

Using Nano- and Micro-Titanium Dioxide (TiO₂) in Concrete to Reduce Air Pollution

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Abstract

A crucial element in construction, tunnels, roads, and more, concrete has become one of the most important materials in the world. At the same time, air pollution, particularly in crowded cities, is increasing, mainly due to industrial activity and transportation. Therefore, one possible approach to reduce pollution is to use “smart” construction materials, particularly those that incorporate photocatalytic active nano- and micro-size structures into concrete. Incorporating titanium dioxide (TiO₂) in roads and pavements could degrade and reduce various pollutants under ultraviolet sun radiation. TiO₂-infused concrete would also maintain its optical characteristics for far longer than traditional concrete mix. This study evaluated the ability of concrete containing nano- and micro-TiO₂ to degrade organic molecules, as assessed by the concrete’s ability to degrade Rhodamine B dye. The amount of nano- and micro-TiO₂ in the concrete samples was 3, 6, 9, 12, and 15% of the cement composition. The resulting concrete blocks were exposed to sunlight for 24, 48, 72, and 96 hours. Both the nano- and micro-TiO₂ significantly degraded the Rhodamine B dye, demonstrating the potential of this approach to benefit the smart construction industry and, as a result, fight certain types of air pollution.

Keywords: Environmental; Nanotechnology; Nanoparticle; Microparticles; Titanium dioxide; Concrete

Introduction

Concrete is a vital building block of modern life, used in homes, roads, airports, skyscrapers, and more. In fact, it is the most common synthetic structural material in the world, with almost 3 tons utilized per person every year [1]. The name itself means “to grow together” in Latin, referring to the process of mixing all of concrete’s components to create a solid from a liquid [2].

Unfortunately, pollution is another fact of modern life. The Environmental Protection Agency tracks emissions of the most hazardous air pollutants that negatively impact human health and the environment; these pollutants include carbon monoxide, sulfur dioxide, particulate matter, volatile organic compounds (VOC), nitrogen oxides (NO_x), and lead. All these air pollutants are increasing worldwide, particularly in crowded cities. As a result, certain health problems are also increasing, such as cardiovascular disease and respiratory issues. Pollution can also affect the nervous system in a variety of ways (i.e., learning, memory, and behavior; IQ loss) and contribute to cancer and premature death [3]. Automobile emissions are a primary source of air pollution; Figure 1 shows other common sources.

A possible solution to the international pollution problem is the use of “smart” concrete that is infused with materials that can break down air pollutants and render them harmless. One such material is titanium dioxide (TiO₂), which is classified as Generally Recognized as Safe (GRAS) by the U.S. Food and Drug Administration [4,5]. Around 4 million tons of TiO₂ are utilized annually in materials such as paints, plastics, food, papers, inks, medicines, toothpastes, and sunscreens [6]. Three forms of TiO₂ particles exist: rutile, anatase, and brookite, with anatase particles becoming rutile at high temperatures [7]. TiO₂ is able to help fight pollution as an additive to concrete, with anatase TiO₂ having the best photoactivity [8]. When heat and light hit the concrete’s surface, TiO₂ uses this energy to break down certain pollutants, such as NO_x and VOCs, changing them from the harmful phase to the harmless phase, as shown in Figure 2 [7].

In this study, we infused nanoscale and microscale TiO₂ into cement to make the resulting concrete photocatalytic. We then measured the efficiency of the photocatalytic concrete to remove organic pollutants, based on their removal of Rhodamine B dye.

Background

Because automobiles are a major source of air pollution, treating air impurities at the site of traffic makes logical sense. To do so, photocatalytic materials can be integrated into the surface of roads, buildings, and pavement. When activated by sunlight, these photocatalytic materials oxidize different kinds of pollutants, which are then precipitated on nearby surfaces and removed by rain or cleaning with water [8-10]. For example, studies have shown that a thin coating containing TiO₂ on a surface near the source of contamination can eliminate a large amount of NO_x and VOC pollutants from the atmosphere. Such a coating would be a non-invasive, affordable method to protect buildings against the effects of biological pollutants and smog. In one study, a single square meter of TiO₂ coating under sunlight was able to remove NO_x and VOC from about 200 m³ and 60 m³ of air per day, respectively [11,12]. A photocatalytic TiO₂-SiO₂ nanocomposite system was designed to coat buildings in order to combat the deterioration caused by air pollutants. The photocatalytic activity of the composite was analyzed by measuring its self-cleaning ability, using Methylene blue, when coated on portions of a real outdoor concrete wall. After a year, the researchers studied the color degradation

