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EVALUATING THE IMPACT OF NANOPARTICLES ON WASTEWATER COLLECTION AND TREATMENT SYSTEMS IN VIRGINIA

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CHARACTERISTICS AND TREATMENT CONSIDERATIONS OF WASTEWATER CONTAINING NANOPARTICLES

The Significance of Nanotechnology

Nanotechnology is perceived as the economic and scientific driver of the 21st Century. Research has been progressing over the last couple decades, and since 1999, countries worldwide have invested billions of dollars into nanotechnology research because of its perceived economic as well as technological advancement potential. The USA has invested $1 billion in research, while other major players such as Japan ($800 million), Western Europe ($600 million), and Korea ($200 million) have been heavily involved. Other countries have invested $800 million (Biswas and Wu, 2005). Simply defined, nanotechnology is…

> *"…the research or development of nanoparticles, and nanoparticles are objects one billionth of a meter in size (0.000000001 m), or from 1 to 100 nanometers (nm) in size, or those particles that have at least one dimension 100 times smaller than a human hair."* – EPA (2007)

Nanoparticles are expected to help improve products used in biomedical, electronics, consumer products, and environmental applications. For example, nanoparticles are being researched to improve drug-delivery in the body, create smaller more efficient electronic components, enhance the properties of auto-parts such as tires and packaging materials, as well as remove contaminants from industrial wastewater. Research has shown that nanoparticles synthetically manufactured behave very differently than similar particles greater than their size, and some can be further modified by attaching specific molecules on them to enhance their properties. It is postulated that some of these modified molecules can for example allow doctors to guide drugs to specific organs of the body whereby the drug is released to that site only.

Types of Nanoparticles

There are two major classes of nanoparticles -- environmental and engineered/manufactured. For the past 20 years, scientists have been discovering that environmental nanoparticles are formed naturally by chemical and biological processes in the environment. These environmental nanoparticles are mainly metal oxides and metal sulfides commonly found as minerals. Unfortunately, environmental nanoparticles are poorly understood and much research must be completed to fully understand their fate, transport, and significance to the environment. Based on available studies to date, researchers suspect that environmental nanoparticles can bind with contaminants and also be responsible for causing chemical reactions in soil and water (Wigginton et al., 2007). Environmental nanoparticles however are not those receiving attention due to the influx of billions of dollars for research.

Engineered nanoparticles are those particles that have been synthetically manufactured. It is the study of these particles which receives much of the research funding. There are four types of engineered nanoparticles being investigated for their significance.

- **Carbon-based** nanoparticles are comprised mostly of carbon. Fullerenes (mostly spherical in shape) and nanotubes (cylindrical in shape) are two of the most popular engineered nanoparticles being researched worldwide. Fullerenes are pure carbon, cage-like molecular composed of at least 20 atoms of carbon. The word fullerene refers specifically to the Carbon-60 (C_{60}) molecule (type of fullerene). C_{60} and C_{70} are two of the most common and easy to produce fullerenes.
- **Metal-based** nanoparticles such as metal oxides, quantum dots, nanogold, and nanosilver are being studied for their ability to bind with other molecules and catalyze chemical reactions. One concern of metal-based nanoparticles is that once they enter the environment, they could release their metal, which may be toxic to organisms. Quantum dots are closely packed semiconductor crystals comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Changing the size of quantum dots changes their optical properties. Specifically, the surfaces of quantum dots can be modified to make the particle more stable.
- **Dendrimers** are the third type of nanoparticle and are constructed from pieces of different nanomolecules called nanopolymers. A dendrimer is a large molecule comprised of many smaller ones (called monomers) linked together. Similar to quantum dots, smaller molecules can be attached to dendrimer surfaces, which enable these dendrimers to perform specific chemical functions. Dendrimers that have these smaller molecules attached to them can have increased water stability or initiate a chemical reaction.
- **Composites** are the final class of engineered nanoparticles and are mixtures of nanoparticles or nanoparticles attached to larger, bulk-materials.

The Fate of Nanoparticles in Wastewater Collection and Treatment Systems

Little is known about the fate and transport of these particles in the environment as well as in wastewater collection and treatment systems (EPA, 2007). Because of this knowledge-gap, it is difficult to predict nanoparticle fate in the Town of Pulaski sewer system or facilities operated by PFRWTA. Several studies have been commissioned by the EPA and other Federal agencies to elucidate these questions. Unfortunately, results of these studies are slow to be released and after they have been completed, there will still be many unanswered questions regarding nanoparticle fate and impact on wastewater facility and treatment operations.

A Typical Wastewater Collection and Treatment System

To understand the potential impact of nanoparticles on wastewater collection and treatment systems, it is first necessary to understand the basics of wastewater treatment systems. Residential, commercial, and industrial waste is typically discharged into a collection system or buried network of plastic and metal pipes. Waste flows through these pipes to the wastewater treatment plant by gravity flow or to a pump station designed to capture the waste and then pump it to the wastewater treatment plant under pressure. Once at the wastewater plant, waste first passes through a bar screen to remove large debris and/or a grit removal facility to eliminate small stone and heavy materials from the flow stream. Following screening and grit removal, waste then travels through large quiescent basins called primary clarifiers where solids are allowed to sink to the bottom. Most facilities are based upon biological treatment. Following the settling process, the biological reactor uses bacterial organisms to reduce the waste to carbon dioxide and water with the addition of compressed air into the basin. The contents of the reactor are directed to secondary clarifiers, where the biological colonies formed in the reactor are settled to the floor of the basins. Supernatant, or liquid at the top of the clarifier, is then directed to a filtration step and/or to a disinfection chamber. Disinfected water is then discharged to a body of water or sent to land irrigation. From the bottom of the clarifiers, slurry or sludge is typically pumped either to the primary clarifier for recycling or to a digester for stabilization and then sent to dewatering equipment for ultimate disposal. Dewatering occurs using a mechanical press and/or by drying in open-air beds to reduce their volume. Depending on the permit of the WWTP, once dried these solids are either transported in a landfill or land applied. Each wastewater treatment facility operates under a discharge permit. The provisions of the permit, when reviewed in the engineering of the plant, generally dictate the specific processes to be designed and used at the facility.

Stability in Water

The stability of nanoparticles in water depends upon their chemical structure, water pH, and temperature. Carbon-based nanoparticles such as C_{60} form negatively charged colloids soluble in water from 0.000000001 mg/l to 100 mg/l (Fortner et al., 2005). It is thought that high water solubility is achieved because in water, C_{60} undergoes a transformation whereby aggregates are formed (diameter 5-500 nm) and outer carbon molecules become oxidized thus making the molecule more water soluble. Another complicating factor with C_{60} is that water pH has been shown to influence the diameter of C_{60} aggregates. Generally, particle size decreased 50% as water pH increased from 3.8 to 10.3 (**Table 1**). Fortner et al. (2005) concluded that C_{60} aggregates are stable in waters with ionic strengths similar to that of ground water and surface water for up to 15 weeks. Studies have also shown that these carbon-based compounds can be chemically altered during manufacturing in an effort to increase their water solubility (10,000 to 100,000 mg/l).

Table 1 - Variation in Particle Diameter of C_{60} Aggregates Based on Water pH*

Water pH	Average Particle Diameter (nm)
3.8	118
5.0	92
7.0	92
9.0	91
10.3	60

* Data from Fortner et al. (2005) and representative of reagent water.

