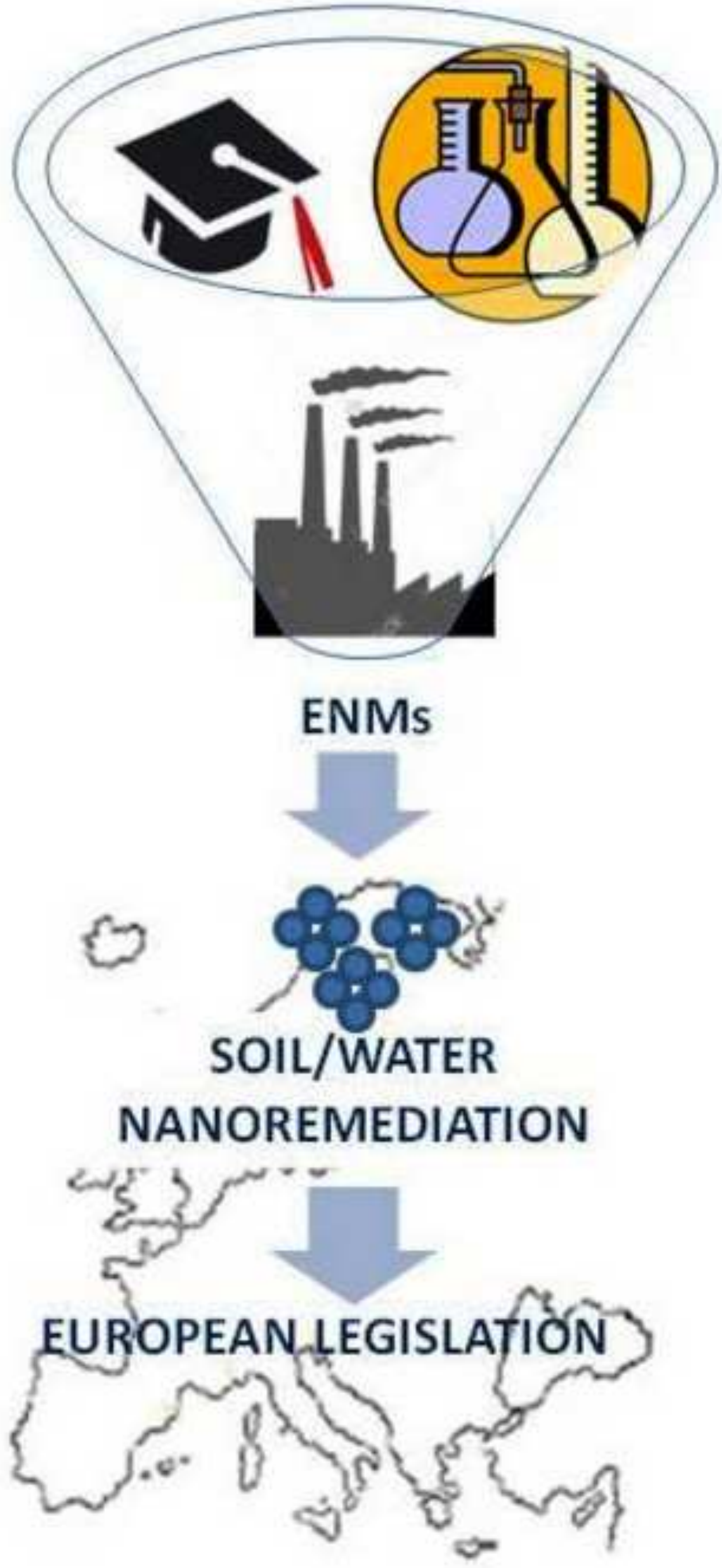
Ecofriendly nanotechnologies and nanomaterials for environmental applications: Key issue and consensus recommendations for sustainable and ecosafe nanoremediation

Graphical Abstract



Highlights

- Nanotechnology represents a breakthrough for environmental remediation
- Ecosafety is a priority feature of ENMs intended for nanoremediation
- Predictive safety assessment of ENMs for environmental remediation is mandatory
- Greener and sustainable (nano) solutions are emerging
- Regulatory framework will support industrial competitiveness of the sector

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, 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 where the number 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 ENMs 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 ENMs 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 (Grieger et al., 2010). Thus, a case-by-case analysis must be undertaken to assess the potential real applicability and need for nanoremediation.

