EXPLORATORY RESEARCH: A SELF-CLEANING DRAINAGE MATERIAL

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PURPOSE OF STUDY

The goal of this mini-grant is to identify the effectiveness of photocatalysis to purify water using a titanium dioxide (TiO_2) catalyst coated on translucent, particulate media. To clean contaminated waters, photocatalysis requires sufficient light to initiate chemical reactions leading to the mineralization of organic contaminants. Thus, we intend to perform a series of laboratory experiments to 1) determine a method to effectively coat crushed glass with a TiO_2 film and 2) quantify the degree of purification with depth within a column of this drainage material.

Progress on this mini-grant has been focused on *Task 1: Catalysis Immobilization on Crushed Glass*. The following sections describe steps taken to accomplish this first task. *Task 2: Column Studies* will be addressed when a coating method and a glass cullet source have been selected.

METHODS FOR GLASS COATING

A variety of methods have been explored for the immobilization of titanium dioxide (TiO_2) photocatalyst on a glass substrate including sol-gel techniques [1], incorporation into zeolites and molecular sieves [2] and the use of binary aerogels (Watson and Cooper, 2004) to name a few. While some of these methods are suitable for the proposed application, the majority are precision methods, more suitable for use with homogeneous substrates from virgin sources. The methods to be explored for coating of the glass for this feasibility study will be limited to those methods that can be carried out at ambient or near ambient temperature, with minimal specialized equipment. Additional methods will likely be explored for the extramurally funded project in order to identify the most appropriate technology for this application.

PEROXOTITANTE METHOD

Gao, et al [3] describe a simple method for the room temperature deposition of anatase TiO_2 thin films at room temperature starting with a solution of metatitanic acid (H_2TiO_3) in hydrogen peroxide (H_2O_2) and aqueous ammonia. The prepared solution is reported to remain stable in a refrigerated environment (< 5°C) for several weeks. The substrate is floated (or soaked) in the solution for approximately 12 hours and air dried.

UREA BASED METHOD

A nucleation method performed at near room temperature was reported by Yamabi, et al [4]. In urea based method, titanyl sulfate ($TiOSO_4$) and urea are sequentially is dissolved in an aqueous solution bath containing hydrochloric acid or sodium hydroxide, and adjusted to a pH range of –0.5 to +1.84. The substrate is placed in the precursor solution at a temperature of 60°C where the reaction occurs over several days (1-10). The introduction of barium chloride is followed by filtration for removal of the sulfate from the solution.

Both methods have been tested on glass substrate, though neither has been used with crushed glass. These methods will be tested for efficacy with a crushed glass substrate as measured by stability, final composition (by XRD) and photocatalytic activity.

TRANSMISSIVITY OF CRUSHED GLASS

A sufficient number of crushed glass (cullet) producers have been identified largely through an internet search. From this search, five major producers were identified in five different states. Glass cullet samples were acquired from one of the larger producers, Universal Ground Cullet, Inc. based in Ohio.

Absorbance and transmissivity of four different samples of glass cullet were tested using UV-Vis equipment. The four samples include clear and mixed glass cullet of two different gradations, M&E 1010 and M&E 1015, as shown in Figure 1. The M&E 1010 is a coarser gradation than M&E 1015; both gradations are relatively uniform.

Values of absorbance and transmissivity were acquired using a quick read procedure, which measures both values at a single wavelength of 920 nm. Three different water samples were used in these tests: de-ionized (DI) water, lake water, and road surface run-off (storm water). The lake water and storm water samples were used to evaluate the effect of particulates on absorbance and transmissivity. The chemical composition of these water samples still needs to be determined. Three samples of each glass cullet were tested using the three different water samples. Thus a total of (3 samples) x (4 glass cullet materials) x (3 water samples) = 36 tests were performed.

