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Engineered nanomaterials for environmental remediation

Cleaning up the environment from various sources of pollution is imperative to not only protect ecological health but also general public health. Having a clean environment is extremely important for us as we significantly depend on clean air to breathe as well clean water to drink and for use in agriculture and industry. Unfortunately, many environmental resources such as groundwater are precious resource which are continuously threatened by various natural and human-made contaminants. To put this in perspective, there are more than 900 sites in the US alone that are prioritized for clean-up by the US Environmental Protection Agency (EPA) (USEPA 2009) and current estimates of polluted sites in Europe are counted in the millions, of which approximately 350,000 sites constitute a potential risk to humans or the environment (EEA 2014).

Pollution in the environment can be cleaned up (also called "remediated") using a range of techniques. The field of study that focuses on investigating the clean up or removal of contaminants from the environment is called "environmental remediation." Environmental remediation techniques use various methods to remove and/or break-down (degrade) environmental contaminants in polluted soils, surface waters, groundwater, as well as in sediments. The overall objective of environmental remediation is to reduce environmental and/or human health risks due to environmental pollution through one or several remediation methods. Some of these involve removing the contaminated soil, sediment, or water from the polluted sites and then treating the pollution aboveground (known as *ex situ* techniques). Other techniques clean up the contamination while it is still in the ground (known as *in situ* techniques) without the need of off-site treatment. There are numerous pressures from financial, legislative, and time-related constraints that drive the need for continued research into new techniques that provide better, faster, and cheaper environmental remediation treatment options. Ultimately, the choice of the "best" remediation technique varies from site to site and depends on site-specific conditions (e.g., hydrology, nature of contaminant etc.) as well as performance, cost, and environmental impacts of the potential clean-up technologies.

To date, extensive research has been carried out to design efficient and cost-effective techniques for treating environmental pollution. Most of the conventional remediation methods presently available are based on classical ex-situ 'pump-and-treat' approaches that involve removal or extraction of the contaminated soils, groundwater, and/or sediments and then treating them using conventional treatment processes. These methods are highly energy intensive, and therefore costly, as well as face challenges to meet permissible cleanup standards. Another limitation of *ex-situ* techniques is that they may leave concentrated hazardous waste residues, which require further disposal. Development of long-term efficient and inexpensive *in-situ* treatment methods has therefore become a research interest of major importance. Various *in-situ* methods have been explored for environmental remediation which vary in their technical approach, cost, and contaminants that may be treated (see US EPA's list of techniques, USEPA 2013).

In recent years, the use of engineered materials, such as nanoparticles, have gained increased amounts of attention as potential remediation techniques, often cited as an attractive, cost-effective alternate to conventional approaches. Engineered nanomaterials are generally defined as specially designed materials with size range of approximately 1-100 nm (1 nanometer is 1^{-9}m). These nano-sized materials often display different properties compared to their bulk-scale counterparts. Due to these novel properties at the nanoscale, a range of engineered nanomaterials are used in a number of consumer products and other applications, including environmental remediation. "Nanoremediation" is therefore the term used to describe various techniques and methods to clean up contaminated sites using engineered nanomaterials. To date, it is estimated that there are between 45 and 70 sites around the world that have used nanoremediation techniques either at pilot or full study scales (Karn et al. 2009; Bardos et al. 2014; PEN 2015). Engineered nanomaterials are also being developed for other environmentally-related activities, such as the use of absorbent nanowires for oil spills, anti-fouling, nanomaterials for desalination processes using reverse osmosis, as well as photocatalytic nanomaterials that can be used for disinfection or decontamination of drinking waters.
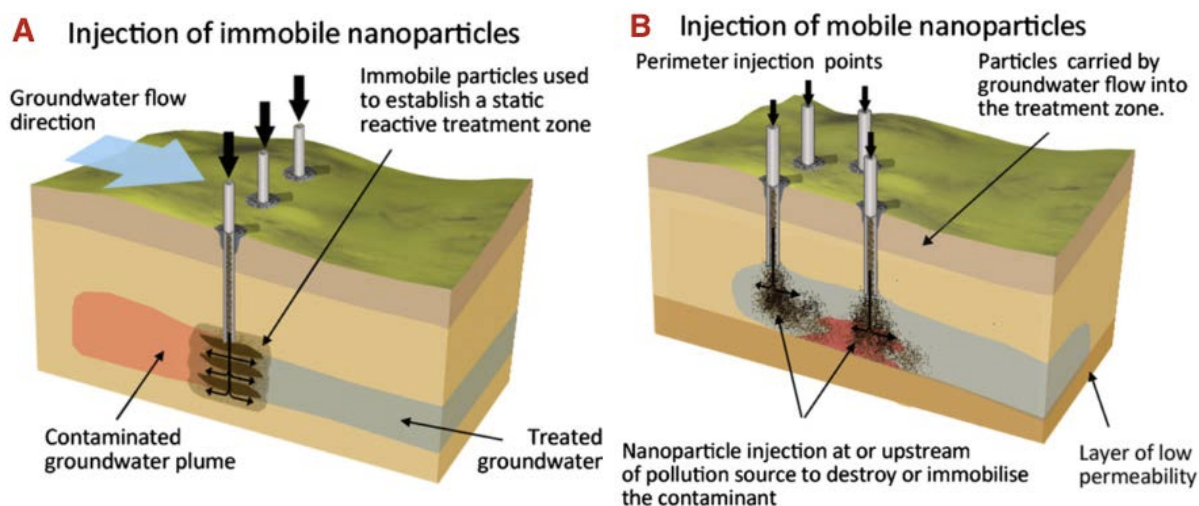

Figure 1: Schematic of how (A) immobile nanoparticles and (B) mobile nanoparticles are injected into the subsurface for groundwater treatment (modified from Crane and Scott (2012)).

