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Evaluation of phosphours removals by biochar-supported nano-scale zero-valent iron

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Abstract

This study evaluated the effectiveness of biochar-supported nano-scale zero-valent iron (nZVI/BC) in removing phosphorus (P) from water. Samples of nZVI/BC were prepared using aqueous nanoparticles synthesis techniques, and were mixed with a stock phosphorus solution. To determine P reductions water samples were tested for P content using the ascorbic acid method. This procedure was repeated for samples of stock P solution, zero-valent iron (ZVI), biochar, and ZVI/BC. nZVI/BC reduced P content by 86% whereas ZVI, biochar, and ZVI/BC removed 6%, -23%, and 17% respectively. This suggests that nZVI/BC has the potential to be an effective method of stormwater remediation.

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1. Background

With the rise in urban land development, natural environmental landscapes are being replaced with impervious surfaces such as roofs, roads, and parking lots. Impervious surfaces prevent the infiltration of water, which can negatively affect local waterways by generating large volumes of runoff at a high velocity. Large amounts of swift moving runoff can adversely affect an eccosytem by increasing sedimentation and erosion in receiving waters. Increased concentrations of sediment lead to a higher level of turbidity, which is a measure of cloudiness in a body of water ('Turbidity: Description, Impact on Water Quality, Sources, Measures - A General Overview', 2008). Elevated levels of total suspended solids can harm aquatic ecosystems by filling in potential habitats, inhibiting plant growth, limiting daytime oxygen release through decreasing photosynthesis, and providing food and shelter for pathogens (Perlman, 2016; 'Turbidity in Lakes', n.d.).

Moreover, runoff can contain elevated concentrations of pollutants such as nutrients, trace metals, and pathogens, which pollute natural surface waters ("Municipal Separate Storm Sewer System (MS4) Program Plan", 2011). Elevated levels of nutrients such as nitrogen and phosphorous contribute to eutrophication which is the natural addition of nutrients to water and its associated effects ('Eutrophication: Causes, consequences, correctives; proceedings of a symposium', 1969). However, the rate and extent of this process can be accelerated by point and non-point discharges of water that contain excess nutrients

(Chislock, Doster, Zitomer, & Wilson, 2013). A point source is defined as any discernible, confined, or discrete conveyance such as discharge from a sewer system, whereas a non-point source is any source that does not meet the legal definition of a point source under the Clean Water Act (CWA) ('What is a non-point source?', 2016). Anthropogenic eutrophication can

adversely affect a body of water by accelerating plant and algal growth which can produce toxic algal blooms, excess detritus, foul tastes and odors, and deplete dissolved oxygen that is vital for fish and other aquatic life. ('Eutrophication: Causes, consequences, correctives; proceedings of a symposium', 1969).

1.1 Stormwater Regulations

The discharge of pollutants and water quality standards for surface waters are overseen by the Environmental Protection Agency through a federal policy enacted by Congress in 1977 called the Clean Water Act (CWA). Under the CWA, it is unlawful to discharge any pollutant into navigable water unless a permit has been obtained ("Summary of the Clean Water Act", 2015). The National Pollutant Discharge Elimination System (NPDES) stormwater program regulates discharge from municipal separate stormwater systems (MS4s), construction activities, and industrial activities ("NPDES Stormwater Program", 2016). Many states, cities, towns, or other public entities use MS4s to manage stormwater. MS4s separate stormwater and sanitary sewage, which results in stormwater draining directly to receiving waters ("Stormwater Discharges from Municipal Sources", 2016). To protect receiving waters, MS4 operators are required to obtain an MS4 permit and develop a stormwater management program. The measures put in place through a stormwater water management program must decrease the discharge of pollutants to the maximum extent practicable (MEP), protect water quality, and satisfy the water quality requirements of the CWA. Best management practices (BMP), such as bioretention cells are used to reduce pollutant levels to the MEP ('Stormwater Phase II Final Rule'. 2005).

1.2 Bioretention Cells

Bioretention cells are an optimal way to treat stormwater runoff because the cells are designed to decrease runoff volume and maximize nutrient removal. Typically, a bioretention cell has a ponding area, an optional layer of vegetation, 2-3 inches of mulch, 2-6 feet of filter media, and an underdrain as seen in Figure 1. ('Virginia DCR Stormwater Design Specification No. 9: Bioretention', 2011).