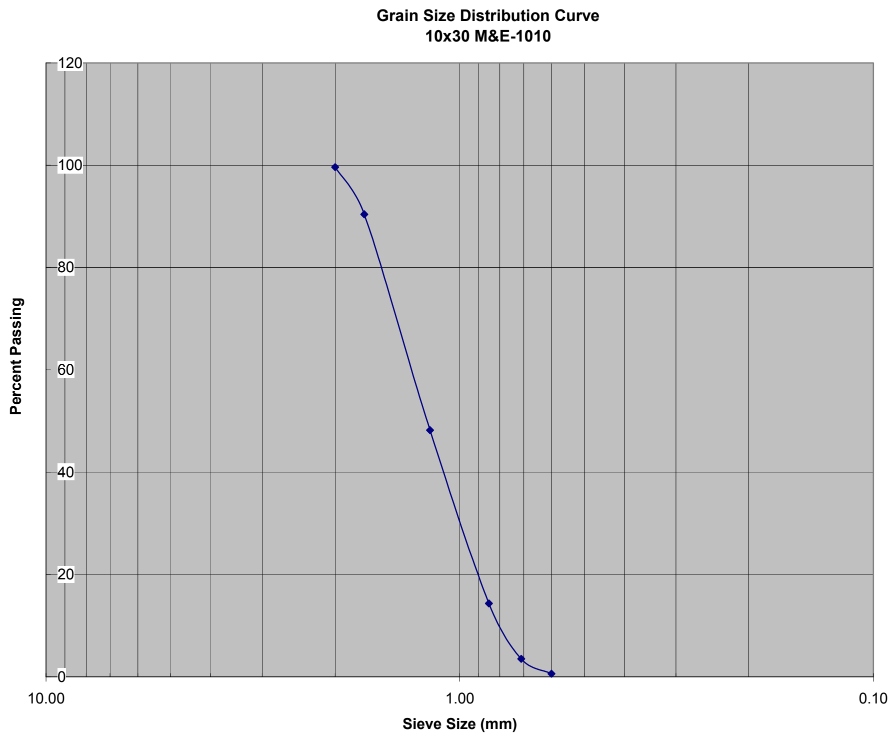
The average absorbance of the three samples for each glass cullet and each water sample are summarized in Figures 2 through 4. Absorbance represents the fraction of input wavelength that is absorbed in the glass-water mixture. The remaining fraction is transmitted, such that the sum of absorbance and transmissivity equals one.

Figure 2 shows two trends with absorbance of glass cullet in DI water. First, the mixed glass seems to absorb more UV light than the clear glass. In these tests, the mixed glass absorbs nearly twice as much UV light as the clear glass. The clear glass has an absorbance of less than 0.30, meaning that its transmissivity is near 0.70. Second, gradation does not appear to influence absorbance of glass cullet when immersed in DI water.

Interestingly, absorbance of glass cullet in lake water (see Figure 3) shows trends that are opposite of those shown in Figure 2. For each gradation, the color (clear or mixed) seems to have minimal effect on absorbance. However, the gradation has a significant effect. A coarser gradation (M&E 1010) absorbs less UV light (absorbance < 0.30) than a finer gradation (absorbance > 0.50). Figure 4 shows the same trends for storm water, although the magnitude of absorbance is higher. The reasons for these findings are not yet understood and need to be investigated.

These observations suggest that a coarse gradation of glass cullet will transmit more UV light. It still needs to be determined if mixed glass or clear glass is more suitable. To this end, translucent properties of different colors of glass need to be identified from literature. In addition, the aforementioned tests need to be repeated when glass cullet is coated with TiO_2 to quantify changes in absorbance when particles are covered with a thin film. These items will constitute the next set of items to be accomplished for Task 1 of this study.

1. Fu, X., et al., *Enhanced Photocatalytic Performance of Titania-Based Binary Metal Oxide: TiO_2/SiO_2 and TiO_2/ZrO_2.* Environmental Science and Technology, 1996. **30**(2): p. 647-653.
2. Anpo, M., et al., *Design and development of titanium and vanadium oxide photocatalysts incorporated within zeolite cavities and their photocatalytic reactivities.* Journal of Industrial and Engineering Chemistry, 2000. **6**(2): p. 59-71.
3. Gao, Y.F., et al., *Room temperature deposition of a TiO_2 thin film from aqueous peroxotitanate solution.* Journal of Materials Chemistry, 2003. **13**(3): p. 608-613.
4. Yamabi, S. and H. Imai, *Crystal phase control for titanium dioxide films by direct deposition in aqueous solutions.* Chemistry of Materials, 2002. **14**(2): p. 609-614.



