Entry into the Stockholm Junior Water Prize 2014

A Novel Photocatalytic Pervious Composite for Degrading Organics and Inactivating Bacteria in Wastewater

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I. ABSTRACT

The goal of this research was to develop a safe, cost-effective, and eco-friendly technique for wastewater purification. The innovative methodology developed in this study integrates an enhanced photocatalytic advanced oxidation process (AOP) with filtration using novel pervious composites. Silver (Ag) doped photocatalytic pervious composites were synthesized using uniformly graded sand, Portland cement, titanium dioxide (TiO_2) and silver nitrate ($AgNO_3$). The ratio of TiO_2: cement: sand was 1: 5: 20 by weight and the optimum amount of Ag was 0.04% by weight of the composite. This composition was determined from photodegradation studies of methylene blue using UV-Vis spectroscopy. The photodegradation of methylene blue conformed to a pseudo-first order kinetics according to the Langmuir–Hinshelwood model. Bacterial inactivation studies with the Ag-doped photocatalytic pervious composite showed 98% reduction in total coliform bacteria immediately after filtration. Subsequent exposure of the filtered water to sunlight inside a beaker containing an Ag-doped photocatalytic composite disc resulted in 100% inactivation of total coliform bacteria in just 15 minutes. This project opens numerous possibilities for sustainable, economically viable, and effective wastewater purification.

II. TABLE OF CONTENTS

III. KEY WORDS

Advanced oxidation process, coliform bacteria, filter, methylene blue, photocatalysis, pervious composite, silver, sunlight, titanium dioxide, wastewater

IV. ABRREVIATIONS AND ACRONYMS

UV: Ultraviolet	Vis: Visible light
SODIS: Solar disinfection	TCC: Total coliform counts
E. coli: Escherichia coli	DNA: Deoxyribonucleic acid

V. ACKNOWLEDGEMENTS

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VI. BIOGRAPHY

Deepika Kurup is a sophomore at Nashua High School South. Recently she received the United States President's Environmental Youth Award from the Environmental Protection Agency. She also received first place in the Environmental Science division at the 2014 and 2013 New Hampshire Science and Engineering Exposition. In 2013, Deepika was the national runner-up for the Stockholm Junior Water Prize. She was also an invited participant at the 2013 White House Science Fair. In 2012, Deepika was named "America's Top Young Scientist" after winning the grand prize in the Discovery Education 3M Young Scientist Challenge. She has been passionate about solving the global water crisis ever since she was in elementary school, as she was exposed to the water problem at a very early age. Deepika challenges herself academically and is a member of the Julian C. Stanley Study of Exceptional Talents. In her free time, she enjoys giving talks to encourage students all around the world to pursue science, technology, engineering and math, and to increase awareness of the global water crisis.

1. INTRODUCTION

1.1 Problem and Need

Fresh water demand for domestic use, agriculture, and industries is increasing significantly due to rising population, industrial development and economic growth. Given the growing scarcity of freshwater and increasing wastewater production, wastewater treatment for reuse is gaining importance. However, it is estimated that around 90% of wastewater generated worldwide remains untreated (Tchobanoglous et al., 2003). Wastewater contains a wide range of chemical and biological pollutants that, if discharged improperly, can result in the pollution of soil, sediments, water bodies and groundwater. Such pollution adversely affects humans, animals, plants, and aquatic life. Waterborne diseases such as cholera and diarrhea caused by bacteria such as Escherichia coli (E. coli), Salmonella, and Shigella are responsible for more than 2.2 million deaths a year; most of the victims are children in developing countries (WHO and UNICEF, 2000). Many organic and inorganic pollutants such as volatile organic compounds (benzene, toluene, xylene, etc.) and heavy metals (lead, cadmium, arsenic, etc.) are toxic to humans and many living species. Some of these pollutants are carcinogens and can cause damage to the kidney, liver, skin, and the respiratory and central nervous system.

Current methods of wastewater treatment include physical means such as sedimentation, filtration, and ultraviolet irradiation (UVC at wavelength, λ = 100-280 nm); chemical means such as chlorination, fluorination, and ozonation; and biological means which may be aerobic or anaerobic processes (Cheremisinoff, 2006). Wastewater is usually treated in large treatment plants that are expensive, energy intensive and use harsh chemicals that can generate compounds leading to secondary pollution, and even leave water with a noticeable odor and taste. As we strive for an eco-friendly world, conventional techniques for wastewater remediation must move towards green and sustainable alternatives. Thus, there is a critical need for safe, affordable, and sustainable water purification techniques.

1.2 Photocatalytic Advanced Oxidation Process (AOP)

Solar disinfection (SODIS) that uses ultraviolet radiation from the sun (UVA, λ = 315-400 nm) is a safe and cost-effective means of purifying water infected by pathogens (McGuigan, 2012). When UV light is absorbed by the deoxyribonucleic acid (DNA) of bacteria, pyrimidine dimers are formed between adjacent thymine or cytosine base pairs. This inactivates the bacteria by

preventing its DNA from replicating. In recent years, photocatalysts such as titanium dioxide (TiO_2) have been used to accelerate the SODIS process (Hashimoto and Fujishima, 2005; Byrne et al., 2011; Barnes et al., 2013). When UVA radiation strikes these photocatalysts, electrons (e^-) from the valence band are energized into the conduction band, thereby leaving positive holes (h^+) in the valence band. Some of the electrons and holes may recombine, but most combine with oxygen and water to create reactive oxygen species such as super oxides (O_2^-), hydroxyl radicals ($^\bullet OH$) and hydrogen peroxide (H_2O_2) (Equations 1-5). Through the advanced oxidation process (AOP), organics such as methylene blue are oxidized by $^\bullet OH$ radicals, into carbon dioxide and water (Houasa et al., 2001; Chang et al., 2004) (Figure 1). The reactive oxygen species also destroy bacteria by damaging their cell structure and disrupting their DNA, thereby preventing them from replicating (Sunada et al., 2003; Nadtochenko et al., 2005).

