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

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Motivation

- Stems from the harmful effects of agricultural practices in the United States
  - Estimated 54.9 million tons of fertilizer, 21.9 million tons of nutrients
- Nutrients in excess can cause nearby water sources to experience eutrophication
  - Examples: lakes, ponds, and even segments of rivers
- Hyper-eutrophic ecosystems are unable to sustain life
- We propose a barrier technology to remove harmful substances in runoff prior to entry into the water system

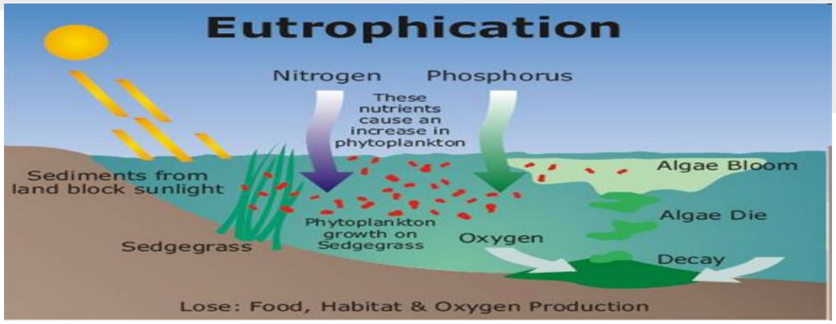

Figure 1. - Eutrophication cycle depicting the intake of nutrients and subsequent decay

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

Background

- Materials Science and Engineering Aspects
  - **Cellulose Foam Matrix**
    - Highly porous, highly absorbent, environmentally friendly
    - Hydroxyl groups
  - **Activated Carbon Black (ACB)**
    - Massive surface area and porosity
    - Ability to adsorb nitrates and environmental merits
    - Specially suited to selectively remove nitrates and heavy metal ions from solution
  - **Kinetics and Transport**
    - Interaction between ACB and cellulose foam matrix
    - Van-Der Waals forces and hydrogen bonding
    - Cellulose pore filling by ACB particles

Design Goals

- **<u>Main goal</u>**: Demonstrate that a porous cellulose matrix embedded with ACB particles is capable of reducing nitrate concentration from runoff water
- **<u>Two main questions addressed:</u>**
  - How do the ACB particles interact with the cellulose matrix?
  - How efficiently is nitrate absorbed into ACB and removed from runoff water?
- To model the porous cellulose matrix, a single pore was isolated
- Langmuir isotherm curves were used to model the nitrates' adsorption behavior
- Amount of total nitrate absorbed into the matrix was determined

Previous Work

1. Conventional bleached kraft pulps are frequently used in water absorbing product applications
   - Barcus and Bjorkquist developed a transesterification approach for crosslinking pulps
   - The thermally cured cellulose-copolymer was then treated with a dilute sodium hydroxide solution

2. The nitrate adsorption properties of ACB have been previously studied using several isotherm models.
   - Zanella et. al. determined that the maximum experimental value of Q_e for the sorption of nitrate $CaCl_2$ modified CB was 1.57 $mg.g^{-1}$
   - For the untreated activated carbon the value was lower than 0.2 $mg.g^{-}$