Figure 1. Diagram of a typical bioretention cell

The ponding area is a shallow, depressed area that allows 6-12 inches of water to pool. This provides temporary storage and allows sediment to settle. Usually, the surface of a bioretention cell is covered with mulch, which acts as a filter for runoff and protects soil from drying and eroding. Bioretention cells can also have a layer of vegetation, which helps to absorb nutrients, prevent erosion, and transpire runoff (Pennsylvania Department of Environmental Protection, 2006). The filter media usually consists of a mixture of sand, soil, and organic material ('Virginia DCR Stormwater Design Specification No. 9: Bioretention', 2011). The layers of filter media in the bioretention cell help to filter out pollutants and allow for the storage and infiltration of runoff ('Pennsylvania Department of Environmental Protection, 2006).

Although bioretention cells are optimally designed to remediate stormwater, there are drawbacks to using this best management practice. Bioretention cells do not always sufficiently remove nutrients such as nitrogen and phosphorus from stormwater and can take up large areas of land. Therefore, it is advantageous to enhance bioretention cells with materials that are able to increase nutrient removal efficiency and make the implementation of this best management practice more economical.

1.2 Bioretention Cell Enhancements

Zero-valent iron (ZVI) is scrap iron filings, and it is able to remove phosphate from solution through precipitation (Chiu 2014). Precipitation is the process in which two ions bind together to form an insoluble compound that can be filtered out of water. Iron (III) and phosphate form iron (III) phosphate (Fe₃PO₄), which precipitates out of solution thereby decreasing the amount of dissolved phosphate. The removal of phosphate by ZVI has been observed under laboratory conditions. Column studies conducted on a mixture of sand and 5% ZVI by volume (7.3% by mass) reported removal efficiencies that ranged from 36-100% due to various influent phosphate concentrations (Chiu, Imhoff, & Culver, 2016). Likewise, zero-valent iron nanoparticles (nZVI) have removed high levels of phosphate under lab conditions. In lab-scale batch reactors nZVI removed 95% of P (Drenkova-Tuhtan, Meyer, & Steinmetz, 2012). Furthermore, another experiment demonstrated that nZVI removed 83.6% of total phosphorus after a contact time of 35 minutes (Tawfik, Harhash, & Saad, 2013). It is hypothesized that nZVI Rossetti

is effective at removing P and other contaminants such as polychlorinated biphenyls and heavy metals due to a larger surface area and high reactivity (Wen, Zhang, & Dai, 2014). However, there are disadvantages to using nZVI in an aqueous environment such as a lack of stability, difficulty separating the nanoparticles, rapid passivation of the material, and limited mobility due to formation of agglomerates (Stefaniuk, Oleszczuk, & Ok, 2016).

In order to improve the dispersion and stability of nZVI, it can be supported on carbon materials, such as biochar. Biochar is biomass that has been heated to high temperatures under low oxygen conditions. This process creates a fine-grained, highly porous charcoal-like material. Because it is highly porous, biochar has a large amount of surface area, which enables it to remove many contaminants such as P, ammonia, and total suspended solids ('Biochar as Filtration Media', 2016). Laboratory studies have shown that biochar supported nZVI has successfully removed trichloroethylene, heavy metals, and dyes such as methyl orange from water (Stefaniuk, Oleszczuk, & Ok, 2016). Moreover, a recent study which evaluated the use of biochar supported nZVI in removing methyl orange dye from waste water showed that there was little decline in methyl orange removal efficiency for 30 days thus indicating that this material could maintain a longer period of efficient pollutant removals than nZVI alone (Han et al., 2015). As both materials have shown the propensity to remove P and other contaminants from water, it would be advantageous to evaluate the efficacy of biochar-supported nZVI for P removals in order to develop this technology for use in stormwater runoff remediation. This study proposes that biochar-supported nanoscale zero-valent iron (nZVI/BC) could be used to increase nutrient removals from stormwater runoff and would remove nutrients more efficiently than a combination of biochar and larger scale zero-valent iron.

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2. Experimental Methods

In order to assess the extent to which nZVI/BC and ZVI with biochar remove P from stormwater, nZVI/BC and ZVI/BC materials were prepared for testing. Next, the samples were mixed with a stock P solution and water samples were taken before and after testing. Last of all, the P concentration of the water samples was determined using the ascorbic acid method ('Standard Methods for the Examination of Water and Wastewater: 4500-P Phosphorus', 1999).