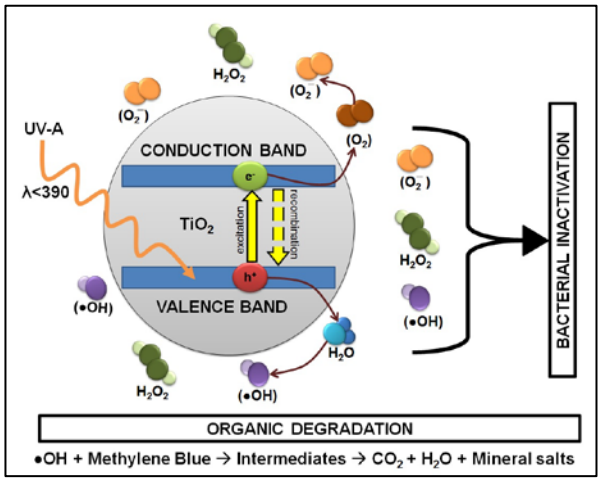

Figure 1. Bacterial inactivation and organic degradation by advanced oxidation process

$TiO_2 + h\nu \rightarrow TiO_2 + (h^+ + e^-)$ (1)

$H_2O + h^+ \rightarrow {}^\bullet OH + H^+$ (2)

$2H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+$ (3)

$O_2 + e^- \rightarrow O_2^-$ (4)

$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2$ (5)

To enhance and extend the photocatalytic activity of photocatalysts from the UV (3% of sunlight reaching the earth) into the visible light spectrum (44% of sunlight reaching the earth), researchers have tried doping the photocatalysts with silver (Ag) (Akpan and Hameed, 2010; Hamal and Klabunde, 2007; Liu et al., 2011; Guin et al., 2007). Doping with Ag introduces an energy level (intermediate band) just below the conduction band, essentially reducing the band gap energy and allowing light absorption in the visible light spectrum. Silver also acts as an electron scavenger (Smith et al., 2009), thereby preventing the recombination of electrons and holes and resulting in increased bactericidal effects due to the generation of more reactive oxygen species. Silver also has inherent bactericidal properties. It binds to and alters bacterial

nucleic acids, disrupts the cell membrane, and deactivates enzymes (Feng et al., 2000; Soo-Hwan et al., 2011; Gupta et al., 2013). In year 1 of this research (2012-2013), the author synthesized a novel UV-Vis Ag-doped photocatalytic. This composite was found to inactivate bacteria under sunlight in 1 hour, visible light in 4 hours, and dark in 8 hours.

1.3 Pervious Concrete

Pervious concrete is a special type of concrete with high porosity that is becoming increasingly popular in the construction of pavements for parking lots and pedestrian walkways (Asadi et al., 2012; Shen et al., 2012). The high porosity is attained by using uniformly-sized coarse aggregates (gravel and stones), little to no fine aggregates (sand), and just enough cement to coat the coarse aggregate particles. The amount of water added to the concrete mix is kept low to attain a water to cement ratio (by weight) between 0.30 and 0.45. After the mix hardens, it results in a pervious concrete with interconnected pores or voids that allow water to flow through. The applications of pervious concrete are recognized by the U.S. Environmental Protection Agency (EPA) as best management practices for storm water mitigation. They reduce runoff from paved areas, permit the use of smaller storm water sewers, eliminate the need for detention ponds and prevent pollutants from being discharged into water bodies. Pervious concrete also has other environmental benefits. It facilitates the recharge of groundwater as water flows through pores and reaches the water table. It also filters water as it percolates through voids, thereby reducing pollutants reaching the groundwater. However, the void size of pervious concrete is typically large (> 0.45μm) and unable to filter bacteria efficiently. It is also prone to clogging by small debris.

1.4 Objective

The overall objective of this research was to synthesize and evaluate novel photocatalytic pervious composites for water purification. It was hypothesized that an Ag-doped photocatalytic pervious composite would be more effective in removing bacteria and degrading organics than a plain pervious composite (without any photocatalyst). A simple method was developed by the author to synthesize the photocatalytic pervious composite using sand, TiO_2, Portland cement, and silver nitrate ($AgNO_3$). The composite is envisioned to have potential applications in wastewater treatment plants, point-of-use water (POU) purification systems, and surface layer coatings for pervious concrete pavements.

2. MATERIALS AND METHODS

2.1 Materials

The pervious composites were synthesized using commercially available Type III (rapid hardening) Portland cement having a specific surface area of 0.50 m^2/g. In an attempt to filter bacteria by reducing void size, the author excluded coarse aggregates (traditionally used in pervious concrete), and instead used uniformly graded silica sand with a mean particle size of 0.55 mm. The uniformly graded sand was prepared by sieving through standard U.S. sieves, with 100% passing through the U.S. Number 20 sieve with a square opening of 0.85 mm, and 100% retained on U.S. Number 40 sieve with a square opening of 0.425 mm.