The solubility of quantum dots with modified surfaces has also been found to be dependent on chemical structure and water pH, but also the presence of specific minerals in water. Zhang et al. (2008) studied the solubility of quantum dots having sulfur and acid groups attached. Results from their study indicated their "functionalized" quantum dots readily bonded with potassium, calcium, manganese, aluminum, each under certain water pH conditions. More specifically, particles aggregated and formed flocs below pH 3 in the absence of monovalent cations, but at about pH 5 these suspensions were clear. Interestingly, Zhang et al. (2008) also found the functional groups attached to the quantum dots prevented aggregation.

No studies were found investigating the water stability of dendrimers and composites; however it can be predicted that these molecules would act similarly to carbon-based and metal-based nanoparticles under similar conditions.

Sorption/Binding

Research suggests that carbon-based nanoparticles sorb to materials commonly used in wastewater systems. Duncan et al. (2008) reported that fullerenes can sorb to natural organic matter. Organic materials are commonly found in domestic wastewater in the form of suspended and dissolved solids, consumer products, and debris and could also be expected to sorb these nanoparticles. Duncan et al. (2008) also found that a C_{60} sorbed to plastic and Teflon. Based on this evidence, it is expected that any plastic and gasket materials exposed to nanoparticles could contain nanoparticle residue. Another aspect of nanoparticle fate in wastewater is that fullerenes have the potential to sorb to organic contaminants such as naphthalene (Cheng and Tomson, 2004). While naphthalene is commonly known as a gasoline contaminant and is unlikely to surface in wastewater, the finding nonetheless demonstrates that carbon-based nanoparticles could sorb to other contaminants which, if not removed during wastewater treatment, could be discharged with the effluent into the environment. While no studies were found evaluating if nanoparticles would sorb into biofilms lining pipe walls as well as basins within the treatment plant, based on previous studies on particle entrapment in biofilms, this could be expected. No data was found regarding the sorption of other types of nanoparticles to infrastructure materials.

Because of their binding potential, metal-based nanoparticles have been used to assist in removing heavy metals from wastewater. Specifically, maghemite nanoparticles at 10 nm in diameter have been found to be effective at binding with chromium (VI), copper (II), and nickel (III) (Hu et al., 2006). Complexation of nanoparticles with metals has also been found to be pH dependent. Maximum maghemite nanoparticle binding and heavy metal removal of chromium (VI) was obtained at pH less than 4, while copper (II) and nickel (III) were removed most effectively at pH 6 and 8, respectively. Other researchers have found that maghemite nanoparticles were effective at binding with chromium, vanadium, lead and arsenic from wastewater (Nurmi et al., 2005; Yavuz et al., 2006).

The binding of nanoparticles to organic matter, metals, and other contaminants could also have other undesirable consequences. For example, nanoparticle concentration in wastewater sludge is also a possibility. Sludge is the result of accumulation of solids removed during clarification. If nanoparticles have bound with solids, they would presumably be settled out and concentrated in the sludge during clarification. Nanoparticles removed in sludge could also end up in the environment if the sludge is land applied or is sent to a landfill.

Toxicity to Biological Processes

Several investigators have postulated that certain nanoparticles can be toxic to fish, humans, and bacteria by themselves or due to transformations they undergo to environmental conditions. By monitoring CO_2 production, Fortner et al. (2005) found that C_{60} inhibited growth of gram-positive and gram-negative bacterial cultures under both aerobic and anaerobic conditions. C_{60} has also been found to be toxic to human skin cells (Sayes et al., 2004). Another concern regarding nanoparticle toxicity is that nanoparticles may react or transform in water and become toxic. Cho et al. (2007) showed that cadmium can be released from cadmium-selenium quantum dots after being exposed to UV light. Cadmium is a known toxic to biological growth. Other nanoparticles have also been found to be acutely toxic to fish because the nanoparticle can initiate oxidative chemical reactions.

Effectiveness of Conventional Treatment Processes

Some data exist that report on the effectiveness of removing nanoparticles using conventional water and wastewater treatment processes. Zhang et al (2008) evaluated the removal effectiveness of functionalized quantum dots using alum coagulation, flocculation, and sedimentation for a local tap water and nanopure water. Results from their work indicated that the removal of quantum dots in tap and buffered nanopure water differed greatly. Due to the presence of divalent cations, quantum dots formed settleable flocs (larger than 2 μm) in tap water even without alum. Removal efficiency by sedimentation was about 70% by mass. The addition of alum did not increase removal efficiencies significantly. Even with an alum dosage of 2.86 meq Al^{3+}/L, the quantum dots removed by sedimentation were still no more than 80% of the total mass. With 0.45μm filtration, quantum dot removal only increased to about 85% regardless of the addition of alum.

Coagulation combined with flocculation, sedimentation, and filtration has been extensively studied for removing copper (II), alumina, and silica nanoparticles from four different semiconductor processing wastewater slurries with turbidity from 100 -1000 NTU and pH 6.8 - 8.6 (Carrerra et al., 2007). Coagulants examined were aluminum sulfate, ferric sulfate, chitosan, polyacrylamide and an anionic polymer. Results indicated that 45% of the copper was initially bound to particles and that most of the copper was removed by gravity settling (60-70%). It was also reported that nanoparticles containing copper (II) ions were also removed during coagulation and filtration.

Nanoparticle removal by coagulation using polyaluminum chloride (PACl) and thermal treatment were studied by Chang and coworkers (2006, 2007). Wastewater from a secondary treatment works serving a high-tech industrial park containing silica based nanoparticles and CaF_2 was examined. Results from Chang et al. (2006) revealed that the size of the wastewater sample particles was segregated into four groups: 30 mm, 1–4mm, 2–5 nm, and 30–300 nm. Experiments revealed that silica-based nanoparticles were not sufficiently removed by coagulation under the conditions tested, but increasing the temperature to 65 degrees C resulted in nanoparticle agglomeration and improved water quality. In a subsequent study, Chang et al. (2007) reported that silica based nanoparticles of 1-5 nm in size contributed COD to the wastewater, but were agglomerated and the particles of size 1–5 nm effectively coagulated using a PACl dose of 2.08 mg/l as Al. However, additional PACl did not cause additional agglomeration and nanoparticle removal, but contact time between the PACl and nanoparticles was proven to result in larger agglomerates.

Electrocoagulation of nanoparticles has also been scrutinized, but is not a standard conventional wastewater treatment process. Electrocoagulation is commonly used to treat industrial wastewaters from semiconductor manufacturing operations (Den et al., 2006).Nanoparticles typically found in these wastewaters are SiO_2, Al_2O_3, or CeO_2. Den et al. (2006) examined the electrocoagulation treatment effectiveness using wastewater from one semiconductor manufacturing plant with an average particle size of 450 nm to 3000 nm. It should be noted that particles greater than 100 nm are not generally considered to be "nanoparticles." A reduction in turbidity was the only measure of treatment effectiveness used in this study. No work was conducted to characterize the size of nanoparticles in the treated water. Den et al. (2006) did find that silica nanoparticles primarily bonded with iron in solution and settled out in sludge and concluded that this phenomenon occurred due to coagulation. Based on these results and the potential of nanoparticles to sorb to organic matter and other contaminants, it could be expected that nanoparticles would concentrate in wastewater sludge.