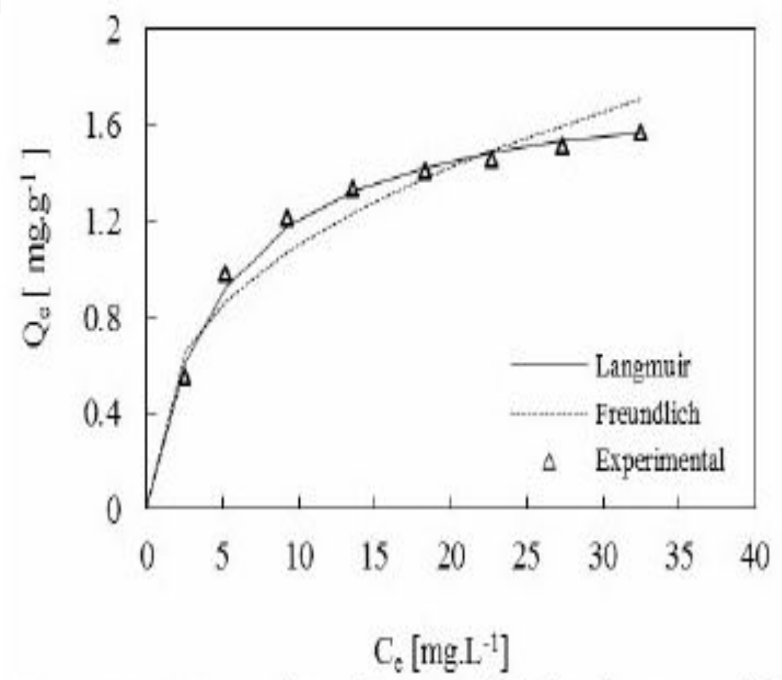

Figure 3. - Langmuir and Freundlich isotherm models and the experimental data sorption of nitrate

Technical Approach

- Several phases of calculations and modeling were designed
  - Interaction mechanisms between:
    - ACB particles and the porous cellulose matrix
    - ACB particles and the nitrate ions
- Cellulose pore structure models constructed
- Data used to calculate the saturation limit and create Langmuir isotherm curves
- Total nitrate adsorption capacity calculated using the saturation limit

Cellulose to ACB Interaction	**Nitrate to ACB Interaction**
A. Hydrogen bonding - Cellulose has many negatively charged hydroxyl groups on surface - Risk of desorption as a result of water **B. Van-Der Waals Force** - Van-der Waals constant is positive and therefore attractive	A. Adsorption - Chemical and physical A. Mechanical Filtration B. Ion Exchange C. Surface treatment with $CaCl_2$ **$-COH^+ + NO_3^- \rightarrow -CNO_3 + OH^-$** - Mechanism mainly due to activation of functional carbon sites

Modeling

- Used to simulate the behaviors and interactions between the ACB particles and nitrate molecules
- Three different models of the cellulose pore structure were constructed
  - Geometrical simplifications
    - Figure 4 SEM Image
- **<u>In each scenario</u>**:
  - The adherence of ACB particles onto the pore's internal surface was varied
  - Pore size was set constant at 300µm in diameter
- Size of ACB particles can be controlled and varied with grinding methods