TiO_2 nanoparticles (Degussa P-25 with 80% anatase and 20% rutile crystal structure) having a mean particle size of 20 nm and specific surface area of 50 m^2/g was used as the photocatalyst. Silver nitrate ($AgNO_3$) from Sigma-Aldrich served as the source for silver in the Ag-doped photocatalytic pervious composites. Preliminary testing was conducted using methylene blue, also from Sigma-Aldrich. The water used for synthesizing the composites and for preparing aqueous samples was deionized and ultrapure (18.2 MΩ·cm resistivity), obtained from a Purelab water purification system (ELGA).

2.2 Synthesis of Preliminary Composite Compositions for Evaluating Organic Degradation

Based on the results of bacterial inactivation studies conducted by the author in year 1, a weight ratio of 1: 25 was used for TiO_2: cement. It was also established that the Ag-doped photocatalytic composite exhibited enhanced bactericidal properties in sunlight, visible light and dark.

To evaluate the efficiency of Ag-doped TiO_2 for degrading organics, six photocatalytic compositions were prepared. Based on permeability and strength tests, a ratio of cement: sand of 1: 4 was selected for the pervious composites. High ratios of cement to sand resulted in a composite that was relatively impervious to water, and low ratios of cement to sand resulted in a composite that fractured easily (low strength). A ratio of TiO_2: cement: sand of 1: 5: 20 was selected for the photocatalytic compositions. For the Ag-doped photocatalytic compositions, six samples were prepared using various amounts of Ag. A seventh sample served as the control and was a plain mixture of cement and sand (in the ratio 1:4) with no Ag or TiO_2. Table 1 shows the weight percent of TiO_2 and Ag with respect to the total weight of the composition.

Table 1. Weight percent of TiO_2 and Ag with respect to the total weight of the compositions

	Preliminary Photocatalytic Compositions						Control
Sample	1	2	3	4	5	6	7
TiO_2 by weight of compositions	3.85%	3.85%	3.85%	3.85%	3.85%	3.85%	0%
Ag by weight of compositions	0%	0.01%	0.02%	0.04%	0.06%	0.08%	0%

The procedure for preparing the composites is illustrated in Figure 2. To synthesize the preliminary photocatalytic compositions (samples 1-6), sand and TiO_2 were proportioned and mixed by rolling in a horizontal ball mill. This resulted in a mixture of sand particles coated by TiO_2 nanoparticles, which will hereon be referred to as photocatalytic sand. A simple, fast, and cost effective methodology was developed to synthesize novel Ag-doped photocatalytic sand. The photodoping procedure involved first preparing an $AgNO_3$ solution in deionized water. Various concentrations of the $AgNO_3$ solution were uniformly mixed with the photocatalytic sand to achieve the composition ratios given in Table 1. The compositions were exposed to sunlight for one hour. The light-colored photocatalytic sand turned dark upon exposure to sunlight. This change in color occurred as Ag was reduced onto the surface of the photocatalytic sand (Equation 6). The samples were calcined at 300^{o}C for 3 hours to form the Ag-doped photocatalytic sand.

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2 \quad (6)$$

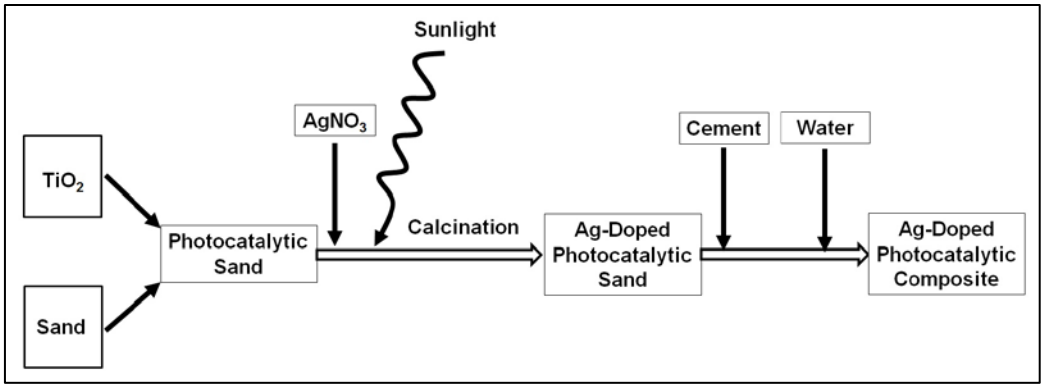

Figure 2. Flowchart illustrating the synthesis of the photocatalytic composites

The photocatalytic composites were prepared by mixing the compositions of samples 1-6 with cement to achieve a TiO_2: cement: sand ratio of 1: 5: 20 by weight. The control was prepared by mixing the composition of sample 7 with cement to achieve cement: sand ratio of 1: 4. Deionized water was added at a water/cement ratio of 0.3 and mixed uniformly to form wet mortars. The wet mortars were placed and lightly compacted to a thickness of 0.3 cm, inside 5 cm diameter, 3.8 cm deep containers, and moist cured for 28 days (Figure 3).

