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Reduction of Nitrates From Runoff Water  
Via Absorbent Cellulose Matrix  
Embedded with Activated Carbon Black

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**Capstone Final Report**

**5/13/2015**

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## **Abstract**

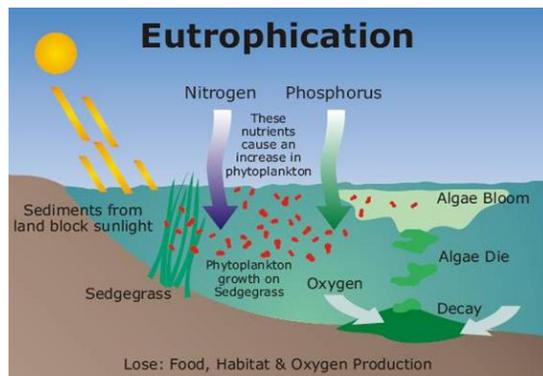
Herein we discuss the design of an absorbent material, composed of a cellulose matrix and activated carbon black particles, to serve as an environmental filtration device. Fundamental kinetic models are used to determine the interactions and adsorption mechanisms of ACB particles within the porous matrix. Pore structure models and langmuir isotherm models were constructed to determine the nitrate adsorption capacity of the designed material. The model suggests that our designed matrix is capable of removing approximately 790 milligrams of nitrate from contaminated water. Experimental data from our fabricated matrix also confirmed successful reduction of nitrate by at least 60%.

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## Motivation

The motivation for this project stems from the harmful effects of agricultural practices in the United States. An estimated 54.9 million tons of fertilizer material is used annually, which includes an alarming 21.9 million tons of nutrients including nitrogen, phosphate, and potash. [9] In excess, these nutrients can cause nearby water sources such as lakes, ponds, and even segments of rivers, to experience eutrophication when rainfall sends runoff water into aquatic ecosystems. Hyper-eutrophic ecosystems are subsequently unable to sustain life due to a surface algae bloom which cuts off light and oxygen below the surface. This often results in the water source becoming an acidic cesspool of dead organisms. Figure 1: Eutrophication [3].



**Figure 1. - Eutrophication cycle depicting the intake of nutrients and subsequent**



**decay [3]**

**Figure 2. - Hyper- eutrophic lake covered in a layer of algae and filled with residue of dead organisms [15]**

In order to decrease the amount of nutrients entering the water system, we propose a barrier technology to remove harmful substances in runoff prior to entry into the water system. This device has the potential to remove nitrates from such water through a carbon filtration system. With the ACB particles hosted in a porous matrix of cellulose, runoff water can be expected to flow in and out of the system with ease.

### **Materials Science and Engineering Aspects**

When designing our filtration device we determined we needed a matrix that can retain both large amounts of runoff water and large amounts of nitrate absorbent, while being environmentally benign. Therefore, through literature research, we selected a highly porous, highly absorbent, environmentally friendly cellulose foam for our matrix. Cellulose foam is synthesized from wood pulp and other natural resources making it an environmentally sensitive option. It also exhibits extremely absorbent behavior, which will allow us to retain more runoff water, allowing for a higher degree of filtration.

ACB was chosen for our additive due to its massive surface area and porosity, its ability to adsorb nitrates, and its environmental merits. ACB is specially suited to selectively remove nitrates and heavy metal ions from solution. Its high microporosity combines with its high surface area to volume ratio to allow for high adsorption of ions, charged particles, and functional groups, which are the primary pollutants in runoff water. Activated carbon is commonly used in filters to create deionized water for chemical labs. [14] By optimizing the amount of activated carbon black within the cellulose foam matrix, a substantial amount of nitrates can be removed from runoff water.

Cellulose pore filling by ACB particles was considered under three different scenarios. The first, and most simplistic, is that a spherical pore of average size would be filled totally with ACB particles to the extent that the volume permits. The second was that only a monolayer coverage of a spherical pore of average size would be present. The third was that the pores, rather than being spherical, would be fibrous cubes without sidewalls. The different scenarios of pore structures will be discussed in further detail in the later sections. These models were iterative, with the first being used as a starting point for calculations. We moved onto the second after considering that ACB particles should only interact with the cellulose matrix through attractive Van-Der Waals forces, which resulted in only monolayer filling. Further investigation

of our matrix lead us to model an average pore as a fibrous cubic shape, leading to the third regime.

### **Previous Work**

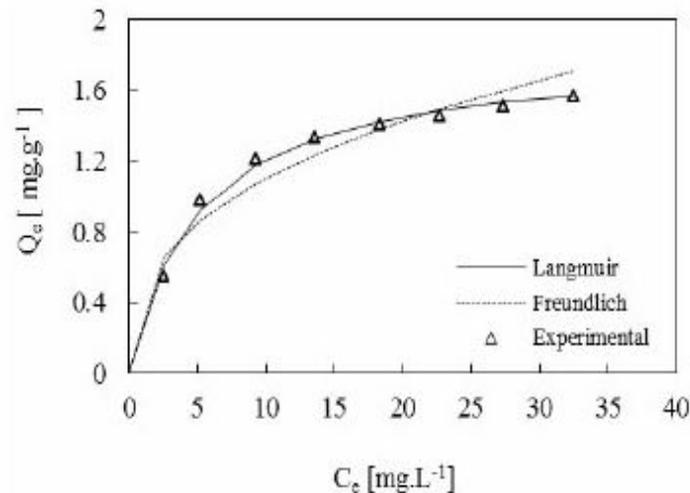
The initial research towards materials selection focused on finding a matrix material that was superabsorbent and an additive substance that could filter nitrates. A discussion of such materials brought us to a cellulose matrix and activated carbon black as an additive. Cellulose hydrogels have potential applications in the fields of food, biomaterials, agriculture, and water purification. There has been a recent interest in cellulose based materials due to its environmental benefits and its abundance. Conventional bleached kraft pulps are frequently used in a host of water absorbing product applications typically absorbing water approximately 20 times their weight. [22] Barcus and Bjorkquist developed a transesterification approach for crosslinking pulps using poly(vinyl methyl ether-co-maleic acid) (PVMEMA) and polyethylene glycol (PEG). The thermally cured wood pulp-copolymer was then treated with a dilute sodium hydroxide solution and the resulting material could achieve water absorbencies of 15–100 g/g. [14] Recently, Goetz et al. reported the preparation and characterization of a nanocomposite film from cellulose whiskers crosslinked with poly(methyl vinyl ether-co-maleic acid) and polyethylene glycol [21]. The synthesized nanocomposites were reported to have a network structure and capable of absorbing up to  $\square$ 900% water by weight of nanocomposite. [21]

Investigation into the adsorption properties of carbon black show that its characteristically large surface area allow for the intercalation of many types of surfactants. [8] The adsorption of anionic, cationic, and nonionic surfactants have been experimentally and mathematically modeled. Results suggest that most possess adsorption isotherms identical to Langmuir's isotherm. In association with our system, given that the toxins being adsorbed into the ACB will possess a charge (as salts often do), we can theoretically conclude that ACB will successfully draw nitrates out of the contaminated runoff water.

