16 in EU (Mueller et al., 2012). In the NANOREM project significant effort was devoted to the development of modelling tools to support the design and field implementation of *in situ* nanoremediation interventions. The design of a field-scale injection of ENP suspensions requires reliable procedures and approaches to effectively assess the expected ENP mobility at the field scale and for a reliable estimation of several operative parameters, such as particle distribution around the injection well, radius of influence (ROI) for a target concentration, number of required injection wells, etc. This information can be typically obtained using an experimental approach, running a wide set of column transport tests under all different field-relevant conditions, and inferring the expected mobility at the field scale from the laboratory results. However, this approach may be time- and cost-consuming, and does not guarantee a direct up-scalability to the field, if not supported by modeling.

The Groundwater Engineering Group of Politecnico di Torino developed MNMs Micro-and Nanoparticle transport, filtration and clogging Model-Suite (http://areeweb.polito.it/ricerca/groundwater/software/MNMs.php), a comprehensive tool for the interpretation of NP transport experiments at the lab scale.

When upscaling from lab to full field scale, the first step in the design of an intervention is the execution of a pilot injection. In field applications, NP suspensions are typically injected into the subsurface via wells or direct push systems, generating a radial flow (Tosco et al., 2014a). MNMs can be used to simulate the particle transport distance in the subsurface and to estimate the expected ROI. For full scale interventions, more complex scenarios can by simulated with the powerful MNM3D tool (Bianco et al., 2016) (http://areeweb.polito.it/ricerca/groundwater/software/MNM3D.php). This software can be used to simulate important operative parameters, including particle distribution, ROI, number of injection wells.

Understanding particle transport and deposition is of pivotal importance not only in the short term, during injection, but also in the long term, to understand the fate of the particles in the environment. NP injection is usually performed at high flow rate in order to achieve high ROIs. When the injection process is interrupted, the particles are subjected to natural flow, and transport velocities become much smaller. In such conditions, the geochemical properties of groundwater and the aquifer heterogeneities become the main driving force governing the particle deposition and release processes. Some particles, such as nZVI, usually are almost immobile under typical aquifer conditions, but other NMs can be significantly mobile in groundwater systems, eg. CarboIronand iron oxide NPs studied for metal immobilization in the framework of the H2020 REGROUND project (G.A. an. 641768) (Tiraferri et al., 2017).

As a consequence, to guarantee the long-term safety of the remediation approach and meet regulator requirements, it is of pivotal importance to provide reliable, quantitative estimations on the long term mobility of the injected particles that may remain in the subsurface after reaction with the contaminant. The NANOTUNE approach was developed at Politecnico di Torino to tune the mobility and potentially immobilize these NPs. Moreover, MNM3D can be used as a tool to evaluate the *post*-remediation fate of NPs employed in groundwater remediation projects.

4. Innovative and sustainable (nano)materials

While several ENMs reported in the literature show outstanding performances, in terms of decontamination efficiency of water and soil, the potential safety drawbacks related to their use in ecosystems suggest the necessity to design new solutions, capable to take into account these critical aspects (Trujillo-Reyes et al., 2014).

In this context, a valuable alternative strategy to overcome the ecotoxicology and legislative issues related to the use of ENM/Ps for environmental remediation consists into the simple concept of moving from *nano-sized* materials to *nano-structured* devices, transferring the advantages of nanotechnology to macro-dimensioned systems. If NMs, such as NPs and nanofibers, are not used directly in the remediation process, but become building blocks of stable nanostructured systems with enhanced micro- and nano-porosity, it is possible to provide a new class of sorbent units with high surface area, capable to remove organic and inorganic pollutants from contaminated water, air, and soil. To reach this goal, an optimized system should preserve the advantages deriving from ENM/Ps and prevent their release in the ecosystem. Moreover, this approach could be considered even much more valuable if the new ENM/Ps are obtained starting from the easy and scalable processing of renewable sources. For this reason, the choice of biopolymers as starting materials is becoming an important target.

