

POTENTIAL IMPACTS OF NANOPARTICLES ON WATER RECLAMATION

Dr. Rajagopalan Ganesh, Kennedy/Jenks Consultants, Irvine, CA
Dr. Lawrence Y.C. Leong, Kennedy/Jenks Consultants, Irvine, CA

Introduction

Nanotechnology is an emerging technology that could impact a wide range of industries in the near future. Nanotechnology involves production and use of extremely small particles (1 – 100 nm size scale), wherein the particle synthesis is controlled or manipulated at the molecular level (1). The nanoparticles are often used for industrial/commercial applications due to their extremely high reactivity compared to commercial grade bulk materials. The high reactivity of the nanoparticles is contributed by several factors. First, the extremely small size of the nanoparticles provides orders of magnitude higher surface area (reaction sites) per unit mass of the media. In addition, the nanoparticles have a larger number of atoms on their surface, higher porosity and small crystallite structures, all of which enhance their reactivity. Yet another reason the nanoparticles use is increasing is that the “bottom-up” approach (synthesis of particles from molecular level manipulation) involved in the production of these particles facilitates incorporation of other desired structural characteristics for optimum contaminant treatment (2). In other words, nanotechnology provides an opportunity to synthesize stable, “new” materials that can not be synthesized using conventional synthesis techniques.

Due to these unique advantages, the market size for nanotechnology products is predicted to grow exponentially to \$1 trillion by year 2015. Just in the recent years over 200 products containing engineered nanomaterials have been introduced into the market (3). The major industries currently using nanomaterials include personal care products, pharmaceutical, automobile, electronics, paints and coating industries. Sun screens, cosmetic products, drug delivery systems, batteries, spill resistant fabrics, wear resistant protective coatings, heat transfer fluids, durable tennis balls and point of use filters are some of the products that contain nanoparticles. The type of nanomaterials used in these products include i) carbon-dots, a carbon based material with a fundamentally unique carbon molecular structure, ii) Single or multi wall nanotubes (SWNT/MWNT) that are less than 10 nm thick and a few micrometer long, and behave as nano “fibers”; iii) metal oxide nanoparticles (e.g. ZnO, TiO₂, SiO₂, CeO₂, LiCoO₂) used in personal care products, semiconductor polishing, batteries and fuel cells, and iv) nanostructured polymers and surfactants used in drug delivery and environmental remediation. Nanoparticles are used as nanopowders, nanofibers or nanoaggregates in various applications.

Although the use of nanomaterials is rapidly increasing, very little is currently known about their fate, transport and toxicity effects of nanoparticles in the environment. EPA and other organizations have recently initiated studies to evaluate some of these issues. Preliminary data from these studies show evidence of adverse health effects due to exposure to nanoparticles, and support the need for detailed evaluation (4). For example, the extremely small size of the nanoparticles may facilitate their transport across human organs or bacterial membranes, and cause cellular, subcellular and protein level damage (5). The nanoparticles, upon their entry into human system, have the ability to generate reactive oxygen species (ROS) and cause lung injury (6). The potential for some nanoparticles to travel throughout the body, deposit in target organs, penetrate cell membranes, lodge into mitochondria and cause injuries has been reported (7). Intradermally injected quantum dots have been found to migrate to regional lymph nodes in animals (8). This could potentially lead to effects on the immune system (7).

The increasing use of nanoparticles in everyday products increases the potential for their release in water sources and wastewater streams. The same unique characteristics for which the nanomaterials are used in manufactured products can affect water reclamation process when they are released into the waste streams. A recent report from EPA indicates that the fate of nano-sized particles in wastewater treatment plants is not well understood (9). The release of nanoparticles into the wastewater streams may have the following implications for water reclamation:

- When present in trace levels ($\mu\text{g/l}$ range), based on toxicity study data, some nanoparticles may potentially be added to the list of constituents to be removed prior to water recharge/reuse applications.
- When present in higher concentration (say, mg/l range) the nanoparticles may impact the performance of waste treatment processes by various mechanisms, including inhibition of microorganisms in activated sludge, increasing the turbidity, fouling of UF/RO membranes or affecting the efficiency of disinfection processes.