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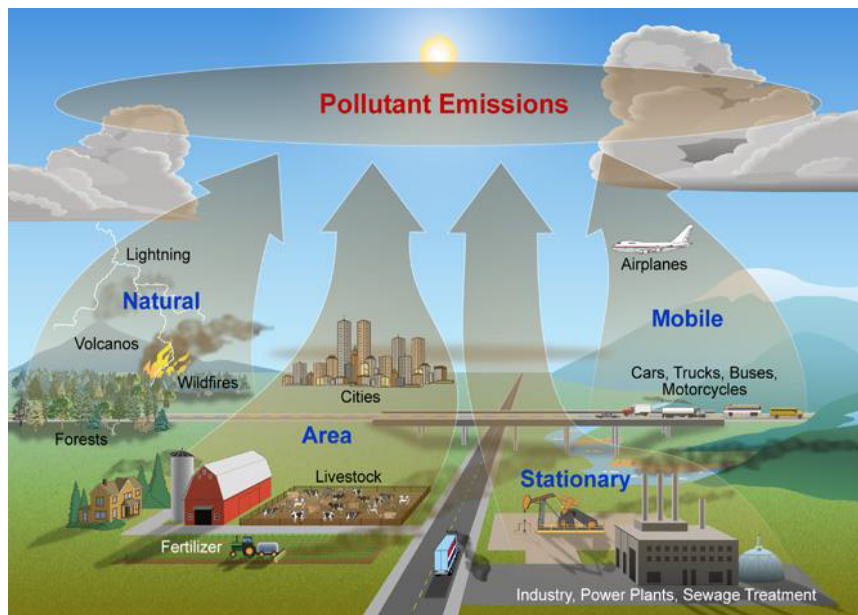


Figure 1: Sources of air pollution [4].

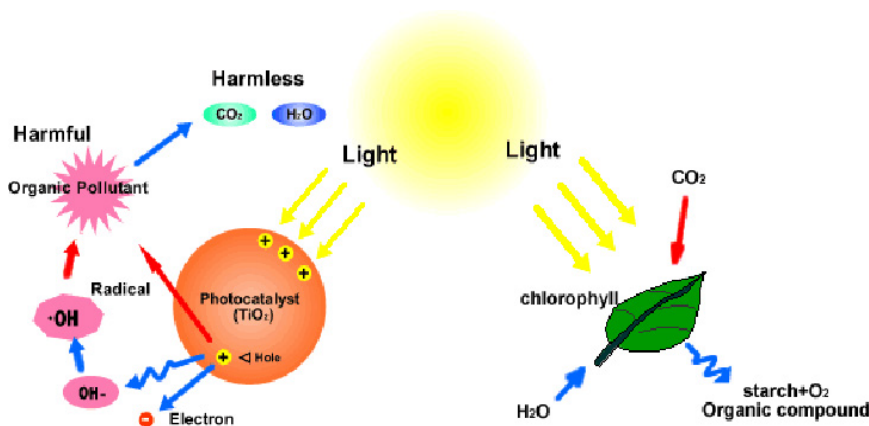


Figure 2: Photocatalytic process triggered by TiO₂ in concrete [9].

and found reasonable results. They also studied the system's ability to protect the concrete from bacterial organisms and found it to have had a good antibacterial effect against most of the tested organisms.

In another project, Beeldens integrated TiO₂ into concrete pavement blocks to test its use as a photocatalytic for air purification, measured in terms of NO_x reduction. In this study, the inlet concentration of NO was equal to 1 ppm. When the UV light was turned on, the concentration dropped by approximately 40%. After 5 hours of UV light exposure, both the NO and the light were turned off for 30 minutes. The NO_x concentration was measured and had notably decreased. The final measurements varied based on the size of the exposed surface, the material itself, the concentration of NO, the light intensity, the flow rate, and the air temperature. The best results were seen under low relative humidity, high temperature (>25°C), long contact time, and high light intensities. These are the conditions seen on hot, sunny days without wind-the same conditions that foster a high risk of smog formation [10].

