Photocatalytic Treatment of Sormwater Runoff using Puralytics LilyPad

by
Jon Laurance

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Abstract approved:

_______________________________________________________

Tyler Radniecki

Stormwater picks up pollutants as it flows over impervious surfaces before ending up in water resources. Best management practices are implemented to remove pollutants from stormwater. Puralytics manufactures a stormwater treatment product called the LilyPad. The LilyPad consists of a titanium dioxide nanoparticle photocatalyst immobilized on polypropylene substrate. Treatment of stormwater by the LilyPad was tested both in the field, at the OSU-Benton County Green Stormwater Infrastructure Research (OGSIR) Facility and in the lab. NO₃⁻, Cu²⁺, and Zn²⁺ removal by the LilyPad was investigated in the field using sunlight and in the lab using UV lamps. Total coliform removal was investigated in the lab using natural sunlight. Algae were more effective at removing NO₃⁻ than the LilyPad in the field. The LilyPad reduced NO₃ to NO₂⁻ and NH₄⁺ in the lab for both collected stormwater and deionized water. Total coliform concentrations were reduced by 50% in the presence of the LilyPad and sunlight. Zn²⁺ removal was observed in the field but not in the lab. Cu²⁺ removal was observed in the lab but not in the field. More work is needed to confirm the LilyPads role in Zn²⁺ and Cu²⁺ removal.

Key Words: stormwater, photocatalysis, titanium dioxide, nanoparticle

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Background

Stormwater

Stormwater runoff is water that flows over impervious surfaces as the result of precipitation [1]. Stormwater runoff picks up pollutants including chemical oxygen demand (COD), total suspended solids (TSS), heavy metals, nitrogen, phosphorus, and human pathogens (e.g. coliform bacteria) [2]. In the National Water Quality Inventory 1996 Report to Congress, urban runoff was the largest source of pollutants causing water quality impairment to ocean shore waters [2]. In 1999, urban runoff impaired 5,000 square miles of estuaries, 1.4 million acres of lakes, and 30,000 miles of rivers [2]. The National Pollutant Discharge Elimination System (NPDES) regulates some stormwater discharges from municipal separate storm sewer systems, construction sites, and industrial activities [1].

Stormwater controls known as best management practices (BMPs) are used to protect water resources. A BMP seeks to reduce stormwater pollution and manage the flow of stormwater while minimizing cost [2]. There are two types of stormwater BMPs, structural and non-structural. Structural BMPs seek to treat stormwater and non-structural serve to limit the amount of stormwater runoff and associated pollution [2]. Examples of structural BMPs are: constructed wetlands, filtration systems, biofilters,
minimizing impervious surfaces, and vendor-supplied systems. Non-structural BMPs include: educating proper waste disposal, community outreach, proper pesticide/herbicide use, and proper fertilizer use.

**Titanium Dioxide Photocatalysis & Adsorption**

Titanium dioxide (TiO$_2$) has been utilized by humans for thousands of years as a white pigment and has been used since the 1980’s in environmental applications [3]. TiO$_2$ acts as a photocatalyst in the presence of UV irradiation, forming electron hole pairs. Holes are able to react with H$_2$O and OH$^-$ to form hydroxyl radicals. Both hydroxyl radicals and holes can oxidize constituents in stormwater, such as organic contaminants [4]. Additionally, the electron from the electron-hole pair can also react with a variety of electron acceptors and take part in a reducing reaction, such as the reduction of nitrate to N$_2$ and NH$_4^+$ [5]. Titanium dioxide exists in three different forms, rutile, anatase, and brookite with particle sizes of greater than 35 nm, 11-35 nm, and less than 11 nm respectively [3]. Most research for environmental TiO$_2$ applications takes place with anatase and rutile which are relatively more common than brookite [3].

TiO$_2$ nanoparticles have large adsorptive capacities due to the large surface area available for adsorption [6]. TiO$_2$ adsorption of metals is influenced by pH. If the pH is below the point of zero charge the surface becomes positively charged, if the pH is greater than the point of zero charge the surface becomes negative [6]. The point of zero charge is 4.8-6.2 for TiO$_2$ [6].

**Nitrogen Chemistry**

Photocatalysis can reduce nitrate in the presence of light [5]. Electrons are excited on the photocatalyst and are transferred to nitrate ions. The excited electron creates a hole that can be filled from an electron donor as the result of an oxidation reaction. The products of the photocatalytic reduction of nitrate are nitrite, ammonia, and dinitrogen [5].
Doudrick et al. tested the effectiveness of several types of titanium dioxide nanoparticles at reducing nitrate in deionized and groundwater, both spiked with nitrate [5]. Different electron donors were tested including oxalic acid, water, and formic acid. Nitrate reduction was only seen with formic acid. This could be explained by the oxidation rate of formic acid being much faster than that of oxalic acid in the presence of TiO$_2$. pH also effects the rate of nitrate reduction. The rate increases as pH decreases because 12 protons are required for nitrate reduction to nitrogen gas. The observed rate of nitrate removal was smaller in groundwater than in deionized water. The decrease is the result of sulfate, carbonate, chloride, perchlorate, and phosphate in the groundwater which compete for electrons, holes, and sorption sites [5].