Previous studies show that nitrate removal systems have been investigated in an effort to improve the quality of groundwater. While our system deals heavily with cleaning surface runoff water, understanding existing mechanisms of toxin removal enhances the design. Hong et al demonstrate that applying granulated activated carbon (GAC) to wheat rice stone (WRS) and

synthesizing the components into biofilm carriers effectively removes nitrates during the denitrification process. [6] WRS serves as a support in the biofilm and as a leaching agent of cations ( $K^+$ ,  $Ca^{2+}$ ,  $Na^+$ , etc.) to promote the denitrification process. Similar to its use in our system, GAC was found to adsorb a large quantity and variety of pollutants and thus was used in the biofilm carrier.

The nitrate adsorption properties of ACB have been previously investigated using several isotherm models. Zanella et al. investigated the effects on the adsorption of nitrates after  $CaCl_2$  treatment of ACB. They successfully modeled the adsorption capacity of treated ACB by using the Langmuir and Freundlich isotherms, determining that the Langmuir isotherm matched experimental data more closely. Figure 3 shows the research groups Langmuir and Freundlich isotherms and the experimental data for sorption of nitrates.



**Figure 3. - Langmuir and Freundlich isotherm models and the experimental data sorption of nitrate [19]**

They determined that the maximum experimental value of  $Q_e$  for the sorption of nitrate on activated carbon modified with  $CaCl_2$  was  $1.57 \text{ mg.g}^{-1}$ , while for the untreated activated carbon the value was lower than  $0.2 \text{ mg.g}^{-1}$ . Namasivayam and Sangeetha investigated the nitrate removal from aqueous solution using  $ZnCl_2$  activated carbon developed from coir pith, which is made of coconut husk. They also utilized both the Langmuir and Freundlich isotherms to describe their experimental results, with the Langmuir isotherm being the best model. Through our literature research we determined the Langmuir model was the best suited for our project.

## **Design Goals**

The project's main goal was to demonstrate that a porous cellulose matrix embedded with Activated Carbon Black (ACB) particles is capable of reducing nitrate concentration from runoff water. In order to achieve this goal, the group focused on two main questions to better understand the performance of the matrix. The first question was to understand how the ACB particles interacted with the cellulose matrix at a microscopic level. The second question was to understand and predict how efficiently nitrate was being absorbed into the system and removed from runoff water.

To model the porous cellulose matrix, a single pore was isolated and constructed to represent the average size, shape, and structure of the randomly distributed pores in the matrix. Three different iterative scenarios were constructed to design the structure of a single pore and model the interactions of ACB particles within the constructed pore. The average sizes of a cellulose matrix pore and ACB particle were taken from previous literature as mentioned above. Langmuir isotherm curves were used to model the nitrates' adsorption behavior on the ACB particles. Using the pore structure design and adsorption calculations, the amount of total nitrate absorbed into the matrix of a specific quantity of runoff water was determined. This value was compared to the average amount of nitrate washed into the Potomac during a moderate rainstorm in order to understand our success relative to real-world application.

## **Technical Approach**

In order to successfully address the two main questions, several phases of calculations and modeling were designed. First, interaction mechanisms between the ACB particles and the porous cellulose matrix were investigated to better understand the adhesion behavior of ACB particles onto the internal cellulose pore surface. Literature research as well as calculations of Van-der Waals forces were used for this phase. Next, interaction mechanisms between the ACB particles and the nitrate ions were investigated to better understand how the ACB particles adsorb nitrate ions from water.

Simultaneously, the cellulose pore structure models were constructed to construct geometrically simplified representations of a single, isolated pore within the randomly distributed porous matrix. This phase was iterative, and three different pore structure models were constructed to best represent the real structure of our cellulose pore. Using the three pore

structure models, total number of ACB particles per pore and number of active sites within the pore were calculated. This data was then used to calculate the saturation limit and create Langmuir isotherm curves for each scenario at varying degrees of porosity. Total nitrate adsorption capacity was also calculated using the saturation limit for each scenario.

### **Cellulose to ACB Interaction**

The interaction between the ACB particles and the porous cellulose matrix is largely attributed to intermolecular forces, mainly Hydrogen bonds and Van-der Waals forces. On a molecular and atomic scale, adhesion is attributed to the constituent parts of the atoms.

First, cellulose has many hydroxyl groups on its surface which can partake in Hydrogen bonding. [4] These negatively charged hydroxyl groups are electrostatically attracted to the positively charged hydrogen ions on nearby molecules, such as those on the activated sites on surfaces of the ACB particles. This attraction will lead to the adhesion of ACB particles onto the internal surface of the cellulose pore. However, because hydrogen bonds depend on the presence of H<sup>+</sup> ions, the addition of water may introduce a competing process by also forming hydrogen bonds with the cellulose matrix. This may also introduce a risk of desorption of the ACB particles from the cellulose matrix, and its potential effect will be further discussed in the environmental impacts section.

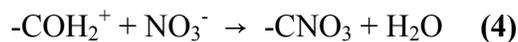
Another large contributor to the attraction between the ACB particles and cellulose is the London Dispersion Van-der Waals force. Van-der Waals forces are those by which any atom or molecule is attracted by another atom or molecule, regardless of material composition or physical appearance [5]. Since the Van-der Waals contribution is positive for both interactions between two ACB particles and ACB particle and the cellulose matrix, the overall Van-der Waals force will be positive and therefore attractive.

