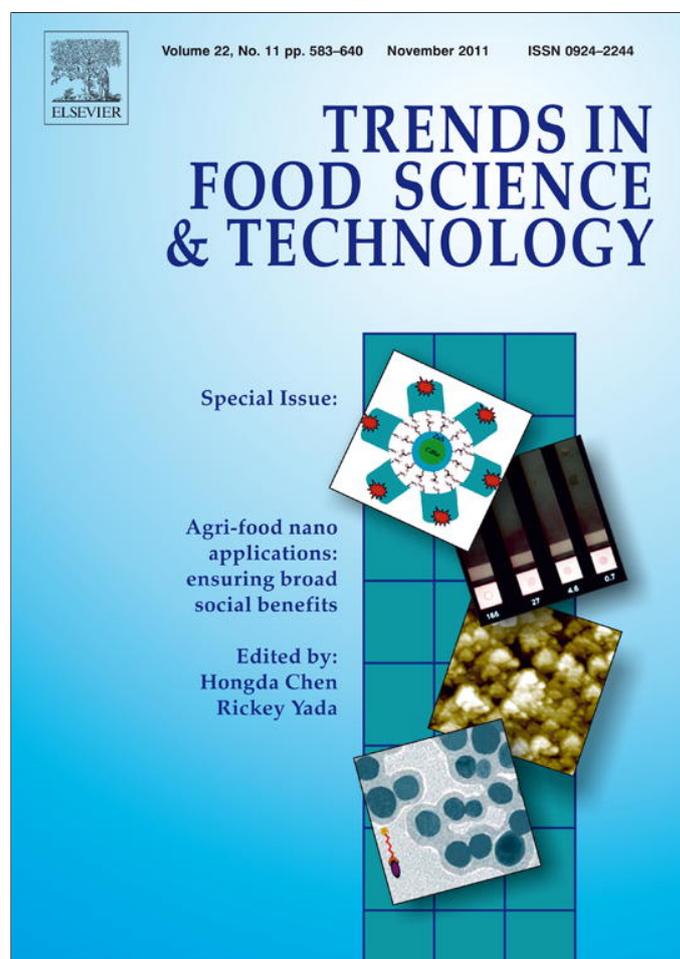


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Nanotechnology-enabled water treatment and reuse: emerging opportunities and challenges for developing countries

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The availability of clean water is necessary for all aspects of food production, preparation, distribution and consumption. Yet the magnitude, intensity and diversity of water pollution and the depletion of some water resources continue to grow, reducing the availability of clean, usable water and raising the potential for a water-related crisis that would have a severe impact on food processes. These impacts could be especially severe in developing nations where water supplies and treatment technologies are limited. Nanotechnology shows great promise as a feasible means of treating both long-standing and emerging water contaminants, as well as enabling technologies such as desalination of seawater to increase water supply. However, some engineered nanomaterials could also become water pollutants that threaten public and ecosystem health. Accordingly, this paper considers both the applications and implications of nanotechnology within the context of water quality and water security for developing countries.

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Introduction

Ensuring reliable access to inexpensive and clean sources of water is an overriding global challenge noted as one of the Millennium Development Goals of the United Nations (to “halve, by 2015, the proportion of the population without sustainable access to safe drinking water and basic sanitation” <http://www.un.org/millenniumgoals/>). This challenge is rapidly growing as the world’s population increases; global climate change threatens to take away a large fraction of already scarce fresh water resource due to seawater intrusion; municipal and industrial wastes continue to pollute water supplies; and larger quantities of water are used to produce increasing amounts of energy from traditional sources. These processes combine to reduce the amount of clean, available water for food production, even as agriculture draws more and more of the diminishing water supply. Additionally the runoff from agricultural use is often laden with pesticides, fertilizers and other chemicals which further limit the availability of clean, usable water. The growing toll of these processes on the water supply will likely result in the need for policy and technology changes to safeguard against shortages in the future.

The need for a sustainable and safe water supply is particularly compelling for developing countries, not only in rural villages but also in metropolitan areas experiencing a tendency towards mega-urbanization coupled with a lack of adequate infrastructure to purify and treat wastewater. The risks associated with water quality deterioration during distribution through aged centralized systems as well as the high energy demand for distributing water call for both a paradigm shift in water management and for technology reform.