Kumar et al. compared doped TiO₂ with 0.2% Ag or 2% Ag to non-doped TiO₂ when both samples were integrated into white cement. Their goal was to produce a concrete that self-cleans under sunlight and UV light. The cement containing doped TiO₂ showed better degradation efficiency than the non-doped cement in both sunlight and UV light. TiO₂-cement slabs with 2% Ag displayed the most efficient color degradation compared with the other samples. Therefore, they concluded that adding TiO₂ to white cement is an excellent method to produce self-cleaning cement, with the surface only needing water (in the form of rain or humidity), sunlight, and atmospheric oxygen to self-clean [13]. However, Dylla et al. found that higher air flows lead to lower NO removal efficiency because the decreased contact of the pollutants with the concrete does not allow enough time for them to be absorbed and removed by the photocatalytic compound [14]. Zhang et al. tested different dosages of TiO₂, between 1% and 6%, in traditional Portland cement mortar to study TiO₂'s self-cleaning ability; 50% slag as cement replacement was included for comparison. The specimens with 1% TiO₂ showed

good self-cleaning and faster rates of recovery to the original color. When the TiO₂ dosage was increased to 2%, the rate of color recovery also increased. In general, the slag mortars showed slightly lower or similar rates of color recovery-less efficient self-cleaning-than the Portland cement mortars [15].

Hassan et al. studied three different methods to apply TiO₂ to concrete. The first method involved applying thin coatings of TiO₂-3% and 5%-to the concrete surface. In the second method, a hardened concrete surface was treated with water-based TiO₂. Finally, the third method consisted of sprinkling nano-sized TiO₂ particles (3% and 5%) on the surface of fresh concrete before it hardened. The results showed that the 5% TiO₂ coating and the water-based TiO₂ removed NO_x from the air the best. The samples treated with the water-based TiO₂ product showed the highest NO removal efficiency [16].

Experimental Details

Materials

Cement: In this research, type I Portland cement obtained from Ash Grove Cement Company was utilized in all mixtures to prevent variation in results. The cement properties are listed in Table 1.

Coarse aggregate: The coarse aggregate was obtained from Webco Mining, Inc. It complies with the grading requirements of ASTM C-136. It has an absorption capacity of 1.2% and specific gravity of 2.57. Table 2 shows the coarse aggregate gradation.

Fine aggregate: Fine aggregate (sand) was purchased from Jeffery Sand Co. It has a specific gravity of 2.62 and absorption capacity of 0.48% and complies with ASTM C-33, as presented in Table 3.

Water: Clean, fresh drinking tap water, free from impurities, was used in all mixes.

TiO₂: Table 4 presents the characteristics of the nano- and microscale TiO₂. The microscale TiO₂ was obtained from Crystal Co., and the nanoscale TiO₂ was obtained from Sigma Aldrich.

Rhodamin B dye: 0.01 millimoles of Rhodamine B dye was used to represent organic pollutants.

Component	Percent by weight
SiO ₂	20.08%
Al ₂ O ₃	4.65%
Fe ₂ O ₃	4.11%
CaO	63.63%
MgO	0.94%
SO ₃	3.19%
Na ₂ O	0.16%
K ₂ O	0.54%
Limestone	2.7%

Table 1: Portland cement properties (Information provided by the Ash Grove Cement Company).

Sieve Size	% Passing as tested
1.5 inch (38 mm)	100
3/4 inch (19.05 mm)	95.1
3/8 inch (9.5 mm)	28.55
#4 (4.75 mm)	5.2
#8 (2.36 mm)	0.4
#16 (1.18 mm)	0.3

Table 2: Coarse aggregate gradation (Information provided by Webco Mining, Inc).