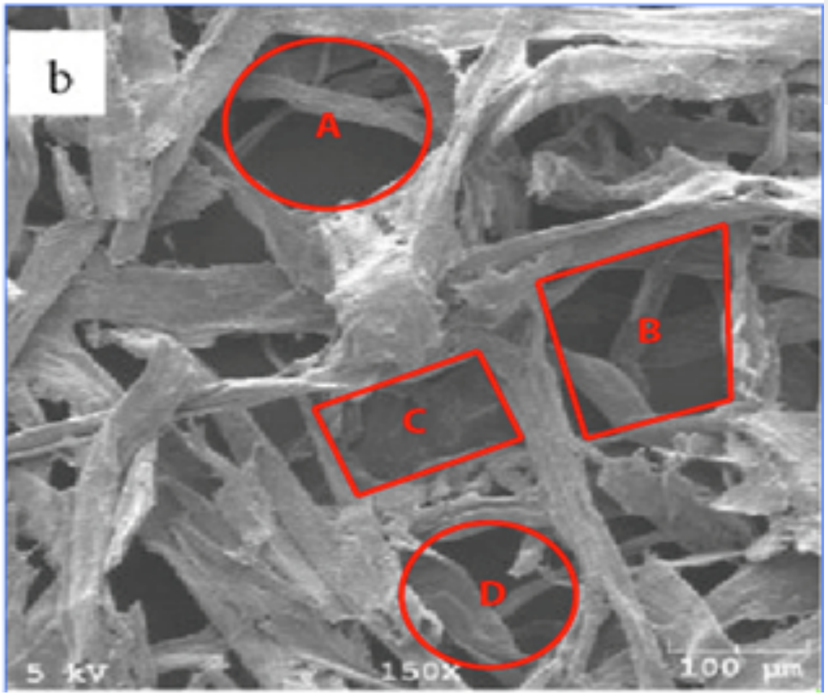

Figure 4. - SEM Image of Cellulose Pore Matrix

Scenario One

- Perfect cube or a perfect sphere with a diameter of 300µm
- Assumed to fill the entire volume of the cellulose pore with maximum packing fraction
- Sizes of the ACB particles varies as number of particles increase
- **<u>Assumptions</u>:** too simplistic to represent the real pore structure
  - Not enough electrostatic force
  - Particles would not have been perfectly entrapped

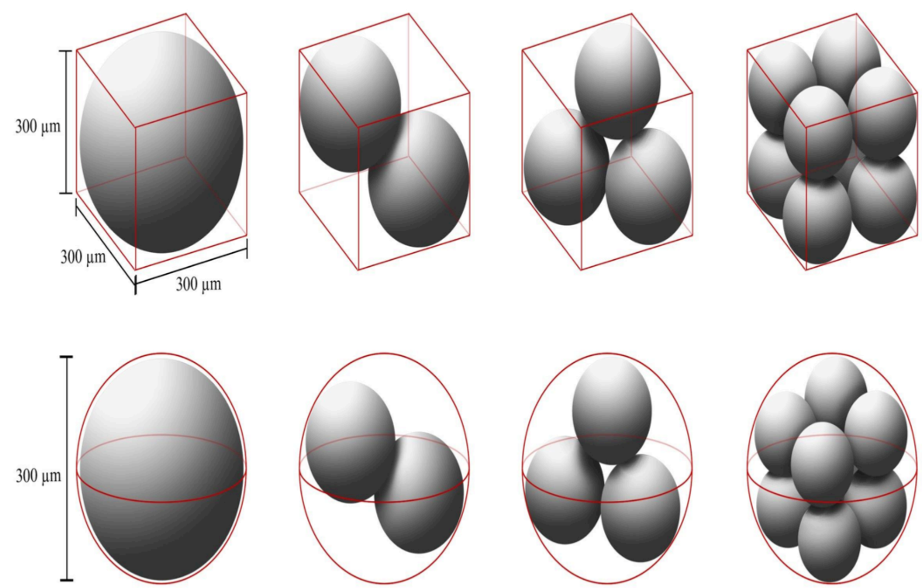

Figure 5. - Pore Structure Models for Scenario #1

Scenario Two

- The pore shape was simplified to a perfect sphere
    - Diameter of 300µm
- ACB particles designed to create a monolayer on the internal surface
    - Interactions between the cellulose matrix and the ACB particles
    - **<u>Figure 5</u>:** cross-sections of the cellulose pores for the first two scenarios
- **<u>Scenario 1:</u>** The particles not in contact with the cellulose pore surface would be less strongly attracted to the matrix
- **<u>Scenario 2</u>:** Particles only attached to the internal surface of the cellulose pore
- **<u>Assumption</u>:** The pore cell would consist of a flat wall like surface with open spaces for the ACB particles to bind to