Polysaccharides well fit most of the requirements for the design of ENM/Ps, as they combine a good chemical reactivity for further nano-structuring processes, due to the presence of several hydroxyl functional groups on the polymer backbone, with their high biodegradability and negligible toxicity. Cellulose represents an abundant, renewable, and low-cost polysaccharide natural source, especially when deriving from agricultural and industrial by-products, for the production of materials for water remediation (Krishnaniandand Ayyappan, 2006). Sugarcane bagasse, fruit peel, biomass, and rice husks have been proposed as cellulose-based matrices for the removal of heavy metal ions from contaminated water. Moreover, waste paper would also represent an alternative, even cheaper source of cellulose, suggesting the virtuous approach of "*recycling to remediate*" (Setyono and Valiyaveettil, 2016).

Nevertheless, what makes cellulose so attractive as source for the design of advanced materials is its intrinsic hierarchical structure (Kim et al. 2015). The cellulose fiber composite is made with macrofibers of cellulose, hemicellulose and lignin. The macrofibers are composed of microfibrils, which in turn are formed with nanofibrils of cellulose. The possibility to cleave the original structure of native cellulose and to produce cellulose nanofibers (CNF) opens interesting perspectives for a wide range of applications, including wastewater treatment. Following the simplest protocol for the production of CNF, cellulose can be preliminary oxidized with the 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO)-mediated system (Pierre et al., 2017), selectively converting primary C6-hydroxyl groups of the glucose units to the corresponding carboxylic groups. Following this protocol, defibrillation of TEMPO-oxidized cellulose nanofibers (TOCNF) can be achieved by increasing the pH of the solution. In fact, the deprotonation of carboxylic groups favor the electrostatic repulsion of negatively charged single fibrils, leading to the physical separation of single fibriles.

Hydrogels obtained from TOCNF have been reported as efficient and reusable adsorbents of heavy metal ions (Isobe et al., 2013). However, TOCNF can be also used for further cross-linking, taking advantage of the new carboxylic moieties introduced on the polymer backbone. While this process would lead to macro-dimensioned nano-structured systems, with all the advantages previously discussed, the choice of the ideal cross-linker would allow to introduce additional properties and functional groups, increasing the versatility of the systems. In this context, we recently reported a thermal route for the production of a new class of aerogels, starting from TOCNF and following a simple thermal protocol in the presence of branched-polyethyleneimine (bPEI) (Melone et al., 2015a). The formation of amide bonds between the carboxylic and the amine moieties favored the high reticulation into sponge-like, water stable systems, which show high efficiency in removing heavy metals and phenolic derivatives from wastewater. The possibility to functionalize selectively the amino groups of the cross-linker (Melone et al., 2015b), and to use these devices as templates for further organic (Panzella et al., 2016) and inorganic (Melone et al., 2013) coating, suggests the potentialities of this new ENM, whose properties can be modulated in order to perform selectively for the absorption and degradation of target contaminants.

In the framework of the NANOBOND project (Nanomaterials for Remediation of Environmental Matrices associated to Dewatering), the specific application of hydrogels obtained from TOCNF and tested for their ecosafety will aim to develop new ecofriendly nanotechnologies for sludge and dredged sediment remediation. Funded in the framework POR CReO FESR Tuscany 2014-2020, the NANOBOND project aims to develop an innovative system for treating contaminated sludge and dredged sediments, by coupling the use of nanostructured *eco-friendly* materials with the classical geotexile dewatering tubes. This new solution, will enable to reduce contaminated sludge and sediments, in terms of volumes and costs of transport, but also to convert the resulting solid and liquid wastes to a renewable clean resource to be use, for instance, in riverbanks settlements and any other applications. By developing nanoremediation techniques associated with dewatering, NANOBOND intends to explore new solutions to dredging and sludge management linked to hydrogeological disruption and maintenance of harbour areas, emerging issues which are tremendously increasingly worldwide. This innovative solution aims to became an efficient strategy to significantly reduce sludge and sediment contamination through nanoremediation since also easily scalable for large-scale *in situ* applications with competitive costs. The NANOBOND consortium made by a 70% of industrial partnership specifically of companies involved in sludge and dredged sediment disposal as well as in their risk assessment and 30% of academia and research institutes for synthesis, ecosafety and life cycle assessment of nanostructured materials accomplished the requirements of technology transfer and business development needed for the development of an ecosafe and sustainable nanoremediation and promote economic development in terms of industrial competitiveness and innovation, both still very little developed in European countries.