Zhang et al. (2008) reported that divalent cations such as manganese and calcium not only affected quantum dot water solubility, but also resulted in these nanoparticles aggregating into 2 μm flocs and being removed by settling up to 70% by mass from tap water. These investigators also found that coagulation using alum only produced marginally better results

(80% removal by mass). Filtration using a 0.45 µm filter achieved 85% reduction in nanoparticle mass regardless of whether or not coagulation was used.

Relevance to Pulaski

The stability of nanoparticles in water and their ability to aggregate and settle out will depend on their design, which includes specific functionalized groups and structure. The inherent variability of ions in domestic wastewater will also complicate this prediction. Since there are countless permutations of nanoparticle design, it is only possible to conclude that water pH may in fact influence nanoparticle stability in the proposed Nano Park. However, without specific details on the actual particles, it will be impossible to predict the solubility of the particles or the pH adjustments that may be required to disassociate the particles from the wastewater. If a pretreatment process at the Nano Park adjusts the pH of the wastewater outside the usual ranges of wastewater pH (generally regulated to pH 6.5 to 8.5), a reciprocal pH adjustment will have to be made to return the pH into the acceptable range before the wastewater is transferred to the PFRWTA system.

Nanoparticles have the potential to sorb and bind with many different surfaces and contaminants in the Town of Pulaski wastewater and system. Nanoparticles can bind with heavy metals, some which may be toxic to treatment biology, or they could hinder treatment by attaching to equipment, piping, tanks etc. Likewise, sorption could allow particles to pass through treatment processes and into the environment where their fate could be equally diverse. In addition, nanoparticles have been shown to react with UV light and release sorbed metals into the water column. Identification of the specific particles to be used will be critical in evaluating their effect on the processes and environment. A treatment process, which will be effective for the situation, needs to be developed based on those specifics.

As mentioned previously, engineered nanoparticles (depending on their purpose) can hinder or destroy biological activity. This is a grave concern to any wastewater treatment facility as biological treatment is the backbone of the facility, and without it significant reduction in contaminant loads would not be achievable. The characteristics of nanoparticles created in the Pulaski Nanotechnology Business Park will be critical to the determination of concerns relative to problems created, and the appropriate solutions in wastewater treatment.

The discharge of nanoparticles to the PFRWTA could be detrimental to the facility's treatment process or could allow the pass-through of substances of concern to the receiving stream. It is apparent that specific engineered nanoparticles can be removed from a liquid waste stream provided the treatment system is designed specifically for the type of particle. The PFRWTA plant cannot be expected to affect significant removals for most nanoparticles. Therefore, the Pulaski Nanotechnology Business Park will need to include provisions for wastewater pretreatment which targets the specific substances. It is unlikely that a single pretreatment process at the Park will allow for proper treatment of the complex of nanoparticles that may be received from the matrix of ten or fifteen potential tenants of the Park. For that reason, the overview of pretreatment required, includes a number of dedicated pretreatment processes (for specific particle removal) followed by a general pretreatment process (for conditioning the pretreated waste prior to delivery to PFRWTA.

Conclusions

The following conclusions were developed based on the literature review and DAA's experience designing, upgrading, and troubleshooting domestic and industrial wastewater collection and treatment systems.

- ❖ Limited data is available for enabling a complete assessment of the impact of waste containing engineered nanoparticles on wastewater collection and treatment facilities and operation.
- ❖ The fate and transport of engineered nanoparticles in the Town's sewer system and PFRWTA will depend on tenant nanoparticle production, nanoparticle interactions with surfaces, other contaminants in the wastewater, particle stability, their ability to bind to surfaces, toxicity to wastewater organisms, and reported removal effectiveness of typical treatment plant processes.
- ❖ The ability of an engineered nanoparticle to impact wastewater treatment operations will depend specifically on the type, quantity and characteristics of that manufactured nanoparticle.
- ❖ Water pH, ionic water quality content, presence of other contaminants, and temperature can affect the stability and aggregation potential of some nanoparticles in water. The effect however is strongly dependent on the characteristics and structure of the predominant nanoparticles.
- ❖ Research has shown that some carbon-based nanoparticles have the potential to bind with themselves as well as with plastic, glass, organic matter, and other contaminants found in water. It is reasonable to presume that some types of engineered nanoparticles could deposit themselves throughout wastewater collection and treatment systems by binding to piping, basin surfaces, and equipment and contaminants in the waste stream. While no studies were found specifically evaluating if certain fluid velocity is needed to prevent surface adhesion or the potential of nanoparticles to bind with biofilms or corroded metal piping tubercles, based on a conservative approach, it seems reasonable to expect these phenomena could occur.
- ❖ It can be expected that bar screening and other mechanical treatment methods will be ineffective at removing any engineered nanoparticles.
- ❖ Wastewater treatment operations with the most potential for removing nanoparticles from wastewater are the Primary and Secondary Clarification basins. Of course, nanoparticle removal potential will rely on the specific characteristics of the nanoparticles. The following research findings facilitate nanoparticle removal: (1) some nanoparticles can bind with organic matter which is ultimately settled out; (2) some nanoparticles have shown that they naturally aggregate with one another thus improving settling; (3) some nanoparticles can bind with organic contaminants; (4) some nanoparticles can adhere to selective surfaces.
- ❖ Sludges, or solids that have been removed during primary and secondary clarification, as well as that matter collected and removed from all basins during regular cleaning, have the potential to contain high concentrations of nanoparticles due to removal of water in a

sludge thickening and dewatering process. In addition, contaminants bound to these nanoparticles (such as heavy metals) could also be present in dried sludge. No studies were found evaluating the potential for engineered nanoparticles in dried sludge to become airborne when the material is agitated or transferred for disposal. This would be a work exposure issue. Industrial concerns may need to consider the hazards associated with airborne particles, and take specific precautions.

- ❖ Engineered nanoparticles pose the greatest risk to the biological treatment processes because some nanoparticles are designed to inhibit or even prevent biological viability. A reduction of biological activity in the wastewater treatment facility by toxic nanoparticles could decrease the contaminant removal effectiveness of the entire facility causing noncompliance with effluent discharge limits. A total failure of the biological portion of the process could be experienced in the worst case. Further, nanoparticles could bind to piping, equipment, basin surfaces, be difficult to remove, and require the complete shutdown and sanitization of the infrastructure affected before treatment could be reinitiated. Unfortunately, limited research has been conducted that would enable further conclusions about the fate of nanoparticles on surfaces.
- ❖ Due to the potential impact of engineered nanoparticle waste on wastewater collection and treatment operations, data should be obtained from the tenant industry regarding wastewater quantity and quality characteristics and specific knowledge as to the characteristics and purpose of the nanoparticles to be discharged in wastewater. These data, along with environmental regulatory requirements, should be used to determine if industrial pretreatment requirements should be established.
- ❖ It is important that nanoparticle fate be considered in sludge sent to landfills or incinerated, even though little work has been published on this topic. Considerations could include whether or not the nanoparticle is destroyed during sludge stabilization, incineration, and if nanoparticles could desorb and enter landfill leachate.

Recommendations

Based on a review of the literature and assessment of engineered nanoparticle impact on wastewater collection and treatment processes, the impact of nanoparticles on the local PFRWTA should be assessed. It is reasonable to allow the facility to receive engineered nanoparticle wastewater if after a review of the nanoparticle characteristics and industrial wastewater quality of the nanotechnology industry, it is determined that the discharge will have no detrimental impact on wastewater operations or permit compliance. The decision to permit the discharge of nanoparticle wastewater to the sanitary sewer should be based, at the minimum, on the systematic approach provided below. Because certain engineered nanoparticles are intentionally designed to be toxic to organisms and bind with surfaces, some nanoparticles have the potential to severely impact wastewater treatment effectiveness, which could result in acute and chronic effluent violations. A three-pronged implementation approach to ensure limited impact on wastewater operations is provided below.