Methods

Traditional concrete mix contains cement, fine and coarse aggregates, and water. In this work, different concentrations of titanium dioxide (3, 6, 9, 12, or 15% (w/w) of the cement composition; 3 samples for each concentration) were also added to the mix. In real situations, this kind of modified concrete mix would be applied as the top layer of concrete, making up about 10% of the thickness of the concrete, because only the surface is involved in the photocatalytic process. Two sizes of TiO₂ were utilized, nanoscale and microscale, both with the same crystal structure (anatase). Table 5 lists the contents of the TiO₂-infused concrete mixes used in this work.

After the concrete samples were prepared, 0.1 ml of (10 mM) Rhodamine B were applied on top to represent organic pollutants. Next, the samples were put under sunlight to mimic real conditions, and the color intensity degradation was measured after 24, 48, 72, and 96 hours. All samples were put out together to avoid unwanted differences between them. ImageJ® software was used to analyze color removal efficiency to identify the optimal dose and size of TiO₂.

Results

Both the nano- and microscale TiO₂ degraded the color on top of the concrete, but the micro-TiO₂ performed better than the nano-TiO₂. The optimal amount of micro-TiO₂ was 9%, which removed 98.25% of the color; the optimal amount of nano-TiO₂ was 3%, which removed 89% of the color. Figure 3 shows the color degradation for 9% micro-TiO₂, and Figure 4 shows it for 3% nano-TiO₂. Overall, results indicate that nano-and microscale TiO₂-infused concrete may be able to remove organic pollutants that come in contact with the concrete surface.

Figure 5 charts the color removal efficiency of all the micro-TiO₂ concentrations, clearly showing 9% to be the optimal amount. Figure 6 charts the same for all nano-TiO₂ concentrations, indicating the optimal amount to be 3%. Figure 7 shows the color intensity degradation caused

Sieve Size	% Passing as tested
3/8 inch (9.5 mm)	100
#4 (4.75 mm)	97
#8 (2.36 mm)	86
#16 (1.18 mm)	80
#30 (600 micro meter)	45
#50 (300 micro meter)	13
#100 (150 micro meter)	0.5

Table 3: Fine aggregate gradation (Information provided by Jeffery Sand Co).

	Nano	Micro
TiO ₂ (Weight)%	99.7	97.5
Type of crystal structure	Anatase	Anatase
Particles size	≤ 25 nm	≤ 850 μm

Table 4: Nano- and micro-TiO₂ characteristics (Information provided by Crystal Co. and Sigma-Aldrich).

Material (gm)	3% TiO ₂	6% TiO ₂	9% TiO ₂	12% TiO ₂	15% TiO ₂
Cement	8.73	8.46	8.19	7.92	7.65
Fine aggregate	25	25	25	25	25
Coarse aggregate	12	12	12	12	12
Water	5	5	5	5	5
TiO ₂	0.27	0.54	0.81	1.08	1.35

Table 5: Components of the different concrete mixes used in this study.



Figure 3: 9% micro-TiO₂ at 0, 24, 48, 72, and 96 hours (left to right).

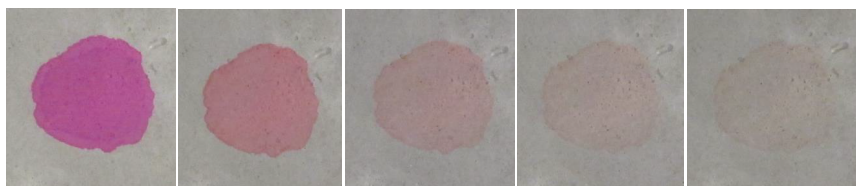


Figure 4: 3% nano-TiO₂ at 0, 24, 48, 72, and 96 hours (left to right).

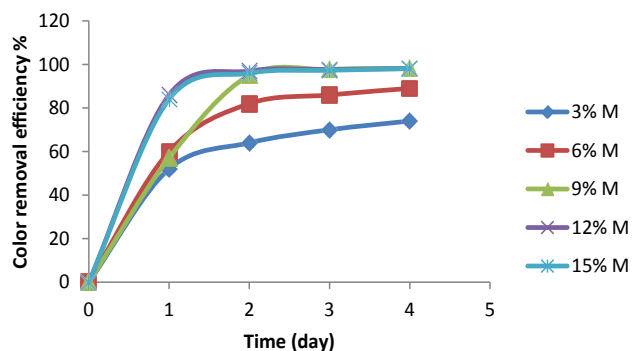


Figure 5: Color removal efficiency of all micro-TiO₂ concentrations with time (day).

