Critical Review of Removal of Nano Materials in Waste Streams

Solomon W. Leung\textsuperscript{1}, Bradley Williams\textsuperscript{1}, Karl De Jesus\textsuperscript{2}, and James C.K. Lai\textsuperscript{3}

\textsuperscript{1}Civil and Environmental Engineering Department at Idaho State University, Idaho, USA
\textsuperscript{2}Chemistry at Idaho State University.
\textsuperscript{3}Pharmacology & Toxicology at Idaho State University College of Pharmacy.

Abstract. Industrial applications of nanomaterials (NMs) are rising drastically in recent years and the commercial value of these materials can reach over $100 billion in 5 years. Major effort in nano research has been devoted to the utilities of the materials, only minimum effort has been directed to the disposal, reuse, and recycle of these new forms of materials. Due to their unique sizes and sharps, nanomaterials possess unique characteristics and toxicity that are not expected from their counterparts in meso/micro forms. At the present time, there are no regulations governing the handling and disposals of NMs, but recent research demonstrated that NMs are more hazardous than we realize. A main reason why less caution is being exercised by the general public regarding NMs is that the measurement and quantitation of NMs are difficult, which lead to difficulties in monitoring, thus regulation. This article critically reviewed over the issues stemming from the development of NMs, especially the challenges of measurement and disposal of these materials in landfills.

1. Introduction

Industrial applications of nanomaterials (NMs) in industries in recent years are expected to reach over $100 billion in the global nanotechnology market in 2021 [1]. Research in NMs and their fate and sustainability in waste streams, eventually the environment, has highlighted some major concerns. This paper will discuss the literature search, current works, findings, and some relevant results that are associated with the generation and removal of NMs.

To begin this process of understanding the current leading edge knowledge and active work in the subject of nanomaterial (NM) as it becomes waste, an extensive literature search was conducted. Hundreds of articles and studies have been published on many different aspects regarding NM, ranging from transport, toxicology, and environmental accumulation, to uptake including in animals and plants. Currently NMs are used in industries worth multibillion dollars and the trend is in the upswing, however, limited amount of commercial effort has been directed to capture and recovery of these new forms of materials.

To better understand the scope of NM impact to human health and the environment, and the need for recovery processes, this paper will highlight the levels of NMs being generated, bioavailability, toxicology, measurement methods, and possible recovery solutions. Most important of all, since NMs are being generated for commercial use, these MNs ultimately end up entering a typical municipal wastewater treatment plant (WWTP) or landfill. Once NMs enter the WWTP they are either captured in the waste solids or are discharged in the effluent. The persistent NMs stay in nano form either in the liquid or solids and then are released to the environment. Waste solids are usually transported to a landfill and are incinerated, or used as mulch or fertilizer onto an open field. Liquid as effluent is...
therefore released back into surface waters. This general practice of NM management can then lead to NMs unintentionally reentry into the environment and possibly the food chain that is not a desirable solution.

2. Nanomaterial Industrial Waste Discharge Amounts (2010 data)

In looking at nanomaterial in waste streams and possibilities for recovery, one of the first items that need to be understood is the amount of industrial nanomaterial being produced and released to waste. A study conducted by Keller et al. [2], based on material flow modeling discharged into waste streams, showed the top 10 (by metric tons/year) most abundant engineered nanomaterials (ENMs) from 2010 global data: the study calculated how much ENM was produced and how much would then be discharged as shown in Table 1. The amount discharged to waste was based on presumptive material flow and then back calculated by knowing the reported amount produced rather than the actual measurement of the true ENM concentration in a waste stream.

Table 1: Top 10 ENMs AND DISCHARGES (YEAR/METRIC TON) IN 2010.

| Engineered nano material | Discharge |
|--------------------------|-----------|
| 1  Silica (SiO₂)         | 95,000    |
| 2  Titania (TiO₂)        | 88,000    |
| 3  Iron oxides           | 41,900    |
| 4  Alumina (Al₂O₃)       | 34,900    |
| 5  Zinc oxides           | 34,100    |
| 6  Nano-clays            | 10,400    |
| 7  CeO₂                   | 10,000    |
| 8  Carbon nano tube (CNT)| 3,276     |
| 9  Cu and Cu oxides      | 497       |
| 10 Ag                     | 424       |