In conjunction, the hydrogen bonds between the cellulose matrix and the ACB particles will be much stronger than the Van-der Waals force between the ACB particles. This leads to the assumption that a monolayer of ACB particles adsorbing onto the internal surface of the cellulose pore is more likely than a fully filled pore; both scenarios are described in the sections below. Furthermore, strong interactions between activated carbon and organic polysaccharides like cellulose have been observed by multiple research groups. Luo et. al. used cellulose beads embedded with activated carbon particles and Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles to confirm a

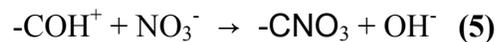
strong attractive interaction between the cellulose beads and activated carbon. [10] Another research group from Japan successfully observed entrapment of carbon black particles within porous alginate matrix, another type of organic polysaccharide similar to cellulose. [18] From this investigation, we concluded that the ACB particles will sufficiently adsorb onto the internal surface of the cellulose pores within the matrix.

### **Nitrate to ACB Interaction**

Activated carbon has both chemical and physical effects on substances where it is used as a treatment agent. Activity can be separated into (1) adsorption; (2) mechanical filtration; and (3) ion exchange [2]. Physical adsorption involves the attraction by electrical charge differences between the adsorbent and the adsorbate. Chemical adsorption is the product of a reaction between the adsorbent and the adsorbate. Mechanical filtration involves the physical separation of suspended solids from a liquid passing through carbon arrayed as a porous media. Ion exchange is defined as a ‘reversible chemical reaction between a solid and an aqueous solution that allows the interchange of ions [2]. Ion exchange can be enhanced by chemical activation. Carbon surfaces have both negative (anionic) or positive (cationic) charges to attract free ions in solution or suspension, depending on how they are treated [2]. Surface treatment with CaCl<sub>2</sub> assigns positive character to the activated carbon sites which allows for the adsorption of nitrate [20]. At a pH < pH<sub>zpc</sub> (zero point charge) the adsorbent surface moves towards a more positively charged one and NO<sub>3</sub><sup>-</sup> adsorption occurs by electrostatic attraction [18].



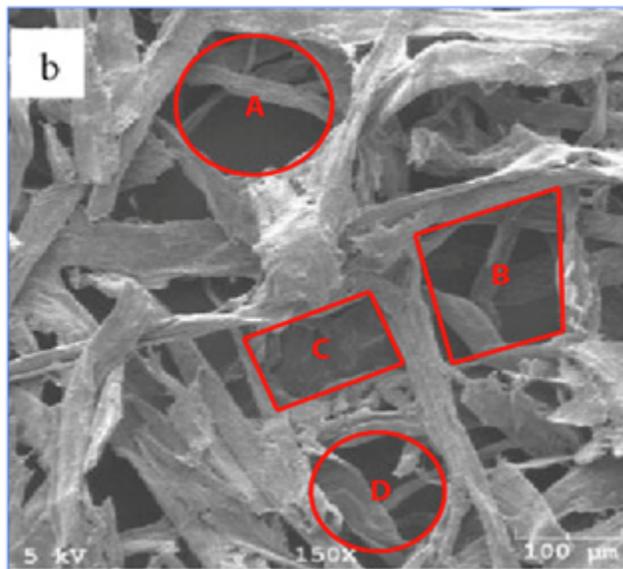
Nitrates can also be adsorbed on the neutral surface of the adsorbent by ion-exchange mechanism [18].



The main mechanism for nitrate sorption does not involve the CaCl<sub>2</sub> directly. It is mainly due to activation of functional carbon sites. Zanella states in [19] that the variation of pH<sub>zpc</sub> suggests that the removal of nitrate, increased for each cycle due to presence of calcium ions in the activated carbon surface. A possible explanation is that calcium ions increase the number of positively charged active sites, providing an augment in the sorption capacity. Further studies should be done in order to identify active sites which contain calcium and whether these sites are responsible for the sorption of nitrate.

## Cellulose Pore Model

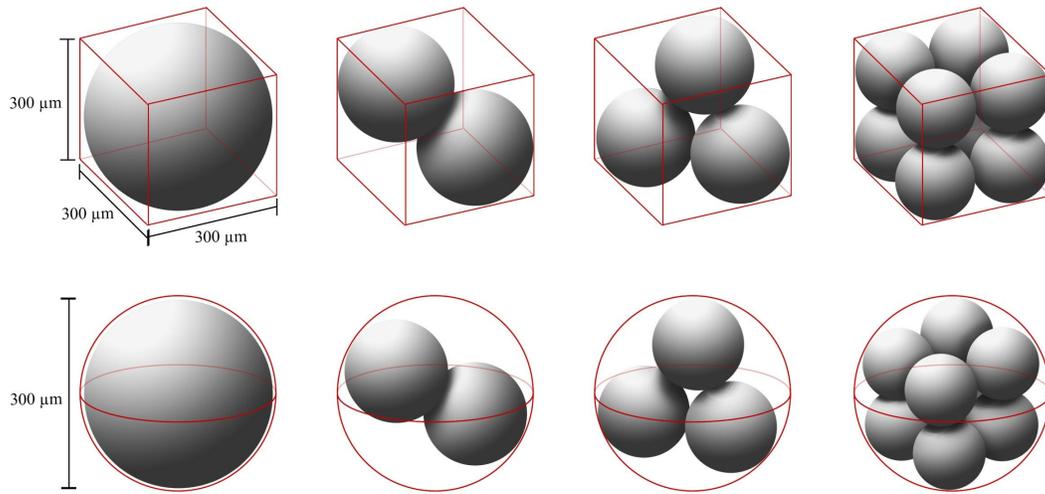
In order to correctly simulate the behaviors and interactions between the ACB particles and nitrate molecules, three different models of the cellulose pore structure were constructed. Geometrical simplifications were made in order to construct the three possible scenarios of isolated pore structure. In each scenario, the adherence of ACB particles onto the pore's internal surface was varied. Pore size was set constant at  $300\mu\text{m}$  in length or diameter for all three scenarios using values of average pore sizes of cellulose matrix from literature. [12] The size of ACB particles can be controlled and varied using different grinding methods. For the first scenario, the ACB particle size was varied from  $150\mu\text{m}$  to  $300\mu\text{m}$ . For second and third scenarios, the ACB particle size was set constant at  $50\mu\text{m}$  in diameter, consistent with the particle size we proposed to purchase for the prototyping phase of the project.