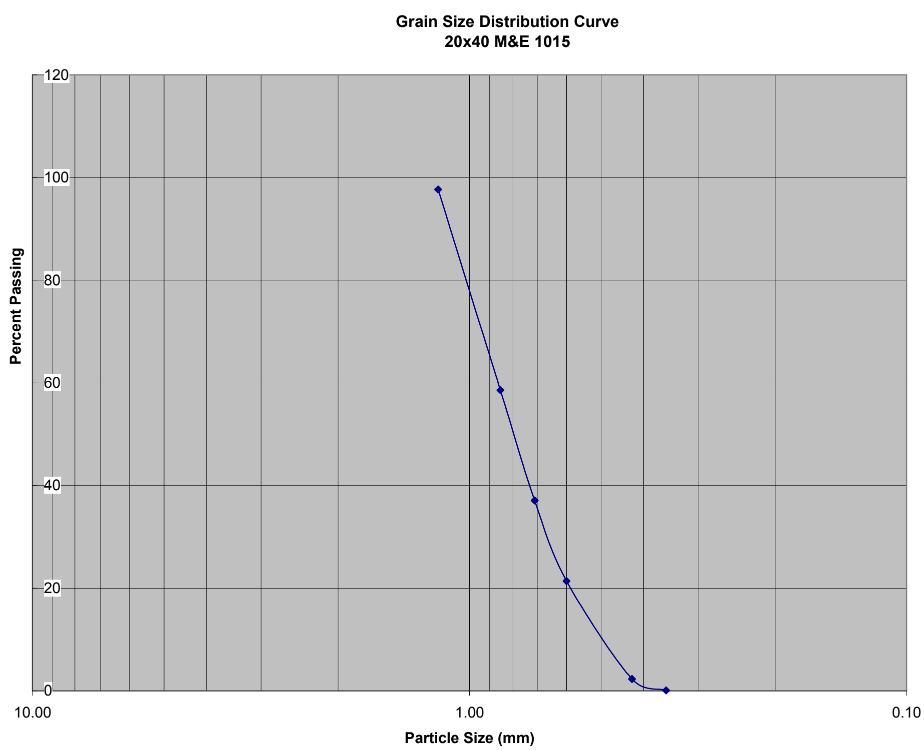


Figure 1. Gradation of M&E 1010 and M&E 1015 Glass Cullet

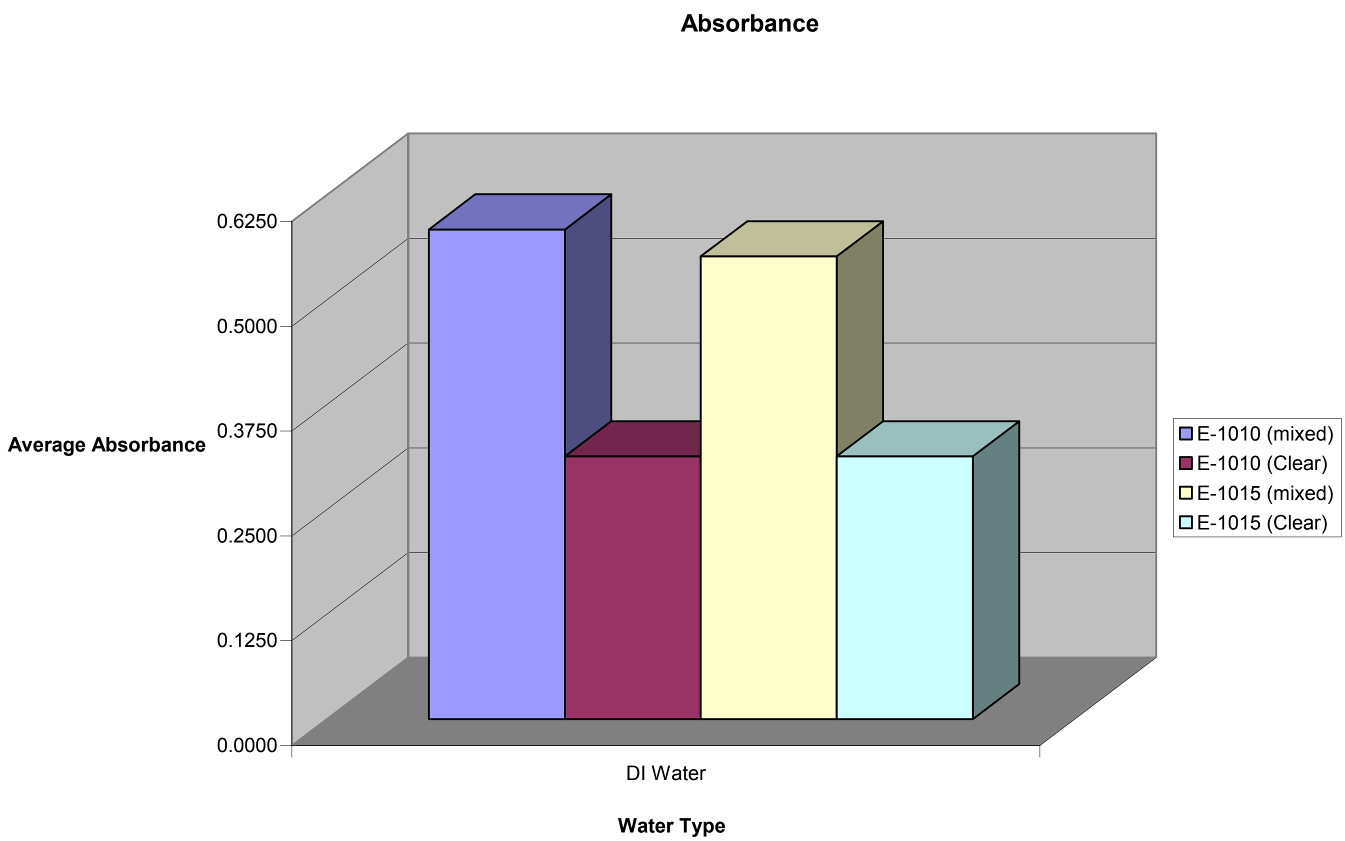


Figure 2. Average Absorbance (at 920 nm) of Glass Cullet in De-Ionized (DI) Water