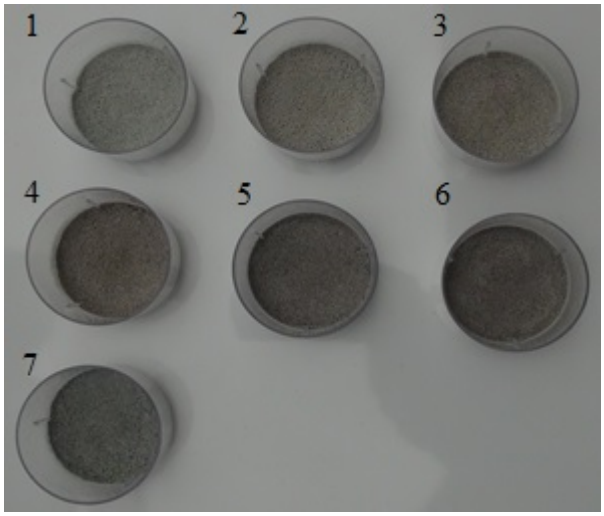

Figure 3. Samples 1-6: Photocatalytic composites with varying wt% Ag, and Sample 7: Plain Composite (control)

2.3 Degradation of Methylene Blue

The photocatalytic activity of the seven preliminary test samples was evaluated by the photodegradation of methylene blue (a model organic dye) under sunlight. The experiments were carried out in the daytime between 11:00 am and 3:00 pm. Testing was done on sunny days when the average UVA intensity was 4.5-6.5 W/m^2 and light intensity was 65,000-95,000 lux, as measured by UVA and light sensors (Vernier Software & Technology).

The color change (from blue to clear) was quantitatively determined from samples taken at various time intervals and analyzed using an Agilent 8453 UV-Vis spectrophotometer. The degradation of methylene blue was the fastest for sample 4 (with 0.04% Ag in composite), and this ratio was selected for fabricating the photocatalytic pervious filter. The UV-Vis spectroscopy results for all seven samples are presented in the results (section 3).

2.4 Pervious Composite Filters for Filtration

Two pervious composites were fabricated: a plain pervious composite filter using the composition of sample 7 (control), and a photocatalytic pervious composite filter using the composition of sample 4. The composite filters (7.0 cm diameter and 2.5 cm thick) were formed by placing the wet mortar inside 10.0 cm long plastic tubes (Figure 4). The mixture was placed in three equal layers, and each layer was lightly compacted (10 blows/layer) using a 335 g

cylindrical weight, free-falling through a height of 2.5 cm. The composite filters were moist cured for 28 days. The final thickness of the composite filters was 2.5 cm. Physical properties determined include bulk dry unit weight, porosity and permeability. Bulk dry unit weight (γ_{dry}) is the weight of dry composite (W_{dry}) per unit bulk volume (V) of the composite (Equation 7). Volume was determined from the measured dimensions (diameter and thickness) of the samples. Porosity (n) of concrete is the ratio of the volume of voids (V_v) to the bulk volume (Equation 8).

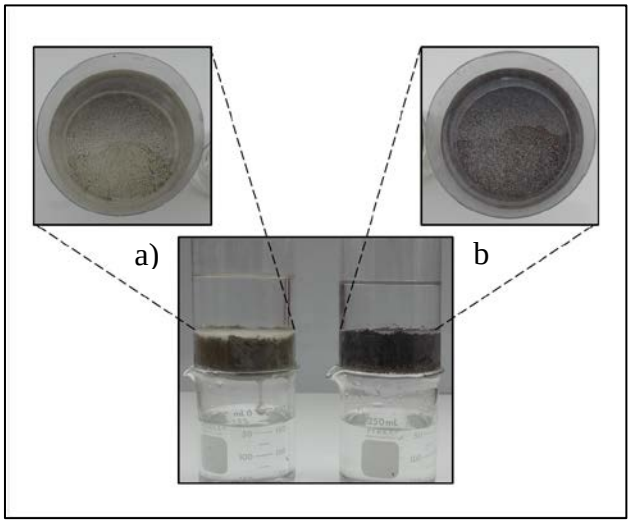

Figure 4. a) Plain pervious composite filter and b) photocatalytic pervious composite filter

$$\gamma_{dry} = \frac{W_{dry}}{V} \tag{7}$$

$$n = \frac{V_v}{V} \tag{8}$$

Permeability to water was determined by the falling head test (Figure 5) using Equation 9. This equation is derived from Darcy's law, which states that the velocity of flow is directly proportional to the total head, inversely proportional to the thickness of the pervious specimen, and is related through the permeability coefficient k.

$$k = \frac{A_1 L}{A_2 t} \ln\left(\frac{h_1}{h_2}\right) \tag{9}$$

where A_1 and A_2 are the cross-sectional areas of the tube and specimen (both 38.48 cm^2) respectively, L is the thickness of specimen (2.5 cm), and t is time in seconds for the total head to drop from an initial value of h_1 to a final value of h_2.

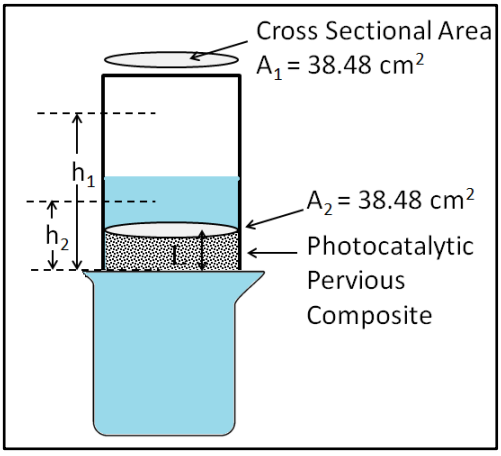

Figure 5. Schematics of the falling head test

2.5 Bacterial Inactivation Studies

The removal of bacteria by the pervious composite filters was evaluated under sunlight exposure. Wastewater for testing was obtained from the Nashua Wastewater Treatment Facility (NWTF) located in New Hampshire. The water used for testing was obtained just after the secondary treatment, but before the addition of hypochlorite (that kills harmful bacteria). Two 200 mL samples of wastewater were taken in glass beakers. The first sample was filtered using the plain pervious composite (control), while the second was filtered using the photocatalytic pervious composite. The filtered water was collected in two glass beakers containing disks (5.0 cm diameter, 0.3 cm thick) made of the respective composite mixtures. The unperturbed water samples were exposed to sunlight for 4 hours. The experiments were carried out in the daytime between 11:00 am and 3:00 pm. Testing was done on sunny days when the average UVA intensity was 7.5-8.8 W/m^2 and light intensity was 108,000-118,000 lux.