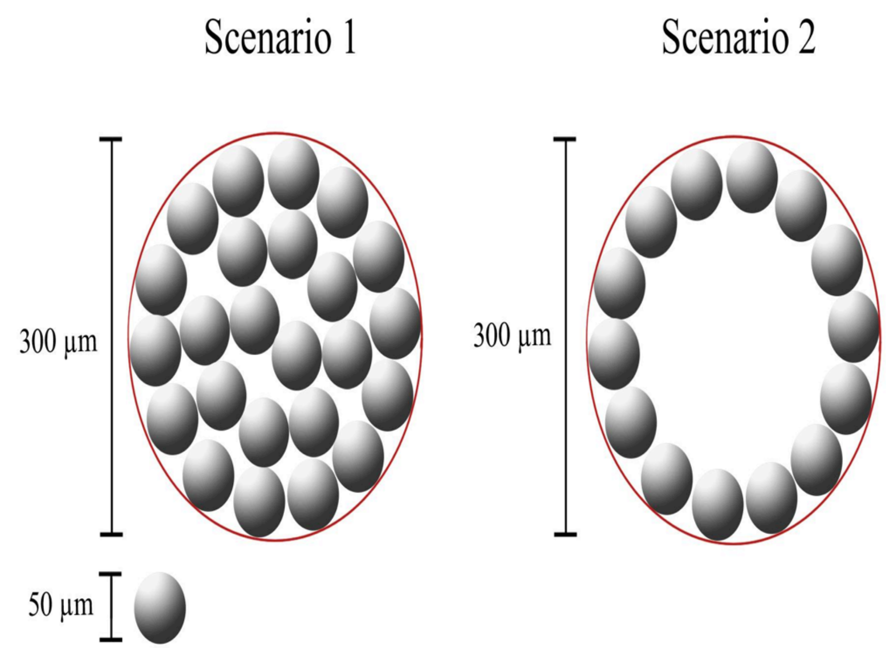

Figure 6. - Cross-Sections of Pore Structure for Scenario #1 and #2

Scenario Three

- The pore shape was changed to a perfect cube with a side length of 300µm
- Edges of the cube structure was modified to resemble a more fibrous structure
- SEM images of pore structure of cellulose matrix
  - Used to measure the width of the pore fibers
  - Average fiber width of 40µm was determined
- Size of the ACB particle set at 50µm in diameter
- ACB particles were designed to linearly fit on top of the inner surface of the fibers

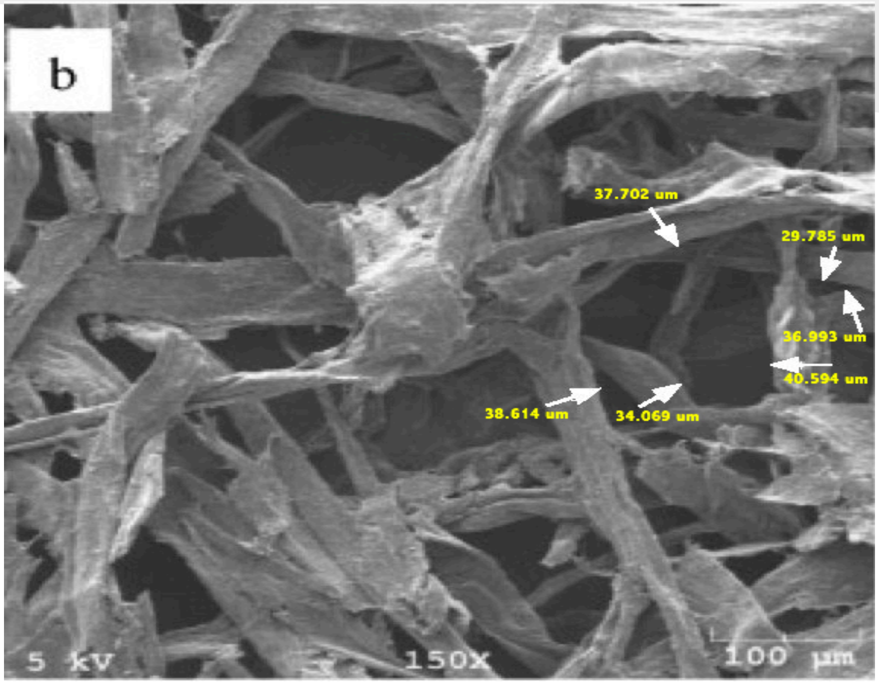

Figure 7. - SEM Image of Cellulose Matrix Pore Structure

Scenario Three (Cont'd)