2.2 Water, wastewaters, groundwater

Among emerging application of nanoremediation there is the global problem of marine contamination both in coastal and off-shore sites. Marine sediments are established as a major sink for environmental pollutants; the increasing number of sites to be remediated, together with significant times/costs of current technologies, are clearly promoting nanoremediation as a promising solution (Otto et al., 2008). However, sediment nanoremediation may pose a potential risk for marine biota, due to partial ENM mobilisation in interstitial waters and/or water column (Karn et al. 2009). This may affect not only sediment dwelling/deposit feeding species, but also other species from different trophic levels (bacteria, phyto-zooplankton, benthic invertebrates) (Kadar et al., 2012; Corsi et al., 2014; Minetto et al., 2016). An increasing number of ENM-based products are being developed specifically for marine applications as *in situ* nanoremediation. Some good examples are absorbent nanowires used for controlling and reducing the impact of oil spills (Yuan et al., 2008).

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 ENMs (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 and a hindrance for the use of ENMs in remediation. 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 ENMs in environmental matrices though some advancements are available for specific ENPs (Nowack et al., 2015).

The many peculiar features of ENMs 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 water. 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 ENMs 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 itself thus affecting uptake and toxicity in exposed organisms (Corsi et al., 2014). The 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).

In wastewater treatment nanotechnology emerged as a robust and efficient technology that overcomes the limits of existing processes, due to the tunable properties and outstanding features of ENMs (Qu et al., 2013). The main advances of nanotechnology applied to this sector rely in the ability to degrade almost completely several types of recalcitrant compounds (Shao et al., 2013; Lofrano et al., 2016). 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 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).

Besides the potential of ENMs to improve the performance of existing water purification processes, nanotechnology would represent a major breakthrough towards the development of next-generation water supply systems, in which centralized water treatment facilities are supplemented with decentralized point-of-use (POU) infrastructures (Qu et al., 2013). Indeed, the application of nanotechnology-enabled devices, which could selectively remove specific class of contaminants, could allow the development of POU systems, which address the specific needs of local communities, allowing efficient wastewater treatment and reuse, boosting a more sustainable water supply (Qu et al., 2013). 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 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 ENMs in water and in sludge, from where they will likely enter natural ecosystems (Nogueira et al., 2015a). 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 engineered nanoparticles (Delnavaz et al., 2015). Up to now few studies investigated the harmful effects of ENMs occurring in wastewater and sludge, highlighting a potential risk for wildlife, related to their application in wastewater processes (Carotenuto et al., 2014; Nogueira et al., 2015b).

The decrease in safe freshwater availability is one of the most challenging issue to be faced by many societies and the World in the 21st century. It can be ascribed to a series of factors such as the population growth, the effects of climate change on the hydrologic cycle, and the increasing pollution. Aquifer systems are depleting due to multiple problems such as overexploitation and salt water intrusion, inadequate sanitation, spread of common and emerging contaminants. If from one side nanotechnologies can be successfully used to treat the water after its exploitation (e.g. to remove salt and contaminants), the *in-situ* use of ENMs is a challenging, but very promising approach. Groundwater (or aquifer) nanoremediation, which exploits ENMs for the treatment of contaminated groundwater, broadens the range and increases the effectiveness of *in situ* remediation options. This approach can be very effective to treat contaminants very close to the source of pollution but, mainly due to the costs of reagents, it is not suitable to target widespread and areal contaminations such as those induced by saltwater intrusion or of agricultural origin (nitrates and phosphates). Several ENMs 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 nanoparticles, both in the form of iron particles alone, and as composite materials. Iron particles include, e.g., nanoscale and microscale ZeroValent Iron (nZVI and mZVI) (Wang and Zhang, 1997), and nano-sized 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 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., 2014). 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.