In terms of cleaning up the environment from chemical pollution, one of the most common types of nanoremediation techniques relies upon the use of nano-scale zero valent iron (nZVI). In general, nZVI can be injected into a site to degrade the contaminant either by creating a "wall" of particles that cleans water as it passes through it, or by using mobile particles small enough to travel through the pores in the soil (Figure 1). Due to their high available surface area compared to larger iron particles, which lead to higher reaction rates, nZVI is an attractive option for *in situ* remediation.

New solutions to old problems

Every environmental remediation technology has its own potential benefits and limitations in effectively clean up a contaminated site. The use of nanoremediation consequently involves weighing the potential benefits as well as draw-backs from using this novel technique at a given site. Some of the main benefits of nanoremediation (especially *in situ*) compared to other remediation techniques include the fact they may provide a faster, potentially more cost-effective manner to clean up contaminated soils, sediments, and groundwater (e.g. Yan et al. 2013; Sridevi and Lakshmi 2013). For example, based on a comprehensive review Karn et al. (2009) concluded that:

> "Nanoremediation has the potential not only to reduce the overall costs of cleaning
> up large-scale contaminated but also to reduce sites cleanup time, eliminate the

need for treatment and disposal of contaminated soil, and reduce some contaminant concentrations to near zero - all *in situ.*" – Karn et al. (2009)

In regards to the concept of being cost-effective compared to other techniques, the use of nZVI has been considered to be generally less expensive than traditional clean-up techniques (Cundy et al. 2008; Karn et al. 2009). In essence, if nanoremediation such as the use of nZVI is equally effective as other methods but is more affordable, it may therefore be a very attractive remediation alternative to conventional treatment options, particularly for government agencies, which often operate on tight funding.

At the same time, however, there are a number of concerns with the use of engineered nanomaterials for remediation. For instance, nanoremediation is largely untested, particularly at field scale. This raises questions on not only the real-world efficacy at large-scale field sites polluted with different kinds of contaminates but also in terms of the behavior of these nanomaterials in different types of environments which vary in, for example, temperature, hydrogeology, and sub-surface conditions like pH and soil porosity.

Questions have also been raised in regards to the potential for their adverse impacts on the environment, such as effects on various organisms in the environment, the potential for bioaccumulation and persistency, as well as long-term changes in microbial communities (Mueller and Nowack 2010; Grieger et al. 2010). While there is on-going research aimed at addressing these issues, many questions still remain unanswered to date, particularly in regards to potential environmental and health impacts, such as: *How mobile are the particles? Do they have the capacity to carry pollution into a new, unintended, environmental compartment? What exposure level is considered safe?* These questions, among others, are discussed more in the following section which focuses on one type of nanoremediation, with the use of nZVI for *in situ* remediation.

Taking a closer look: nZVI

As mentioned briefly above, nZVI is one of the most commonly used engineered nanomaterials for environmental remediation. Its use for *in situ* remediation has received increased levels of attention in the past decade, attributed to several factors. First, nZVI may provide faster clean-up compared to conventional techniques due to increased contaminant degradation rates (e.g. Karn et al. 2009). Second, nZVI can be used on a wide range of environmental contaminants (such as polycyclic aromatic hydrocarbons (PAHs), pesticides, heavy metals, and various other chemical pollutants), and hence has broad applicability (Elliott and Zhang 2001). Third, these nanoparticles may potentially able to reach hard-to-access areas for *in situ* use. Finally, it has often been cited to be potentially more cost-effectiveness compared to alternative techniques.

The use of nZVI for remediation is also considered to be a sustainable application of nanotechnology or nanomaterials research. For instance, it is commonly listed among other "green" nanotechnology-related applications that may benefit environmental health (Tratnyek and Johnson 2006; Karn et al. 2009). While the potential benefits of selecting a remediation technique which may be more effective at cleaning up a range of contaminants at lower costs seem attractive, others have also questioned whether these potential benefits of using nZVI may actually outweigh the potential environmental and health risks and uncertainties associated with using this novel remediation technique (Grieger et al. 2010; Crane and Scott 2012; Grieger et al. 2012). In fact, there has been a growing debate on the true benefits to the environment following the use of nZVI.

What are the real benefits and risks?