**Figure 4. - SEM Image of Cellulose Pore Matrix**

### Scenario #1 - Fully Filled

For the first scenario, the pore shape was simplified to be a perfect cube or a perfect sphere with a diameter of  $300\mu\text{m}$ . The ACB particles were assumed to fill the entire volume of the cellulose pore with maximum packing fraction. The sizes of the ACB particles were varied as the number of particles increased from 1 to 8 particles, as shown below in Figure 5.

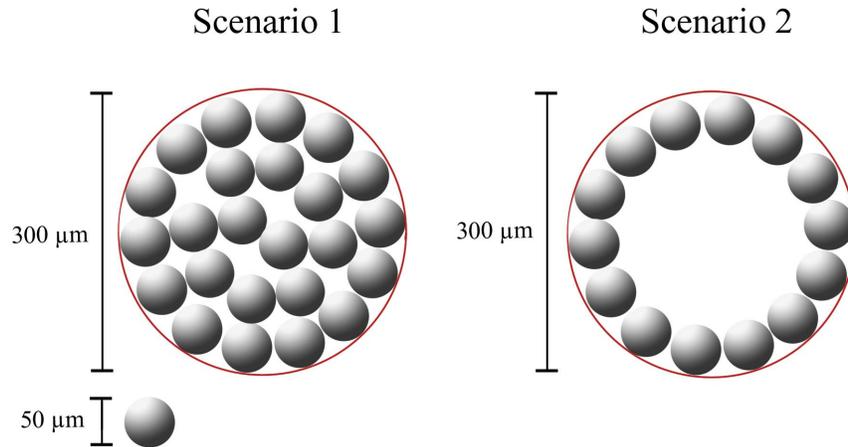


**Figure 5. - Pore Structure Models for Scenario #1**

Using the geometry and size of the cellulose pore and the ACB particle, volume and surface area of the particles were calculated for the varying number of particles per pore and pore shape. For the Langmuir isotherm and nitrate adsorption calculations, particle size of 50  $\mu\text{m}$  and total 216 particles per pore were used. This scenario consisted of various assumptions that were too simplistic to represent the real pore structure. There was not enough electrostatic force between the ACB particles to bind to each other and form a buildup in order to completely fill the pore. Also, particles would not have been perfectly entrapped into the pores due to large variability in pore shape and size. The next scenarios were constructed to address these assumptions and model the pore structure more accurately.

### **Scenario #2 - Monolayer**

Similarly for the second scenario, the pore shape was simplified to be a perfect sphere with a diameter of 300 $\mu\text{m}$ . The cubic pore shape was not considered for this scenario. Instead of filling the entire volume, the ACB particles were designed to create a monolayer on the internal surface of the cellulose pore, with a layer thickness of 50 $\mu\text{m}$ . The size of the ACB particle was also set constant at 50 $\mu\text{m}$  in diameter for the second scenario. The cross-sections of the cellulose pores for the first two scenarios are shown and compared below in Figure 6.



**Figure 6. - Cross-Sections of Pore Structure for Scenario #1 and #2**

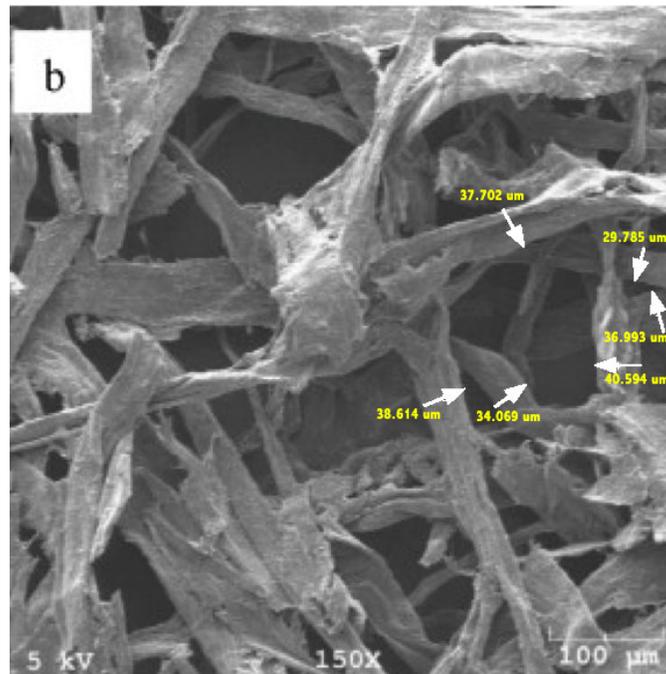
This scenario is more realistic than the previous scenario due to the interactions between the cellulose matrix and the ACB particles. In cases where the ACB particles filled the entire pore, the particles not in contact with the cellulose pore surface would be less strongly attracted to the matrix and would either be removed from the matrix entirely or would migrate to an open space on the cellulose pore. There is also evidence that the cellulose matrix will entrap the activated carbon black particles and the ACB particles would only be attached to the internal surface of the cellulose pore, not occupying the void space like it did the previous scenario.

To calculate the number of particles per pore we took a spherical pore and determined the volume of the shell pore from the edge of the pore to 50 microns into the pore. We then divided this shell volume by the volume of an individual ACB particle and determined the maximum amount of ACB particles per pore. Although more accurate than the previous scenario, the assumption was made that the pore cell would consist of flat wall like surface with open spaces for the ACB particles to bind to. As seen the SEM micrographs previously, the cellulose matrix consist of intersecting network of long fibers that create randomly distributed pores. The next scenario was constructed to better model the fibrous structure of the pore surface of the cellulose matrix.