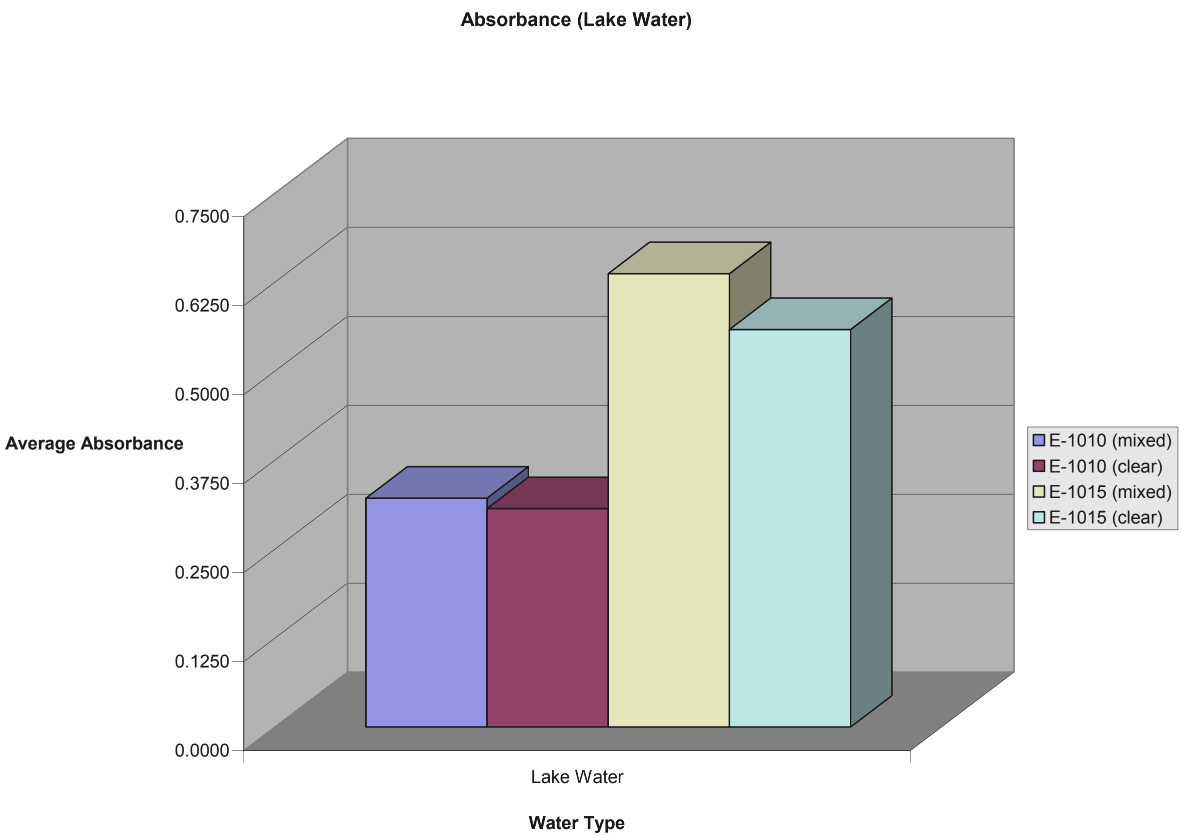


Figure 3. Average Absorbance (at 920 nm) of Glass Cullet in Lake Water