Total coliform counts (TCC) were determined with 3M Petrifilms before filtration (initial bacteria count), and immediately after filtration at 0h, 0.25h, 0.5h, 1h, 2h, 3h, 4h. The 3M Petrifilms for enumerating bacteria have culture media that contain standard nutrients and a gelling agent incorporated into them. They also have an indicator dye that colors the bacterial colonies to facilitate counting. The Petrifilms were inoculated with 1 mL of the sample and incubated for 48 hours at 34^{o}C. The colonies were then counted automatically with a 3M Petrifilm Plate Reader, and also verified by manual counting. Ten-fold serial dilutions were performed for samples with high concentrations of bacteria.

3. RESULTS

3.1 Physical Properties

The physical properties of the plain pervious composite filter and the photocatalytic pervious composite filter are shown in Table 2.

Table 2. Physical properties of the pervious composite filters

	n (%)	γ_{dry} (g/cm^3)	k (cm/s)
Plain pervious composite filter	31%	1.71	3.30×10^{-3}
Photocatalytic pervious composite filter	44%	1.52	4.88×10^{-3}

3.2 Photocatalytic Degradation of Methylene Blue

Methylene blue absorbance spectra for the six preliminary photocatalytic composites and the control after 2 hours of sunlight exposure are shown in Figure 6. The degradation was studied by monitoring the absorbance of the methylene blue solution at the peak absorption wavelength of 664 nm. It can be seen that the control with no photocatalyst showed the least degradation of methylene blue, and sample 4 with 0.04% Ag in the photocatalytic composite, showed the most degradation of methylene blue.

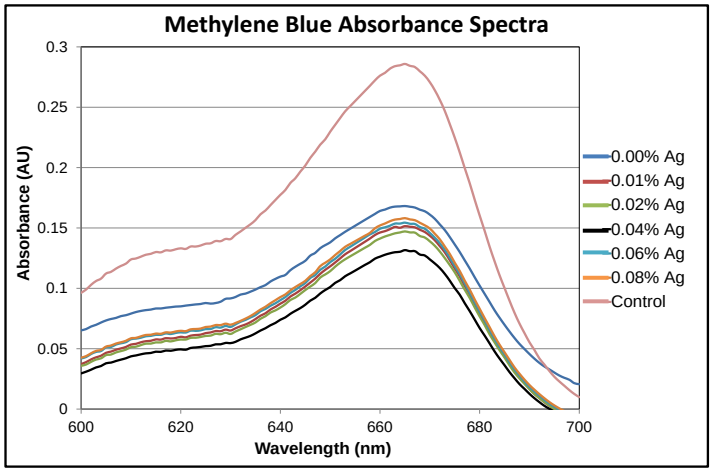

Figure 6. Methylene blue absorbance spectra for preliminary composites after 2 hours sunlight exposure

3.3 Bacteria Count Results

Figure 7a shows the average of the total coliform counts (TCC) for the photocatalytic pervious composite filter and the plain pervious composite filter. The TCC for the photocatalytic pervious composite filter dropped from an initial average value of 225 to 5 colony forming units per milliliter (cfu/mL) immediately after filtration. This value further dropped to 0 cfu/mL after 15 minutes of sunlight exposure following filtration. The TCC for the plain pervious composite filter dropped from an initial average value of 191 to 152 cfu/mL immediately after filtration.

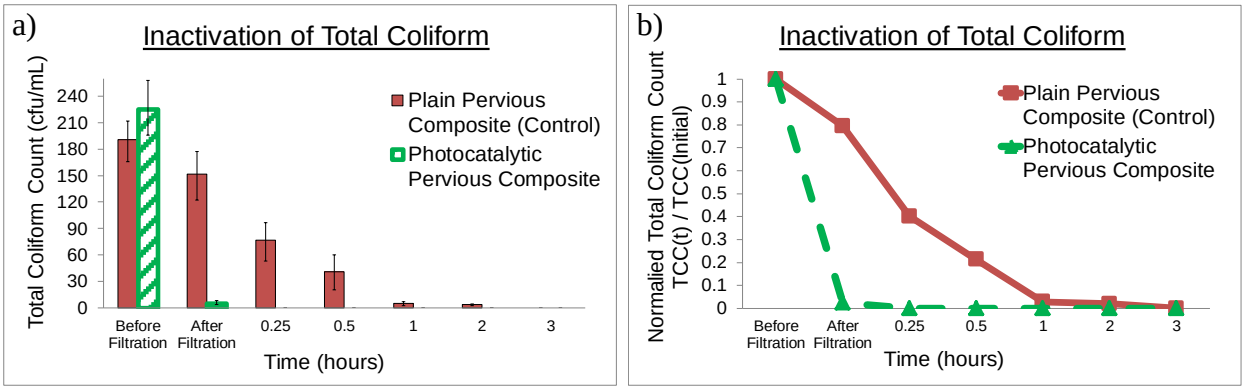

Figure 7. a) Total coliform counts (TCC) and b) Normalized TCC for the plain pervious composite (control) and the photocatalytic pervious composite

It took 3 hours of sunlight exposure following filtration for this value to drop to 0 cfu/mL. Figure 7b shows the normalized TCC values. The average TCC at different time intervals (t hours) were normalized with respect to their initial counts (before filtration) in order to easily compare the effectiveness of the photocatalytic pervious composite and the control.

