

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

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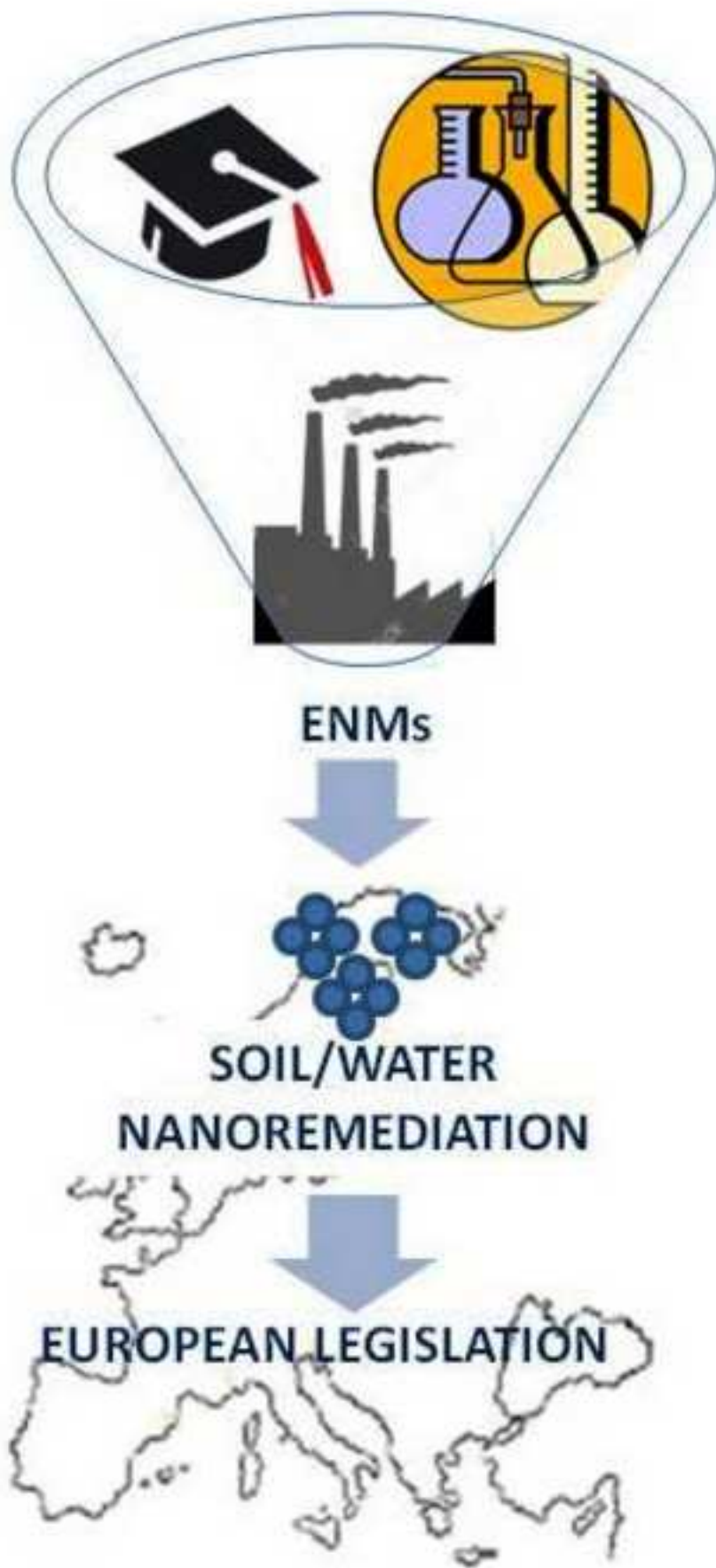
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Highlights

- 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

1 ***Ecofriendly* nanotechnologies and nanomaterials for environmental applications:**
2 **key issue and consensus recommendations for sustainable and ecosafe**
3 **nanoremediation**

4

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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.

58 The application of nanotechnology includes the use of engineered nanomaterials (ENMs) to clean-
59 up polluted media as soils, water, air, groundwater and wastewaters from which the current
60 definition of *nanoremediation* (Karn et al., 2009; Lofrano et al., 2017a). Contamination by
61 hazardous substances in landfills, oil fields, manufacturing and industrial sites, military installation
62 including private properties represent a global concerns need to be remediated since it poses serious
63 risk for health and well-being of humans and the environment (USEPA, 2004; PEN, 2015).