2.1 Material Preparation

Four types of materials were evaluated in this study: nZVI/BC, ZVI, biochar, and ZVI and biochar. A stock P solution with a concentration of 50 milligrams (mg) P per liter (L) was used as a control. The stock P solution was made by dissolving 219.5 mg of potassium dihydrogen phosphate in distilled water and diluting to 1000 milliliters (mL) (Doolittle, 2014)).

The nZVI/BC samples were prepared by combining iron salt with biochar in an aqueous solution. Iron (II) sulfate heptahydrate and biochar with a ratio of 1 mole of carbon to 1 mole of iron were mixed under argon gas for fifteen minutes to remove oxygen and allow substances to completely mix. Once complete, sodium borohydride was added dropwise to the solution at a ratio of 2.5 moles of sodium borohydride to 1 mole of metal. The solution was placed under a vacuum and mixed for another 15 minutes. Then the solution was centrifuged and resuspended in 25 mL of water. The remaining samples consisted of 1 g total of either ZVI, biochar, or ZVI/BC.

2.2 Sample Evaluation

To test the nZVI/BC in the stock P solution, 50 mL of the stock P solution was diluted to a concentration of 1 mg P per L and added to the nZVI/BC sample. Once the sample was prepared, an initial sample was taken from the mixture to determine the initial P concentration. Then the mixture was mixed for 1 hour to allow the nZVI/BC to react with the stock P solution. After the sample was completely mixed, an aliquot of the water was taken to determine the final P concentration. The final sample taken from the mixture was centrifuged in order to separate the solid particulate material from the remaining aqueous solution. In addition to centrifugation, each water sample was filtered using a syringe filter (0.20 micrometer (μ m) pore size) and the liquid was subsequently evaluated for its P concentration using the ascorbic acid method. This process was repeated for the remaining materials pictured in Figure 2, and each sample was evaluated in triplicate.



Figure 2. Samples of biochar, ZVI, ZVI/BC and stock P solution

2.3 Ascorbic Acid Method

In the ascorbic acid method, ammonium molybdate and antimony potassium tartrate react in an acid medium with P to form an antimony-phospho-molybdate complex. This complex turns shades of blue that are proportional to the amount of total phosphorus present when reduced with ascorbic acid, as seen in Figure 3. (Hach Company, 2008).



Figure 3. Samples of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mg per L of P reduced with ascorbic acid

The combined reagent used in this method is comprised of a potassium antimonyl tartrate solution, an ammonium molybdate solution, and an ascorbic acid solution. The potassium antimonyl solution was made by dissolving 1.3715 g of K(SbO)C₄H₄O₆·1/2H₂O in 400 mL of distilled water in a 500-mL volumetric flask and diluted to volume. The ammonium molybdate solution was prepared by dissolving 20 g of (NH₄)₆Mo₇O₂₄·H₂O in 400 mL of distilled water. A solution of 0.1 molar (M) ascorbic acid was made by dissolving 1.76 g of ascorbic acid in 100 mL of distilled water. 5 normal (N) sulfuric acid was prepared by diluting 70 mL of sulfuric acid to 500 mL with distilled water. The combined reagent was made by mixing 50 mL of 5 N sulfuric acid, 5 mL of potassium antimonyl tartrate solution, 15 mL of ammonium molybdate solution, and 30 mL of ascorbic acid solution. Each reagent was added in the order stated above, and the solution was mixed after each addition.

The samples were analyzed by adding 8.0 mL of the combined reagent and mixing it thoroughly with a 50 mL water sample. The absorbance of each sample was measured using a UV-VIS spectrophotometer at a wavelength of 880 nm. Turbidity was corrected for by subtracting the absorbance of a sample of turbid water from the absorbance readings. These values were compared against a standard calibration curve in order to determine the concentration of P in each sample ('Standard Methods for the Examination of Water and Wastewater: 4500-P Phosphorus', 1999). The calibration curve is shown in Figure 4.