**Coliforms**

Ireland et al. found that TiO$_2$ photocatalysis is a viable process for the disinfection of bacteria in both pond water and dechlorinated city water [7]. Continuous reactors were used and consisted of TiO$_2$ immobilized on fiberglass mesh and UV light exposure in the 300 to 400 nm range. Initial *E. coli* concentrations in dechlorinated city water were $10^5$ to $10^9$ CFU/100 mL. The city water was dechlorinated two different ways, with sodium thiosulfate and by UV exposure for 48 hr. There was no reduction in *E. coli* when sodium thiosulfate was used. *E. coli* were reduced to less than 1 CFU/100 mL within 9 min of UV exposure when UV exposure was used. The lack of deactivation was attributed to thiosulfate reacting with hydroxyl radicals, produced by TiO$_2$ to form SO$_2$ gas, which was smelled by the researchers. Pond water was also run through the reactor with a starting total coliform concentration of $1.7 \times 10^2$ CFU/100 mL and a total organic carbon (TOC) level of 20 mg/L. Total coliforms were reduced to 1 CFU/100 mL within 6 min of exposure and to less than 1 CFU/100 mL within 18 min. The main method of total coliform inactivation is thought to be oxidation by hydroxyl radicals [7]. The presence of TOC competed with bacteria for hydroxyl radicals lowering the rate of inactivation in TOC rich waters.
Heavy Metals

Engates *et al.* found that the aqueous Cu$^{2+}$ partition coefficient to the solid TiO$_2$ phase, was greater than that for Fe$_3$O$_4$ nanoparticles, commercial activated carbon, and commercial self-assembled mercaptan on mesoporous silica [6]. At the copper concentrations and pH typical in stormwater, it is unlikely for copper to precipitate out of solution [8] [9]. At pH values below the point of zero charge for TiO$_2$, Cu$^{2+}$ is the dominant form of copper and it is repulsed by the positively charged TiO$_2$ surface. Acidic environments also promote competition between H$^+$ and Cu$^{2+}$ for cation adsorption sites. For the pH range of 1-6, the copper adsorption capacity of TiO$_2$ increased as pH increased, reaching a maximum between pH 5-6 [9]. pH values of 1 and 6 had adsorption capacities of 0.05 and 0.2 mmol/g respectively [9]. Bekkouche *et al.* also found that Zn$^{2+}$ and Cu$^{2+}$ adsorption onto TiO$_2$ was less in the presence of phenol, possibly due to competition for adsorption sites [9].

Puralytics LilyPad

Puralytics is based in Beaverton, OR where they produce products to purify water. Puralytics overall process is marketed as consisting of five photochemical processes including photocatalytic oxidation and reduction, photolysis, photoadsorption, and photodisinfection [10]. According to Puralytics website, photochemical oxidation is the activation of the nanotechnology by LEDs or sunlight to produce hydroxyl radicals which break apart chemicals. Photochemical reduction reduces oxidized chemicals such as Hg (II), As (V), and Cr (IV) to more easily adsorbed forms. Photolysis is the disassociation of contaminants by high intensity UV light. Photoadsorption is the adsorption of contaminants such as lead and mercury to the surface of the nanoparticles. And photodisinfection is the deactivation of pathogens by high intensity UV light. Puralytics uses their process in products designed to purify both drinking water and stormwater.

The Puralytics LilyPads are a class of products that are designed to float on water and provide continuous treatment when exposed to sunlight. Three prototypes exist, each consists of photocatalyst immobilized on a mesh material. The photocatalyst is 75% TiO$_2$ in the anatase form [3]. For prototypes 1, 2, and 3 the photocatalyst was
immobilized on ceramic mesh, polypropylene mesh, and a polypropylene-polyethylene blend, respectively. Puralytics states that 1 m² of LilyPad material can treat 1 m³ of water to a 1-log reduction of contaminants in 1 day of exposure to sunlight [11]. The LilyPad material costs between $100-$200 per square meter of material [3]. Figure 1 shows pictures of each prototype.

![Figure 1](image)

Figure 1. LilyPad prototypes 1, 2, and 3 correspond to L1, L2, and L3 respectively. Cutouts are 11.6 cm in diameter. The ceramic L1 sits between polypropylene mesh to prevent the LilyPad from sinking. Both L3 and L2 float. Picture courtesy of Lopez [3].