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

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

78 Despite such promising expectations, nanoremediation has been slowly applied in Europe (JRC,
79 2007) probably as a consequence of various factors as for instance the emerging societal worries on
80 nanotechnologies and the current lack of regulatory and proper legislative supports (Nature
81 Nanotechnology, 2007; Grieger et al., 2012).

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

86 In Europe, it has been estimated that there are more than 2.5 million potentially polluted sites
87 which need to be remediated and that 350,000 sites may cause a potential risk to humans or the
88 environment (EEA, 2014). Here, the current debate relies on the balance between known benefits

89 and potential risks associated to the use of nano-scale materials in terms of mobility, persistency
90 and ecotoxicity, other than on the current technical limitations in detection and monitor
91 nanoparticles in the environment as well as in proper risk assessment procedures (Nowack et al.,
92 2015).

93 The present paper summarizes the findings from the workshop :“Ecofriendly Nanotechnology:
94 state of the art, future perspectives and ecotoxicological evaluation of nanoremediation applied to
95 contaminated sediments and soils” convened during the Biannual ECOtoxicology Meeting 2016
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97 state of the art of nanoremediation, which represents a breakthrough in pollution control, the
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100 remediation is mandatory; (iii) greener, sustainable and innovative nano-structured materials should
101 be further supported; (iii) those ENMs that meet the highest standards of environmental safety will
102 support industrial competitiveness, innovation and sustainability. The workshop aims to favour
103 environmental safety and industrial competitiveness by providing tools and modus operandi for the
104 valorization of public and private investments. An overview of three European nanoremediation
105 projects (i.e. two still ongoing) was presented with the aim to provide insights into the state of the
106 art of collaborative research across Europe.

107

108 2. *State of the art of nanoremediation*

109 2.1 *Sediment/soil*

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

119 assessment about nanoremediation is further away to be completed, even though some countries are
120 already at the field scale (PEN, 2015).

121 Several papers, since the beginning of the nano-era, focused on the dichotomy of the effects of
122 micro- (MP) and nano-sized particles (NP). Are NPs better than MPs? Of course, as usual, it
123 depends. Costs and benefits are not always easy to define especially for emerging materials where
124 the number of pros and cons are almost the same, at least at the beginning when unexplored aspects
125 are still present, and contradictory results exist considering both human health and environmental
126 effects (Lofrano et al., 2017b). Certainly, some concerns occur regarding the use of ENMs in
127 contaminated soil/sediment: once dispersed in a contaminated site would ENMs be mobile to a
128 point that they could be taken up by plants or animals at the site or further away, and adversely
129 affect them? How to consider the environmental benefits and risks of ENMs for *in situ*
130 applications? Does their use and behavior pose questions regarding environmental fate and impact?
131 Do they provide easier and better results than the relative MPs? Moreover, a remediation
132 technology must attend to cost-benefit approaches considering practical immediate issues and long-
133 term expectancies. For example, nano-iron has an average cost of about 100 €/kg compared to 10
134 €/kg of iron MPs (SiCon, 2016), mainly due to the relative economies of scale. The very high
135 reactivity of iron NPs makes its *in situ* application sometimes difficult and the remediation activity
136 could present a limited long-lasting ability (Grieger et al., 2010). Thus, a case-by-case analysis must
137 be undertaken to assess the potential real applicability and need for nanoremediation.

138

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

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

159 Exposure scenarios, as well as patterns of uptake and toxicity, are substantially still unknown for
160 natural marine environment (Koelmans et al., 2015) and represent a major challenge for marine
161 nano-ecotoxicologists and a hindrance for the use of ENMs in remediation. Bridging current
162 knowledge acquired from lab-controlled experimental conditions to environmental realistic
163 scenarios resembling natural ecosystems is therefore their featured mission (Gottschalk et al.,
164 2013). This is further complicated by the general lack of appropriate methodologies able to detect
165 and quantify ENMs in environmental matrices though some advancements are available for specific
166 ENPs (Nowack et al., 2015).