A further examples is the INTERREG EUROPE project TANIA (TreAting contamination through NanoremedIAtion) with the aim to improve EU regional policies on treating contamination through nanoremediation in European countries. Funded under the 2nd Call for proposal 2016 under the Axis IV “Environment and Resource Efficiency and leaded by Tuscany Region, TANIA aims to improve the implementation of regional development policies and programs in the field of the environmental prevention and protection by pollutants and specifically addresses to innovative and low cost technological solution for the (nano)remediation of contaminated soil and water. Green nanotechnology refers to the use of nanotechnology to enhance the environmental sustainability of processes producing negative externalities. It also refers to the use of nanotechnology products to enhance sustainability. It includes making green nano-products and using nano-products in support of sustainability. Green nanotechnology has two goals: producing nanomaterials and products without harming the environment or human health, and producing nano-products that provide solutions to environmental problems. The concept of nanoremediation fits into this second objective. However, the technology is currently not widely diffused despite an ever-increasing number of sites requiring swift treatment to combat contamination. Being so innovative, there is still resistance to their large-scale application and to policies that support it. There is a lack of information and knowledge on their safety and potential, leading to much misinformation. Therefore, in order to further promote the application of nanoremediation techniques and technologies, regional policy makers must work together and with main stakeholders in order to: (i) support continued research and innovation into the identification and production of eco-compatible and eco-sustainable nanotecnologies for treatment of contaminated soil and water; (ii) define a standardized methodology to evaluate the effectiveness, economic sustainability and the environmental safety and impact of ENM/Ps for contamination treatment, within the context of existing environmental regulations at National and European level.

Environmental safety is particularly relevant to *in-situ* remediation where reactive products must be checked in terms of their reaction with and impact on treated compounds; (iii) support patenting and pilot applications of new ENM/Ps developed on the basis of safety by design concepts; (iv) develop a policy framework to provide incentives for *in-situ* use of ENM/Ps for treatment of contaminated soil and water; (v) raise awareness on the process of nanoremediation, its benefits and means of application. In this context TANIA aims to improve the policy instruments of 5 different EU Regions, sharing also practices and results with the whole INTERREG EUROPE community. TANIA is coordinated by the Development Agency for the Empolese Valdelsa (ASEV Lead Partner – ITALY) and involves all the managing authority of the policy instrument on which it addresses own attention. TANIA's partnership includes Regional Agencies representative of several European countries (Italy, France, Finland, Greece and Hungary).

An important role must be played also by the other stakeholders. Academia, one of this, has to play a major role for supporting and organizing this type of research that overlaps several different fields and that cannot be faced by single research groups or departments. As an example even in the case previously briefly described before in the present paper, it is easy to identify how, to concretely operate in real case, the contribution originates by inorganic and organic chemist, applied chemists, analytical chemists, industrial and processes engineers, biologists, toxicologists, ecologists and expert of regulatory matter. It is clear that such a huge amount of competences is not easy to be assembled: for this reason a pivot role must be played be large organization, like national research institution, such as ISPRA, or aggregation of University, such as the case of NANOBOND project under the flag of the Consortium INSTM (National Universities Consortium for the Science and Technology of Materials, www.instm.it).

5. Business development of the sector

In the field of environmental remediation and the related treatments and disposal of the various solid and liquid matrices, strong collaboration between industrial sector and research is absolutely needed. Specific issues related to waste or site typologies and the resulting innovation from the applied nanotechnologies and their development, will increase the competitiveness of companies involved in the environmental sector with also benefit from applied research as the increase of patents. A role that must be played together by researchers and industries is in the choice of strategies that will allow the scale-up of the material and techniques developed, taking in mind that the amount of materials to be employed is measured in tons or kilotons, as like as the cost of production must be affordable for concretely tackle large scale case. This aspect not necessarily must be considered as mass production because it can also have success with an approach for niche production, but for sure the valley between the laboratory bench production and an industrial product ready for commercialization must be cross, keeping in mind all the classical problems that this pathway usually meet.