Vision for distributed nanotechnology-enabled water treatment and reuse

Nanotechnology can enable a distributed water reuse and treatment paradigm and offer leapfrogging opportunities to obviate concerns of water quality degradation within distribution networks, alleviate dependence on major system infrastructure, exploit alternative water sources (e.g., recycled new water) for potable and agricultural use, and abate energy consumption. This vision may be particularly appropriate for developing countries that face rapid degradation of water quality with increasing pressure for cleaner water to meet more stringent environmental, public health and food safety standards. This scenario underscores the

need for a new class of “high performance” water treatment technology. Future urban systems in developing countries will likely increasingly rely on nanotechnology-enabled water monitoring, treatment and reuse systems that target a wide variety of water pollutants and are affordable and easy to operate. This will also contribute towards a zero-discharge paradigm, which is an ultimate goal of sustainable urban water management. Examples of engineered nanomaterials (ENMs) that can enable this vision are summarized in Table 1. Such novel technologies for water treatment at both point-of-use and community scale are of great value for increasing the effectiveness and robustness of water distribution networks, allowing access to clean water to users that are not connected to a central network, and for emergency response following catastrophic events.

Examples of research and development activities

Although nanotechnology-enabled water treatment and reuse is still far from full-scale application, there is considerable lab scale research activity that has yielded promising results, and several pilot-scale and commercial applications are beginning to emerge (Haldane, 2010; He, Zhao, & Paul,

2010; Radjenovic, Sirtor, Petrovic, Barcelo, & Malato 2009). ENMs primarily silver nanoparticles, have been used in household water filters (Oyanedel-Craver & Smith, 2008). Current research on nanotechnology-enabled water treatment has focused on four major areas: 1) adsorptive removal of pollutants; 2) catalytic degradation; 3) disinfection and microbial control; and 4) membrane filtration and desalination (Li et al., 2008).

Nanomaterials can be superior adsorbents because of their extremely high specific surface area. Magnetic nano-adsorbents are particularly attractive as they can be easily retained and separated from water. The high adsorptive efficiency of magnetite nanoparticles can be used for removing heavy metals (e.g., arsenic) and radionuclides from water. The super-paramagnetic properties of nano-magnetite allow separation under low magnetic fields to enable recycling and reuse (Mayo et al., 2007). This technology was selected by Forbes magazine as one of the top five nanotechnology breakthroughs of 2006, and is currently being tested by Rice University at the pilot-scale in sand filters in Mexico. (http://www.forbes.com/2006/12/26/nanotech-breakthroughs-ibm-pf-guru-in_jw_1227soapbox_inl.html)

Many nanomaterials have catalytic and photocatalytic properties that can be used for oxidative or reductive degradation of chemical pollutants commonly associated with agriculture (e.g., pesticides and antibiotics) as well as for disinfection. Potent bacterial and viral inactivation capacity has been demonstrated for functionalized fullerenes and TiO₂-based nanocomposites in the presence of visible and UV light (Dunlop, Byrne Manga, & Eggins, 2002). This approach represents a significant improvement over current chemical disinfection methods that produce harmful disinfection byproducts and are ineffective to disinfectant-resistant pathogens such as *Cryptosporidium* and *Giardia*. The same process can be used to treat recalcitrant pollutants such as pesticides, residual antibiotics, pharmaceutical compounds and other endocrine disruptors (Lee et al., 2009). Superior (hyper)catalysts, consisting of palladium-coated gold nanoparticles, have also been developed to promote rapid dechlorination of organic solvents such as trichloroethylene (Nutt, Hughes, & Wong, 2005; Wong et al., 2008).

The remediation of groundwater contaminated by oxidized pollutants can be significantly enhanced by the use of nano-scale zero-valent iron (NZVI), a powerful reductant ($E_h^\circ = -409$ mV) that can be used to dechlorinate TCE or reductively immobilize some heavy metals such as Cr(VI) or radionuclides such as U(VI). Pilot field studies have demonstrated the feasibility to inject NZVI into contaminated aquifers to create reactive zones or permeable reactive iron barriers that intercept and destroy priority pollutants (He et al., 2010). NZVI is particularly attractive for source-zone remediation.