167 The many peculiar features of ENMs as chemical core, size, shape and surface energy have been
168 shown to substantially affect their final properties once released in complex natural environmental
169 media as for instance sea water. In this context, marine waters are even more diverse since physico-
170 chemical parameters, and inorganic and organic composition, substantially differ from surface,

171 column and deep waters as well as in lagoon, estuaries, coastal areas and deep oceans (Nowack et
172 al., 2012).

173 The ENMs fate, in terms of dispersion, might be triggered by parameters as pH, osmolarity and
174 natural organic matter (NOM) mainly based on colloids and proteins, which are able to interact with
175 the specific properties of the ENM itself thus affecting uptake and toxicity in exposed organisms
176 (Corsi et al., 2014). The outcome of such interactions is also affected by the biological status of the
177 organism itself as for instance its ability to face and react to such exposure. Further effects could
178 also be seen at higher level from organism, to population and community and the entire ecosystem
179 (Matranga and Corsi, 2012).

180 In wastewater treatment nanotechnology emerged as a robust and efficient technology that
181 overcomes the limits of existing processes, due to the tunable properties and outstanding features of
182 ENMs (Qu et al., 2013). The main advances of nanotechnology applied to this sector rely in the
183 ability to degrade almost completely several types of recalcitrant compounds (Shao et al., 2013;
184 Lofrano et al., 2016). The three main applications are: i) nano-adsorbents: made of either carbon-
185 based or metal-based NMs, such application has high efficiency on adsorption of organic pollutants
186 and also for metal removal, due to extremely high specific surface area, more accessible sorption
187 sites and lower intraparticle diffusion (Lofrano et al., 2016); ii) membrane systems based on
188 nanofibers or nanocomposites, which offer a great opportunity to improve the membrane
189 permeability, fouling resistance, mechanical and thermal stability, and to provide new functions for
190 contaminant degradation (Liu et al., 2015); iii) nano catalysts, with focus on photocatalyst such as
191 TiO_2 (Carotenuto et al., 2014; Lofrano et al., 2016). This application for the wastewater treatment
192 allows fast and efficient removal of metals, and several types of organic pollutants such as for
193 instance hydrocarbons, perfluorooctanoic acid, pharmaceuticals and personal care products as well
194 as of antibiotic resistance bacteria and genes (Shao et al., 2013; Bethi et al., 2016).

195 Besides the potential of ENMs to improve the performance of existing water purification
196 processes, nanotechnology would represent a major breakthrough towards the development of next-
197 generation water supply systems, in which centralized water treatment facilities are supplemented
198 with decentralized point-of-use (POU) infrastructures (Qu et al., 2013). Indeed, the application of
199 nanotechnology-enabled devices, which could selectively remove specific class of contaminants,
200 could allow the development of POU systems, which address the specific needs of local
201 communities, allowing efficient wastewater treatment and reuse, boosting a more sustainable water
202 supply (Qu et al., 2013). Based on the achievements obtained so far, nanotechnology holds great

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

207 Future studies need to assess the applicability and efficacy of different nanotechnologies under
208 more realistic conditions. For instance, most of the studies were based on relatively short time
209 exposure periods, while the long-term performance of these nanotechnologies is largely unknown.
210 Moreover, avoiding of unintended consequences on natural environments is the main issue for the
211 effective adoption of this technology. In fact, the application of nanotechnology will inevitably lead
212 to the release of ENMs in water and in sludge, from where they will likely enter natural ecosystems
213 (Nogueira et al., 2015a). Currently several methods are available, mostly involving the exploitation
214 of magnetic properties of some inorganic material, cross-flow filtration, and centrifugation.
215 Recently great effort has been devolved to develop treatment systems with immobilized engineered
216 nanoparticles (Delnavaz et al., 2015). Up to now few studies investigated the harmful effects of
217 ENMs occurring in wastewater and sludge, highlighting a potential risk for wildlife, related to their
218 application in wastewater processes (Carotenuto et al., 2014; Nogueira et al., 2015b).