The next important factor to take into account when evaluating nanomaterial in waste streams is how long will each ENM remain in nanoparticle form. This means that ENMs that are soluble and would quickly go into solution immediately are no longer in the nanoparticle form; also ENMs that aggregate are becoming larger than the original nanoparticles would be classified as bulk material. For examples: Iron, Zinc, and Cu oxides would likely not last very long in the nanoparticle form as they are more soluble. On the other hand, TiO2 is one of the least soluble among ENMs and would likely stay in the nanoparticle form for much longer. SiO2 would also be very similar to TiO2 with a low solubility. The top 3 industries that account for 42% of the total ENMs release are: 1) Coatings, 2) Paint and Pigments, and 3) Cosmetics. Nearly all the ENMs are released into landfills and/or soils, with the remaining in wastewater streams [2]. Some of these releases to the landfills come originally from municipal wastewater and then are collected as sludge of the treatment plant and eventually end up in landfills.

3. Case Studies: True Measurements of NM

Two case studies are cited in this study to elucidate some of the difficulties that are encountered in NM measurements. The first case study was conducted in Rome, Italy. This study measured concentration of nanocontaminants (NCs) that entered the municipal wastewater treatment plants (WWTPs) and then the concentrations in the effluent. In addition bulk samples were taken in the receiving waters to measure the concentrations of the same NCs [3]. It was found that three NCs had high pass through and posted risk in the environment. They are:
1) Carbamazepine with 0.24 µg/l;
2) Estrone with 0.56 µg/l;
3) Gemfibrozil with 0.11 µg/l.

It should be noted that estrone showed basically no removal in the WWTP. It is one of several natural estrogens that is carcinogenic to females and can cause erectile dysfunction to men. Next was a study of Darwin Harbor Estuary in northern Australia [4]. This study took samples throughout water bodies adjacent to a heavily populated municipality. The location was selected due to a high rate of population growth in the area. In this study, carbamazepine, estrogen, and testosterone concentrations were found in concentrations up to 0.5 µg/l, 0.33 µg/l, and 6.29 ng/l, respectively.

Even though the above studies did not look for ENMs specifically, there were significantly large amounts of hormones and pharmaceutical wastes found and with increasing concentrations near populated areas. These studies indicated that more hazardous wastes are discharged into our surface waters system that we are not aware of at metropolitan areas.

On a good note, it has been shown that wetland can be used to treat NCs to undetectable levels. A study from the Czech Republic showed that wetlands removed all incoming hormones to below detection limits [5]. The incoming levels of wastes that had 55 ng/l of estrone and 11 ng/l of testosterone initially were all removed by constructed wetlands.

4. Modeling and Transport of NM

There are two aspects in looking at modeling of NMs: First is the overall mass balance of how much NMs are produced, and then the eventual final disposal of the NMs. The latter is the more detailed studies of targeted NMs and their movements through waste streams and the resultant environmental impacts. A study of global life cycle release of NMs showed excessive amount of releases from cosmetics, textiles, paint and coatings, and filtration industries [2]. Majority of these wasted NMs are to be deposited in landfills and soil, with quite a large portion of such remains in waste water that is discharged into the surface waters.

There were two case studies that modeled NMs passing through WWTP and were field sprayed onto the soils. Both studies showed that NM concentrations were increasing [6]-[7]. But when these models were compared to actual measurements the modeled values were still less than the measurements, which suggests that the models are conservative and the emissions of NMs may be greater than originally expected.

5. Bioavailability of NM

A number of different studies have shown that nanoparticles are taken up by plant life either from the soil or water column. These particles maintain their nano size and therefore would be also suspected to have toxic effects. One study showed application of carbon nanomaterials to rice plants, the nanomaterial have been observed existing in various tissues of the plants [8]-[10]. This suggests that as environmental levels on ENMs increase, there is a higher risk of the nanomaterial to reenter the food chain. Another study showed that ZnO nanoparticles had a phytotoxic impact on Ryegrass [11]. The key point of bioavailability is that either ENMs are released to the environment via WWTP effluent as suspending solids, or are trapped in waste solids that are used as mulch or fertilizer, there is a clear evidence that NMs will be taken up by plant life, and may eventually be part of the human food-chain. In addition, how long and how many cycles these NMs remain in nano sizes and their toxicity are not known at this time.