Biofilm formation in water distribution and storage systems harbors pathogens and can cause biocorrosion. A promising approach to prevent these problems without formation of disinfection byproducts or use of toxic biocides is

| Desirable ENM properties | Examples of ENM-enabled technologies | References |
|---|--|---|
| Large surface area to volume ratio | Superior sorbents with high, irreversible adsorption capacity (e.g., nano-magnetite to remove arsenic and other heavy metals) and reactants (NZVI) | Mayo et al. (2007) |
| Enhanced catalytic properties | Hypercatalysts for advanced oxidation (TiO ₂ & fullerene-based photocatalysts) & reduction processes (Pd/Au) to treat residual pesticides and other priority pollutants | Hoffman et al. (1995), Nutt et al. (2005) |
| Antimicrobial properties | Disinfection without harmful byproducts (e.g., enhanced solar and UV disinfection by TiO ₂ & derivatized fullerenes) | Lee et al. (2009); Yang et al. (2009) |
| Multi-functionality (antibiotic, catalytic, etc.) | Fouling-resistant (self-cleaning) multi-functional filtration membranes that inactivate virus and destroy organic contaminants | Zodrow et al. (2009) |
| Self-assembly on surfaces | Surface structures that decrease bacterial adhesion, biofilm formation and corrosion of water distribution and storage systems | Nel et al. (2009) |
| High conductivity | Novel electrodes for capacitive deionization (electro-sorption) and low-cost, energy-efficient desalination of high salinity water | Oren (2007) |
| Fluorescence | Sensitive sensors to detect pathogens and other priority pollutants | Bogue (2009) |

to create biofouling resistant surfaces by manipulating surface physical structures at the micro and nano-scale, a mechanism used by marine organisms (dolphins and sharks) and plants (lotus leaf) to prevent bioadhesion. A combination of advanced photolithography, nanoparticle surface assembly and novel nano-template based methods could be used to create surface patterns that inhibit bacterial adhesion (Nel *et al.*, 2009).

Development of multi-functional membranes is another area where nanotechnology may revolutionize water treatment. The application of membranes for drinking water and wastewater treatment is rapidly growing. Especially for areas where fresh water supply is limited, the need for brackish ground water and seawater desalination as well as potable reuse of wastewater requires high-efficiency membrane systems. In spite of the advantages membrane systems offer, the inherent problem of membrane fouling, e.g., scaling, organic fouling and biofouling, poses the biggest obstacle to their broader application. In addition, the large plethora of contaminants in water and the diversity in their properties usually requires multiple stages of treatment. Incorporation of functional (e.g., adsorptive, (photo) catalytic and antimicrobial) nanomaterials into water treatment membranes offers the opportunity to achieve multiple treatment goals in a single step while protecting membranes from fouling (Zodrow, Brunet, Mahendra, Li, & Alvarez, 2009). For example, when irradiated by low energy UV light, TiO₂ is bactericidal and can degrade a wide range of organic contaminants including natural organic matter, a major membrane foulant. Furthermore, Ag(0) nanoparticles (and the Ag⁺ that they release) can inhibit bacterial adhesion and growth (Yang, Lin, & Huang 2009). While they have many advantageous properties, there may be several drawbacks to the use of such metal-based nanoparticles, including a potential co-selection for antibiotic-resistance in bacteria that harbor metal-resistance and antibiotic-resistance genes in the same operon (Baker-Austin, Wright, Stepanauskas, & McArthur, 2006).

Nanotechnology could also help improve the energy efficiency of existing desalination technologies and develop novel, low energy consumption methods for desalination (Lind, Jeong, Subramani, Huang, & Hoek 2009). Seawater is becoming an important source of water supply in many areas in the world, and as freshwater reserves continue to shrink, more and more of the world may require desalination for domestic, industrial and agricultural water supply. However, existing seawater desalination technologies are highly energy intensive. Utilization of nanomaterials has been explored to increase efficiency of membrane based desalination. Capacitive deionization (CDI) is a process that promises to provide a low-cost, energy-efficient technology for desalination. Removing salts by cation and anion electro-sorption in electrically conducting and porous electrodes, CDI avoids the high pressure required in reverse osmosis (RO) and high temperature required in multi-stage flash processes, and provides high water recovery (Oren,

2007). The theoretically calculated as well as experimentally estimated energy consumption of CDI is more than an order of magnitude lower than RO. The current technology limitation lies in the low conductivity and low specific surface area of electrodes. Novel electrodes with super high conductivity and surface area are being developed by employing vertically aligned carbon nanotubes, and their applicability for use in CDI treatment of high salinity water is being tested.