219 The decrease in safe freshwater availability is one of the most challenging issue to be faced by
220 many societies and the World in the 21st century. It can be ascribed to a series of factors such as the
221 population growth, the effects of climate change on the hydrologic cycle, and the increasing
222 pollution. Aquifer systems are depleting due to multiple problems such as overexploitation and salt
223 water intrusion, inadequate sanitation, spread of common and emerging contaminants. If from one
224 side nanotechnologies can be successfully used to treat the water after its exploitation (e.g. to
225 remove salt and contaminants), the *in-situ* use of ENMs is a challenging, but very promising
226 approach. Groundwater (or aquifer) nanoremediation, which exploits ENMs for the treatment of
227 contaminated groundwater, broadens the range and increases the effectiveness of *in situ* remediation
228 options. This approach can be very effective to treat contaminants very close to the source of
229 pollution but, mainly due to the costs of reagents, it is not suitable to target widespread and areal
230 contaminations such as those induced by saltwater intrusion or of agricultural origin (nitrates and
231 phosphates). Several ENMs have been studied in the last years for groundwater remediation
232 purposes. Even if the use of other materials has been explored, most of the particles which are
233 currently being tested and show a good performance for groundwater remediation are iron-based
234 nanoparticles, both in the form of iron particles alone, and as composite materials. Iron particles

235 include, e.g., nanoscale and microscale ZeroValent Iron (nZVI and mZVI) (Wang and Zhang,
236 1997), and nano-sized iron oxides, such as goethite for heavy metals sorption, and ferrihydrite for
237 improved microbial-assisted degradation of organic contaminants (Bosch et al., 2010). Examples of
238 iron-based composite nanomaterials include CARBO-IRON®, where nZVI is embedded in a
239 carbon matrix to promote mobility and contaminant targeting (Mackenzie et al., 2012), bimetallic
240 particles, and emulsified zero valent iron (EZVI). Granular, millimetric zero-valent iron (ZVI) is
241 one of the most successful reagents for groundwater remediation deployed in Permeable Reactive
242 Barriers (PRBs). A PRB is a passive technology for *in situ* treatment of contaminated groundwater
243 plumes (Di Molfetta and Sethi, 2006). Due to its capability of degrading a wide range of organic
244 contaminants, and of reducing and immobilizing metal ions, ZVI has been employed in hundreds of
245 PRBs worldwide. However, installation and construction limitations restrain the application of this
246 technology, making the treatment of deep contaminations impracticable, for instance. Moreover,
247 PRBs target only the dissolved plume and cannot be used for direct treatment of the source of
248 contamination. Wang and Zhang (1997) proposed the use of nanoscale nZVI as an alternative to
249 granular iron. Owing to its small particle size (less than 100 nm), nZVI is characterized by a high
250 specific surface area (10-50 m²/g) and consequently exhibits a significantly faster contaminant
251 degradation rate (Tosco et al., 2014). Furthermore, nZVI aqueous suspensions can be directly
252 injected in the subsurface, directly targeting the plume close to the source of contamination and
253 attaining higher depths than with PRBs. nZVI's small size and high reactivity alone, however, are
254 not sufficient to ensure an effective remediation. In recent years, several laboratories worldwide
255 have been seeking solutions to some of nZVI's main limitations, that must be addressed in regard to
256 the effectiveness and feasibility in field-scale applications. They include in particular stability
257 against aggregation, short and long-term mobility in aquifer systems, and longevity under
258 subsurface conditions.

259 In the framework of the FP7 UE project AQUAREHAB (G.A. n. 226565) single and mixtures of
260 guar gum and xanthan gum have been proved to be suitable for particle stabilization and delivery
261 (Xue and Sethi, 2012; Aquarehab, 2014) while in NanoRem (FP7 EU funded project- Taking
262 Nanotechnological Remediation Processes from the Lab Scale to End User Applications for the
263 Restoration of a Clean Environment, G.A. n. 309517) a hybrid experimental and modeling
264 procedure was developed in order to design pilot and full scale interventions. The procedure is
265 supported by the softwares MNMs and MNM3D (Tosco et al., 2014b) that can be used to interpret
266 the laboratory results and therefore to simulate important field parameters including particle

267 distribution, ROI, number of injection wells in the field. Understanding particle transport and
268 deposition is of pivotal importance not only in the short term, during injection, but also in the long
269 term, to understand the fate of the particles in the environment. Some particles, such as nZVI,
270 usually are almost immobile under typical aquifer conditions, but other NMs can be significantly
271 mobile in groundwater systems, eg. CarboIron and iron oxide NPs studied for metal immobilization
272 in the framework of the H2020 REGROUND project (G.A. an. 641768) (Tirafferri et al., 2017). As a
273 consequence, to guarantee the long-term safety of the remediation approach and meet regulatory
274 requirements, it is of pivotal importance to provide reliable, quantitative estimations on the long-
275 term mobility of the injected particles that may remain in the subsurface after reaction with the
276 contaminant.