**Materials and Methods**

**LilyPad Material**

All experiments took place with the second prototype. LilyPad material was provided in 5 ft. by 10 ft. rolls. The thickness varied greatly, ranging from 1 mm to 5 mm. Cutouts used in laboratory experiments were 11.6 cm in diameter and weighed 1.5-2.5 g [3]. Prior to each experiment, all cutouts were weighed, then rinsed by gently squeezing in deionized water. The rinse water was replaced with fresh deionized water and the process was repeated 3 times. Previous research found a significant amount of TOC is introduced into solution by the LilyPad. Rinsing tests showed that rinsing a LilyPad cutout in 0.5 L of deionized water increased the DOC concentration by 1 ppm. However, after 3-30 rinses, the DOC only increased an additional 0.1 ppm [3].
Analytical Methods

Dissolved Oxygen

Dissolved oxygen was measured with a *HATCH SENSion DO6* Portable Dissolved Oxygen Meter. The probe was calibrated before each measurement following the manufacturer's instructions.

pH

For field experiments, an *Accumet AR20* Panel with an *Orion 9156BNWP* pH probe was used. For the metals and coliform tests a *Fisher Scientific Accumet Model 25 Panel* with a *Fisher Scientific* probe was used. Both probes were calibrated using pH buffers of 4.0 and 7.0 following the manufacturer's instructions.

Solids Analysis

Total suspended solids (TSS) was measured using Method 2540 from Standard Methods for the Examination of Water and Wastewater [12]. *Whatman 934-AH™ 0.45 µm Glass Microfiber Filters* were prepared by filtering 20 mL of deionized water then igniting at 550 °C for 15 min. The prepared filters were stored in a desiccator prior to their use.

During their use, prepared filters were weighed immediately before a sample of known volume was filtered through them. The sample volume was chosen to yield at least 2.5 mg of dried residue on the filter. The filter with solids was placed in a 105 °C oven for 1 hr. to dry completely. The filters were then allowed to cool to room temperature in a desiccator for 15 min before being weighed. The weight of the filter and residue was then subtracted from the empty weight to find the weight of the TSS. The weight of solids was then divided by the sample volume to calculate the TSS concentration.

Total volatile suspended solids (TVSS) was measured by igniting the filter containing the TSS at 550 °C for 20 min. The filter was allowed to cool in air to slightly above room temperature for five minutes. The filter was placed in a desiccator to cool
completely before being weighed. The weight of the filter and remaining residue was subtracted from the original weight to find the weight of TVSS. This weight was divided by the sample volume to calculate the concentration of TVSS.

**Conductivity**

Conductivity was measured using an *Accumet AR20* panel with an *Accumet* conductivity probe. The system was calibrated using a 960 µS/cm standard following the manufacturer's instructions.

**Turbidity**

Turbidity was measured using a *Hach 2100 ISO Portable Turbidimeter*. The instrument was calibrated before each use using 50 and 590 NTU standards.

**Dissolved Organic Carbon**

Dissolved organic carbon (DOC) was measured using a *Shimadzu TOC-VSCH Combustion Carbon Analyzer*. The CCAL method was used [13]. Calibration standards were made using potassium hydrogen phthalate between 0.2 and 7.0 ppm as carbon. All samples were filtered through *Whatman 934-AH™ 0.45 µm Glass Microfiber Filters* before DOC measurements were made.

**Cations**

Iron, copper, zinc, magnesium, and calcium were measured with a *Prodigy Inductively Coupled Plasma Optical Emission Spectrometer* (ICP-OES) using radial view [14]. Standards were made with serial dilutions of 1000 mg/L AAS Standard. Prior to measuring, all samples were filtered through *Whatman 934-AH™ 0.45 µm Glass Microfiber Filters* and acidified to 1% v/v ACS grade HNO₃.

**Anions**

Nitrate and nitrite were measured using a *Dionex DX500 Ion Chromatograph*. The eluent consisted of 0.168 g NaHCO₃ and 0.742 g Na₂CO₃ dissolved in 2.0 L of
Deionized water. Prior to measuring, all samples were filtered through Whatman 934-AH™ 0.45 µm Glass Microfiber Filters. EPA method 300.0 was followed [15].

**Ammonium**

Ammonium was measured using a colorimetric assay, EPA Method 351.2 [16]. Standard curves were made for every experimental run using (NH₄)₂SO₄.

**UV Flux**

UV intensity was measured using a Lutron Electronic Enterprise UV-340A light meter per manufacturer's instructions.

**Total Coliforms**

Heterotrophic bacteria enumeration was made utilizing tryptic soy agar spread plate assays. Sample volumes of 10 µL and 100 µL were spread on separate plates and incubated at 35°C for 12 hr. This provided an order of magnitude estimate of the concentration of total coliforms.

Samples were then diluted to reduce the number of total coliforms to less than 2 million per 100 mL. The total coliforms in the dilutions were then enumerated using the IDEXX Colilert Test Kit and IDEXX Quanti Tray Sealer per the manufacturer's instructions. Enumerations from the IDEXX kit were then used to calculate the total coliform concentration in the samples.