While all of these advances have significant technical merit and innovation potential, it is important to determine when it is feasible to incorporate them either as a starting place, or for replacing or augmenting existing technologies. ENM-enhanced water treatment is best suited for situations in which 1) current technologies for removing specific contaminants are not sufficient to meet water quality standards (or to protect public health if specific standards have not been developed yet); 2) removal of hazardous and recalcitrant micro-pollutants that escape wastewater treatment plants are necessary to ensure beneficial disposal of the effluent (e.g., as agricultural irrigation water; 3) there is insufficient infrastructure for conventional water treatment and one must rely on point-of-use technologies; and/or 4) the nanomaterials enhance the cost-effectiveness of the treatment process. Several of these conditions are often met in developing nations, especially where there is water scarcity, limited water treatment infrastructure in place, and the lack of funding for centralized facilities. The potential of nanotechnology to support decentralized water/wastewater systems that allow differential treatment and multi-purpose reuse while minimizing transport-related energy consumption and water quality deterioration makes it very attractive for developing countries that are starting to establish their water and wastewater systems.

Potential risks to human and ecosystem health

The nanotechnology revolution has a great potential to enhance not only water purification but also a wide variety of products, services, and industries, including the food sector. This promise, however, may be offset by the concern that some ENMs are toxic and may become a new class of hazardous pollutants that threaten public and ecosystem health if accidentally or incidentally released to the environment. Therefore, it is important to understand how released ENMs migrate, behave, and interact with living organisms and the abiotic components of the environment, and take proactive steps towards the long-term goal of safer design and disposal of ENM-containing products (Alvarez, Colvin, Lead, & Stone, 2009; Klaine *et al.*, 2008). Although the recognition of the environmental, health and safety issues of ENMs have been rising, research activities in this area are comparatively low, producing only about 5% of the total papers in environmental nanotechnology (Fig. 1).

Whether ENMs could be designed to be “safe” and still display the properties that make them useful is an outstanding question. Focusing on exposure control rather than

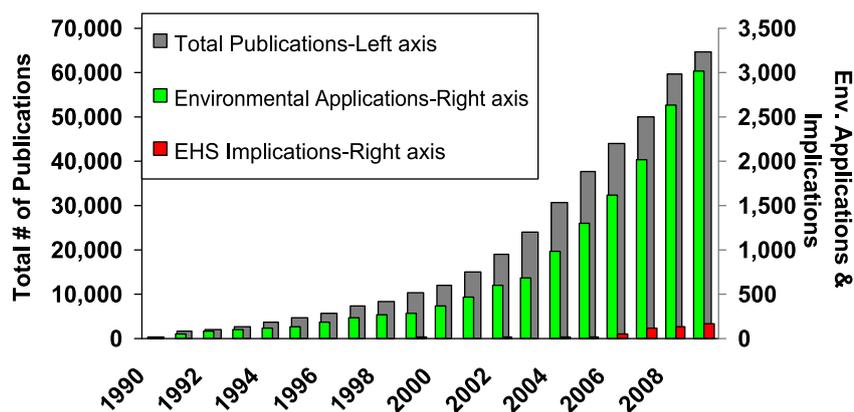


Fig. 1. Comparison of the total number of nano-related publications to the number of publications on environmental applications and implications (i.e., environmental health and safety, EHS) of nanotechnology (Source: ISI Web of Science, May 2010).

suppressing intrinsic reactivity that contributes to toxicity might be appropriate in many cases. Thus, risk abatement options worthy of consideration include tailored coatings that reduce bioavailability or mobility, on-board packaging, and special disposal strategies. The modern chemical industry has demonstrated that some substances can be re-engineered to create safer, greener, and yet effective products. Encouraging examples include the replacement of branched alkylbenzene sulfonate surfactants, which caused excessive foaming in the environment, with biodegradable linear homologues, as well as the replacement of ozone-depleting chlorofluorocarbons by less harmful and less persistent hydrochlorofluorocarbons. Thus, it is important to discern the functionalities and physicochemical properties that potentially make ENMs harmful, and determine which ecological receptors and ecosystem services might be at higher risks. Accordingly, priority research areas to inform the eco-responsible design and disposal of ENMs include (for details, see Alvarez *et al.*, 2009):