Waste Quality Assessment and Facility Impact

For any industry that uses or plans to discharge waste containing nanoparticles, it is highly recommended that the Town and PFRWTA obtain a full characterization from the industry about the wastes, and nanoparticles expected to be present in the wastes before the industry is permitted to discharge to the sanitary sewer. This information can be used to determine if and what industrial wastewater pretreatment requirements are necessary to avoid the wastes from damaging facilities resulting in permit violations.

Inquiry to the interested industry should include the following general questions. Does the industry plan to discharge waste/rinse water containing nanoparticles to the POTW on a continuous basis? Does the industry plan to discharge such wastes intermittently during regularly scheduled equipment/laboratory cleaning operations? If yes or maybe is provided to either of the above questions, the following questions should be asked of that industry:

- What are the types of nanoparticles they are using or plan to use? (e.g., carbon-based, metal-based, quantum dot, dendrimer, composite)
- What is the intended purpose of the nanoparticles? (e.g., sterilization, chemical reaction, binding with other compounds)
- Has the industry determined if their nanoparticles are stable in aqueous suspensions at water pH values typical of PFRWTA?
- Is their waste toxic to bacteria? Other organisms?
- What are the characteristics of their waste? (concentrations of TSS, BOD5, COD5, TN, TP, pH, turbidity)
- What volume of waste do they expect to generate peak, max day, avg day?
- Will there be any equipment cleaning periods where they expect to rinse equipment and discharge waste to the sanitary sewer? What volume could be expected?
- What are the occupational exposure hazards associated with handling the engineered nanoparticles? Is there an MSDS for the nanoparticle or object containing the nanoparticle planned to be discharged to the sanitary sewer? Once sludge dries, it is conceivable that the nanoparticles (if not bound to the organic matter or unbound due to environmental conditions) could become airborne and pose an occupational hazard. What are/could be their fate in a landfill matrix?

Bench-Scale Study

A more conservative, less risky approach to be more certain the proposed nanoparticle waste does not adversely impact wastewater treatment operations would be to conduct a simple bench-scale study using industrial waste containing the industry-specific nanoparticles. Such a study should be conducted following or in parallel with the previous recommendation. A bench-scale study would help quantify the impact of subject industrial waste on wastewater treatment operations. Due to the high-profile nature of nanoparticle fate and impact on wastewater, it is possible that State, Federal, and nonprofit agencies may provide financial assistance in funding such an investigation. This alternative would require approval of the industries under consideration as well as a financial commitment by the wastewater treatment facility, and potentially local and regional governments.

Engineering and Scientific Evaluation

Finally, due to the complexity and infancy of the world's understanding of engineered nanoparticles in the environment and impact on wastewater operations, additional technical assistance should be sought where the impact of nanoparticles can not easily be determined or the impacts can be complicated by many variables. Such help can be located through consulting engineers and research centers.

TARGETED NANOTECHNOLOGY WASTEWATER PRETREATMENT ORDINANCE AND DISCHARGE PERMITTING SURVEY OF U.S. MUNICIPALITIES

Purpose and Methods

A targeted national telephone survey of wastewater utilities and public works departments was conducted to determine (1) whether local pretreatment ordinances and/or (2) discharge permits exist for nanoparticle sanitary sewer discharges in the USA. Several agencies and localities, serving nanotechnology production companies, were contacted based on data for the more than 280 nanotechnology companies identified in the Virginia Tech Economic Development Report. Specifically, municipalities were selected based on the abundance of nanotechnology businesses in their State, the number of agencies in major metropolitan sanitary sewer areas, and geographic region. The locations and proximity of nanotechnology businesses to wastewater collection systems was determined by visiting the company's worldwide web address (provided in the VT report) and by contacting municipal governments. All respondents who had not heard about nanoparticles were provided a brief three minute verbal explanation of nanoparticles (organic and inorganic), their production, and usage in society. In addition, wastewater professionals were also told that there were currently no Federal regulations for industries 1) to disclose nanoparticle wastewater characteristics or 2) limit nanoparticle discharge.

Results

According to the Virginia Tech Economic Development Report, there are 11 States and Commonwealths that are home to 71% of all nanotechnology based companies in the continental USA (**Table 2**). The State of California and Commonwealth of Massachusetts were home to the largest number of nanotechnology companies (30% and 14% of the total, respectively). A total of 13 different wastewater utilities and public works departments in the primary States/Commonwealths were contacted. These wastewater utilities served from 280,000 to greater than 2,500,000 customers, with 204 – 6429 miles of sanitary sewer line, and managed a combined total of 45 wastewater treatment plants. Major metropolitan utilities located near nanotechnology businesses identified in the VT report were contacted. In particular, two municipalities near the Nation's advanced research technology centers in California and North Carolina were contacted. Telephone discussions were held with pretreatment managers, wastewater facility superintendents, sewer and distribution chiefs, industrial waste compliance managers, and industrial waste discharge permit writers.

Table 2 - Top Eleven American States/Commonwealths Home to Nanotechnology Based Companies and Agencies Contacted

Rank	State Abbreviation	Number of Companies	Locations of Agencies Contacted
1	CA	62	San Jose, Santa Clara, and Oakland
2	MA	28	Boston and Cambridge
3	NY	21	Albany
4	TX	18	Austin and Houston
4	PA	18	None
6	OH	11	Cleveland
6	MI	11	Ann Arbor
8	NC	9	Charlotte and Durham
8	VA	9	Fairfax County
8	IL	9	Chicago and Evanston
8	FL	9	Boca Raton

* States not listed were home to 8 or fewer nanotechnology companies per State. There were a total of 287 companies identified in the Virginia Tech Economic Development Report.

Generally, the industrial wastewater representatives contacted were unaware of nanoparticles and whether any industries in their service area were producing or discharging them to their sanitary sewer. In many cases, these representatives were responsible for approving industrial pretreatment discharge permits to the sanitary sewer and inspecting the industries for compliance. A minority of representatives explained that they had heard of nanotechnology but were unaware that nanotechnology industries could generate wastewater containing nanoparticles. Several wastewater pretreatment professionals were aware of EPA's efforts to investigate nanoparticle fate and impact in wastewater collection and treatment systems. These representatives confirmed that there were no specific regulatory requirements in their systems. One representative thought that if nanoparticles were regulated, his utility would likely monitor their discharge by measuring total suspended solids (TSS) quality of the wastewater. It is noted that this measurement technique could provide a correlation to the presence of nanoparticles, but is highly dependent upon the type of particles and the environment of the wastewater. The procedure more likely would provide trend information, but not necessarily good quantitative results. This representative seemed to have the best grasp on nanotechnology in wastewater treatment, for the group surveyed. The survey shows a general lack of understanding of nanoparticles in wastewater and a need for further education in this area as the nanotechnology fields mature.