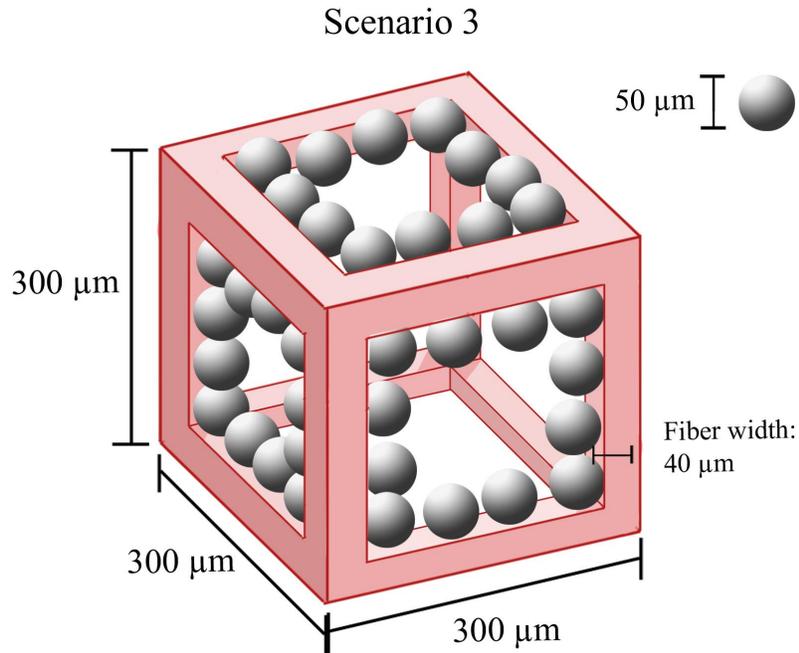
### **Scenario #3 - Fibrous**

For the last scenario, the pore shape was changed to a perfect cube with a side length of 300 $\mu\text{m}$ . The edges of the cube structure was modified to resemble a more fibrous structure than a

fully filled surface. This was observed in SEM images of pore structure of cellulose matrix, as shown below in Figure 7 [2]. ImageJ was used to measure the width of the pore fibers, and an average fiber width of 40 $\mu\text{m}$  was determined for our design. In order to incorporate this fibrous structure into our design, each edge of the cube was constructed as a square base column, with a width of 40 $\mu\text{m}$ . The sides of the cube were left open. The size of the ACB particle was again set constant at 50 $\mu\text{m}$  in diameter for the third scenario. The ACB particles were designed to linearly fit on top of the inner surface of the fibers, as shown below in the schematic in Figure 8.



**Figure 7. - SEM Image of Cellulose Matrix Pore Structure [12]**



**Figure. 8 - Pore Structure Models for Scenario #3**

### **Analysis**

Using the volume of the pore and the volume of individual particles, the maximum number of ACB particles that can be adsorbed onto the internal surface of a single pore was calculated for the three scenarios. It is noted that the number of particles per pore is a slight overestimation since we assumed the space between individual ACB particles would be negligible.

For each scenario, using the number of ACB particles per pore, the maximum absorbance limit,  $Q_m$ , was calculated, in milligrams of nitrate molecules per cubic centimeter of volume. Then a full langmuir isotherm curve was created for each scenario, to show the relationship between  $Q_m$  and  $C_e$ , equilibrium concentration of nitrate molecules in milligrams per liter of runoff water.

### **Particles Per Pore Calculations**

In order to calculate the efficacy of our design in nitrate removal, we needed to model a representative cellulose pore saturated with ACB particles. In our first scenario, we were operating under the condition of a single cellulose pore being spherical, and filled to its

volumetric limit with ACB particles. Investigation of SEM micrographs allowed us to estimate the average pore radius, and the ACB particles used in our design have an average radius of 25 microns. From here, calculation of the average number of particles per pore was simple division of the average pore volume by the average particle. The second scenario we considered called for monolayer coverage of the interior of a spherical pore. Here, calculating the average number of particles per pore was done in a mostly similar way. The difference lied in the available volume for the particles. Here, the volume of the interior of the sphere, that is, any volume not occupied by a monolayer, was removed from the sphere volume number. The third scenario called for a different approach. A computer model of the fibrous cube with adhered ACB particles was generated, and then used to determine the number of particles per pore. Using these values enabled us to calculate the langmuir isotherm for each scenario, as shown below.

### Langmuir Isotherms

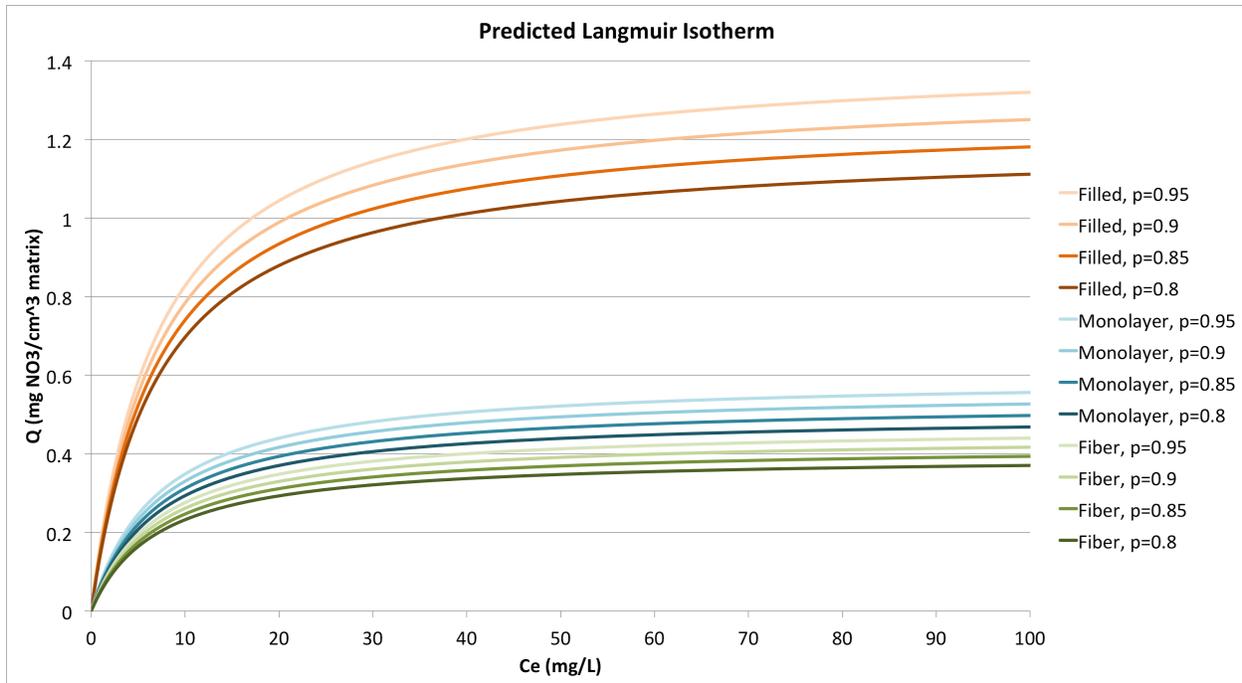
The basic Langmuir equation is:

$$q = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where  $q$  is the ratio of adsorbate (nitrate) to adsorbent (ACB),  $Q_m$  is the saturation limit for  $q$ , representing the maximum possible adsorbate adsorbed for the system,  $K_L$  is a material constant relating to surface energy, and  $C_e$  is the equilibrium concentration of adsorbate in solution. In order to depict the isotherm for the varying scenarios, we needed to determine  $Q_m$  for each. In order to do this, we needed the number of total adsorption sites in a single cell of equivalent size for each scenario. The calculation is shown below:

$$S_t = S_d P_d \quad (7)$$

where  $S_t$  is the total number of open sites in a unit cell,  $S_d$  is the number of open sites per particle, a value derived from literature, and  $P_d$  is the number of particles per pore. Given  $S_t$  for each scenario, we then determined  $Q_m$  for each, given the mass of a nitrate particle. We then plotted  $q$  for a range of  $C_e$  values, resulting in the graph shown below. Additionally, our values were modified by a porosity value which varied from 0.8 to 0.95 to represent a range of potential curves.



**Figure 9. - Langmuir Isotherm Curve for Scenarios #1, #2, and #3**

### Nitrate Adsorption

Given  $Q_m$  values for each scenario, determining the saturation adsorption nitrate levels for a mat of a given size is relatively trivial, simply multiplying  $Q_m$  by the given mat's volume. This allows us to estimate the upper level of our adsorption abilities for each scenario.

Through our analysis, we were able to predict the efficacy our nitrate removal via Langmuir isotherms. We expect the data presented to be a slight overestimation as it does not account for competing adsorption and other potentially negative contributors. However, we feel the data we have presented is encouraging, and represents a new possibility for nitrate filtration.

### Reliability of Model

Our design was based on literature found regarding general particle systems, ACB filtration systems, and kinetics theory. Given the significant lack of literature information regarding the attraction between ACB and cellulose, we needed to rely heavily on theoretical models to describe the atomic Van der Waals forces. In this sense, we believe that with further experimentations and attractive force measurements gained by either optical tweezers or atomic force microscopy, we will be able to accurately describe the London Van der Waals forces in further detail.

Another consideration in examining the reliability of our design is the variability in the cellulose foam pore sizes and the ACB particle sizes. As these estimates were used to generate the Langmuir isotherms, the isotherms were likewise affected and possess large error bars. In addition to the size variability, the models are based on a number of assumptions including; no desorption or competitive adsorption in our system and a saturated density of ACB particles (an overestimate of particles in the structure,

### **Prototype**

Carbon black powder was obtained through Sigma Aldrich, and was activated through the procedure used by Zanella et. al. [19] To do this process, 10 grams of carbon black powder and 2 grams of calcium chloride, or  $\text{CaCl}_2$ , were added to 1 L of deionized water in a beaker. The solution was then stirred for an hour at a speed of 120 rev/min. The modified carbon black particles were then separated from the solution using filtration paper. The collected activated carbon black particles were then allowed to dry for 24 hours.

In order to produce our cellulose hydrogel matrix we needed to obtain chemical and commercial supplies. We obtained cellulose fibers from commercial grade sawdust. Poly(vinyl methyl ether-co-maleic acid) (PVMEMA), Polyethylene glycol (PEG), Hydrochloric Acid (HCl) and deionized water all were bought through Sigma-Aldrich Products. Filter paper and aluminum foil were obtained through local commercial vendors. Dry saw dust was first disintegrated using manual manipulation and then further disintegrated using a mechanical blender. This was performed until we acquired a fluffy fiber.

To prepare the hydrogel we began with deionized water that had its pH adjusted to 2.88-2.98 by addition of 0.50M HCl solution. Once this pH was achieved, PVMEMA was added and the mixture was stirred at 65°C for about one hour. Once the PVMEMA had been fully dissolved, the PEG was added and once again the mixture was stirred for about one hour. The mixture was then allowed to cool to room temperature, and then the cellulosic fines and prepared ACB particles were added. The mixture will once again be stirred for an hour. This mixture was then poured onto a cast made from aluminum foil and dried at 65°C until sample had achieved a constant weight. Finally the cast mixture was cured at 130°C for 6.5 minutes using a curing oven. The prepared sample was then dried and used to conduct a nitrate adsorption experiment as described below.

## Experiment

Reduction of nitrate concentration was tested using a nitrate adsorption testing kit acquired through Engineers Without Borders. The testing method used an indicator solution, which when added to a solution containing nitrate, caused a color change in the solution that corresponded to an approximate level of nitrate concentration in units of milligrams per liter.

First, the adsorption of nitrate through ACB particles by itself was tested to acquire a comparison point. A solution with an initial concentration of 30 mg/L of nitrate was prepared using sodium nitrate dissolved in deionized water. This solution was set aside and used as our control. Approximately 2 grams of ACB particles was added to 50 mL of the prepared solution, which was then stirred for 5 minutes at a speed of 100 rev/min. The ACB particles settled to the bottom of the beaker containing the prepared solution, and a sample of the solution was extracted out of the beaker using a pipette to test the nitrate concentration. A nitrate adsorption testing kit was used to determine the final concentration of nitrate in the solution.

Next, the adsorption of nitrate through our fabricated sample matrix embedded with ACB particles was tested. The control nitrate solution with 30 mg/L concentration was poured onto the top surface of the sample and diffused through the matrix. The outflow solution was then captured and its final nitrate concentration was determined using the same kit. The two final concentrations are shown and compared in the results section below.