Figure 4. P Calibration Curve

2.4 Data Analysis

For each material, the initial and final P concentrations were calculated using equation 1, which is the trend line from the P calibration curve graph solved for concentration.

$$\frac{y - 0.0452}{0.4471} = x \tag{1}$$

y = absorbance

$$x =$$
concentration of P (mg/L)

The percent reduction in P concentration was calculated for each sample using equation 2.

$$\frac{X_i - X_f}{X_i} = \% reduction \tag{2}$$

 X_i = Initial concentration of P (mg/L)

 X_{f} = Final Concentration of P (mg/L)

3. Results and Discussion

The average P reductions for each material are enumerated in Table 1. nZVI/BC reduced P by 86%; ZVI reduced P by 6.0%; biochar reduced P by -23%; and ZVI/BC reduced P by 17%.

Material	Average percent reduction
nZVI/BC	86%
ZVI	6%
Biochar	-23%
ZVI/BC	17%

Table 1. Average P reduction for each material

The average percent reduction in P concentration by nZVI/BC found in this study is similar to the P percent removals from a study assessing the impact of nZVI on a sand filter. The P reduction value reported in that study was 83.6% (Tawfik, Harhash, & Saad, 2013). The high level of P reduction in this experiment and the consistency with other studies suggests that nZVI/BC can reduce P concentrations in stormwater.

However, ZVI only reduced P by 6%; this value is much lower than the P percent removals reported for ZVI which ranged from 36-100% (Chiu, Imhoff, & Culver, 2016). The difference in P removals for ZVI could be due to a variety of reasons such as particle diameter, volume/mass of ZVI used, contact time, and agglomeration of particles during experimentation. This experiment used a small amount of finely ground ZVI and P reduction was evaluated over a short period of time whereas Chiu, Imhoff, & Culver looked at a greater amount of larger sized particles of ZVI over a longer period of time. In addition, it was observed during this experiment that the ZVI particles agglomerated which could have limited the surface area available for P Rossetti

removal. Conversely, the sample of pure biochar did not reduce the P concentration but increased the P concentration. This result was unexpected but not surprising as literature suggests that biochar can adsorb nutrients as well as release them back into the water (Mukherjee and Zimmerman, 2013). The biochar samples used in this experiment mostly consisted of fine particulate matter which dissolved during experimentation. Since biochar is organic matter, the dissolution of it during experimentation could have resulted in the increase in P content in the water. In addition, biochar can easily be produced from various waste products under different pyrolysis conditions; this can result in a lack of consistency in the capability of biochar to adsorb certain contaminants (Yao et al, 2012). The sample of ZVI/BC reduced P by 17%. This shows improved removal from pure biochar and indicates that the addition of ZVI to biochar can improve P removals. During the evaluation of these samples, it was noted that there was less agglomeration of the ZVI particles which could explain the higher level of P removal from this combination of materials. The P removals of nZVI/BC exceeded the P removals for the other materials. This suggests that nZVI/BC has the potential to be a viable tool for stormwater remediation more so than the other materials evaluated in this study.

4. Sources of Error

In this experiment, there were many potential sources of error. First of all, the samples containing biochar were very turbid which could have limited the accuracy of the absorption readings. In addition, due to processing multiple samples at one time there were differences in the duration of the ascorbic acid reduction. This could have produced the variance present in the absorption data for each sample.

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5. Future Work

The experiment should be carried out in a way that limits the turbidity of the samples in order to improve the accuracy of the absorbance data. In this experiment, the samples containing biochar resulted in very turbid samples as seen in figure 5. Consequently, the samples were filtered to try and limit the turbidity of the water samples used in the ascorbic acid testing. In this experiment, the samples were filtered with coffee filters which resulted in water samples that were less turbid. This method was used because cellulose acetate syringe filters with pore size of 0.20 and 0.45 µm were an inefficient method of filtering due to constant clogging. The turbidity of the sample could be limited by using samples of biochar that contain larger pieces of biochar instead of finer pieces which dissolved during experimentation as seen in figure 5 and 6. If turbidity persists in the sample; the turbidity should be corrected during absorbance reading using the method described in *Standard Methods for the Examination of Water and Wastewater:* 4500-P Phosphorus.



Figure 5. Sample of water treated with biochar

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Figure 6. Fine particulate biochar and larger pieces of biochar (l-r)

In addition, it would be advantageous to repeat the experiment with a larger mass of samples in order to produce a more accurate assessment of the phosphorus removals of each material. If the experiment is successful on a larger scale, the next step is to assess the stability of the nZVI/BC particles by evaluating their removals of phosphorus over a longer period of time such as a period of 30 days.

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