**Experiments using Lamp Array**

The lamp array procedure utilized was previously developed, and is further explained, by David Lopez in his M.S. Thesis [3]. The lamp array consisted of ATR 32 watt UV lights with 1 in spacing. Shelves were placed under the array to allow 2 in clearance between the UV lights and the top of the 2 L beakers. The outside of the beaker was covered in aluminum foil to ensure an even flux of light into each beaker. All experiments took place with an initial volume of 0.5 L and contained an 11.6 cm diameter LilyPad cutout. UV intensity ranged from 1600 µW/cm² to 1900 µW/cm². Figure 2 shows the lamp array setup.
Nitrogen & Heavy Metals

The lamp array was used to test the LilyPad performance at removing NO$_3^-$, Cu$^{2+}$ and Zn$^{2+}$ from deionized water, synthetic stormwater, or filtered collected stormwater. Filtered collected stormwater was prepared by filtering collected stormwater through Whatman 934-AH™ 0.45 µm Glass Microfiber Filters. Synthetic stormwater was based on the ionic strength of highway stormwater runoff and contained 0.185 mM NaHCO$_3$ and 1.0 mM NaCl, pH adjusted to 6.5 with NaOH or HNO$_3$ [17] [18].

To adjust for evaporation losses, the solution volume in the beakers was replenished to a volume of 0.5 L. For the NO$_3^-$ tests, the whole solution was poured into a graduated cylinder and then brought back to 0.5 L with deionized water. For the dissolved metals tests, the volume was replenished by adding deionized water up to a line drawn with a permanent marker that was approximately 0.5 L.

For NO$_3^-$, samples were filtered, then 10 mL was placed into a new 15 mL centrifuge tube with a serological pipette. For metals, samples were filtered and 9 mL was placed in a 14 mL polystyrene culture tube containing 1.0 mL of 10% v/v HNO$_3$.

Metals samples were stored at 40 °C and nitrogen samples were frozen at -80 °C until analysis.
Experiments using Natural Sunlight

Coliforms

LilyPads were rinsed 3 times and cut into 11.6 cm diameter circles and placed in 2.0 L beakers filled with 1.0 L of stormwaer. Aluminum foil was wrapped around the outside of each beaker up to the water level. This was to prevent light from entering from the side of the beaker. Five treatments were tested in triplicates:

1. LilyPad in sunlight
2. LilyPad in sunlight on magnetic stir plate (100 rpm)
3. LilyPad in dark
4. No LilyPad in dark
5. No LilyPad in sunlight

All beakers were placed on the roof of Merryfield Hall for approximately 5 hours at Oregon State University. The LilyPad in the dark was placed in a cardboard box. Figure 3 shows the experimental setup on the roof.

![Figure 3. Experimental setup for coliform removal](image)

Coliform experiments took place on 10th and 15th of December 2015. Figure 31 shows that the measured solar intensity during the experiments ranged between 2 and 601 µW/cm². The weather was cloudy and foggy during that week. Stormwater and centrifuged stormwater were tested on the 10th and 15th of December respectively.
100 mL samples were taken four times spaced throughout the experiment and stored at 40 °C until analysis. Coliform concentration was analyzed for the initial and final samples only.

**Field Experiment**

The field experiment took place at OSU-Benton County Green Stormwater Infrastructure Research (OGSIR) Facility at 360 SW Avery Ave, Corvallis, OR 97333. Figure 4 is an overview map of the OGSIR facility and the runoff collection area.

![Figure 4. OGSIR drainage basin overview map. Blue star designates area that hose was turned on during Field Experiment 3. Modified google map (Google, 2015). Figure courtesy of Lopez [3].](image)

The total drainage area is about 100,000 ft² and all stormwater is diverted to an underground storage tank. A pump is activated when there is 1.0 in. of water in the underground tank, and stormwater is pumped into the OGSIR sedimentation basin (RGSB). Weirs located on the side of the RGSB can be controlled to allow stormwater flow into cells 1-3. Figure 5 is a map of the OGSIR facility. The field experiment was conducted in cell 1.
Cell 1 is lined with a 24 mil thick impermeable membrane to prevent LilyPad interactions with the soil. Cell 1 contains a mixing system composed of a 0.25 hp Eco-Flo sump pump attached to a 2 in. schedule 40 PVC pipe that runs the entire length of the cell. McMaster pipe nipples were installed every 2.5 ft. along the length of the 2 in. PVC pipe. The pump was attached to a timer that controls when the pump runs. See Figure 6 and David Lopez's Master's thesis for a more detailed description of the OGSIR design [3].

Figure 5. OGSIR facility map. FE3 took place in cell 1. Map produced by Livingston and modified by Lopez [19] [3].

Figure 6. a) RGSB looking east. b) Cell 1 looking south toward the RGSB. The white PVC pipe is the mixing system. The sump pump sits in the lowest point of cell 1 and pumps water into the PVC mixing system. The orange ruler was correlated to the volume of water in Cell 1.
The field experiment took place from August 14, 2015 to October 8, 2015. A mixture of stormwater stored in the underground tank and tap water from the City of Corvallis was used. First, the RGSB and Cell 1 were swept out and rinsed with tap water, the sump pump was used to remove any excess water from the sedimentary basin and cell 1. The stormwater stored in the underground tank was pumped into the RGSB and the volume was calculated. The area of the RGSB was measured to be 12.20 m² and stormwater volume was calculated using

\[ V = 12.20 \text{m}^2 \times h \times \frac{1000 \text{L}}{\text{m}^3} \]

where \( V \) is the volume in the RGSB and \( h \) is the height of water in the RGSB. The sump pump was used to pump the stormwater into cell 1 after the volume was determined. This was repeated until the underground tank was emptied. The total volume of stormwater was 3,900 L. See Figure 7 for description of the stormwater pumping procedure.