- The pore shape was changed to a perfect cube with a side length of 300µm
- Edges of the cube structure was modified to resemble a more fibrous structure
- SEM images of pore structure of cellulose matrix
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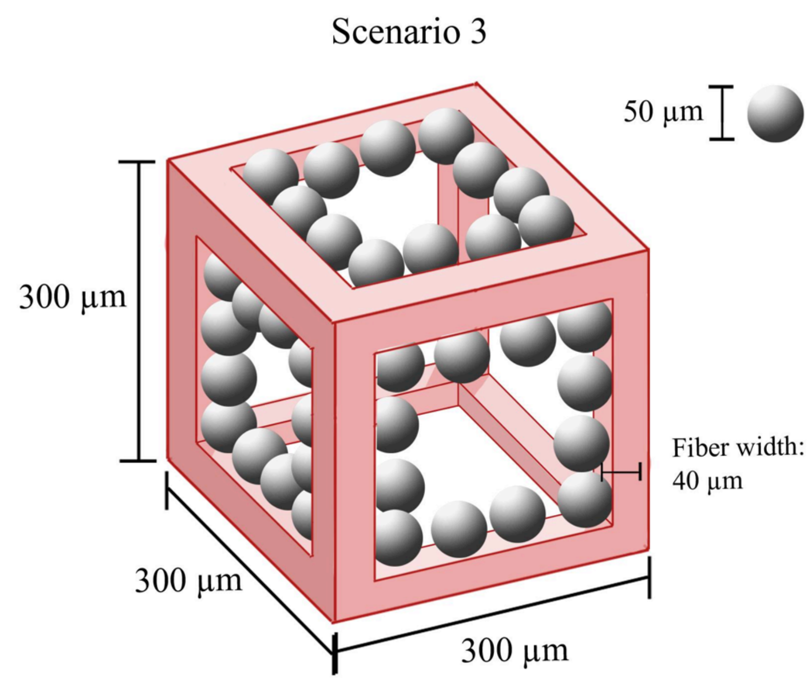
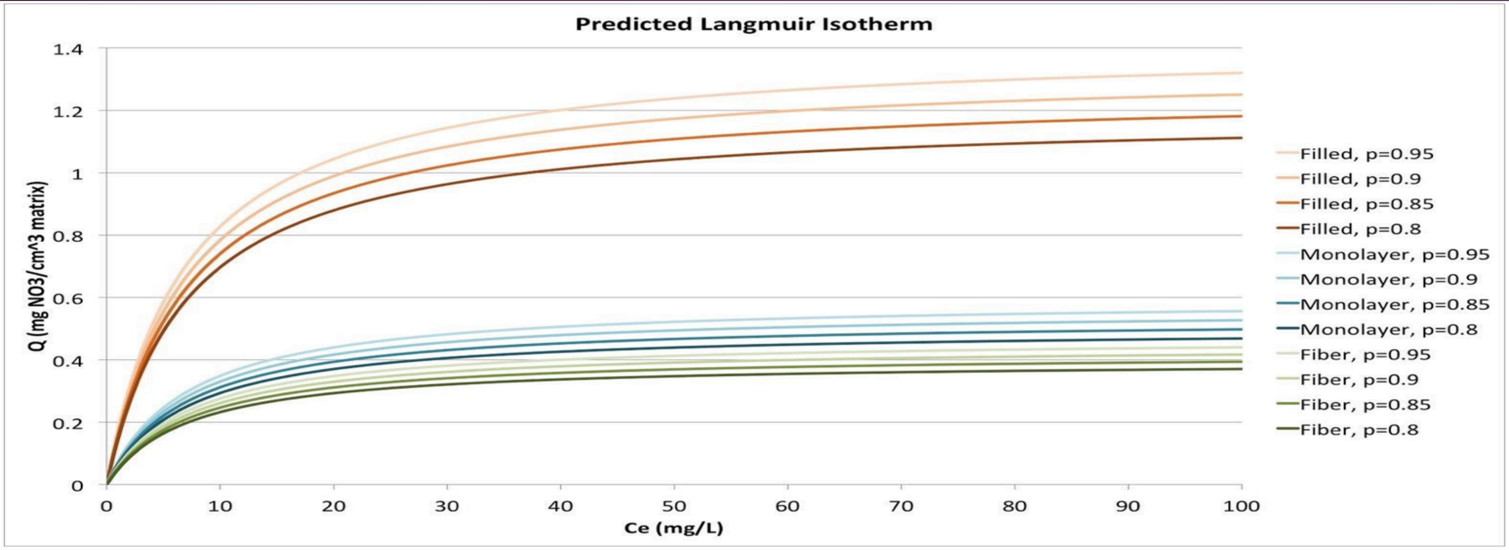