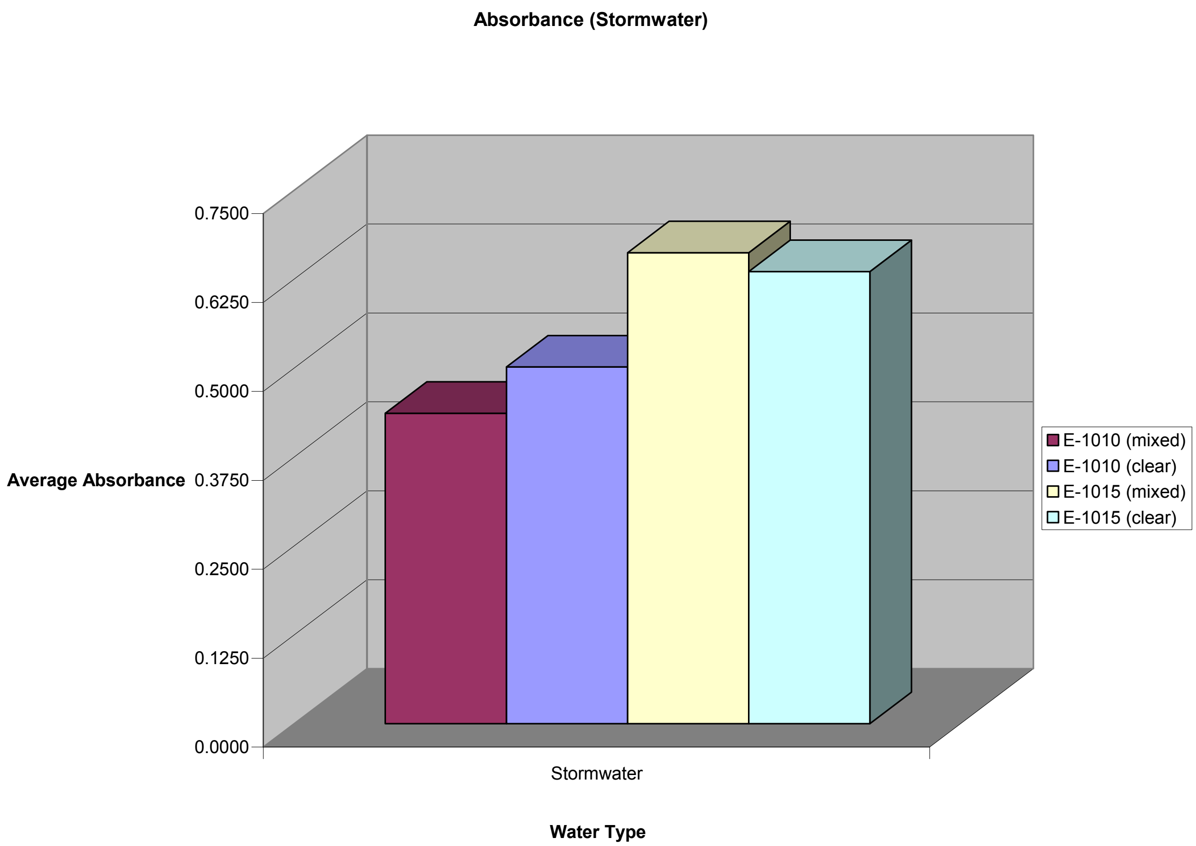


Figure 4. Average Absorbance (at 920 nm) of Glass Cullet in Storm Water