It is a well known fact that particle size distribution in wastewater streams can impact the efficiency of particles removal during water reclamation (10). While the mechanisms of particle transport and the impact of particle size during wastewater treatment are well studied for conventional, micron-sized pollutants, very little information is currently available on the fate of nanoscale materials (naturally occurring or engineered) in treatment processes. Only recently a limited number of studies have been initiated to elucidate fate of nanoparticles in aquatic environment by i) refining the existing transport models (11), and ii) preliminary laboratory scale studies (12). In addition to their smaller particle size, yet another factor that could complicate the fate of nanoparticles in water reclamation is the functionalization of these particles for several applications. Functionalization is the process by which organic/surfactant molecules are attached to the nanoparticles to keep them in dispersed state. As a result, nanoparticles may behave very differently than conventional, dissolved contaminants as well as micron sized suspended particles during wastewater treatment. This paper attempts to summarize available information from literature on the potential impact of nanoparticles during water reclamation.

Fate of Nanoparticles on Water Reclamation Processes

Figure 1 is a schematic of various process units involved in water reclamation. The reclamation processes typically include primary settling, activated sludge process, secondary sludge settling, filtration and disinfection. Coagulation and membrane filtration are also used in water reclamation.

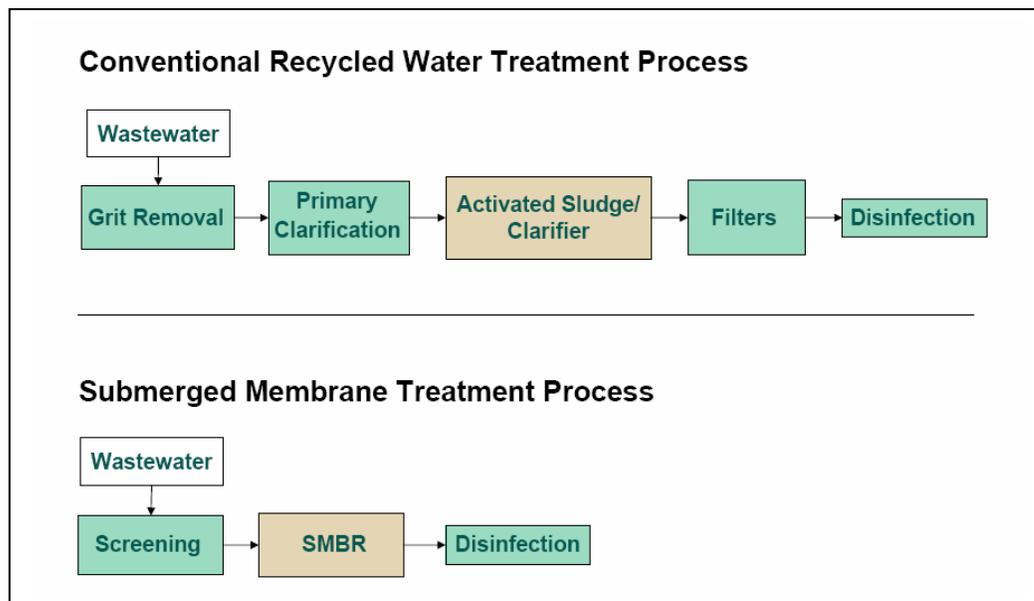


Figure 1. Simplified schematic of water reclamation processes

Nanoparticles in Primary Settling

Primary settling process is a solids-liquid separation process intended for removal of suspended, micron sized or larger inorganic particles. Under laminar flow conditions particle settling in sedimentation tank can be expressed by the following equation:

$$V_s = \frac{g}{18\mu} * (\rho_s - \rho) * d^2 \quad (1)$$

Where:

V_s = Settling velocity; g = Acceleration due to gravity; ρ_s = Mass density of the particle; ρ = Mass density of water; d = diameter of the particle.

As indicated in the above equation, settling velocity of particles is an exponential function of particle size. Accordingly, settling velocity of nanoparticles will be several orders of magnitude slower and hence, settling time orders of magnitude higher than micron/submicron sized particles of the same material. Hence, without the addition of coagulant and flocculants to enhance the mean particle size, or

without the adsorption of nanoparticles to large inorganic particles, nanoparticles are unlikely to be removed in the primary sedimentation tanks.