1. *Structure–activity relationships for ENMs in the environment.* Modifying the physical and chemical properties of an ENM to affect its mobility, reactivity, bioavailability and toxicity.
2. *Metrology, quantification and tracing of ENMs.* Analytical capabilities are needed to quantify ENMs in complex environmental and biological matrices (without alteration during separation and concentration) and determine the form that will reach receptors after they aggregate, dissolve, acquire/lose coatings, or undergo other transformations in the environment.
3. *Bioavailability and sub-lethal effects.* Standardized protocols are needed to investigate ENM cellular uptake mechanisms, trophic transfer and biomagnification potential (including discerning likely entry points into food webs) and sub-lethal effects that can also influence ecosystem services such as primary productivity, nutrient cycling, and waste degradation.
4. *Predictive modeling of multimedia fate and transport.* Computational models that predict the form and

concentration of ENMs at the point of exposure will be important to identify the most susceptible compartments and ecological receptors and assess the associated risks.

5. *Disposal scenarios and release dynamics.* Immobilization and separation technologies need to be developed to retain ENMs in systems where their functions are desired. Meanwhile, sources and discharges into various compartments must be quantified (including ENM leaching from products) as a first step to predict exposure and to evaluate the need for interception or remediation technologies.

Sustainability of nanotechnology requires that nanomaterials be more than just “safe”. Adopting principles of industrial ecology and pollution prevention should also be a high priority to steward ecologically-responsible nanotechnology (Table 2. See also Alvarez *et al.*, 2009; Anastas & Zimmerman, 2003; Klaine *et al.*, 2008; Lee, Mahendra & Alvarez, 2010). For example, antimicrobial nanoparticles made of natural materials such as peptides and chitosan (Li *et al.*, 2008) can be used in place of those containing heavy metals (e.g., nanosilver); stimuli-responsive surface coatings can be developed to control stability of the nanoparticles so that they disperse or coagulate as needed; low-cost, locally available raw materials (e.g., clay, biomass and other carbon forms, and iron rust) as well as green synthesis methods should be considered first. Such measures can help apply nanotechnology for sustainable water management while avoiding unintended impacts.

Barriers for implementation in developing countries

Insufficient technical capacity/knowledge needed to apply an advanced technology might be an initial implementation barrier that could be relatively easy to overcome with an appropriate technology transfer program. This premise is supported by the widespread use of cell phones in developing nations.

Table 2. The 12 principles of ecologically-responsible nanotechnology (adapted from Anastas & Zimmerman, 2003)

1. Inherent rather than circumstantial (use raw materials and elements that are inherently non-hazardous if dissolved or otherwise released)
2. Prevention rather than treatment (containment, minimize exposure by choosing appropriate coatings, *design away hazardous functionalities or features without impacting useful functions*)
3. Design for separation and purification of nano construction wastes (take advantage of magnetic properties for separation, stabilized coatings that can be intentionally removed after use to coagulate and precipitate ENMs, introduce surface properties to enable facile aggregation after environmental release)
4. Maximize mass, energy, space, and time efficiency (use multi-functional ENMs, quality > quantity, need > greed, enough > more, long-term > short-term)
5. "Output-pulled" rather than "input-pushed" use of energy and materials (drive manufacturing reactions to completion by removing products rather than increasing inputs of materials or energy, according to Le Châtelier's principle [Sawyer, McCarty, & Parkin 2003]).
6. Find opportunities for recycle, reuse or beneficial disposal
7. Target durability rather than immortality (avoid indefinite persistence)
8. Need rather than excess - don't design for unnecessary capacity – avoid "one size fits all" (incorporate just what you need, avoid excess ENMs in commercial products)
9. Minimize material diversity to strive for material unification and promote disassembly and value retention (minimize variability and sources of a given ENM)
10. Integrate local material and energy flows (holistic life cycle analysis perspective, look for interconnectivity, system of systems)
11. Design for commercial "afterlife" (enable recycling, remanufacturing and/or reuse opportunities, beneficial disposal)
12. Use renewable & readily available inputs through life cycle (minimize carbon, land use and water footprint)