277

278 *3. Recommendations*

279 *3.1 Ecotoxicological testing and predictive safety assessment tools*

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

- 282 a) estimate the behavior of ENMs in the media to be remediated, with particular focus on
283 the physico/chemical modifications induced by environmental factors, which might affect
284 their reactivity and fate;
- 285 b) consider the nature of the pollutants and the characteristics of the polluted media/area and
286 its surroundings;
- 287 c) identify possible toxicological targets of ENMs and provide a mechanism-based
288 evaluation of ecotoxicity in different species and more important at ecosystem level.

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

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

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

315 Investigations of the most common used ENMs for remediation, nanoscale zero valent iron (nZVI)
316 showed that it might cause hazardous effects to organisms in the environment, especially
317 microorganisms (Grieger et al., 2010). A review of the recent published literature showed that
318 although nZVI is a reactive substance with toxic properties, it could also stimulate microbiota
319 through its influence on environmental parameters (Semerad and Cajthaml, 2016). Results show
320 clearly that there is a need for further investigations to achieve a deeper understanding on how
321 nZVI, as well as other ENMs applied for remediation, affect organisms in areas surrounding their
322 applications. However, it should be considered that the purpose of *in-situ* nanoremediation is to
323 reduce the toxic pollutants in a contaminated area and that the application of ENMs may reduce the
324 overall toxicity of the contaminated site even if it has properties which could cause toxic effects on
325 biota (Semerad and Cajthaml, 2016). Currently a certain level of uncertainty in risk assessment
326 approaches is related to ENMs instability in water media, as for instance the tendency to form
327 aggregates with different physical/chemical characteristics, with respect to the bare
328 particles/materials (Lowry et al., 2012).

329 In order to optimize a remediation process, any potential fate scenarios need to be predicted from
330 the ENM introduction into a polluted site until their removal or degradation upon elimination of the
331 target pollutants (Stone et al., 2010; Nowack et al., 2012). Despite lack of methods for *in-situ*
332 assessment of ENM speciation, ageing and agglomeration/aggregation state (Peijnenburg et al.,
333 2016), predictive fate and transport models for ENMs are useful tools in the design and selection of
334 a nanoremediation strategy for a specific contaminated area.

335 Different approaches have been used for describing the aggregation processes, which typical fall
336 into two categories, one based on particle number (Praetorius et al., 2014) and another based on
337 mass (Dale et al., 2015; Markus et al., 2015). The particle number based approach describes the
338 aggregation kinetics using an attachment efficiency, a collision frequency and the particles
339 concentrations, whereas in the mass based approach the attachment efficiency and collision
340 frequency is replaced with a mass based rate of aggregation (Dale et al., 2015). The development of
341 these models has primarily been driven by the need to understand the fate of ENMs in the
342 environment and their possible environmental risk. Although deep insight on the environmental
343 effect and fate of ENMs is still in its infancy, the model is able to compare and screen the impact of
344 different ENMs when injected or dosed in a contaminated sediment layer. It is possible to apply the
345 proposed concept to assess ENMs properties, which are crucial for their fate and transport. It can be
346 used to explore the consequences of different input values such as pollutants, ENMs, salinity and
347 sediment/soil properties. The concept provides the basic for ecosafe design of the ENM and choice
348 of strategy for remediation (Figure 1).

349

350 3.2. Greener and sustainable (nano)solutions for remediation

351 While several ENMs reported in the literature show outstanding performances, in terms of
352 decontamination efficiency of water and soil, the potential safety drawbacks related to their use in
353 ecosystems, associated to possible bioaccumulation due to ingestion, dermal contact, and inhalation,
354 are still controversial (Trujillo-Reyes et al., 2014). A multitude of studies have failed to reveal a risk
355 of materials in the nano-dimension *per se*, as it is hard to differentiate ENMs effects to those of bulk
356 materials (Laux et al., 2017). Nevertheless, under this uncertainty national and international
357 regulations often adopt a conservative approach, banning the use of ENMs on field. This suggests
358 the necessity to design new solutions, capable to take into account these critical aspects.