Nanoparticles in Activated Sludge Process

No systematic studies have been performed to date to evaluate i) removal of nanoparticles in activated sludge process, and ii) impact of nanoparticles to the biomass. Ivanov et al., (13) evaluated retention of nano/micro latex beads (0.1, 0.6 and 4.2 μ) and cells of *E. coli* by microbial self-aggregated granules in wastewater treatment plants. Microbial granules are spherical biofilm structures where microbes are attached to each other and embedded in an extracellular matrix (13). Approximately 10 % of 0.1 and 0.6 μ particles were removed by the biofilm after 60 minutes of incubation. Furthermore, these particles penetrated only to the top 250 to 300 μ m from the edge of the granule. Cells of *E. Coli* on the other hand penetrated to approximately 800 μ m of the biofilm. Results from these studies indicated that some nanoparticles can be removed by adsorption to activated sludge. However, more studies are required to evaluate the extent of nanoparticles adsorption to activated sludge, their removal in secondary clarifiers as well as their fate during sludge digestion processes.

Fortner et al., (14) evaluated the toxicity of nanoscale carbon fullerene (nano-C60) to two facultative nitrate reducing soil bacteria. Nano-C60 is unique type of carbon nanoparticles that are candidates for a variety of applications including drug delivery and energy conversion (15). One of the bacteria used in this study (*E. Coli*) is a gram negative bacterium, and the other bacterium (*B. subtilis*) is a gram positive bacteria. Nano-C60, at 0.4 mg/l concentration, inhibited the growth of both the microorganisms when grown in a basic media. Furthermore, when 4 mg/l of nano C-60 was added to these bacterial cells during their log growth phase, their respiration rate slowed down significantly. Although these studies were performed using soil microorganisms, results suggested that nanoparticles have the potential to inhibit activated sludge process during water reclamation.

Removal of Nanoparticles During Granular Filtration

In water and wastewater treatment, filtration theories have long been developed to describe particle transport in the filter media. The major mechanisms that impact the filtration of particles during water treatment include interception, sedimentation, and Brownian diffusion (14). Interception of particles in the filter bed occurs when the particles come in contact with the media due to their finite size. This mechanism of immobilization is generally more relevant for particles of larger size (e.g. 0.4-0.6 μ m range) than nanoscale materials. Immobilization through sedimentation occurs when the densities of the particles are significantly higher than those of the surrounding media, or the velocity of flow is significantly lower. Brownian diffusion causes agglomeration of smaller particles (e.g. nanoparticles) with each other and with filter grains, and results in their immobilization. Models describing these interactions have been developed over several decades for effective filtration process design. Recently, Tufenkji, & Elimelech (15) have developed the following empirical model, further refining the previous equations to incorporate hydrodynamic interactions and universal van der Waals attractions, to describe the filtration process for water treatment:

$$\eta = 2.4A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.554A_S N_R^{1.675} N_A^{0.125} + 0.22N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053} \quad (2)$$

Where

η - collector efficiency; A_S – Porosity Function; N_R – Aspect ratio of particle

N_{Pe} – Peclet number characterizing the ratio of convective to diffusive transport

N_{vdw} – van der Waals number characterizing the van der Waals interaction energy to particle thermal energy

N_A – Attraction number describing influence of van der Waals forces and fluid velocity on particle deposition

N_G – Gravity number describing the ratio of Stokes particle settling velocity to approach velocity of the fluid