4. DISCUSSION

4.1 Kinetic Studies for Modeling the Photocatalytic Degradation of Methylene Blue

Figure 8 shows the photodegradation efficiency ($\frac{C_0-C}{C_0} \times 100\%$) of the plain pervious composite and photocatalytic pervious composite (using the optimum composition of sample 4) calculated from the UV-Vis spectra of the methylene blue solution at its maximum absorption wavelength (664 nm). C_o represents the initial concentration of the dye solution and C represents the concentration of the dye at sunlight irradiation time (t).

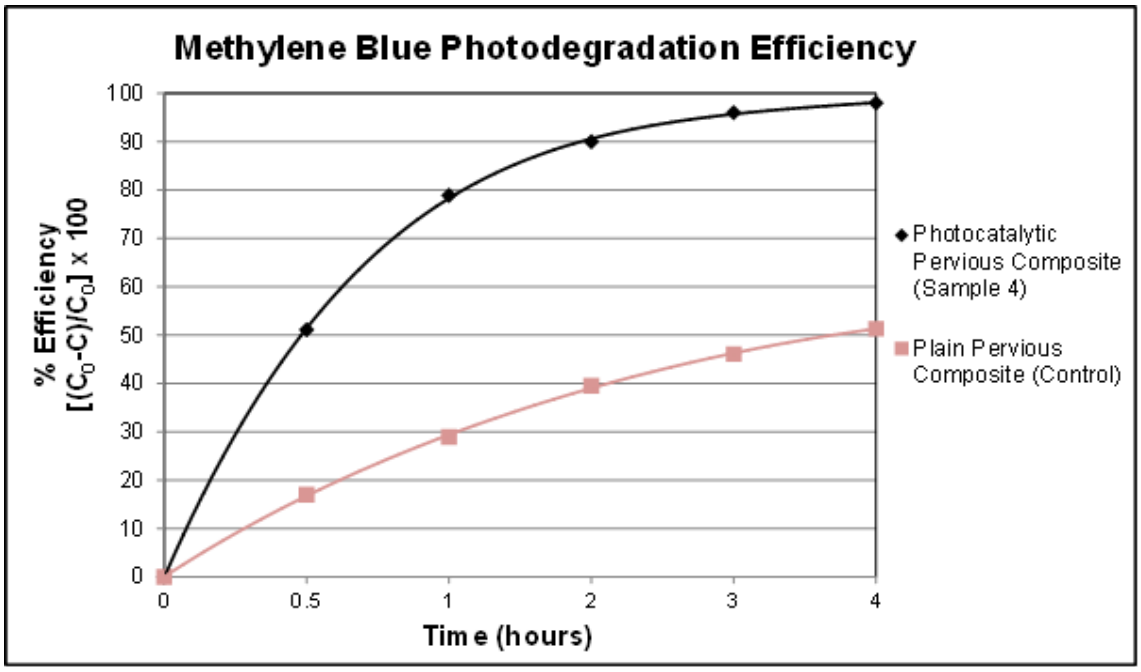

Figure 8. Methylene blue photodegradation efficiency for the photocatalytic pervious composite and the plain pervious composite

The photocatalytic AOP is a heterogeneous process since the reaction occurs at the surface of the catalyst. The Langmuir–Hinshelwood model (Equation 10) can be used to describe the kinetics of the photocatalytic degradation of aqueous methylene blue on a heterogeneous catalytic system (Chang et. al., 2004; Shaban, 2014).

$$r = -\frac{dc}{dt} = \frac{k_r K_{ad}}{1+K_{ad}C} \quad (10)$$

where r is the degradation rate, C is the concentration of aqueous methylene blue at time (t), k_r is the rate constant, and K_{ad} is the adsorption equilibrium constant. When the adsorption is weak and/or methylene blue concentration is low, the Langmuir–Hinshelwood model simplifies to a pseudo-first order kinetic model (Equation 11).

$$\ln\left(\frac{C_0}{C}\right) = k_r K_{ad} t = k_a t \quad (11)$$

where k_a is the apparent first order rate constant. Figure 9 shows linear relationships between $\ln(C_o/C)$ and sunlight irradiation time for the plain pervious composite and photocatalytic pervious composite. This linear relationship confirms that the photocatalytic degradation of methylene blue obeys pseudo-first order kinetics according to the Langmuir–Hinshelwood model. The apparent first order rate constants of photocatalytic degradation by the plain pervious composite and photocatalytic pervious composite are 0.1784 h^{-1} and 0.9780 h^{-1} respectively. The higher rate constant of the photocatalytic pervious composite signifies greater photocatalytic activity in degrading organics, when compared with the plain pervious composite.