Although the manufacturing costs of some ENMs (e.g., nano-magnetite) are predicted to be relatively low in the near future, the current high cost of many ENMs is and may remain the main barrier for application in the water sector, especially in developing nations. Current costs of some ENMs are known (Table 3) but the cost normalized to the volume of water treated is unknown since their lifetime capacity (including recyclability) has rarely been tested to exhaustion. In addition, currently available cost information for many ENMs is based on small scale production and research-grade materials. These complications preclude meaningful cost comparison with existing technologies. Despite the current high cost of nano-enabled products, their use in the water sector is likely to increase at the point-of-use/entry scale because of (1) highly valuable properties imparted at relatively low additive ratios; (2) rapid development of new applications harnessing unique nano-scale properties; (3) decreasing trend in cost of nano-enabled products; and (4) savings on capital investment for centralized infrastructure. The feasibility of ENMs

Table 3. Prices of selected nanomaterials of interest to the water sector

| Nanomaterial | Price in 2010 (US\$/gram) |
|-------------------------------|---------------------------|
| Nano zero-valent iron | 0.14 |
| Nano TiO ₂ | 0.18 |
| Nano-Magnetite | 0.44 |
| Nano Iron-Oxide | 1.20 |
| Nano Silver | 19.60 |
| Fullerenes (C ₆₀) | 330.00 |

Zero-valent Iron, TiO₂ and Magnetite are currently available in (semi) bulk quantities. Others are more expensive research-grade materials.

for water treatment could be significantly enhanced by their ability to be reused multiple times. ENM-enabled point-of-use technologies could be particularly beneficial in rural developing countries or expanding megacities, where large-scale centralized water treatment is impractical or unfeasible.

Large-scale treatment plants can provide treated water at costs of as little as US \$0.1 to \$0.3 per 1000 gallons of treated water. However, the initial capital cost of constructing the facilities is prohibitively large for developing countries (millions of dollars). Smaller point-of-use treatment systems provide relative independence from extensive infrastructure and are much more reasonable in initial cost (on the order of US \$100) but may require much higher operating costs—as much as \$100 per 1000 gallons treated for highly advanced point-of-use treatment systems. In order to be economically competitive in this cost range, current prices of nanomaterials would require that 1000 gallons of water be treated by 200 g of titanium dioxide or 100 mg of fullerenes. As technology grows and prices of nanomaterials fall, and ENM recycling opportunities are identified, the feasibility of ENMs to purify water will increase—especially in view of the enhanced capabilities that can be imparted at low additive ratios.

Food industries in developing nations generally have access to water that has been treated to some extent. However, as demand for water quantity and higher quality continues to grow, high performance water treatment technologies will become vital for the safe production and distribution of food throughout the world. Furthermore, ENMs may enable treatment of processed and wastewater from food production for reuse and recycling, adding further benefit to the industries and communities they serve. While ENM-enhanced water treatment may remain too expensive for the general population in developing countries for some time, the food industry could provide an impetus for positive change while finding ways to better meet their own needs and opportunities through the use of nanotechnology.

Conclusions

Food industries provide a unique nexus between demand and impact in water usage. Agricultural and production

demands for water are rapidly increasing in developing countries, while the importance of clean and safe water will continue to grow as health and environmental standards become more stringent. ENMs have great potential to meet current and growing clean water demands throughout the world as cost and technical capacity barriers are overcome. As the science and engineering of nanomaterials continue to grow, these improvements will likely come more and more rapidly. For instance, the ability to use low-cost, natural source materials and green manufacturing will reduce the environmental footprint and cost of nanomaterials. Additionally many of these technologies can take advantage of regeneration, reuse and recycling of ENMs to increase yield and further reduce cost – which is perhaps the most critical current barrier for developing nations. As the range and scope of pollution in water systems continue to increase we may see specialized treatment processes wherein nanotechnology can fill the gaps where conventional water treatment is either marginally effective or not feasible. Finally, efforts to control the release of ENMs into water systems will mitigate the environmental risk (and associated potential liabilities) until fate, transport and eventual impact of these materials are better understood.