Figure. 8 - Pore Structure Models for Scenario #3

Langmuir Isotherm



Basic Langmuir Eq:

$$q = \frac{Q_m K_L C_E}{1+K_L C_E}$$

- q is the ratio of adsorbate (nitrate) to adsorbent (ACB)
- Q_m is the saturation limit for q
- K_L is a material constant relating to surface energy
- C_e is the equilibrium concentration of adsorbate in solution.

- The Langmuir Isotherm was used to determine the maximum amount of sorption of nitrates per gram of ACB.
- Can be used to determine the max amount of nitrates adsorbed for a specific device volume.
- The model shows that the adsorption capacity reduces as we go from scenario one to three.

Results & Discussion

- Main quantitative difference: density of particles packed into a representative pore
- Lead to the variation between Q_m as well as the variation of the Langmuir isotherms
- Scenario 3 is the most realistic and experimental data would fit that curve the closest

	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^3	**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_m (mg/cm^3)	**1.19040759**	**0.501514309**	**0.39680253**

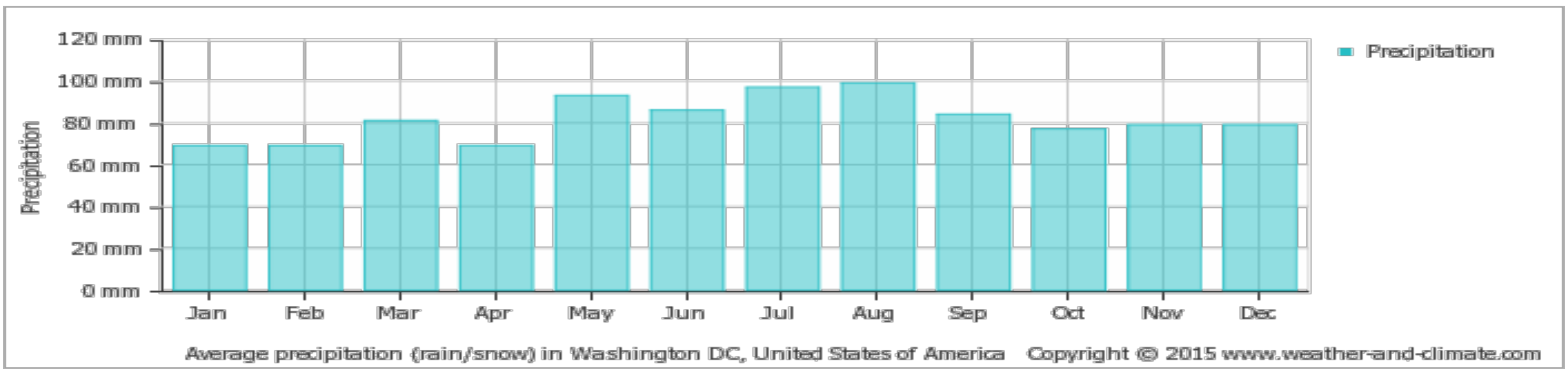
Prototype Development

- To produce our cellulose hydrogel matrix we needed to obtain chemical and commercial supplies
    - Cellulose fibers from ground treated sawdust
- Began preparing the cellulose hydrogel:
    - Deionized water with pH adjusted to 2.88-2.98
    - PVMEMA was added to the mixture and stirred for 1 hour
    - After fully dissolved, the PEG was added and stirred for 1 hour
    - Cellulosic fines added after cooling to room temperature
    - Mixture poured onto a cast made from Al foil