## Results and Discussion

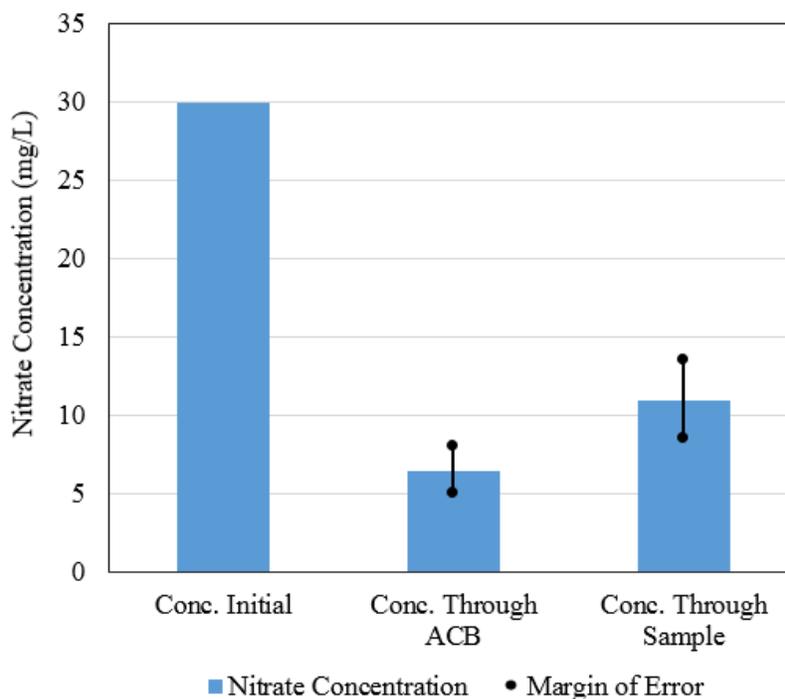
The main quantitative difference between our three scenarios is the density of particles packed into a representative pore. This lead to the variation between  $Q_m$  as well as the variation of the Langmuir isotherms, as shown below in Table 1.

**Table 1. - Comparison of Predicted Scenario Parameters**

	Scenario 1	Scenario 2	Scenario 3
$P_d$ (particles/pore)	216	91	72
$S_t$ (open sites/pore)	2.04307E+14	8.60737E+13	6.81023E+13

Active sites/m <sup>3</sup>	1.15614E+25	4.87078E+24	3.8538E+24
Max adsorbed nitrate for 10 cm x 10 cm x 2 cm matrix (g)	2.380815181	1.003028618	0.79360506
Q <sub>m</sub> (mg/cm <sup>3</sup> )	1.19040759	0.501514309	0.39680253

The isotherms shown are a prediction of what we'd see if we had time to fully synthesize and test our device. It is our belief that scenario 3 is the most realistic, and that any experimental data would fit that curve the closest. Unfortunately, our fabrication attempt was not wholly successful, and so we could not test our data. These predicted results based on our design stand on their own and are encouraging.



**Figure 10. - Graph of Nitrate Concentration Before and After Adsorption Through Sample**

The final nitrate concentrations of the prepared solution from the experiment is shown in Figure 10 above. The initial nitrate concentration was 30 mg/L. When treated with bare solution containing the ACB particles, the final concentration was reduced to 8 mg/L with a error of  $\pm 2$  mg/L. When treated through our prepared matrix prototype, the final concentration was reduced to approximately 11 mg/L with a error of  $\pm 2$  mg/L. Our designed matrix showed about 63%

reduction compared to the initial concentration. Although our experiment was preliminary and needed to be confirmed using multiple trials, the observed reduction of nitrate concentration is very promising and agrees with our model that our design achieved the proposed goals.

### **Ethics and Environmental Impact**

The materials used to produce our design were specifically chosen to have the smallest impact possible on the environment, except for the the removal of nitrate for the runoff water. The components of our product are sustainable and relatively abundant. Our cellulose matrix is composed of a stabilizing polymer agent in acidic conditions, and sawdust . Carbon black is common as well, although the particular carbon black we used was purchased for high purity and surface area.

We examined MSDS statements from each of our materials to ensure that our components are safe and nontoxic. Our carbon black samples are suspected of being carcinogenic in their raw form, but are completely safe once added to our matrix. If carbon black were to leak through our system due to poor processing, that could theoretically cause health problems; however, following our procedures correctly should prevent this issue. PEG and carbon black are both slightly toxic, but only in very high concentrations, on the par of 8-50 g/kg in mammals. Carbon black can also become toxic to marine life, but also only in very high concentrations. Our design does not involve quantities of carbon black large enough to make toxic effects a real risk.

Due to our sustainable product design, disposal requires no special treatments or post-consumption processes. Carbon black could, in theory, be collected and recycled after use. Because the reactivity of our design is so low, our product can theoretically be left undisturbed for several weeks after its use, with no resultant environmental deterioration or effects. Because a primary component of our design is cellulose, it is susceptible to biodegradation on a relatively short timeline.

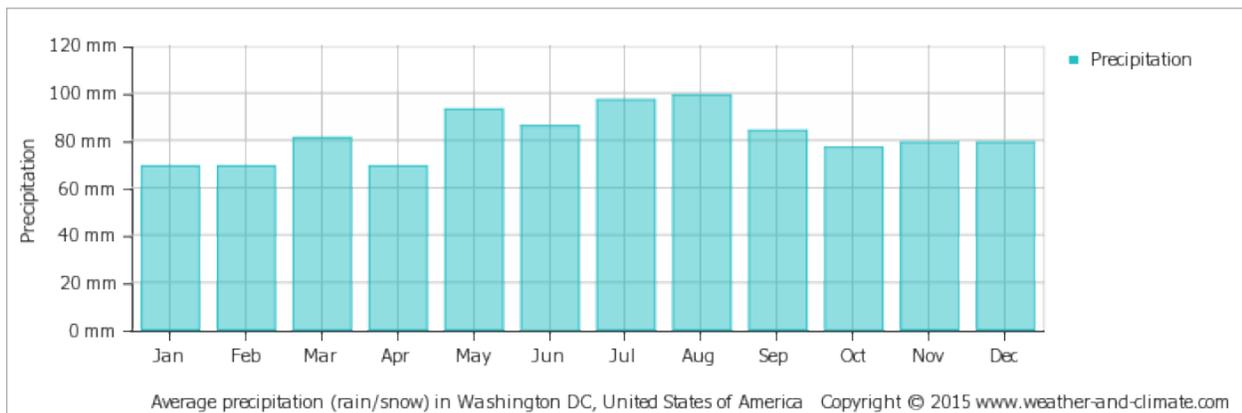
### **Intellectual Merit**

Scientific insight gained from the research and development of this project includes a greater understanding of absorbent cellulose matrix in its application of selective absorbance. It constitutes an analysis of cellulose microstructure and identifies methods of solid-solid

interaction with non-ionic activated carbon black particles. With the use of the Langmuir Isotherm and predictions through structural analysis concerning packing behavior with a cellulose pore structure, accurate conjecture can be made regarding behaviors and interaction between ACB particles and a cellulose matrix. Using these predictions, the amount of nitrates removed from runoff can be calculated, allowing for future development in optimal operation. Currently, there is no literature concerning the interaction and kinetics of transport between a cellulose matrix and ACB. Another contribution to this project includes greater insight towards the development of a bio-compatible product that can selectively remove toxins.