Schrick, et al., (11) used this filtration model to partially explain delivery of zerovalent metal nanoparticles in soil. Based on the above model, they developed a relationship between the particle size and the filtration length (distance traveled by nanoparticles in the soil column at which the particle concentration falls to $1/e$ of the initial concentration). Results from their work suggested that the filtration length for iron particles is the highest at a particle size range of 0.4 to 0.6 μm . At typical nanoparticle sizes of < 200 nm, particles are often immobilized quickly due to Brownian collisions. Aim et al., (16) evaluated filtration of micron and sub-micron sized latex microspheres (0.46 μ , 0.87 μ and 3 μ) in laboratory scale granular bed filtration columns. Three sizes of filter grains (0.1, 0.175 and 0.45 mm) were used in these columns. Clean bed filtration efficiency (initial stage) as well as transient stage (after filter ripening) filtration were evaluated. During the initial stages, prior to filter ripening, removal efficiency for the 0.8 μ size particles was significantly lower than that for 0.4 μ or 3 μ sized particles in all the three filter media. This is somewhat consistent with the prediction of Schrick, et al (11). However, this trend no longer existed after filter ripening. Smaller size particles (0.4 μ) broke through more rapidly than the larger size particles in all the three columns. The largest size particles were retained better in all the studies. These observations indicated that long term studies need to be performed to evaluate nanoparticles transport in filter units.

Nanoparticles Removal in Membrane Processes

The impact of colloidal particles size on the fouling of pressurized membranes (UF, MF, NF and RO) has been evaluated through modeling and laboratory scale studies (17, 18). In general, during membrane treatment, colloidal/suspended particles are subjected to various forces including van der Waals attraction, permeation drag and sedimentation that pull the particles closer to the membrane surface and inertial lift, double layer repulsion, axial drag and drag torque and Brownian diffusion that move the particles away from the membranes (17). The net effect of these forces on the particles depends on the particle characteristics and flow conditions. Wiesner and Chellam (17) developed a theoretical model that included these interactions. Accordingly, the predominant force acting on particles larger than 20 μm is the inertial lift, which prevented these particles from fouling the membranes. For particles smaller than 20 μm , the key forces that keep the particles away from the membrane surfaces (and hence, prevent fouling) are the back-brownian diffusion and shear-induced diffusion. By assuming a constant shear rate, they calculated the particle diffusivity as a function of particle size. Accordingly, the Brownian diffusion and orthokinetic forces are the lowest for particles at the size range of 0.1 μ (100 nm). These evaluations indicate that individual or agglomerated nanoparticles of about 100 nm have the highest potential to foul the membranes during treatment. At sizes smaller than 100 nm, the particles are likely to pass through the membranes, and may require pre or post treatment for their removal.

Aim et al., (16) evaluated removal of micron and sub-micron particles in dynamic microfiltration using a Couette system made of two coaxial cylinders. The Al_2O_3 microfiltration membrane had an average

pore size of 2 to 8 μm . Removal of suspended synthetic alumina particles of size 0.1 to 32 μm was evaluated. Their studies indicated that a decrease in particle size decreased the efficiency of particles removal. Only about 50% of the smallest size fraction ($d_{50} = 2.5 \mu$) was removed by the microfiltration membrane. Approximately 70 and 90% of larger size fractions ($d_{50} = 3.8$ and 4.2μ , respectively) were removed. The profile of particle size over time indicated that approximately 50% of the particles in the permeate stream were less than 0.5 μ (500 nm). Kwon and Vigneswaran (1998) evaluated influence of particle size (0.46, 3.2 and 12 μ) on cross flow microfiltration and reported that the increase in resistance of the membranes (0.2 μ pore size) was more sensitive to fouling by 0.46 μ particles than that by the larger particles. These findings are in general, in agreement with the predictions by Wiesner and Chellam(17).

Huang et al., (19) evaluated removal of nanosilica (80 to 200 nm) from semiconductor CIP water using pre-coagulation and microfiltration process (average pore size 0.45 μ). The initial nanosilica concentration was about 800 mg/l. The results indicated that, without any pre-coagulation, only about 50% of the nano-silica was removed by the membranes. Furthermore, significant fouling of the membranes was also observed under these conditions. Pre-coagulation with 30 mg/l of polyaluminum chloride (optimum dose) increased the filtration efficiency to 90%. The effluent nano-silica concentrations were still very high (~ 80 mg/l) in these samples. Roorda et al., (20) evaluated the impact of micro/nano particles (0.1 to 200 μ) on microfiltration. Their study indicated that, among the various fractions of particle size evaluated, a significant resistance to filterability (40 to 57%) was caused by particles of size 0.1 to 0.2 μ . Particles less than 0.1 μ caused about 12 to 29% of the resistance to flow. Particles larger than 0.2 μ size caused 30 to 36% resistance to filterability. All of these observations, in general, agree with the impact of particle size predicted by Wiesner and Chellam (17) that particles of about 0.1 μ are likely cause the most fouling during membrane treatment. Recently, Cho et al., (21) evaluated the Brownian and shear-induced diffusivity of nano and microparticles on cellulose membrane (1000 MW cutoff) using nano and micro particles (90 nm to 1 μ). Their studies indicated that minimum diffusion and hence, the highest fouling was observed for particles of 0.5 μ size. Particles smaller than that apparently passed through the membrane, and particles larger than that did not offer significant resistance to flow.