    - Cast mixture was cured at 130°C for 6.5 minutes using a curing oven

Figure. 8 -Images taken during prototype development

Broader Impact

- Simulated a trial with similar conditions to the Potomac river
- DC: Average annual precipitation of about 1009 mm over 114 days of bad weather
- 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
- Not enough nitrates in the water can be problematic for algae growth in ecosystems as well
    - Carbon black matrix can be treated for specific regional demands, in order to ensure appropriate regulation of nitrates



Conclusion

- Design for the fabrication of an absorbent cellulose matrix doped with ACB for use as a nitrate filtration system for run off water
- Main design goals were to fabricate a filtration mat that is harmless to the environment
    - Can filter out harmful pollutants such as phosphates, nitrates, and heavy metal ions
- Difficult to design for the removal of all three pollutants so we focused on just nitrates
- Lack of literature on our design suggests that ACB particles have not yet been used in conjunction with a cellulose matrix
- 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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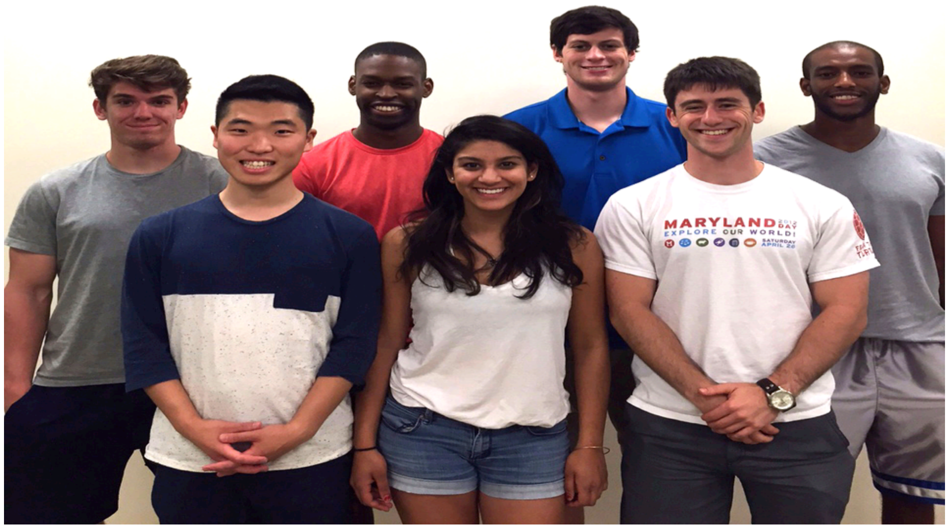

Works Cited

[1] "Activated Carbon." *Activated Carbon Technical Information Bulletin*. Sigma Aldrich Co LLC, 2015. Web. 15 Apr. 2015.

[2] "Activated Carbon Processing." *Agricultural Marketing Service*. USDA National Organic Program, 10 July 2002. Web. 15 Apr. 2015.

[3] Csaba, Pregun. "Water Resources Management and Water Quality Protection| Digitális Tankönyvtár." *Water Resources Management and Water Quality Protection*. N.p., 2011. Web

May 2015.