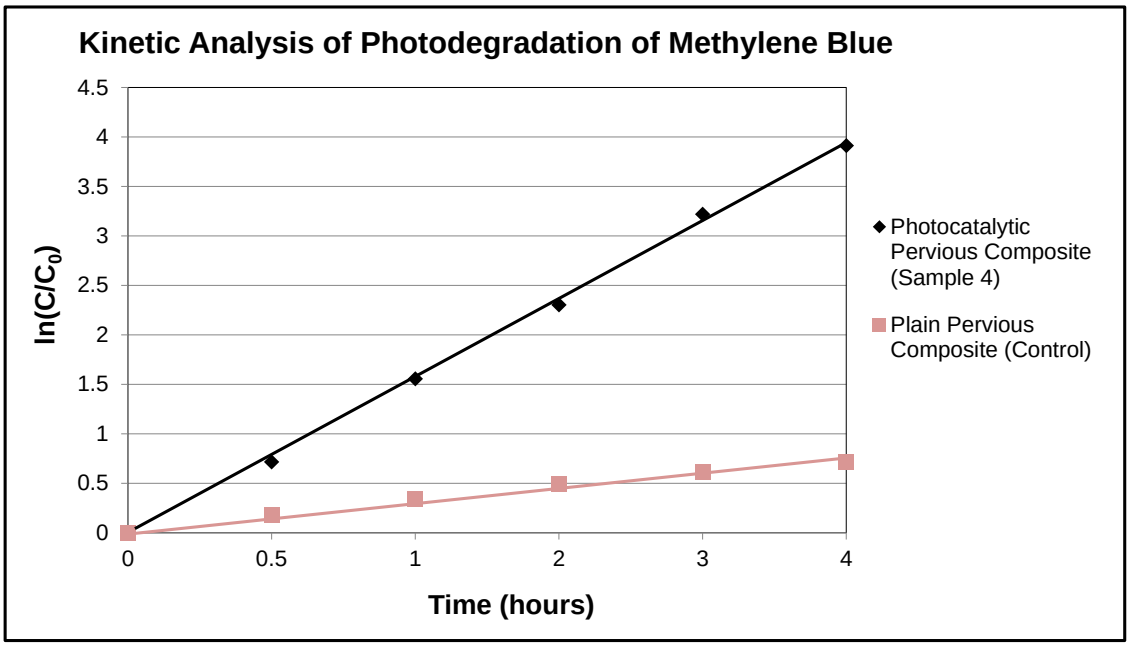

Figure 9. Kinetic analysis of photocatalytic degradation of methylene blue for the photocatalytic pervious composite and plain pervious composite

4.2 Filtration and Bacterial Inactivation by the Pervious Composites

Comparison of the total coliform counts before and immediately after filtration by the plain pervious composite showed only a 20% reduction in total coliform bacteria. Water flows in the pervious composite only through the interconnected voids. These voids, of varying shape and size, form channels that follow a tortuous path. Some of the voids and channels may be small enough to trap bacteria, but many are large and allow water containing bacteria to flow through. The size of coliform bacteria is from 0.5 to 2μm, and would normally require membrane filters with a pore size less than or equal to 0.45 μm to filter them. In fact, most in-home filters will not filter coliform bacteria, and EPA recommends boiling water or treating water using chlorine, ultra-violet light, or ozone to inactivate coliform bacteria. Subsequent exposure of the filtered water to sunlight inside a beaker containing the 5.0 cm diameter 0.3 cm thick, plain composite disc resulted in 100% inactivation of total coliform bacteria in 3 hours.

The photocatalytic pervious composite showed 98% reduction in total coliform bacteria immediately after filtration. Exposure of the filtered water to sunlight inside a beaker containing the 5.0 cm diameter 0.3 cm thick, photocatalytic composite disc resulted in 100% inactivation of total coliform bacteria in just 15 minutes. This rapid filtration and inactivation of bacteria is due to the synergistic effect of photocatalysis by the Ag doped TiO_2 composite filter and the inherent bactericidal properties of silver.

4.3 Applications

The photocatalytic composite developed in this research has diverse applications, such as in wastewater treatment plants, POU purification systems, and surface layer coatings for pervious concrete pavements. Typically in wastewater treatment plants, chlorine-based compounds are used to disinfect water after secondary treatment. However, when chlorine is in contact with certain types of organic matter found in wastewater, it may create more hazardous compounds such as trihalomethanes.

The photocatalytic pervious composite developed in this study may be used to reduce or eliminate the need for treatment with chlorine or other chemicals at wastewater treatment plants. Large water tanks may be constructed with a pervious photocatalytic composite bottom, supported by a gravel drain (Figure 10). The filtered water may be led to a second tank with its inner surface coated with the photocatalytic composite. Photocatalytic rods made from the

composite may also be placed in tank to increase the photocatalytic surface area in contact with water. In this study the filtered water in the glass beakers was not stirred, however in wastewater treatment plants, water may be gently mixed to speed up organic degradation and bacterial disinfection. Various types of POU water purification systems can also be constructed for house-holds or industry to treat water on-site. These include treatment tanks similar to those described earlier for wastewater treatment plants, but smaller in size. Existing water tanks can also be coated with the photocatalytic composite. After the composition has set and hardened, the tank may be filled with contaminated water and exposed to sunlight until purified. Photocatalytic pervious water filters can also be fabricated for purifying water for potable use. A prototype water filter made by the author is shown in Figure 11.

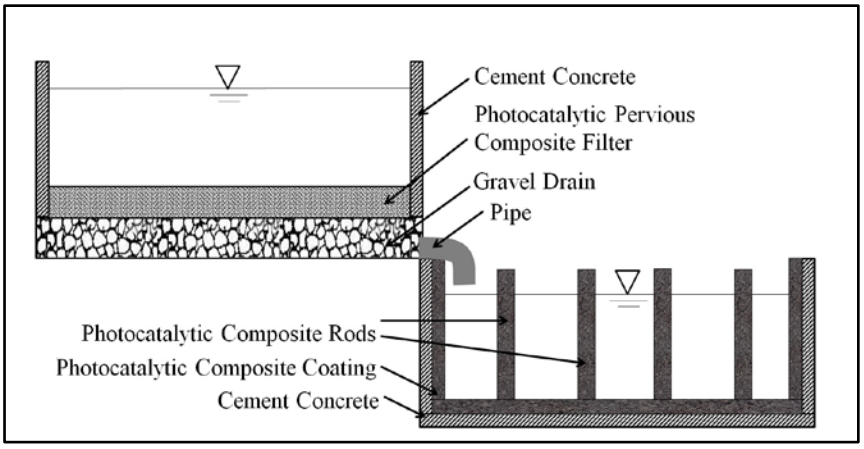

Figure 10. Envisioned deployment of the photocatalytic pervious composite in a wastewater treatment plant

Figure 11. POU photocatalytic filter

The largest use of pervious concrete is in pavements. The most common problem relating to the long term performance of pervious concrete pavement is clogging of the voids by debris. The photocatalytic pervious composite may be used as a surface layer on top of traditional pervious concrete pavements in order to facilitate easy maintenance using pressure washing, and mechanical (bristle), air, and vacuum sweeping.