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

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

381 Nevertheless, what makes cellulose so attractive as source for the design of advanced materials is
382 its intrinsic hierarchical structure (Kim et al. 2015). The cellulose fiber composite is made with
383 macrofibers of cellulose, hemicellulose and lignin. The macrofibers are composed of microfibrils,
384 which in turn are formed with nanofibrils of cellulose. The possibility to cleave the original
385 structure of native cellulose and to produce cellulose nanofibers (CNF) opens interesting
386 perspectives for a wide range of applications, including wastewater treatment. Following the
387 simplest protocol to produce CNF, cellulose can be preliminary oxidized with the 2,2,6,6-
388 tetramethylpiperidinyloxy (TEMPO)-mediated system (Pierre et al., 2017), selectively converting
389 primary C6-hydroxyl groups of the glucose units to the corresponding carboxylic groups.
390 According to this procedure, defibrillation of TEMPO-oxidized cellulose nanofibers (TOCNF) can

391 be achieved by increasing the pH of the solution. In fact, the deprotonation of carboxylic groups
392 favor the electrostatic repulsion of negatively charged single fibrils, leading to the physical
393 separation of single fibriles. Hydrogels obtained from TOCNF have been reported as efficient and
394 reusable adsorbents of heavy metal ions (Isobe et al., 2013). However, TOCNF can be also used for
395 further cross-linking, taking advantage of the new carboxylic moieties introduced on the polymer
396 backbone. While this process would lead to macro-dimensioned nano-structured systems, with all
397 the advantages previously discussed, the choice of the ideal cross-linker would allow to introduce
398 additional properties and functional groups, increasing the versatility of the systems. In this context,
399 we recently reported a thermal route for the production of a new class of aerogels, starting from
400 TOCNF and following a simple thermal protocol in the presence of branched-polyethyleneimine
401 (bPEI) (Melone et al., 2015a). The formation of amide bonds between the carboxylic and the amine
402 moieties favored the high reticulation into sponge-like, water stable systems, which show high
403 efficiency in removing heavy metals and phenolic derivatives from wastewater. The possibility to
404 functionalize selectively the amino groups of the cross-linker (Melone et al., 2015b), and to use
405 these devices as templates for further organic (Panzella et al., 2016) and inorganic (Melone et al.,
406 2013) coating, suggests the potentialities of this new ENM, whose properties can be modulated in
407 order to perform selectively for the absorption and degradation of target contaminants. Moreover,
408 the implementation of these systems for biomedical applications in the field of drug-delivery
409 (Fiorati et al., 2017) enforce their safe use for environmental remediation.

410 In the framework of the NANOBOND project (Nanomaterials for Remediation of Environmental
411 Matrices associated to Dewatering), the specific application of hydrogels obtained from TOCNF
412 and tested for their ecosafety will aim to develop new ecofriendly nanotechnologies for sludge and
413 dredged sediment remediation. Funded in the framework POR CReO FESR Tuscany 2014-2020,
414 the NANOBOND project aims to develop an innovative system for treating contaminated sludge
415 and dredged sediments, by coupling the use of nanostructured *eco-friendly* materials with the
416 classical geotextile dewatering tubes. This new solution, will enable to reduce contaminated sludge
417 and sediments, in terms of volumes and costs of transport, but also to convert the resulting solid and
418 liquid wastes to a renewable clean resource to be use, for instance, in riverbanks settlements and
419 any other applications. By developing nanoremediation techniques associated with dewatering,
420 NANOBOND intends to explore new solutions to dredging and sludge management linked to
421 hydrogeological disruption and maintenance of harbour areas, emerging issues which are
422 tremendously increasingly worldwide. This innovative solution aims to become an efficient strategy

423 to significantly reduce sludge and sediment contamination through nanoremediation since also
424 easily scalable for large-scale *in situ* applications with competitive costs. The NANOBOND
425 consortium made by a 70% of industrial partnership specifically of companies involved in sludge
426 and dredged sediment disposal as well as in their risk assessment and 30% of academia and research
427 institutes for synthesis, ecosafety and life cycle assessment of nanostructured materials
428 accomplished the requirements of technology transfer and business development needed for the
429 development of an ecosafe and sustainable nanoremediation and promote economic development in
430 terms of industrial competitiveness and innovation, both still very little developed in European
431 countries.