A multidisciplinary approach must be applied at the forefront of the most advanced nanotechnological solutions to be tunable according to different situations. Remediation should accomplish several aspects according to national regulation, human and environmental safety and contract management economics.

The global nanotechnology market in environmental applications reached $23.4 billion in 2014. This market is expected to reach about $25.7 billion by 2015 and $41.8 billion by 2020, registering a compound annual growth rate (CAGR) of 10.2% from 2015 to 2020 (https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-applications-market-nan039c.html). The urgent need to develop commercially-deployed remediation technologies at European level have seen the involvement of service providers and site owners or managers which are now finally considering their potential applications as well as implications for their business activities. Only in Tuscany Region (Central Italy), sites under remediation are around 3.700 (approx. 17.000 hectares), and more than 50% are considered potentially contaminated (ARPAT, 2016). The dimension of the phenomenon linked to dredging activities is identified by the following data: in Italy, the average dredging is 6 million cubic meters per year. From 10 to 25% by weight of these materials is contaminated (Bortone, 2007). Sea areas falling within the perimeter of Sites of National Interest to be reclaimed are over 124,000 hectares

(Legambiente, 2014). Only in the harbor area of Livorno (one of the major harbour of Tuscany Region), about 1.8 million cubic meters of sediments have been dredged in the decade 2006-2016.

Currently the remediation sector in Italy is in a stalled state due to the lack of adequate investments and also often farraginous administrative procedures (Legambiente, 2014).

In terms of land, this solution accounts for 50% of land reclamation, while technological processing solutions represent minority percentages (EEA, 2012). In the case of dredged sediment management, the traditional approach involves storing in collapsed crates or CDF (Confined Disposal Facility), capping or conferral in a controlled landfill.

An increase of sustainable environmental remediation solution is therefore mandatory so that the benefit of the remediation action will be greater than the impact of the action itself (SuRF Italy, 2014). This is particularly evident in recovery of former industrial areas, which, apart from limiting soil consumption, can produce benefits beyond the cost of the interventions themselves (APAT, 2006). Today, more than ever, these interventions become significant given the wide presence of dismantled industrial areas, transformed into large "urban voids", following the progressive outsourcing of western economies.

The approach to re-use (both the areas to be reclaimed and the environmental matrices) is the aim of numerous studies that highlight the possibilities of recovery. In the case of dredged sediments, for instance, recovery is possible by using them as materials in the building industry (Hamer et al., 2005; Dang et al., 2013; Aouad et al., 2012), or as infrastructural components (Sheehana and Harringtonb, 2012).

The European Community promotes the more efficient use of resources: in the logic of the circular economy, the circle closes with the transformation of waste into resources (European Commission, 2014). The innovative approach of the circular economy aims to bring greater resource efficiency and material savings, based on the life cycle principle (Kobza et al., 2016).

Identifying nanomaterials as a technological solution for remediation can be a decisive turning point and is perfectly in line with the principles of circular economy. In fact, the project is characterized by a high degree of flexibility with regard to incoming material streams (treatment of sediments of different nature and contamination) and a high level of sustainability (technologies that aim at material recovery, low impact on the configuration plant engineering). It could successfully enter the industrial economic system by proposing lower costs than those currently on the market for sediment treatment, with additional strengths, such as lower transport costs, linked to the elimination of the need to travel long distances for specific treatments and the possibility of reuse of processed material, possibly for port infrastructure (extensions) and other uses (eg watering of streams).

Concluding remarks

As the potential and efficacy of nanotechnology is well established, several drawbacks related to the full-scale application should be overcome. In particular great efforts should be devoted to develop (nano)materials which own ecosafe features such as limited release in environmental matrices and any toxicity for natural ecosystems. Ecotoxicology can be used to develop *ecofriendly* nanotechnology and (nano)-materials and to support decision-makers.

The development and production of innovative nanotechnologies, applied to water and soil/sediment remediation, must fill current gaps on their environmental impact. Moreover, a specific legislation at European level is necessary to regulate their emissions and field application.

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