While no industrial wastewater pretreatment ordinances or wastewater discharge permit restrictions were found that specifically regulated nanoparticle wastewater, some utilities had enacted local pollutant discharge limits inadvertently affecting nanoparticle waste. For example, one utility located in the Eastern US required that a nanoparticle production industry not exceed a permitted discharge limit for antimony (on a concentration basis). It happened to be that antimony was used in the manufacture of that industry's nanoparticles. Thus, in this case, limiting antimony discharge to the sanitary sewer limited nanoparticle discharge as well. However, a Western wastewater utility had a very different experience. Within their sanitary sewer system, a nanoparticle production industry produced aluminum oxide nanoparticles using a production method not regulated in the Code of Federal Regulations and there was no local aluminum discharge limit. As a result, this facility was not required to limit aluminum discharge to the sanitary sewer which happened to contain nanoparticles.

Conclusions

Results from this survey revealed several key findings pertinent to the Pulaski Nanotechnology Business Park. They are:

- Generally, industrial wastewater professionals at utilities and public works departments across the US are unaware of or don't know if nanotechnology companies discharge waste containing nanoparticles to their sanitary sewer. This lack of knowledge is likely amplified to community leaders. By conducting this scoping study, Pulaski has positioned itself ahead of other communities for anticipating the challenges that may follow the production of industrial wastewater containing nanoparticles.
- No pretreatment ordinances or wastewater discharge permit restrictions were found specifically regulating nanoparticle wastewater discharge to sanitary sewer.
- Some utilities/localities are likely limiting nanoparticle discharge to the sanitary sewer using discharge limits for regulated chemicals (e.g., antimony, aluminum) which could be bound to nanoparticles in certain industrial applications. At the majority of the facilities however, nanoparticles could already be discharged to the sanitary sewer and not be detected or removed under the existing Federal and local discharge standards.

CONCEPTUAL PLAN FOR WASTEWATER TREATMENT AT THE PULASKI NANOTECHNOLOGY PARK

Background and Chosen Concepts

The literature research and discussions with nanotechnology and environmental engineering experts nationwide have revealed that nanotechnology industry is growing by leaps and bounds. However, nanotechnology is also a field that is in its infancy. The possibilities for application of nanotechnology sometimes seem endless. As part of a parallel study, a Virginia Tech Economic Development Report was compiled with a list of U.S. firms involved in nanotechnology applications. The list includes over 280 firms in various phases of research, development, or production of nanoparticle materials. Any number of those firms could potentially show interest in occupancy at the Pulaski Nanotechnology Business Park. Several of the firms provide research or products which would make their local presence in Pulaski quite attractive to other local businesses in this region. Because the Business Park planning is in its initial stages, at this time, it is difficult to predict the business makeup of the Pulaski Nanotechnology Business Park. For that reason, it is equally difficult to predict the type of waste that would be generated from a nanotechnology facility.

At the present time, there are no specific regulations pertaining to nanoparticle production or disposal of waste that contains nanoparticles, regardless of whether the discharges are in solid, liquid or gaseous form. Regulations have not been proposed primarily because there is an overall lack of understanding about nanoparticle characteristics, and their fate in infrastructure and environmental systems. The U.S. Environmental Protection Agency (EPA) is now conducting the fact finding and data collection phase to determine if nanoparticles pose a risk to humans and the environment. Typically, a mandate for regulation of a complex matrix of substances like nanoparticles could take years, possible decades to promulgate. Several studies have been initiated to elucidate these questions. Unfortunately, once these initial investigations are complete, more questions will remain. One very significant question will concern whether the conclusions associated with the studied nanoparticles can be used to predict results for nanoparticles that have not been studied. The lack of knowledge has translated to a nearly total absence of regulation for the discharge of these particles. A mandate for regulating nanoparticles by the EPA could take years, possibly decades to promulgate.

In the previous section, the nationwide canvass of wastewater system managers and operators revealed the absence of regulation of nanoparticles in discharged wastewater. It was found that most localities are currently reviewing the apparent constituents of discharged wastewater and setting pretreatment limits for traditional parameters such as heavy metals, pH, dissolved solids, toxicity, etc. On the surface, this methodology would appear to serve the purpose of general protection of the environment and human health. Just the same, there is concern that nanoparticles, with their unique characteristics, could defy detection through currently accepted laboratory tests and procedures used in the wastewater industry. The impact of nanoparticles on the environment is largely unknown, which may raise the risk to the quality of the environment. One community has required nanoparticle industries to provide full disclosure of their operations to assess the known impacts of the particles that will be produced at the industrial site. This seems like a good effort, on the part of the locality, to define the particular impacts for a specific situation. However, since little to nothing is known about nanoparticles, there is still a significant risk that the barn door will be closed well after the horses have scattered in all directions. This scenario of risk, in producing a material whose impact is largely unknown, reminds us of past episodes involving substances that were better known such as lead, asbestos, PCB's and the like.

Because there may be as many as ten or fifteen industrial clients in the Pulaski Nanotechnology Business Park, the type and quantity of nanoparticles discharged to the sanitary sewer may vary greatly. A wastewater pretreatment model was created based upon traditional wastewater parameters and the presumption that the following specific pretreatment measures could be required. This model may or may not meet the final needs of the Park.

- Heavy metal precipitation (for copper, lead, etc)
- Other coagulation and precipitation process (for dissolved substances)
- Membrane filtration or reverse osmosis (removal of small particles or sulfates)
- Deionization (removal of specific dissolved chemistry or sulfates)
- Sulfate removal (specific process for more economical high concentration sulfate removal)

These five (5) parallel processes would be followed by one last stage of pretreatment for pH adjustment and final settling of solid materials. A monitoring station would be located at the entry point of the facility waste stream to the Town of Pulaski sewers. Treatment unit configuration would be similar to that shown in Figures 1 through 6. For solids handling (due to precipitation, settling, particles entrapped on filters), sludge storage and dewatering equipment will be needed. Until clients in the Business Park are identified along with their business plans, there is no way to predict the final treatment requirements or projected flow rates. Lack of client business plans and waste characteristics also could cause the assumed process elements, sizes, and sequence to differ from those ultimately required. However, the treatment scenario provided enables a general layout of the Business Park's wastewater treatment needs.

Heavy Metals Precipitation

Nanoparticle production can involve heavy metals or materials with ionic characteristics similar to dissolved metals. Wastes from these production processes could be directed to a pretreatment train that includes chemical addition and solids precipitation. The precipitation process would use Sodium Hydroxide (Caustic Soda) or Calcium Hydroxide (Lime) to adjust pH, and Aluminum Sulfate (Alum) and/or Polymer to coagulate and flocculate the metal precipitates. The process will form solid materials for removal from the liquid waste stream.

Adjustment of water pH is the fundamental mechanism for successful precipitation of heavy metals. Changing pH changes the solubility of metals in water. By increasing pH to a value around 9.0, most metals will be insoluble and can be settled out using a coagulating chemical. Some of the more common metals treated in this manner include Copper, Silver, Nickel, Lead, Cadmium, Chromium, and Zinc. The metal precipitation process will include "pretreatment" for pH adjustment, Alum addition for "precipitation", and gentle mixing for "flocculation" and "settling" of the solids in a clarifier. To maximize the effectiveness of the metals precipitation process, the wastewater composition, volume, and quantity of metals in wastewater must first be determined. Depending upon the nature of the process, and the tendency for some heavy metals to resist flocculation and settling, there may be elevated levels of metals in the effluent from this segment of the wastewater treatment operations. In the event discharge concentrations must be kept at levels less than possible by the described process, a final filtration step may be necessary to maintain compliance. A process schematic diagram is presented in Figure 1.