**Figure 7.** a) RGSB filled with stormwater from underground tank where volume was determined. b) Known volume of stormwater was pumped into cell 1 using the sump pump.
To increase the volume of stormwater for the experiment, city of Corvallis tap water was sprayed over the parking lot and next to paint bins located at the facility. The blue star in Figure 4 is the area over which water was sprayed. The tap water flowed into the underground tank, was pumped into the RGSB, and flowed through the weir into cell 1, until a total volume of 15,600 L was reached. Figure 8 shows cell 1 full.

![Image](image)

**Figure 8.** Cell 1 with 15,600 L of stormwater-tap water mixture.

On August 14, after the cell was full, 190 g of KNO₃ dissolved in 5 L of DI water was added along the length of the cell and the pump was set to mix continuously. Nitrate was added to make the concentration similar to previous field experiments [3]. The targeted concentration was 1.7 ppm NO₃-N and the actual measured concentration the morning after spiking was 1.58 ppm NO₃-N. Starting the morning of August 15, samples were taken twice daily, between 8:00 AM and 10:00 AM, and again between 3:00 PM and 5:00 PM. On August 18, at 9:45 AM, the volume in cell 1 was 14,002 L and the nitrate-N concentration was 0.65 ppm. The decision was made to fill cell 1 and spike in more nitrate before addition of the LilyPad. On August 18 city water was again sprayed in the parking lot until an additional 1,700 L was collected in cell 1. An additional 108 g KNO₃ was dissolved in 5 L of DI water and dispersed through the basin. Eight new 5 ft. by 10 ft. LilyPads were added on August 19, at 10:45 AM. Figure 9 shows the LilyPads directly after deployment.
Puralytics correlated the volume in Cell 1 to the height of a ruler located on the north end of the cell. This method of volume measurement only works when the cell has more than 9,600 L. Figure 6 b) shows the location of the ruler.

**Results and Discussion**

**Nitrogen**

In previous studies with the LilyPad at OGSIR, nitrate removal was observed [3]. Figure 10 shows removal of nitrate in field experiments 2 and 3. The field experiment discussed in this paper is field experiment 3 but will be referred to as the field experiment.
Figure 10. Nitrate removal in field experiments 2 & 3 provided by Lopez [3]. Field experiment 3 is the field experiment discussed here. Field experiment 2 took place in June 2015 and the stormwater contained about 1.5 ppm nitrate-N. Nitrate was spiked into the field experiment 3, to a concentration comparable to field experiment 2. Nitrate removal was seen in both field experiments with and without the LilyPad.

The rate of nitrate removal was compared with and without the LilyPad to investigate the effect of the LilyPad on nitrate removal. The rate of nitrate removal in field experiment 2 and field experiment 3 decreased after the addition of the LilyPad.

Nitrate was spiked into Cell 1 on days 0 and 4 of the field experiment and LilyPads were deployed on day 4.3 (Figure 11). See the Field Experiment section under Materials and Methods for a more detailed description of the nitrate spiking procedure.
Dissolved nitrate was removed from the cell with and without the LilyPad in the field experiment. The observed zero order rate of nitrate removal was significantly smaller in the presence of the LilyPad (p=0.002) as seen in Figure 12.

Figure 11. Nitrate mass in OGSIR cell during the entirety of FE3. Nitrate was spiked into cell 1 on days 0.0 and 4.0 to compare rate of nitrate removal with and without the LilyPad. The LilyPads were deployed on day 4.3. Error bars are the 95% confidence level.

Figure 12. Observed zero order rate of nitrate removal during FE3. The observed zero order rate of nitrate removal with the LilyPad is significantly less than without the LilyPad (p=0.002).
More work is needed to determine if the LilyPad is the cause of the decrease in rate of nitrate removal. The LilyPad could potentially be blocking sun, leading to decreased algae growth and photosynthesis. Another potential cause is algae death by the products of TiO\textsubscript{2} photocatalysis.

Lab tests with deionized water were performed to test LilyPad removal of nitrate in deionized water. High concentrations of nitrate-N in stormwater in an urban area in Maryland were measured to be 4.3 ppm [20]. This initial concentration was used for a lab-scale test and the LilyPad was found to remove nitrate (Figure 13). However, as the nitrate was removed, dissolved nitrite and ammonium increased indicating that nitrate was being reduced. The reduction of nitrate by titanium dioxide nanoparticle photocatalysis has previously been observed [5]. The mass balance in Figure 13 does not sum to the amount at t=0 possibly due to escape of gaseous nitrogen species such as ammonia and nitrogen gas [5].

![Figure 13](image.png)

**Figure 13.** Nitrate removal was observed with the LilyPad at the lab-scale in deionized water. Some of the nitrate appears to be reduced to ammonium and nitrite. Previous studies have observed nitrate reduction to N\textsubscript{2} and NH\textsubscript{3} gas in the presence of TiO\textsubscript{2} which might explain the decrease in nitrogen over the experiment [5]. Error bars are the 95% confidence level.