6. Toxicity of NM

Although NMs are recent discovery, considerable amount of research has been conducted on the topic. Majority of the results were verified by laboratory experiments. NMs have shown a unique toxicological effect that is not previously expected. For many cases when one would consider the toxicity of a bulk substance that appears to be benign, the size and shape of the same substance in nano form would now make it toxic to living cells. A basic explanation is that with particles that are so
small that they can pass through cell walls that they will likely have a different impact on that cell than the same bulk substance that cannot pass through the cell wall.

A second part to toxicity is the inclusion of hormones and pharmaceuticals. In the nano contaminant (NC) form many hormones and pharmaceuticals will reenter the body and cause developmental and adverse impacts on human health. In the case of ENMs, they are designed to maintain the size and shape for an extended life depending on the application. But in the case of hormones and pharmaceuticals they are not intended to still be functioning after their initial use in the body. Their persistence in the environment is causing unexpected health consequence.

With all the variety of ENMs, TiO2 seems to have a large number of related studies. This is likely due to TiO2 being one of the more stable ENMs and is used in many industrial and domestic applications, thus exists in high abundance. Taking this in mind most of the following discussion is in reference to TiO2 [12]-[13].

TiO2 is classified as a Group 2B carcinogen, with nano-TiO2 having stronger catalytic activity than its non-nano counterpart; the nano particle has gained much more toxicological attention in recent studies [14]. Exposure to nano-TiO2 can induce inflammation, cytotoxicity, genotoxicity, and phototoxicity depending on the cells and form of exposure. [15]-[16]. Nano-TiO2 particles have many different pathways to enter the human body: 1) Injection in to the blood; 2) Inhalation in to the respiratory tract; 3) Ingestion into the gastrointestinal tract; and 4) Dermal through the skin. It was shown that nano-TiO2 can penetrate the skin causing damage to different organs [17]. Also nano-TiO2 (anatase) is phototoxic to skin due to its photo-reactivity when exposed to UV light [18]. This is a concern because one of the major uses of nano-TiO2 is in sunscreen. TiO2 has been shown in many different studies to have the ability to be transported to many different organs along with its ability to crossing over the blood brain barrier. Liver and kidney were shown to easily accumulate nano-TiO2. Toxic effects have been observed in tests on specific cells in rats or mice, showing impairment and/or cell death. It has been shown that exposure of TiO2, specifically to brain cells, can cause damage leading to neurodegenerative diseases [19].

7. **Challenges in Accurate Measurements of NM**

As the toxicity of NMs was unexpected, also as difficult is the current methods to accurately measure the sizes and concentrations of NMs in environmental samples on a broad scale. Acquiring real concentrations of NMs are difficult at best when the NMs being measured are actually known to be existing, let alone the presence of NMs in a sample are unknown. When looking at NMs there are many characteristics that need to be evaluated, such as the average particle size, shape, elemental composition, and mass concentration. Size and shape can be very critical in relating to toxicity [20].

Especially the size and shape of NMs, these characteristics are dependent of the bulk properties of the environmental media, such as pH, chemical affinity between the NMs and the solution they are in, and the ability of polymerization by the NMs. For example, if a NM has the size and shape that allows it to cross the blood brain barrier, then there is a very high risk to human health regardless of the material composition. NM is very difficult to differentiate between ENM and its natural counterparts in an unknown waste sample. As imaging and material science are advancing, better characterization and measurement techniques are definitely in demand.

8. **Measurement Methods**

There have been extensive studies evaluating specific NMs. In doing so, each study has to have a method for analyzing the concentration, chemical makeup and particle size of the nanomaterial. Each method is a little different depending on the sampling medium. For liquid samples such as WWTP effluents, large volume samples need to be collected and concentrated using a process such as rotary-evaporation and dialysis then freeze drying [21]. Then ICP (inductively coupled plasma), EDX (energy-dispersive X-ray) and TEM (transmission electron microscopy) analysis are performed on the samples.

Just as important in the analysis is the separation of different colloids. This is done by acid reduction depending on the types of colloid of interest such as organic or inorganic. This works on ENM such
as TiO$_2$ because it mostly remains in its original form. Other ENMs that may dissolve or react and transfer into other forms must be analyzed by different methods.

9. Removal mechanisms

By the nature of NM, being of such a small particle size, normal particle settling dynamics are not relevant. Next important characteristic to know about persistent NMs is that some of these particles also resist aggregation due to the surface chemistry and surface charge [22]. Nanoparticles that cannot be aggregated will then subsequently end up in the WWTP effluent. Nanoparticles that can be aggregated will be collected in the WWTP solids [23]-[24].