### Broader Impact

In order to confirm successful implementation of our design, we simulated a trial with similar conditions to the Potomac river. Washington DC receives an average annual precipitation of about 1009 mm over 114 days of bad weather. [17] As shown in Figure 9 below, the average rainfall in Washington DC is the highest during the month of August, peaking at about 100 mm.



**Figure 11: Average precipitation in Washington DC by month. [17]**

Assuming that it rains on ten days within that month, rainfall per day is about 10 mm/day, which is an adequate approximation of the average rainy day in Washington DC. 10 mm of rain over 1 acre (4047 m<sup>2</sup>) of land is approximately 38443 L of water. Assuming that rainfall occurs over 4 acres, that the water flows directly into the Potomac watershed, and using a 1m x 1m x 10mm sample of our carbon black doped polymer matrix, about 784 L of water will flow through the mat.

Total nitrogen data for the Potomac watershed revealed total nitrate concentrations of between .40 and 2.71 mg/L in the rainy months of 2008. [16] A maximum value of 2125 mg, or

2.125 grams, of nitrates would be expected to pass through our sample from four acres of rain over the course of a day, which is an accurate representation of the demand for the Potomac river area. Our analysis predicts that a 1m x 1m x 10mm sample of our carbon black doped polymer matrix will be able to remove up to 5 g of nitrate, which exceeds the need in this example.

Not enough nitrates in the water can be problematic for algae growth in ecosystems as well. In application, our carbon black matrix can be treated for specific regional demands, in order to ensure appropriate regulation of nitrates.

### **Future Work**

Many problems arose in our design and research that should be further investigated. The most important of these is the study of the specific sorption mechanism occurring at the active ACB sites. Better understanding this mechanism would allow us to optimize our design further. How the calcium ions are dispersed among the ACB structure and how they affect adsorption is something that can be further investigated. Also to be investigated are the effects from competing sorption: Our device will be exposed to many agents in runoff water that may inhibit our nitrate sorption.

### **Conclusion**

In this paper we have detailed a design for the fabrication of an absorbent cellulose matrix doped with ACB for use as a nitrate filtration system for run off water. Our main design goals were to fabricate a filtration mat that is harmless to the environment and can filter out harmful pollutants such as phosphates, nitrates, and heavy metal ions. After literature research we determined it would be too difficult to design for the removal of all three pollutants so we focused on just nitrates.

Our final design is the accumulation of information obtained from literature, professors, and personal knowledge. We set out to create a model for a novel polymer matrix. The lack of literature on our design suggests that ACB particles have not yet been used in conjunction with a cellulose matrix. The models we developed are simply a theoretical proposal; there is still work to be done mathematically and experimentally to verify if even our basic modeling assumptions were accurate. However, using these assumptions we were able to design a device that can theoretically filter out significant amounts of nitrate from runoff water. Using our model we can

determine the maximum amount of nitrates that can be absorbed for a given device dimension. Overall, we were able to select appropriate materials for an environmentally friendly device, develop models for the adsorption mechanism of our device, determine theories for the molecular interactions occurring between the cellulose and the ACB and between the nitrates and the ACB.

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## Appendix

### A. Calculations

#### Maximum capacity of sorption calculations

Specific surface area of activated carbon black (ACB) particle [3]: 1500 m<sup>2</sup>/g

Density of ACB : .45 g/cm<sup>3</sup>

Diameter of ACB : 50 μm

Langmuir Model equation [18]:  $q_e = q_m \cdot K_L \cdot C_e / (1 + K_L \cdot C_e)$

- $q_e$  equilibrium capacity of adsorption (mg·g<sup>-1</sup>)
- $q_m$  maximum capacity of sorption (mg·g<sup>-1</sup>)
- $K_L$  constant of surface energy (L·mg<sup>-1</sup>)
- $C_e$  equilibrium concentration (mg·L<sup>-1</sup>)

#### Solving for $q_m$ using design parameters and values from literature:

$$S_t = P_d \cdot S_d = (9.459 \cdot 10^{11}) \cdot (216) = 2.043 \cdot 10^{14} \text{ [scenario 1]}$$

$$S_t = P_d \cdot S_d = (9.459 \cdot 10^{11}) \cdot (91) = 8.607 \cdot 10^{13} \text{ [scenario 2]}$$

$$S_t = P_d \cdot S_d = (9.459 \cdot 10^{11}) \cdot (72) = 6.810 \cdot 10^{13} \text{ [scenario 3]}$$

$$q_m = S_t \cdot (\text{pores/m}^3) \cdot (N_A \cdot M_{\text{nitrate}}) \cdot (1000/100^3) =$$

$$(2.043 \cdot 10^{14}) \cdot (56588424210) \cdot (6.022^{23} \cdot 62.0049) \cdot (.001) = 1.190 \text{ mg/cm}^3 \text{ [scenario 1]}$$

$$q_m = S_t \cdot (\text{pores/m}^3) \cdot (N_A \cdot M_{\text{nitrate}}) \cdot (1000/100^3) =$$

$$(8.607 \cdot 10^{13}) \cdot (56588424210) \cdot (6.022^{23} \cdot 62.0049) \cdot (.001) = 0.5015 \text{ mg/cm}^3 \text{ [scenario 2]}$$

$$q_m = S_t \cdot (\text{pores/m}^3) \cdot (N_A \cdot M_{\text{nitrate}}) \cdot (1000/100^3) =$$

$$(6.810 \cdot 10^{13}) \cdot (56588424210) \cdot (6.022^{23} \cdot 62.0049) \cdot (.001) = 0.3968 \text{ mg/cm}^3 \text{ [scenario 3]}$$