In summary, the theoretical as well as experimental observations indicate that, without any pretreatment such as coagulation, nanoparticles will either foul the membranes or will pass through the membranes requiring additional treatment for their eventual removal.

Coagulation and Precipitation of Nanoparticles

Coagulation and chemical precipitation are sometimes used as pretreatment for sedimentation or microfiltration during water reclamation. Coagulants are added to destabilize the suspended particles by charge neutralization or double layer compression. Very little information is currently available on the impact of particles size, particularly in the nanoparticle size range, on the efficiency of their removal by coagulation/flocculation mechanisms. Kvinnesland and Odegaard (22) evaluated coagulation of humic substances of size less than 0.1 μm using several cationic polymers. They defined coagulation as the filterability of polymer added humic substance by a 0.1 μ filter, and flocculation as filterability using 1.2 and 11 μ filters. Their study indicated that about 95% of the humic substances can be removed by coagulation using any of the polymers tested. Efficiency of polymer dose, in general was proportional to the charge density of the polymers. Approximately 1.5 to 2 mg of polymer per mg of carbon was required for the removal of nanosized humic substance. The flocculation efficiency, however, appeared

to be influenced by factors other than charge density of the polymers alone. A weak polycation chitosan polymer was more effective than some other polymers with higher charge.

Sanchis et al., (23) evaluated particle size distribution in a slaughterhouse wastewater before and after coagulation-flocculation treatment. Suspended particles were grouped into 0.5 μ size intervals up to 10 μ size. Efficiency suspended particles removal using alum alone was compared with that using alum and five different coagulation aids (activated silica, powdered activated carbon, precipitated calcium carbonate, polyacrylic acid and anionic polyacrylamide). Without any coagulation aid, alum removed about 87% of the suspended particles from the waste stream. Approximately 88% of removal was observed for particles smaller than 0.5 μ . All coagulation aids, except activated silica enhanced removal of particles smaller than 0.5 μ in their study. Polyacrylic acid was the most effective (99.3%) in removing particles of this size range in this study. Note that the concentration of suspended particles in the slaughterhouse waste is extremely high (~ 25,000 particles/ μ l) in these studies.

Recently, Westerhoff et al., (12) performed bench scale studies to evaluate removal of metal oxide nanoparticles (10 mg/l of aluminum, iron, titanium metal oxides and cadmium quantum dots) using various coagulants. Their studies indicated that, coagulation and sedimentation alone removed only 40 to 60% of the nanoparticles from the water. Filtration (0.45 or 3 μ filters) removed additional 50 to 80% of the remaining nanoparticles. Approximately 10 to 30% of the initially added nanoparticles still remained in the water after filtration.

Summary

In summary, the market for commercial and industrial products containing nanoparticles is increasing rapidly. Nanomaterials are significantly small, extremely reactive and behave very differently than micron-sized counterparts. Health impacts of exposure to nanoparticles are not currently well understood. Very limited information is available on the fate and transport of nanoparticles. Transport mechanisms for nanoscale materials in the water reclamation process are likely to be very different than conventional pollutants. More studies are required to understand the fate of nanoparticles during water reclamation.