In viewing ENMs for removal, we should first consider the most environmentally persistent NMs. TiO$_2$ is one of the most environmentally persistent NMs and is a good candidate as an ideal surrogate for removal and recovery study. To begin understanding possible ENM removal solutions, it is important to highlight the key examples that showed some kind of characteristics that supported aggregation. In a study that concentrated on the aggregation behavior of nanoparticles in WWTP, showed that no aggregation was observed for a variety of nanoparticles in wastewater effluent [25]-[26]. But then when the test was repeated with wastewater containing dissolved organic matter (DOM), aggregation was observed. This demonstrated how the change of surface chemistry induced by organic matters may affect the state of NMs.

Furthermore, vast majority of nanoparticles that are captured in the WWTP processes utilize organic processes such as activated sludge or trickling filter. This identifies a possible mechanism for changing the surface chemistry to allow for aggregation. Also shown in studies is that ENM will be adsorbed to biomass [12].

The next step to be considered is recovery. This is because even though the NPs are adsorbed to biomass, many will still maintain their nano size or be very loosely aggregated, meaning even though NPs are incorporated onto the bulk solid they maintain the characteristics of NM. Often, when NPs are captured in a solid, the clean-up/disposal may have been considered completed. But with NPs, they maintain their nano-characteristics and are just temporarily “stored” in the bulk solid, a good example is sludge in WWTP. A general practice for sludge management is to spread the sludge in an open field as final disposal. If the NPs captured in the sludge retain the nano-properties, field application would unintentionally allow the NPs return to the environment. Thus, it becomes clear that immediate NM recovery is necessary. In doing the recovery to make the ENMs viable again for commercial use they have to be separated from the bulk mass and the surface properties restored. For example, the ENMs would need to be separated into an identifiable specific nanoparticle (e.g., TiO$_2$) with a reasonable level of purity to enable recycling. Further research is needed to encourage this recycle/reuse initiative.

10. Possible Removal Techniques

Taking the characteristics that are favorable for separation and isolation, techniques for actually removing and capturing nanoparticles needs to be developed. One such method is the modification of procedures during incineration of the WWTP solid effluent, which is already a normal practice with many plants. Taking this process and adding scrubbing technique of the exhaust gases would likely result in reasonable nanoparticle capturing rate. One possibility may be spraying the exhaust gases with a solution of calcium carbonate that is widely used in the industry. At this point the nanoparticles would be suspended in solution that are mixed with other particles (such as carbon ash and other metals) and require further separation and drying.

For treatment and removal, in applications that do not go through a WWTP or that are in the liquid effluent of the WWTP, an organic based coagulation and settling type process would be needed to pull the nanoparticles from suspension. It was shown in a number of studies that nanoparticle removal rate was greatly increased by the presence of organics [25].

In all, the removal and capture of nanoparticles will take a series of steps incorporating two main processes: The first step is changing the surface chemistry to allow aggregation and then settling of the NPs. The next step is drying the solids and then remove the intermediate material that was used to promote aggregation in the first step. A process to get reusable original form nanoparticles may be
challenging, experimental trials are needed to ensure a practical and working process. At this time, there is no one known universal removal/recycle technique for these multifaceted properties of NPs.

11. Summary
Nanomaterials have been proven to be very useful in many applications and are being produced at ever increasing rates. At the same time, NMs possess unexpected toxicity and risk to human health due to size and shape that are not typically observed in their bulk material counterparts. Furthermore, NMs are not being captured or recovered by the vast majority of waste treatment methods and they are being released into the environment at an alarming rate. Whether the NMs are in the effluent or the waste solids of the WWTPs, some of them remain their unique characteristics that they can be a health concern if they are released into the environment and be part of the food chain. The next critical point is that measurement of unknown waste or environmental samples for NMs is inaccurate and often near impossible. Currently, there are no regulations governing NM disposal that is becoming a public health concern.

In summary, we could be just seeing the tip of the iceberg of a possible significant environmental impact on human health that would be reminiscent of such events seen during the industrial revolution. The alarming issues with NMs are the difficulties of detection and measurement, then the realization of hazard, in addition to the disposal of the wastes. The fact that the secondary environmental concentrations are non-existing because these materials cannot be practically sampled. Disposal of NMs is an imminent issue that deserves more research and regulatory attention.

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