Developing nations have a distinctive window of opportunity to adopt novel, appropriate water treatment technologies. Locations currently lacking extensive water infrastructure (e.g., expanding megacities) are less constrained to follow traditional paradigms (e.g., centralized treatment) and can more easily adopt point-of-use water treatment strategies that hold many significant advantages to traditional centralized systems. These ENM-enabled technologies require far less initial capital, eliminate the need for skilled operators of complex systems and allow for differential treatment of water (e.g., drinking, domestic and agriculture uses require different treatment levels). While the immersion of new technology in these areas can be difficult, the rapid dissemination of cell phone technology (which obviated the need for traditional infrastructure, such as land lines) shows that these problems can be overcome.

As water becomes scarcer and more contaminated the food industry stands to gain much from advanced technology that would provide cleaner and more plentiful water supplies. Nanotechnology has the potential to meet these water-related needs in an inexpensive, efficient, yet flexible way that is crucial for developing nations. It is important to capitalize on the leapfrogging opportunities offered by nanotechnology to improve and protect water quality and quantity. Furthermore, proactively assessing and mitigating potential environmental impacts of nanotechnology in the early stages of its development may result in better, safer products and less long-term liability for the industry. Indeed, due diligence is needed to ensure that nanotechnology evolves as a tool to improve material and social conditions without exceeding the ecological capabilities that support them.

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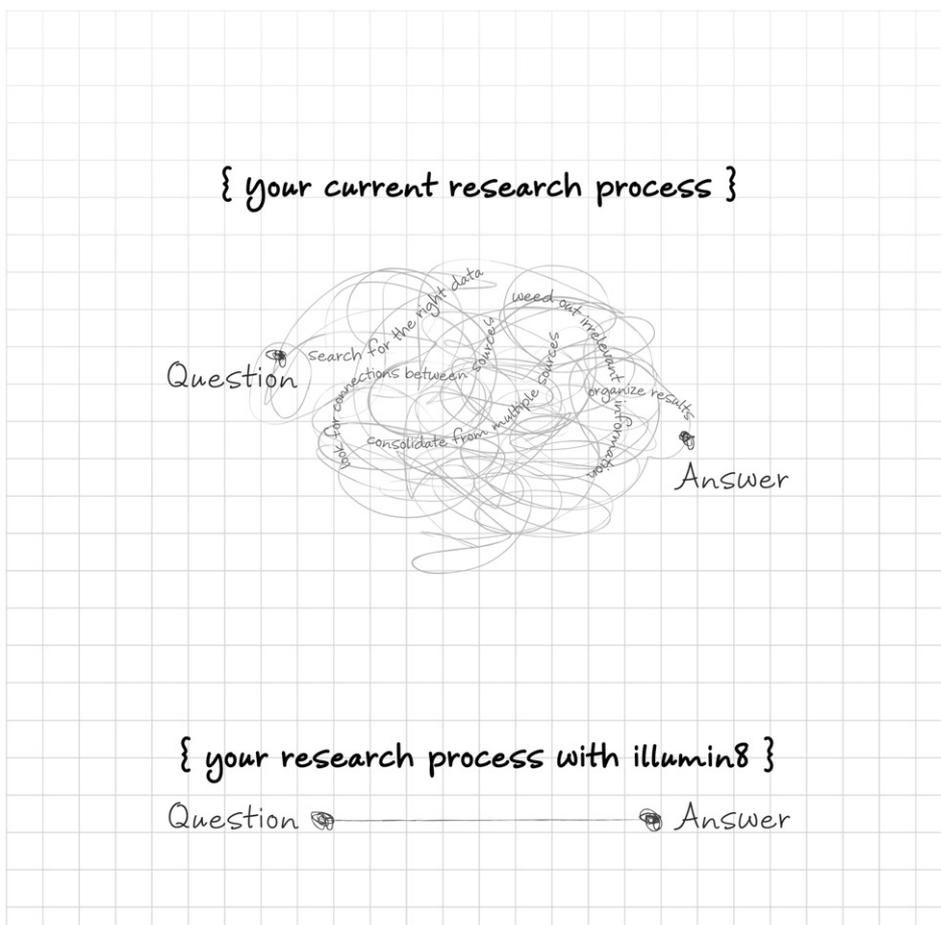
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