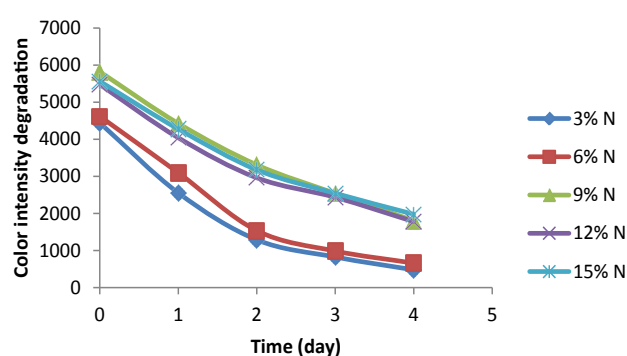


Figure 7: Color intensity degradation by nano-TiO₂ over time (day).

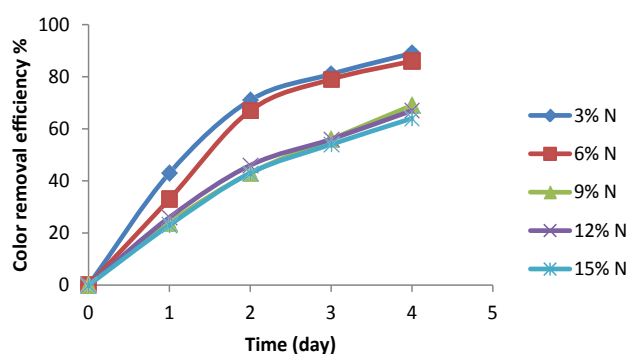


Figure 6: Color removal efficiency of nano-TiO₂ over time (day).

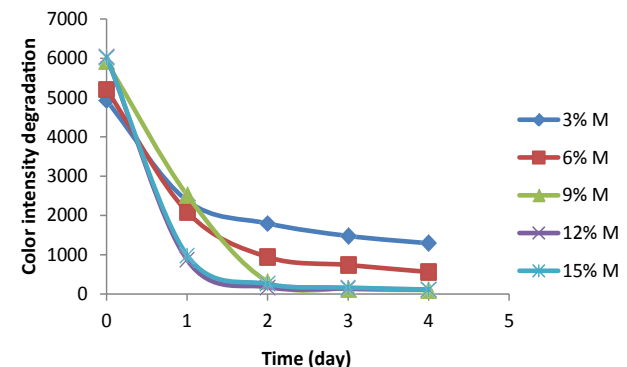


Figure 8: Color intensity degradation by micro-TiO₂ over time (day).

by nanoscale TiO₂, and Figure 8 shows the color intensity degradation caused by microscale TiO₂.

Conclusion

Studies have shown that titanium dioxide helps produce a concrete that can clean itself and the air around it by various mechanics, particularly photocatalysis. To evaluate this concept, we measured the pollutant removal efficiency of TiO₂ by applying Rhodamine B dye on the surface of TiO₂-infused concrete mixes and calculating the surface's

removal efficiency, which represents its potential removal efficiency of air pollutants and certain organic contaminants. Our results indicated that both nano- and micro-TiO₂-infused concrete can remove organic pollutants that interact with concrete's surface. Microscale TiO₂ showed more efficient color removal than the nanoscale samples. The optimal dose of microscale TiO₂ was 9% of the cement concentration, with its color removal efficiency reaching up to 98.25%. The optimal dose of nanoscale TiO₂ was 3% of the cement concentration, having color removal efficiency of 89%. Therefore, our study clearly shows

that mixing small amounts of TiO₂ (either nano-or micro- size) into cement mixtures can have drastic effects on the overall ability of the resulting concrete to remove pollutants and self-clean. In the future, we will investigate other photocatalytic active agents in order to further optimize the photoactivity of cement.

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