In the framework of the FP7 UE project AQUAREHAB (G.A. n. 226565) single and mixtures of guar gum and xanthan gum have been proved to be suitable for particle stabilization and delivery (Xue and Sethi, 2012; Aquarehab, 2014) while in NanoRem (FP7 EU funded project- Taking Nanotechnological Remediation Processes from the Lab Scale to End User Applications for the Restoration of a Clean Environment, G.A. n. 309517) a hybrid experimental and modeling procedure was developed in order to design pilot and full scale interventions. The procedure is supported by the softwares MNMs and MNM3D (Tosco et al., 2014b) that can be used to interpret the laboratory results and therefore to simulate important field parameters including particle distribution, ROI, number of injection wells in the field. 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. Some particles, such as nZVI, usually are almost immobile under typical aquifer conditions, but other NMs can be significantly mobile in groundwater systems, eg. CarboIron and 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 regulatory 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.

3. Recommendations

3.1 Ecotoxicological testing and predictive safety assessment tools

To implement the effective application of nanotechnology, a thorough ecosafe predictive assessment approach should be performed addressing the following key aspects:

a) estimate the behavior of ENMs in the media to be remediated, with particular focus on the physico/chemical modifications induced by environmental factors, which might affect their reactivity and fate;

b) consider the nature of the pollutants and the characteristics of the polluted media/area and its surroundings;

c) identify possible toxicological targets of ENMs and provide a mechanism-based evaluation of ecotoxicity in different species and more important at ecosystem level.

Ecotoxicology can provide suitable tools able to select ecofriendly and sustainable ENMs for environmental remediation (Corsi et al., 2014). Together with the needs of a regulatory framework, the most important topics discussed during the workshop has been the absence of reproducible, standardized hazard testing methods for ENMs which is currently limiting the development of a safety risk assessment also for those intended for environmental application as nanoremediation (Zhou et al., 2016; Petersen 2015, Corsi et al., 2014; Kühnel and Nickel , 2014). Therefore, there is a urgent need to develop a comprehensive guidance on how to perform ecotoxicological testing of

ENMs in order to address current limitations and difficulties and support regulatory measures and environmental policies. Regulators expect to take decisions on the permitted level of ENMs released in the environment, as strongly required by stakelholders and industries. While standardized *ad hoc* ecotoxicity bioassays can be used as screening tools for selecting the best ecosafe design of ENMs used for remediation, any risk associated with their fate, behavior and interaction with biological components of the media under remediation should be carefully investigated by using a more ecosystem-scale approach.

Relevant environmental exposure scenarios which will include micro- and mesocosm studies and multi-trophic effects approach are thus particularly needed in order to address ENMs hazard at ecosystem level (Corsi et al., 2014). *Trojan horse* mechanism in cellular uptake of ENMs enhancing bioavailability and accumulation of contaminant to be remediated as well as its trophic transfer up to the food chain leading to biomagnification should be carefully considered and addressed by ecotoxicologists using an ecosystem-based approach. A more ecologically oriented hazard assessment of ENMs entering the natural environment has already been proposed and can take several advantages from the application in nanoremediation where size, properties and quantities of ENMs are known, as well as their potential biological effects from organism to population up to ecosystem level (Corsi et al., 2014). Therefore, the validation of standardized ecotoxicological testing methods as predictive safety assessment tools able to satisfy regulatory needs, should be the next EU target that will promote their eco-friendly application in remediation strategies.

Investigations of the most common used ENMs for remediation, nanoscale zero valent iron (nZVI) showed that it might cause hazardous effects to organisms in the environment, especially microorganisms (Grieger et al., 2010). 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 ENMs 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 ENMs 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). Currently a certain level of uncertainty in risk assessment approaches is related to ENMs instability in water media, as for instance the tendency to form aggregates with different physical/chemical characteristics, with respect to the bare particles/materials (Lowry et al., 2012).

In order to optimize a remediation process, any potential fate scenarios need to be predicted from the ENM introduction into a polluted site until their removal or degradation upon elimination of the target pollutants (Stone et al., 2010; Nowack et al., 2012). Despite lack of methods for *in-situ* assessment of ENM speciation, ageing and agglomeration/aggregation state (Peijnenburg et al., 2016), predictive fate and transport models for ENMs are useful tools in the design and selection of a nanoremediation strategy for a specific contaminated area.