While the development and use of nZVI as a sustainable, environmentally-beneficial nanotechnology was initially regarded as a promising example of "green nanotechnology," the development of this remediation option has been slower than primarily anticipated (Bardos et al. 2014). While it seems relatively clear that nZVI may indeed provide an efficient technique to remove a wide range of environmental contaminants, there are also concerns related to its ability to be used in the real-world, field scale applications and its ability to be an cost-effective

alternative (Crane and Scott 2012). For example, realizing the full potential of nZVI for field-scale use would require the ability to inject nZVI into the environment (i.e. into the subsurface) and transport these particles to the contaminant source zone, where they can rapidly degrade the contaminants of concern. However, nZVI particles tend to cluster together and quickly aggregate in the environment (due to their colloidal chemistry), thereby limiting their flow and ability to maintain contact with the contaminants. One potential solution to this problem is to coat the nanoparticles with different organic or polymer substances to improve their mobility in the environment. Researchers are currently in progress with experimenting different coatings for nZVI particles in order to maintain their high levels of reactivity while also improving their mobility in the environment. Ideally, these coatings should be nontoxic, biodegradable, and improve the functionality of nZVI in the field (e.g. Li et al. 2010; Zhou et al. 2013).

While nZVI has frequently been cited as a cost-effective remediation option, others have also questioned the validity of this statement. For instance, some researchers have proposed that long-term studies are needed to fully investigate the remediation capacity of nZVI and that the inclusion of all costs for development through deployment are required to substantiate nZVI's true cost-effective potential (Mueller and Nowack 2010; Crane and Scott 2012). Some have also suggested that in order to be truly cost-effective, the cost of nZVI should be reduced between one-fifth and one-tenth of current rates (Crane and Scott 2012).

Another serious challenge related to the use of nZVI for *in situ* remediation is its potential to cause adverse impacts to ecological organisms in the environment, especially microbes. To date, some studies have suggested that nZVI may be toxic to bacterial communities (Kumar et al. 2013), while other studies have found conflicting results (Kirschling et al. 2010). Questions have also been raised regarding the potential for nZVI to persist and/or bioaccumulate in the environment, although these aspects are largely unknown at the current time and remain a topic of on-going research. Given the fact that nZVI may be used in the environment to clean up contaminated soils, sediments, and groundwater, researchers are currently investigating the potential for nZVI to impact other ecological receptors in the environment as well. Furthermore, there are also concerns related to the ability of nZVI to migrate in the environment. While the *in situ* use of nZVI is intended to be injected directly into the environment to clean up contaminants, questions have also been raised regarding any potential unwanted or unexpected migrations of nZVI following injection. For example, if the use of various coatings are being developed to enhance nZVI's ability to migrate in the environment, is it possible that these coatings may allow for unwanted migration? In addition, if there is unwanted or unexpected migration in the environment, what are the maximum distances expected under certain environmental conditions? It is also unclear if nZVI can migrate into sensitive areas or impact unique habitats or ecological communities. While some research has started to address these issues, these questions largely remain unanswered.

While nZVI has already been used in many different sites around the world *for in situ* remediation, there has been little (if no) public engagement on the issue (Grieger et al. 2012). This means that citizen groups and the public have largely been absent from decision-making processes regarding the use of nZVI to clean up contaminated environmental sites; despite the fact that this is still an emerging technology with many uncertainties and data gaps. This lack of involvement seems concerning since the environmental impacts as well as migration potential of nZVI in the environment is not yet well understood.

Moving forward

Developing efficient, cost-effective environmental remediation technologies remains an important research field, given the staggering number of contaminated sites that require clean-up initiatives, particularly when financial resources are limited. The use of engineered nanomaterials for environmental remediation necessitates the careful balancing of the potential benefits as well as risks and uncertainties together with site characteristics in order to decide upon the best treatment option for a given site. This is not an easy task, neither for scientists and researchers nor for political decision makers, given the fact that there are numerous data gaps and uncertainties surrounding the potential risks of nanoremediation techniques, such as in the case of nZVI. One must balance the

existing risks of the contamination at the given site together with potential risks of the treatment option, including its unknown, long-term consequences and uncertainties. The case of nZVI presents an interesting illustration whereby the promises of this emerging technology may not be fully realized given the potential risks and concerns related to its long-term effectiveness of an *in situ* remediation technique as well as unknown "down-stream" consequences of its use.

Given this situation, it is recommended that further research is conducted on the impacts of nZVI to its surrounding environment, focusing on the impacts of nZVI to environmentally-relevant microbial communities. In relation to potential toxic responses, it is also important to understand the specific "mode of action" (meaning, a better understanding of the mechanisms of change) driving each response. Second, it is recommended that additional research activities focus on the potential for nZVI to migrate in the environment with the application of various coatings. This will enable scientists, researchers, and developers to understand and predict the behavior of these novel materials in the environment. Third, research dedicated to a better understanding of nZVI's use in large scale remedial studies is needed to fully evaluate its potential as a cost-effective, efficient, and promising *in situ* remediation technology. Finally, it is recommended that there should be a greater role of public participation in the decision-making process involving nZVI in order to ensure its sustainable development and use.

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