The experiment in deionized water was performed again to test the removal of nitrate at concentrations more similar to values observed in the field experiments. Samples
with 1.5 ppm nitrate-N both with and without LilyPads present was tested under the lamp array (Figure 14). In the presence of the LilyPad, nitrate-N was removed, the control did not have statistically significant removal.

![Figure 14](image.png)

**Figure 14.** Nitrate removal in the lab with deionized water was replicated over a longer time period [3]. A control was run that did not contain the LilyPad. The concentration of nitrate-N was similar to FE2. The total volume of the experiment was 0.5 L. Error bars are the 95% confidence level.

Figure 15 shows less nitrate removal over 17 days in filtered stormwater with nitrate-N concentrations similar to the field experiment. In filtered stormwater, nitrate removal was 22% and 19% over the first 11 days with and without the LilyPad respectively; 92% removal was observed in the field experiment. All samples taken on day 17 show increases in nitrate. Possible sources of contamination include nitrate residue in the ion chromatograph sample holder or column.
Doudrick et al. suggests that the presence of anions and organics can slow the rate of nitrate reduction due to competition for adsorption sites and photogenerated holes and electrons [5]. The stormwater had a significantly higher pH (8.5) as compared to the deionized water (5.5). Photocatalytic reduction reactions occur more readily at low pH values [5]. As the pH increases and the environment becomes less reducing, the rate of nitrate reduction decreases. This could explain the decrease in rate of nitrate removal in filtered stormwater as compared to deionized water.

Doudrick et al. found that nitrate reduction in the presence of TiO₂ did not take place in pure deionized water [5]. Lopez found that the LilyPad introduces dissolved organic matter into solution, which could be acting as an electron donor, allowing the nitrate to be reduced.

Lopez proposed that nitrate removal in field experiment, 1 and 2 was due to algae uptake [3]. Figure 16 shows dissolved oxygen during the field experiment over days 4-8. Oxygen was measured twice daily, once between 8:00 AM and 10:00 AM and again between 3:00 PM and 5:00 PM. Dissolved oxygen concentration is above the saturation concentration in the afternoon and approaches saturation during the night. This is indicative of algae growth [21]. See Figure 33 in Appendix A for oxygen
saturation as a function of temperature for the specific conductance measured during the field experiment [22].

Figure 16. Dissolved oxygen was measured twice daily at around 9:00 AM and 4:00 PM. The oxygen concentration measured in the evening is above the saturation concentration for the measured temperature. Measurements were made at the OGSIR. Lopez suggested this might be due to algae growth.

Figure 17 shows afternoon oxygen concentration and nitrate concentration. The average DO concentration between days 0 and 11 is about 14 mg/L, about 6 mg/L above the saturation limit. Once dissolved nitrate is removed, afternoon oxygen concentrations begin to decline between days 11 and 25. After day 25 the afternoon oxygen concentration drops to within 1 mg/L of the saturation limit. It is proposed that algae growth declined after dissolved nitrate was removed.
Figure 17. Afternoon oxygen concentration decreased after all of the nitrate was removed. This is thought to be a decrease in algae production due to decreased nitrate availability.

An empirical chemical formula for algae provided by Darlymple et al. is C\textsubscript{106}H\textsubscript{263}O\textsubscript{110}N\textsubscript{16} [23]. Assuming all of the 35 g of nitrate added during the field experiment went to creating algae biomass, a total of 550 g of algal biomass was produced. Figure 18 shows that the total volatile suspended solids (TVSS) increased by 260±40 g over the course of 5 days. The non-volatile portion of the suspended solids was constant at about 100 g, indicating that the increase in suspended solids could be due to algal biomass production. TVSS increase has been used by Li as a surrogate for algal biomass production [24].
A total of 20±3 g of nitrate-N was consumed during the first 5 days of the field experiment which represents a potential algal biomass increase of 300±40 g. There is no statistical difference between the increase in TVSS and the calculated algal biomass increase due to nitrate utilization (Figure 19). This is assuming all of the nitrate was utilized by algae and the increase in TVSS was due to an increase in algal biomass.
It is hypothesized that algae and any nitrate that they contain were removed by filtering through 0.45 µm filter paper.

**Metals**

Zn\(^{2+}\), Cu\(^{2+}\), Fe\(^{2+}\), Ca\(^{2+}\), and Mg\(^{2+}\) concentrations were monitored over time during the field experiment. When the data is reported on a mass basis, accounting for evaporation losses from the cell, Ca\(^{2+}\) and Mg\(^{2+}\) stayed constant (Figure 20). On day 4 of the experiment there is an increase in Mg\(^{2+}\) and Ca\(^{2+}\) that was due to addition of city tap water to Cell 1. City tap water contains Ca\(^{2+}\) and Mg\(^{2+}\) at concentrations sufficient enough to account for the increase in mass.