Different approaches have been used for describing the aggregation processes, which typical fall into two categories, one based on particle number (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. Although deep insight on the environmental effect and fate of ENMs is still in its infancy, the model is able to compare and screen the impact of different ENMs when injected or dosed in a contaminated sediment layer. It is possible to apply the proposed concept to assess ENMs properties, which are crucial for their fate and transport. It can be used to explore the consequences of different input values such as pollutants, ENMs, salinity and sediment/soil properties. The concept provides the basic for ecosafe design of the ENM and choice of strategy for remediation (Figure 1).

3.2. Greener and sustainable (nano)solutions for remediation

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, associated to possible bioaccumulation due to ingestion, dermal contact, and inhalation, are still controversial (Trujillo-Reyes et al., 2014). A multitude of studies have failed to reveal a risk of materials in the nano-dimension *per se*, as it is hard to differentiate ENMs effects to those of bulk materials (Laux et al., 2017). Nevertheless, under this uncertainty national and international regulations often adopt a conservative approach, banning the use of ENMs on field. This suggests the necessity to design new solutions, capable to take into account these critical aspects.

In this context, a valuable alternative strategy to overcome the ecotoxicology and legislative issues related to the use of ENMs 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 ENMs, 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 ENMs and prevent their release in the ecosystem. Moreover, this approach could be considered even much more valuable if the new ENMs 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 ENMs, 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 (Krishnani and 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 to produce 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. According to this procedure, 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. Moreover, the implementation of these systems for biomedical applications in the field of drug-delivery (Fiorati et al., 2017) enforce their safe use for environmental remediation.

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 become 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.

Further examples include 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 and to implement regional development policies in the field of the environmental prevention and protection by pollutants. TANIA specifically addresses innovative and low cost technological solutions 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.

3.3. Environmental safety and industrial competitiveness

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 meets. 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.

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. 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) or as infrastructural components using geotubes (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 and Schuster, 2016).

4. 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 innovative, green and sustainable (nano)solutions, which own ecosafe features such as limited mobility in environmental media and no toxicological effects for humans and wildlife.

To further promote the application of nanoremediation regional policy makers must work together and with main stakeholders in order to: (i) support research and innovation for identification of ecosafe and sustainable (nano)solutions; (ii) define a standardized methodology to evaluate ENMs effectiveness, ecosafety and economic sustainability within the context of existing environmental regulations at National and European level; (iii) support patenting and pilot applications of new ENMs developed on the basis of ecosafety by design concepts; (iv) develop a policy framework to provide incentives for *in-situ* use of ENMs for treatment of contaminated soil and water; (v) raise awareness on the process of nanoremediation, its benefits and means of application. In this context ecotoxicology, as well as predictive models, can be extremely helpful in risk assessment for regulatory needs. Greener and sustainable solutions as *ecofriendly* (nano)materials will be also mandatory for supporting industrial competitiveness, innovation and sustainability of the sector. A specific legislation at European level is necessary to regulate their emissions and field application.

Overall, the generation of ENMs that meet the highest standards of environmental safety will therefore support the effective deployment of nanoremediation at European and international level.

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Table

Table 1. List of the most commonly successfully used ENMs for groundwater, water and wastewater remediation for which ecotoxicity[§] 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, liological contaminants, Cr		Marine and freshwater organisms (bacteria, algae, invertebrates, marine mammals)	Baun et al., 2008 Minetto et al., 2016 Ma et al., 2013
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

[§]Ecotoxicity data are referred to bare particles and cannot be generalized to the diversity of specific particles used in remediation.

PCE (Tetrachloroethylene); TCE (Trichloroethylene); DCE (1,2-dichloroethane); TCP (tetrachlorophenol); 2,4 DCP (2,4-diclorophenol); NOM (natural organic matter)

Figure

Sustainable and ecosafe nanoremediation

A way forward to overcome current limitations

BENEFITS

(compared to conventional techniques)

-Less costly

-More effective

-Easiest to apply for *in situ* application

RISKS

(*mostly related to the in situ application*)

Uncertanties on ENMs mobility, reactivity, persistence, environmental and human safety

RECOMMENDATIONS

- Recognize ecosafety as a priority feature
- Validate ecotoxicity testing and predictive assessment tools
- Support research and innovation for greener, sustainable and innovative (nano)materials

GOALS

-Satisfy regulatory requirements

-Boost circular economy

-Support a fully effective deployment of nanoremediation