Other Coagulation and Precipitation

Colloidal substances and dissolved materials can be coagulated, flocculated and settled much the same as in a conventional water treatment process. Coagulation and precipitation treatment has been used in the past for wastes which do not contain heavy metals, but include other byproducts of nanotechnology industries, such as Fluoride. In general, Calcium Chloride and Aluminum Hydroxide, both specific for Fluoride removal, and Alum and Polymers, for colloids, could be used in the process for removal of such materials. The basic flow diagram is presented in Figure 2.

Membrane Filtration or Reverse Osmosis

Removal of nanoparticles from the waste stream could be accomplished with nanofiltration or reverse osmosis. These membranes have the capability of removing very small suspended or dissolved particles from water because of their small pore size. These membrane processes rely on high energy input and moderate cost equipment maintenance and replacement. Membrane filtration equipment and energy costs can be significantly greater than other treatment options. However, membrane filtration is highly effective in comparison to many other treatment processes (e.g., flocculation, settling). A flow schematic is provided as Figure 3.

Deionization

Deionization and water softening processes make use of ion exchange technology. For the Nanotechnology Business Park it is more likely that deionization will be required, since the process generally deals with dissolved metals rather than water hardness. In the deionization process, the waste liquid is passed through a cation rich resin with an excess of positively charged hydrogen ions. As the liquid is passed through the exchanger, hydrogen ions are moved from the resin to the waste while metal ions are taken from the waste and sorbed onto the resin. At some point, the resin loses its ability to sacrifice more hydrogen ions, and the exchange stops. At such a time, the exchanger must be regenerated with an acid wash. Following the cation exchange is an anion exchange step. In this case negatively charged hydroxide anions are available on the resin for exchange with negatively charged particles in the wastestream. The hydroxide replacement of anions in the waste allows the hydrogen cations and hydroxide anions to combine into water molecules. The offensive metal salts have been removed from the waste and replaced with water. A flow schematic is provided in Figure 4.

Sulfate Removal

Sulfate is a specific parameter of concern for the Peppers Ferry Regional Wastewater Treatment Authority (PFRWTA), which receives wastewater from the Town of Pulaski and from its customers. The Nanotechnology Business Park may or may not have industries discharging significant amounts of sulfur compounds. However, due to the regional concern for sulfates, sulfate removal treatment processes were examined. The process used in the model is based upon anaerobic treatment. A schematic is provided in Figure 5.

General Pretreatment Process

Following the five (5) specific processes for treatment of wastewaters, the discharges will be combined together into a single flow stream and delivered to a combined pretreatment process. The process will be oriented toward pH adjustment, to assure that pH is maintained within the allowable discharge limits. In adjusting pH, there may be further precipitation of solids from the wastewater stream. A settling tank will remove any additional settleable solids prior to discharge to the Town of Pulaski sewers. Another common component of the General Pretreatment system will be the sludge handling required from the five preliminary processes and the common process. Figure 6 identifies the typical pretreatment scheme anticipated.

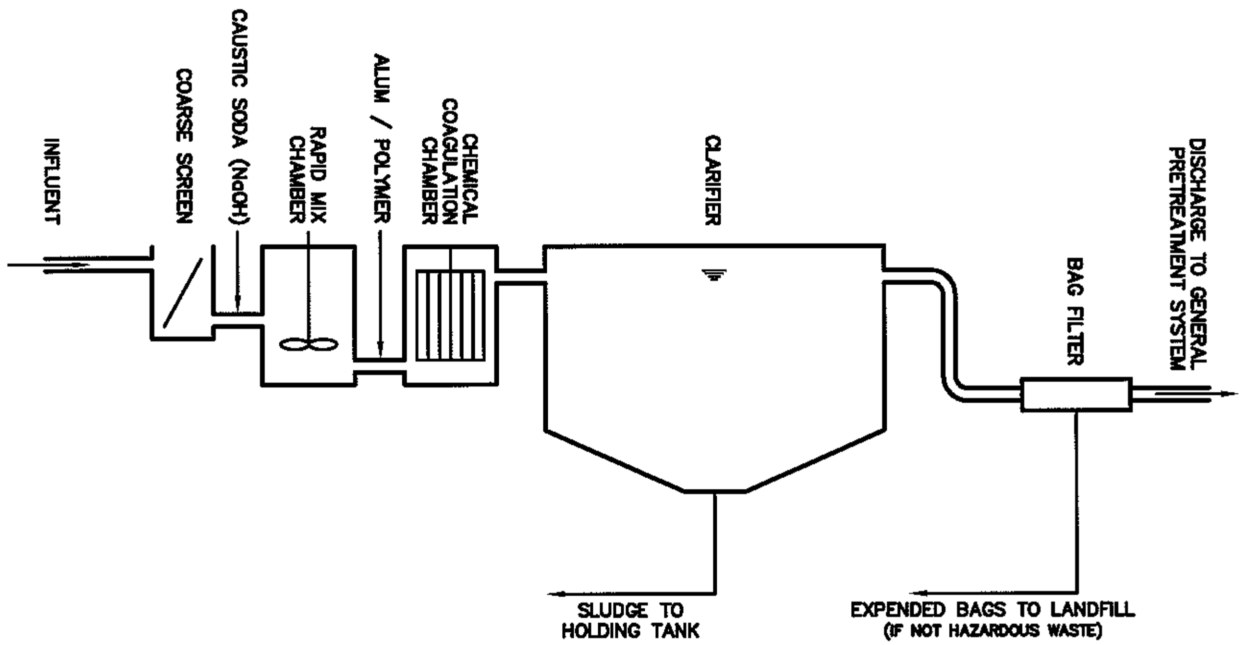
Summary

Pretreatment of wastewater at the Pulaski Nanotechnology Business Park could include a number of distinctive wastewater treatment processes. The model provided includes five specific targeted pretreatment trains and one general pretreatment facility for conditioning wastes prior to discharge into the Town of Pulaski sewers.

CONCLUSIONS AND RECOMMENDATIONS

With limited knowledge of the ultimate tenancy of the park and limited knowledge of the impact of nanoparticles in wastewater treatment or in the environment, rational judgments have been made to prescribe a pretreatment protocol for the park, which would be implemented to meet the needs of the town and regional wastewater treatment authority.

In establishing the Nano Park, it will be beneficial to the Town to thoroughly review the prospect tenants for their potential waste characteristics through identification of materials used in their production process and/or sampling and testing of the waste product. If the waste product can be judged safe for the wastewater collection and treatment system, it could be allowed in the town sewers with little or no pretreatment. However, if the presence of sulfates, objectionable nanoparticles or chemistry is noted, then a properly sized targeted wastewater treatment process, potentially derived from the model presented in this report, should be constructed at the park.