432 Further examples include the INTERREG EUROPE project TANIA (TreAting contamination
433 through NanoremedIation) with the aim to improve EU regional policies on treating contamination
434 through nanoremediation in European countries and to implement regional development policies in
435 the field of the environmental prevention and protection by pollutants. TANIA specifically
436 addresses innovative and low cost technological solutions for the (nano)remediation of
437 contaminated soil and water.

438 Green nanotechnology refers to the use of nanotechnology to enhance the environmental
439 sustainability of processes producing negative externalities. It also refers to the use of
440 nanotechnology products to enhance sustainability. It includes making green nano-products and
441 using nano-products in support of sustainability.

442

443 *3.3. Environmental safety and industrial competitiveness*

444 In the field of environmental remediation and the related treatments and disposal of the various
445 solid and liquid matrices, strong collaboration between industrial sector and research is absolutely
446 needed. Specific issues related to waste or site typologies and the resulting innovation from the
447 applied nanotechnologies and their development, will increase the competitiveness of companies
448 involved in the environmental sector with also benefit from applied research as the increase of
449 patents. A role that must be played together by researchers and industries is in the choice of
450 strategies that will allow the scale-up of the material and techniques developed, taking in mind that
451 the amount of materials to be employed is measured in tons or kilotons, as like as the cost of
452 production must be affordable for concretely tackle large scale case. This aspect not necessarily
453 must be considered as mass production because it can also have success with an approach for niche

454 production, but for sure the valley between the laboratory bench production and an industrial
455 product ready for commercialization must be cross, keeping in mind all the classical problems that
456 this pathway usually meets. A multidisciplinary approach must be applied at the forefront of the
457 most advanced nanotechnological solutions to be tunable according to different situations.

458 Remediation should accomplish several aspects according to national regulation, human and
459 environmental safety and contract management economics.

460 The global nanotechnology market in environmental applications reached \$23.4 billion in 2014.
461 This market is expected to reach about \$25.7 billion by 2015 and \$41.8 billion by 2020, registering
462 a compound annual growth rate (CAGR) of 10.2% from 2015 to 2020
463 ([https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-applications-market-nan039c.html)
464 [applications-market-nan039c.html](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-environmental-applications-market-nan039c.html)). The urgent need to develop commercially-deployed
465 remediation technologies at European level have seen the involvement of service providers and site
466 owners or managers which are now finally considering their potential applications as well as
467 implications for their business activities.

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

472 An increase of sustainable environmental remediation solution is therefore mandatory so that the
473 benefit of the remediation action will be greater than the impact of the action itself (SuRF Italy,
474 2014). This is particularly evident in recovery of former industrial areas, which, apart from limiting
475 soil consumption, can produce benefits beyond the cost of the interventions themselves. Today,
476 more than ever, these interventions become significant given the wide presence of dismantled
477 industrial areas, transformed into large "urban voids", following the progressive outsourcing of
478 western economies.

479 The approach to re-use (both the areas to be reclaimed and the environmental matrices) is the aim
480 of numerous studies that highlight the possibilities of recovery. In the case of dredged sediments,
481 for instance, recovery is possible by using them as materials in the building industry (Hamer et al.,
482 2005) or as infrastructural components using geotubes (Sheehana and Harringtonb, 2012).

483 The European Community promotes the more efficient use of resources: in the logic of the
484 circular economy, the circle closes with the transformation of waste into resources (European
485 Commission, 2014). The innovative approach of the circular economy aims to bring greater

486 resource efficiency and material savings, based on the life cycle principle (Kobza and Schuster,
487 2016).

488

489 4. *Concluding remarks*

490 As the potential and efficacy of nanotechnology is well established, several drawbacks related to
491 the full-scale application should be overcome. In particular great efforts should be devoted to
492 develop innovative, green and sustainable (nano)solutions, which own ecosafe features such as
493 limited mobility in environmental media and no toxicological effects for humans and wildlife.

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

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

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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
TiO₂		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)

Sustainable and ecosafe nanoremediation

A way forward to overcome current limitations