[4] Chang, Chunyu, and Lina Zhang. "Cellulose-based Hydrogels: Present Status and Application Prospects." Carbohydrate Polymers, Feb. 2011. Web. 8 May 2015.

[5] Corn, Morton. "The Adhesion of Solid Particles to Solid Surfaces,." Journal of the Air Pollution Control Association, Mar. 2012. Web.

[6] "Fertilizer Statistics FAQ." *Frequently Asked Questions About Statistics | TFI*. The Fertilizer Institute, n.d. Web. 7 May 2015.

[7] "Granular Activated Carbon (GAC) Selection." *How to Select the Best Granular Activated Carbon Type for Your Application*. TIGG Corporation, 2014. Web. 15 Apr. 2015.

[8] Gupta, Sachin. "Adsorption of Surfactants on Carbon Black−Water Interface."*Taylor & Francis*. Journal of Dispersion Science and Technology, Aug. 2007. Web. 6 May 2015.

[9] Hong, Siqi, et al. "Enhancement of nitrate removal in synthetic groundwater using wheat rice stone." *Water Science and Technology* 66.9 (2012)

[10] Luo, Xiogang. "High Effective Adsorption of Organic Dyes on Magnetic Cellulose Beads Entrapping Activated Carbon." *High Effective Adsorption of Organic Dyes on Magnetic*

Cellulose Beads Entrapping Activated Carbon. Journal of Hazardous Materials, n.d. Web. 6

May 2015.

[11] Namasivayam, C., and D. Sangeetha. "Removal and Recovery of Nitrate from Water by ZnCL2 Activated Carbon from Coconut Coir Pith, an Agricultural Solid Waste." *Removal and Recovery of Nitrate from Water by ZnCl 2 Activated Carbon from* (n.d.): n. pag. *Niscair Online Periodicals Repository*. Indian Journal of Chemical Technology, 7 July 2005. Web.

Works Cited

[13] R.L. Barcus, D.W. Bjorkquist Poly(methyl vinyl ether-co-maleate) and polyol modified cellulosic fiber, Vol. 5049235U.P. Office, USA (1991)

[14] "Ultrafiltration of Natural Organic Matter and Black Carbon: Factors Influencing Aggregation and Membrane Fouling." *Ultrafiltration of Natural Organic Matter and Black*
Carbon: Factors Influencing Aggregation and Membrane Fouling. Web. 7 May 2015.

[15] "Water Pollution:Eutrophication." *Pollution Effects*. N.p., n.d. Web. 8 May 2015.

[16] Water Quality Analysis of Eutrophication for the Potomac River Washington County Watershed, Washington County, Maryland (n.d.): n. pag. Potomac River Washington County
WQA, Sep. 2010.

[17] "World Weather & Climate Information." *Weather and Climate: Washington DC, United States of America, Average Monthly , Rainfall (millimeter), Sunshine, Temperature (*
(celsius), Sunshine, Humidity, Wind Speed. N.p., Feb. 2010. Web. 6 May 2015.

[18] Y.-B. Lin, B. Fugestsu, N. Terui, S. Tanaka Removal of organic compounds by alginate gel beads with entrapped activated carbon J. Hazard. Mater., 120 (2005), pp. 237–241

[19] Zanella, Odivan, Isabel C. Tessaro, and Liliana A. Feris. "Nitrate Sorption on Activated Carbon Modified with AcAl2: Equilibrium, Isotherms and Kinetics." *SCIENTIFIC PAPER*
NITRATE SORPTION ON ACTIVATED CARBON MODIFIED WITH CACL 2 : (n.d.): n. pag. *Doiserbia*. Federal University of Rio Grande Do Sul, Department of Chemical Engineering, 17 Jan. 2013. Web. 15 Apr. 2015.

[20] Zanella, Tessaro, and Feris. "Study of CaCl2 as an Agent That Modifies the Surface of Activated Carbon Used in Sorption/Treatment Cycles for Nitrate Removal." *Brazilian*