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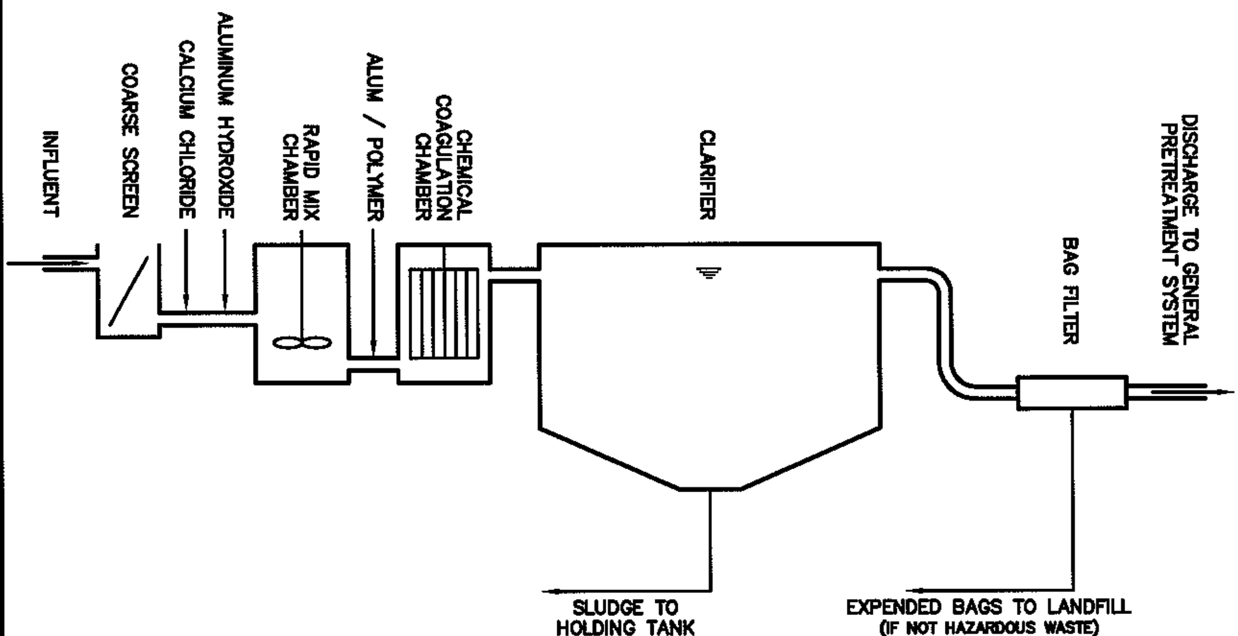
HEAVY METAL PRECIPITATION TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 1



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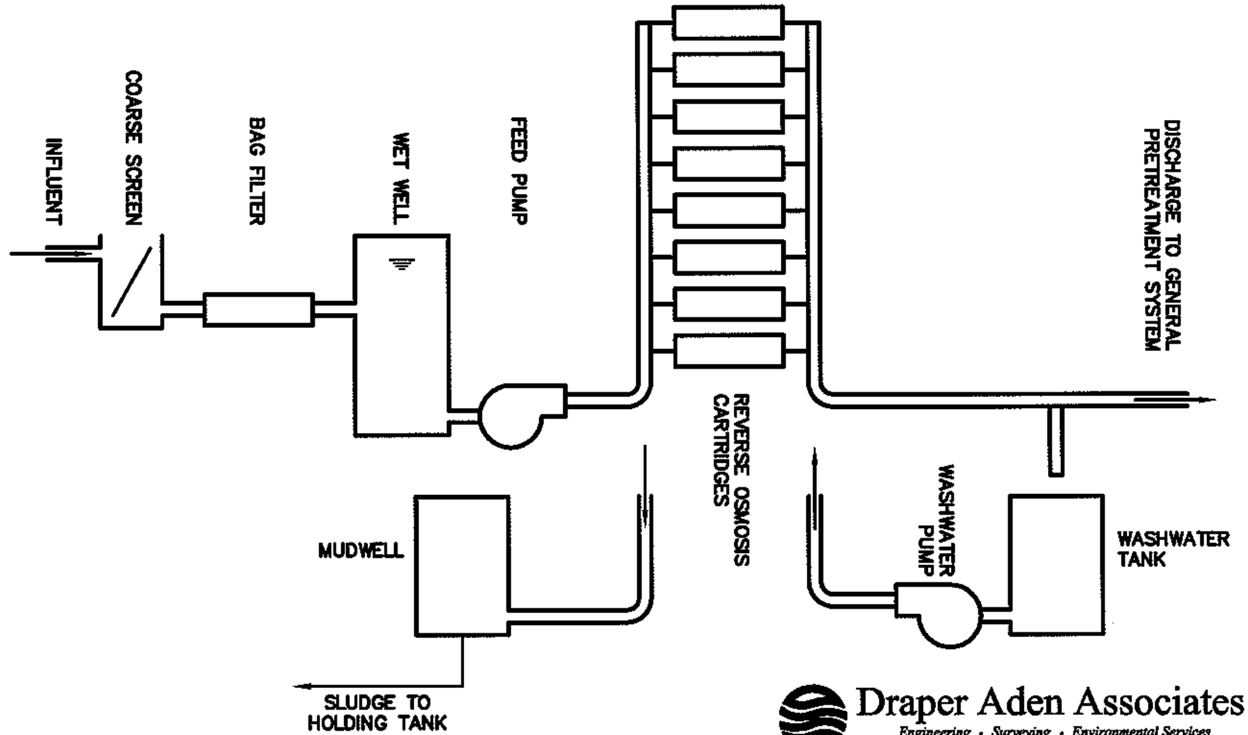
FLUORIDE / COLLOID PRECIPITATION TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 2



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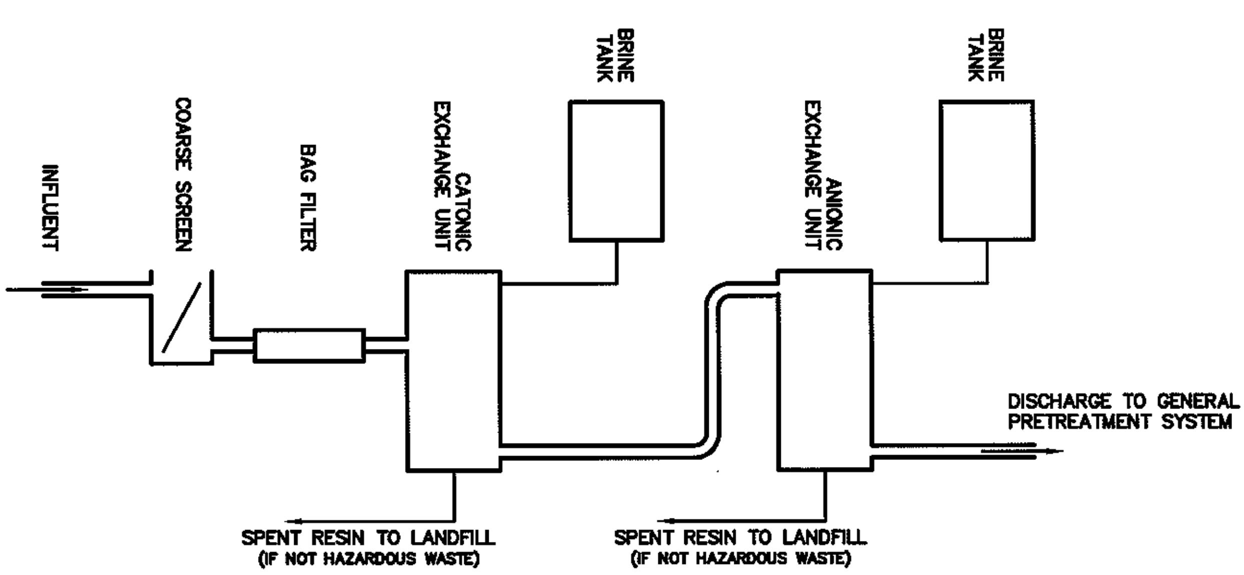
MEMBRANE FILTRATION TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 3