4.4 Cost Analysis

The photocatalytic pervious composite is cost effective since the materials used to synthesize it are inexpensive and abundantly available. Table 3 shows an approximate estimate for the material cost of the photocatalytic pervious composite synthesized in this study.

Table 3: Cost Analysis of Photocatalytic Pervious Composite

Raw Material Cost		**Cost of Material in 1 kg of Composite**	
$AgNO_3$	\$650.00 /kg	\$0.260	0.4 g ($AgNO_3$)
TiO_2	\$20.00 /kg	\$0.770	38.5 g (TiO_2)
Cement	\$0.24 /kg	\$0.046	192.2 g (Cement)
Sand	\$0.0034 /kg	\$0.003	768.9 g (Sand)
Total Cost of 1 kg of Composite		**\$1.079**	**1000.0 g (Composite)**

4.5 Sustainability

As we strive for an environmentally-friendly world, conventional techniques for wastewater remediation must move towards green and sustainable alternatives. The photocatalytic water purification technology developed in this research could become a vital instrument in this endeavor. The technology is safe and does not produce any toxic byproducts. It uses only solar energy (does not require an external power source), which is abundant in developing countries that lack large and expensive infrastructure for wastewater treatment. Also, the photocatalytic composite is capable of repeated use without loss of photocatalytic activity because it is a catalyst and does not get depleted. However, the long-term performance of the composite has to be evaluated.

4.6 Safety

Toxicity, safety and environmental impacts of any new technology have to be evaluated before the technology can be deployed with confidence. Silica sand and Portland cement have been used in the construction of water tanks for over a century and are considered to be safe. However, the safety and long-term effects of nanoparticles are not fully understood, and their environmental impacts are an area of active research in the field of nanomaterials. TiO_2 is a safe inert material and has been used for decades in many applications including food, pharmaceutical products, sunscreens and paint. However, its nanoparticle form could be cause of concern if inhaled or consumed. One of the drawbacks of current TiO_2 enhanced SODIS methods is the difficulty in recovering TiO_2 nanoparticles from the TiO_2-water slurry following disinfection. In the photocatalytic pervious composite developed in this study, the TiO_2 particles coated on the photocatalytic sand are bound by Portland cement. Measurements made using an EC500 ExStik

II pH/Conductivity/TDS Meter have shown that the TiO_2 particles do not wash of even after repeated use.

Argyria, an irreversible discoloration of the skin can be caused by ingesting high concentrations of silver (>1 g). Since silver is not considered to be toxic to human health, the U.S. EPA has not set a maximum contaminant level (MCL). Instead, the EPA has set a non-mandatory secondary maximum contaminant level (SMCL) of 0.1 mg/L to serve as a guideline in water quality. The amount of silver present in the photocatalytic pervious composite is only 0.04% by weight of the composite, and is bound (photodoped) to the TiO_2 coated photocatalytic sand. The photocatalytic sand particles are further bound by cement, thus particulate silver is absent in the water. Detailed analysis using inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) should be conducted to determine the concentration of silver ions in water.

4.7 Future Work

Further research should be conducted to: i) investigate the inactivation of different types of pathogens (including protozoa and viruses); ii) study the feasibility of degrading different types of organics and pesticides; iii) study the feasibility of removing heavy metals and other inorganic water pollutants; and iv) characterize the void size and its distribution; and v) evaluate the safety and performance of the composite filters over time.

Although the study reported in this paper focused on water purification using sunlight, future research should investigate its efficacy under artificial light. For any pervious material, clogging is a potential problem. Further research should be conducted to develop simple and easy techniques to address this issue.

5. CONCLUSIONS

Simple methodologies were developed to fabricate two pervious composite filters for wastewater treatment. The plain pervious composite filter had a weight ratio of cement: sand of 1: 4 and a water/cement ratio of 0.3. The optimum composition of the Ag-doped photocatalytic pervious composite filter consisted of 0.04% Ag by weight of composite with a weight ratio of TiO_2: cement: sand of 1: 5: 20.

Filtration by the plain pervious composite showed only a 20% reduction in total coliform bacteria, whereas the photocatalytic pervious composite showed a 98% reduction in total coliform bacteria. Subsequent exposure of the filtered water to sunlight inside beakers containing the composite discs made of their respective compositions, resulted in 100% inactivation of total coliform bacteria by the plain composite disc in 3 hours and by the photocatalytic composite disc in just 15 minutes.

The photocatalytic degradation of methylene blue obeyed pseudo-first order kinetics according to the Langmuir–Hinshelwood model. The apparent first order rate constants of photocatalytic degradation by the plain pervious composite and photocatalytic pervious composite were 0.1784 h^{-1} and 0.9780 h^{-1} respectively. The photocatalytic pervious composite showed greater photocatalytic activity in degrading organics, when compared with the plain pervious composite.

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