![Figure 20](image)

*Figure 20. a) Shows Ca\(^{2+}\) over time. b) Shows Mg\(^{2+}\) over time. Both Ca\(^{2+}\) and Mg\(^{2+}\) mass increases on day 4 of FE3 when city water was added to the cell in order to prolong the experiment. Ca\(^{2+}\) and Mg\(^{2+}\) concentrations were 18.1±0.5 mg/L and 2.62±0.1 mg/L respectively. The calculated hardness is 1.1 meq/L. Assuming Ca\(^{2+}\) and Mg\(^{2+}\) are the only contributors to hardness.*

The hardness of the water was a concern because hardness has been found to foul TiO\(_2\) photocatalysts [3]. The calculated hardness of the stormwater was 1.1 meq/L, assuming only Mg\(^{2+}\) and Ca\(^{2+}\) are the major contributors to hardness. Water with this hardness is classified as soft and is not thought to be an issue for TiO\(_2\) photocatalysis [25]. This was confirmed in previously conducted tests for fouling where no negative effects were observed [3].

In contrast to Mg\(^{2+}\) and Ca\(^{2+}\), dissolved Zn\(^{2+}\) removal was observed over the entirety of the experiment (Figure 21).
Figure 21. Dissolved Zn$^{2+}$ mass over time during FE3. The spike in Zn$^{2+}$ concentration on day 24 could be due to contamination with first-flush stormwater that was stored in the sedimentary basin from a rain event on days 19-21 of the experiment. Error bars are the 95% confidence interval.

The spike in Zn$^{2+}$ mass that occurred at approximately day 25 of the experiment is thought to be from contamination of first flush stormwater. There was a first flush rain event during this period. The weir that allows water to flow from the RGSB was sealed off with Plexiglas and a clamp. The seal failed and stormwater leaked into cell 1 for up to 12 hr. and created a visible brown plume. The change in volume was not detectable with the ruler. This stormwater was thought to have contained high levels of Zn$^{2+}$.

To see if Zn$^{2+}$ removal could be repeated at the lab-scale, Zn$^{2+}$ removal was investigated in stormwater and synthetic stormwater under the lamp array. The purpose was to investigate adsorption and removal kinetics of Zn$^{2+}$ in the presence of the LilyPad. Figure 22 shows the data collected.
Figure 22. a), b), c), and d) Zn$^{2+}$ concentrations over time in synthetic stormwater in the presence of the LilyPad with starting concentrations of 1000, 500, 250, and 100 ppb respectively. pH was approximately 6.5 at beginning and end of experiment. e) Collected and filtered stormwater concentration over time. Initial pH was 7.8. Error bars are the 95% confidence interval.

The beakers sat open to the air for about 8 days under the lamp array. The location of the lamp array is dusty and the blankets that are used to protect lab workers from UV exposure were deteriorating and would create dust when moved. This might be the cause of contamination.
The collected data was not able to be fit to isotherm models and Zn\(^{2+}\) did not adsorb significantly to the LilyPad. Future work could repeat the experiment in a cleaner environment to avoid Zn\(^{2+}\) contamination. Additionally, dissolved Zn\(^{2+}\) concentrations in the collected stormwater did not change significantly over the experiment. This is unlike what was observed in the field experiment in which dissolved Zn\(^{2+}\) concentrations decreased by second order kinetics (Figure 23).

![Graph showing dissolved Zn\(^{2+}\) removal](image)

**Figure 23.** The observed dissolved Zn\(^{2+}\) removal followed second order kinetics in FE3. Dissolved Zn\(^{2+}\) in Collected and filtered stormwater did not follow second order kinetics.

Freitas *et al.* found algae are able to adsorb Zn\(^{2+}\) and 75% of the total uptake takes place within minutes [26]. Thus, one possible mechanism for Zn\(^{2+}\) removal in the field experiment is adsorption onto algal biomass. Freitas *et al.* measured the biosorption capacity of algae to be 19-32 mg Zn\(^{2+}\)/g algae [26]. An estimate of algal biomass production during the field experiment is made in the Nitrate section of Results and Discussion and found to be about 300±40 g over the first 5 days of the experiment. The mass of zinc in Cell 1 over the same time period decreased by 3870 mg. The calculated biosorption value in the field experiment is 13 mg/g. This is lower than the biosorption capacity value from Freitas *et al.* and could explain the decrease in Zn\(^{2+}\).
Figure 24 shows dissolved copper concentrations during the field experiment. There was no significant removal observed.

![Figure 24: Dissolved Cu²⁺ concentrations for entirety of FE3. Error bars are the 95% confidence interval](image)

To see if Cu²⁺ could be removed at the lab-scale, Cu²⁺ removal was investigated in stormwater and synthetic stormwater under the lamp array. The purpose was to investigate adsorption and removal kinetics of Cu²⁺ in the presence of the LilyPad. Figure 25 shows the data collected.
Figure 25. a), b), c), and d) Cu$^{2+}$ concentrations over time in synthetic stormwater in the presence of the LilyPad with starting concentrations of 1000, 500, 250, and 100 ppb respectively. pH was approximately 6.5 at beginning and end of experiment. e) Collected and filtered stormwater concentration over time. Initial pH was 7.8. Error bars are the 95% confidence interval. 