References

1. National Nanotechnology Initiative (NNI): www.nano.gov.
2. Rolison, D.R. (2003), Catalytic Nanoarchitectures – the Importance of Nothing and the Unimportance of Periodicity. *Catalysis*. 299: pp. 1698 – 1701.
3. Woodrow Wilson International Center for Scholars. 2006. Project on Emerging Nanotechnologies. A nanotechnology Consumer Products Inventory. <http://www.nanotechproject.org/index.php?id=44>
4. Royal Society, London (2004), Nanoscience and nanotechnologies: Opportunities and Uncertainties”. <http://www.nanotec.org.uk/finalreport.htm>
5. Colvin, V.L. (2003), The Potential Environmental Impact of Engineered Nanoparticles. *Nature Biotechnology*. 21: pp. 1166 – 1170.

6. Donaldson, K. et al., (2004), Nanotoxicology. *Occupational and Environmental Medicine*. 67:727-728.
7. Nel, A., et al., (2006), Toxic potential of Materials at the Nanolevel. *Science*. 311: 622 – 627.
8. Kim, S. et al., (2004), Near-Infrared Fluorescent type II Quantum Dots for Sentinel Lymph Node Mapping. *Nature Biotechnology*. 22: 93 – 97.
9. United States Environmental Protection Agency (2005). Nanotechnology White paper. External Review Draft. December.
<http://es.epa.gov/ncer/nano/publications/whitepaper12022005.pdf>.
10. Lawler, Desmond, F. (1997), Particle Size Distribution in Treatment Processes: Theory and Practice. *Water Sci. Technol.* 36(4): pp 15-23.
11. Schrick, B. et al., (2004), Delivery Vehicles for Zerovalent Metal Nanoparticles in Soil and Groundwater. *Chem. Mater.* 16: pp. 2187 – 2193.
12. Westerhoff, Paul, et al., (2005). The Fate, Transport, Transformation and Toxicity of Manufactured Nanomaterials in Drinking water. 2005 Progress Report. EPA STAR Grant R831713.
http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/7387/report/0
13. Ivanov, V., Tay, J.H., Tay, S.T., Jiang, H.L. (2004), Removal of Micro-Particles by Microbial Granules used for Aerobic Wastewater Treatment. *Water Sci. Technol.* 50(12): pp. 147-154.
14. Fortner, J.D., Lyon, D.Y., Sayes, C.M., Boyd, A.M, Falkner, J.C., Hotze, E.M., Alemany, L.B, Tao, Y.J., Guo, W., Ausman, K.D., Colvin, V.L. and J.B. Hughes. (2005), C60 in water: Nanocrystal Formation and Microbial Response. *Environ. Sci. Technol.* 39:4307-4316.
15. Tufenkji, M. and Elimelech, M. 2004. *Environ. Sci. Technol.* 38(2):539-536
16. Aim, R. Ben., et al., (1997), Influence of Particle Size and Size Distribution in Granular Bed Filtration and Dynamic Microfiltration. *Water Sci. Technol.* 36(4): pp 207-215.
17. Wiesner, Mark, R. and Chellam, Shankararaman. (1992), Mass Transport Considerations for Pressure-Driven Membrane Processes. *J. AWWA*. January, pp. 88-95.
18. Kwon, D.Y. and Vigneswaran, S. (1998), Influence of Particle Size and Surface Charge on Critical Flux of Crossflow Microfiltration. *Water Sci. Technol.* 38(4-5): pp 481-488.
19. Huang, C. et al. (2004), Nanosilica Removal from IC Wastewater by Pre-Coagulation and Microfiltration. *Water Sci. Technol.* 50(12): pp 133-138.
20. Roorda, J.H. et al. (2004) The Role of Microparticles in Dead-End Ultrafiltration of WWTP-Effluent. *Water Sci. Technol.* 50: pp 87-94.

21. Cho, J., et al. (2006), Determining Brownian and Shear-Induced Diffusivity of Nano- and Micro-Particles for Sustainable Membrane Filtration. *Desalination*. 188: pp 213-216.
22. Kvinnesland, T. and Odegaard, H. (2004), The Effects of Polymer Characteristics on nano Particle Separation in Humic Substances Removal by Cationic Polymer Coagulation. *Water Sci. Technol.* 50: pp 185-191.
23. Sanchis, Maria, I.A. et al., (2003), Particle Size Distribution in Slaughterhouse Wastewater Before and After Coagulation-Flocculation. *Environmental Progress*. 22(3): 183 – 188.