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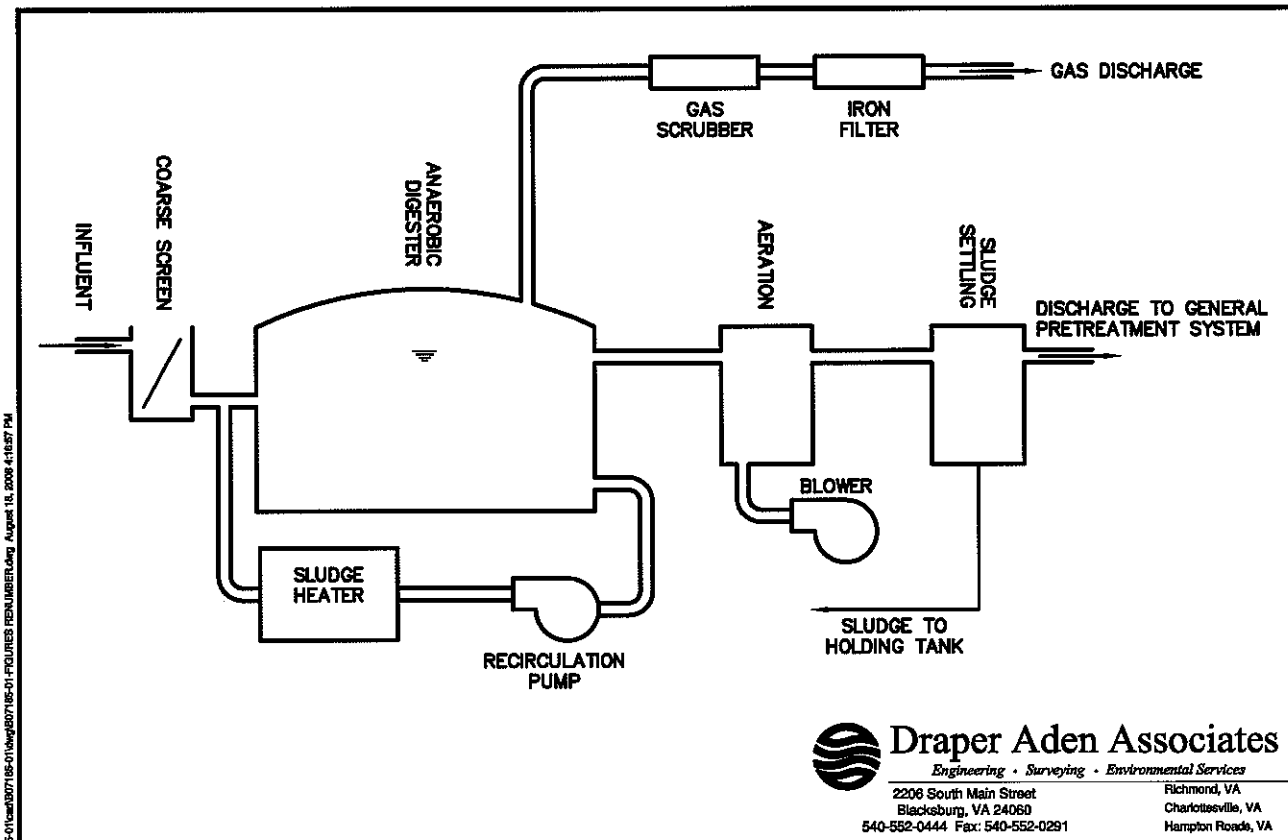
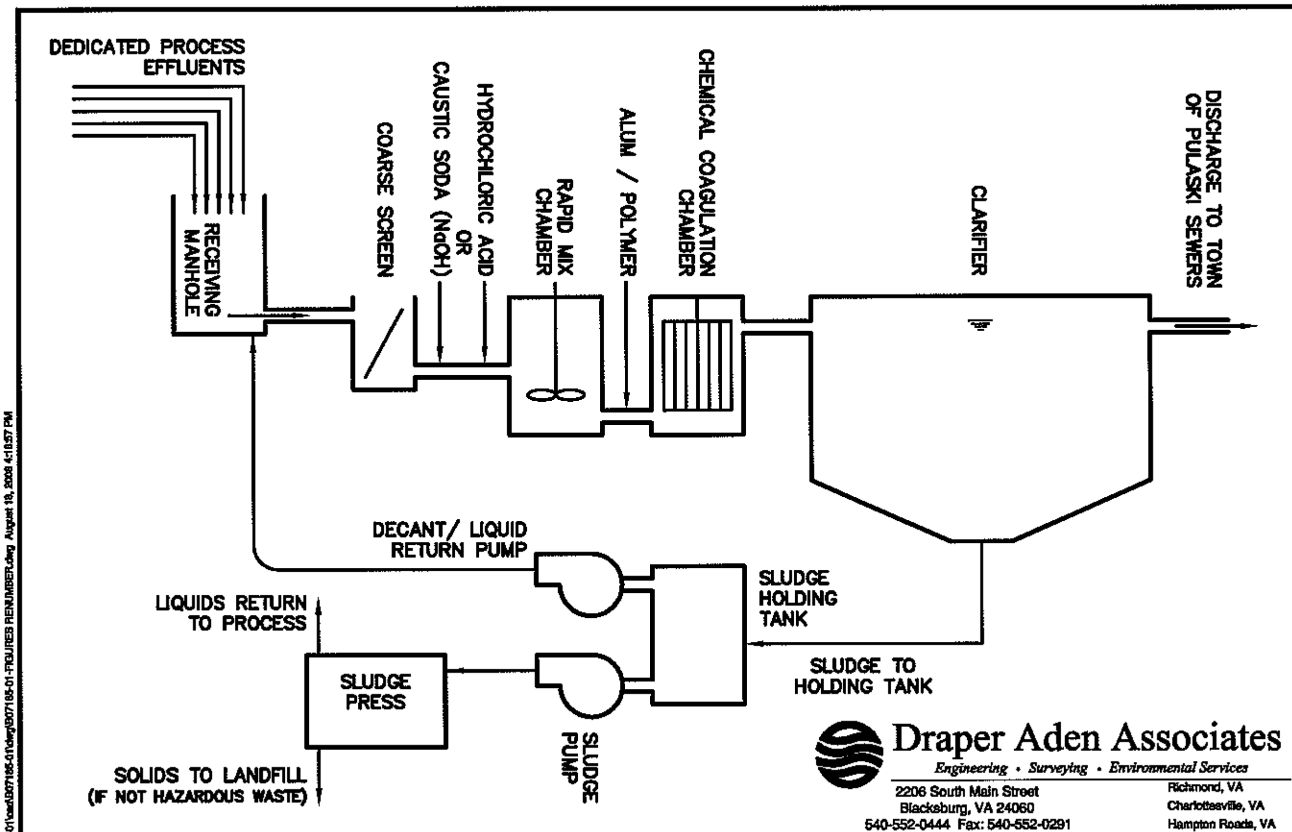
ION EXCHANGE TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 4



SULFATE REMOVAL TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 5



GENERAL PRETREATMENT SYSTEM TOWN OF PULASKI / PULASKI COUNTY NANOTECHNOLOGY BUSINESS PARK - WWTP	DESIGNED GRM DRAWN DLD CHECKED GRM DATE 04/16/08	PROJECT: B07185-01 SCALE: NONE	FIGURE 6

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