Cu$^{2+}$ concentrations increased over time in the beakers that had starting concentrations of 100 and 250 ppb. Copper (II) had maximum removals of 93% and 77% for starting concentrations of 1000, 500 respectively. The beaker with collected and filtered stormwater had a removal of 94%. The average mass of the LilyPad cutout used was 2.3±0.1 g. From Figure 25 a), b), and e) it was thought that the
LilyPad was acting as an adsorbent with the capacity to adsorb all of the copper added. If this was true, Figure 25 c) and d) would have to have been contaminated with more copper than was used in the 1000 ppb treatment. Figure 26 shows the observed first order removal of copper at the lab-scale.

![Figure 26. Observed first order removal of Cu$^{2+}$ in lab-scale experiments.](image)

More work is needed to determine the LilyPads role in meal removal.

**Coliforms**

The removal of coliforms by the LilyPad was investigated in collected stormwater. The stormwater contained 367,000±198,000 CFU/100 mL and there was not significant coliform removal for any of the treatments investigated (Figure 27).
Figure 27. Coliform concentration in collected stormwater. Beginning is the starting concentration and all other treatments were measured after 5 hours. Error bars are the 95% confidence level.

The effects on turbidity were investigated by centrifuging the stormwater. Puralytics suggested that turbidity has a large effect on LilyPad performance and that performance would be best below 30 NTU. Turbidity as a function of centrifuge time at 8000 rpm was investigated for 15, 20, and 25 minutes (Figure 28).

Figure 28. Turbidity as a function of centrifuge time. Error bars are the 95% confidence level.
A centrifuge time of 15 minutes reduced the turbidity by 93% to 28±1 NTU. The collected stormwater had an original CFU concentration of 135,000 CFU/100 mL and was reduced by 73% to 36,100±13,000 CFU/mL as a result of centrifuging. Centrifuging did not change the DOC concentration significantly (Figure 30). A centrifuge time of 15 minutes was chosen for all of the treatments because it reduced the turbidity to the target goal, and was assumed to remove the least amount of coliforms. The treatments with the LilyPad that were exposed to sunlight had significant coliform removal (ANOVA single factor, (p=0.023 for Mixed+LP+Light and p=0.025 for Light+LP)). Total coliforms were reduced from 36,108 to 18,355 and 17,500 CFU/100 mL for mixed and non-mixed treatments respectively. Figure 29 summarizes the LilyPad performance for centrifuged stormwater.

![Figure 29](image_url)

**Figure 29.** Total coliform concentration for LilyPad treated stormwater. Stormwater was centrifuged for 15 min at 8000 rpm. Significant reduction in coliforms was seen for the treatments containing the LilyPad that were exposed to light. Error bars are the 95% confidence interval. * indicates significant reduction in coliform concentration.

Dissolved organic carbon concentration and pH were in ranges that can support coliforms. As expected, centrifuging did not change the pH or the DOC concentration as seen in Figure 30.
None of the treatments tested resulted in the 1-log reduction in coliform concentration goal. One possible reason is the solar intensity available during the experiment. The experiments took place in December on cloudy days. Figure 31 compares the measured solar power during the coliform experiments to a typical sunny day in August in Corvallis, OR. The maximum solar power was only 11-15% of a typical August day.

Figure 30 a) pH for coliform test did not change as a result of centrifuging or after contact with the LilyPad. b) Dissolved organic carbon concentration did not change significantly over the experiment.

Figure 31. Solar power measured during a typical August day during FE3 and the measured solar power during the coliform experiments. Both coliform experiments took place on cloudy days in December.
More coliform removal is expected on a sunny day and is currently being investigated with a solar simulator. The LilyPad did not achieve a 1-log removal of coliforms over 1 day during a cloudy December day as stated on the Puralytics website [11].

**Conclusion**

Nitrate was primarily removed by algae in the field experiment, but was reduced to ammonia in the lab in both deionized water and collected filtered stormwater. The rate of nitrate removal in the collected stormwater was smaller than in deionized water. This could be due to other constituents in the stormwater that interfere with the reduction of nitrate. The role of the LilyPad in Cu$^{2+}$ and Zn$^{2+}$ removal is inconclusive.

Over the course of 5 hours of sunlight exposure, the LilyPad was able to reduce the total coliform concentration by 50% in centrifuged stormwater. Total coliform removal was not observed in un-centrifuged stormwater, due to high levels of turbidity. Coliform removal tests took place in December with low solar intensity, the role of solar intensity on coliform removal is currently being investigated in a solar simulator.

**Appendices**

**Appendix A**

![Figure 32](image.png)

*Figure 32.* Volume measured during FE3 using ruler located on the north end of Cell 1 that was correlated to stormwater volume by Puralytics.
Figure 33. Solubility of oxygen in water at various temperatures at the average specific conductance measured in FE3 of 241 μS/cm. Data generated by U.S. Geological Survey [22].

References


