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THE IMPACT OF PHOTOCATALYTIC ON DEGRADATION OF POLY AROMATIC HYDROCARBONS THROUGH PERMEABLE CONCRETE

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ABSTRACT

Permeable concrete can be a sustainable solution for storm water management systems in urban environments. However, quite often these waters contain harmful contaminants such as poly aromatic hydrocarbons (PAH), which are known as carcinogens and mutagens. Recently, photocatalysts have been used in various mediums for the degradation of organic pollutants. Under UV light, photocatalysts are able to breakdown organic pollutants into simple substrates through the generation of an electron hole pair and the formation of hydroxyl radicals. Titanium dioxide (T_iO_2) is the most commonly used photocatalyst in construction materials, as it is readily available, chemically stable, not subject to photo decomposition, effective under weak solar irradiation and has shown to have pozzolanic properties. Permeable concrete is an ideal medium for the use of photocatalytic T_iO_2 due to the large surface area created by the voids. In this paper, an experimental investigation on the effect of adding T_iO_2 to permeable concrete to reduce PAH in storm water has been discussed. The degradation of Naphthalene, the simplest PAH, was analysed through a photocatalytic reactor cell. High Performance Liquid Chromatography (HPLC) was used for the quantitative analysis of simulated fluid loads containing naphthalene. The analysis has shown that photocatalytic permeable concrete is effective in the degradation of naphthalene by more than 90% in 4 hours.

KEYWORDS

Photocatalyst, permeable concrete, naphthalene, degradation, TiO_2.

INTRODUCTION

Permeable concrete is also known as Pervious Concrete, Porous Concrete, and No Fines Concrete (Kevern et al. 2006, Lian and Zhuge 2010, Park and Tia 2003). Although it is a relatively low-strength structural concrete made from the same cementitious materials and aggregates to traditional concrete, permeable concrete has a continuous interconnected void network. This is created by the reduction of fine material in the mix that allows water to be able to pass through the concrete. Permeable concrete has only been widely used in Australia for the last decade and has shown to be a positive sustainable solution to urban waste water management (Lian and Zhuge 2010). Urban catchments such as roads, footpaths and car parks all form major catchments for runoff water and road and car park runoff waters are exposed to vehicle pollution. The main pollutants are polycyclic aromatic hydrocarbons (PAH), mineral oils, and heavy metals (Schipper et al. 2007). Schipper et al. (2007) conducted field trials for 13 months, examining road runoff and vehicle spray on two motorways. Their findings showed that pollutants negatively affected the top soils, ground water and surface water, and that the concentration of contaminants over time exceeded standard limits.

Over the past decade there has been significant research and development in the area of photocatalysts (Shi et al. 2009). One of the major applications has been photo-induced redox reaction and super-hydrophilic conversion of T_iO_2 for its degradation of organic pollutants (Shi et al. 2009, Chen and Poon 2009). Chen & Poon's (2009) paper on photocatalytic construction materials discussed the application of titanium dioxide (T_iO_2) being added to construction material products such as tiles, glass, concrete, and paints. It was found that the products could be used for water and air purification, self-cleaning, and self-disinfecting.

Although the fundamental mechanisms of the photo-induced redox reaction and the super-hydrophilic conversion of T_iO_2 for the degradation of organic pollutants are understood, some complex reactions are still unknown. The reactions take place on the surface of the TiO_2, (Figure 1) and when T_iO_2 absorbs UV light (300-400nm), a photon of energy is absorbed. If the energy is equal to or greater than the T_iO_2 band gap (3.2ev), this can then produce an electron/hole pair. This is caused by electrons being promoted from the valence band and being transferred to the conductive band, as expressed in Equation 1. The positive holes in the valence band can then react with any water on the surface to produce hydroxyl radicals.

$$TiO_2 \xrightarrow{hv} TiO_2 + e^- + H^+ \quad (1)$$
$$H_2O \leftrightarrow OH^- + H^+ \quad (2)$$
$$OH^- + H^+ \rightarrow OH^\cdot \quad (3)$$
$$e^- + Ti^{4+} \rightarrow Ti^{3+} \quad (4)$$
$$4H^+ + 2O^{2-} \rightarrow O_2 \quad (5)$$

The key point is that hydroxyl radical and the electron holes have sufficient energy to oxidize organic pollutants such as aliphatic, aromatics, detergents, dyes, pesticides and herbicides (Bhatkhande et al. 2001).

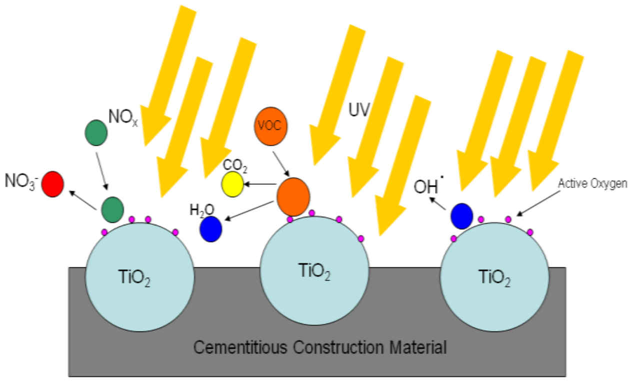


Figure 1. T_iO_2 Construction Material Reaction Mechanisms

Although there are research conducted on photocatalytic construction materials degrading organic pollutants in water, research into photocatalytic permeable concrete has been rare (Shen et al. 2012). Shen et al. (2012) compared different methods to apply T_iO_2 onto the surface of pervious concrete. However, the effect of void ratio was not investigated. This paper presents a research project aimed at investigating the incorporation of photocatalytic titanium dioxide (T_iO_2) within permeable concrete to promote the degradation of organic pollutants in water passing through the concrete. Investigations included the comparison of a standard concrete mix to permeable concrete mixes (with varying void ratios of 20%, 25% & 30%), both incorporating varying percentages of photocatalytic T_iO_2 (5%, 10% & 15%). The breakdown of a poly aromatic hydrocarbon (PAH) (naphthalene) for each mix design was compared.

METHODOLOGY

The photocatalytic permeable concrete specimens were cut into 300mm X 300mm X 100mm samples. The methods and materials used for the permeable concrete samples have been described in previous work (Bolt et al. 2011).

Fluid Sample Preparation

A standard solution of 50µg/L of naphthalene was prepared using Merck Schuchardt OHG > 99% pure naphthalene. Research has shown that storm water samples taken from the side of roads had PAH concentrations between 50µg/L and 20µg/L (Schipper et al. 2007). The solution was then sealed and allowed to stand for 1 hour before being introduced into the testing apparatus.

Testing Apparatus

The testing apparatus was constructed of M16 stainless steel as indicated in Figure 2. Above the injector pipe was the lid, which incorporated a Phillips Actinic BL TL 8 Watt UV providing UV – A radiation in the 350 – 400nm range. The testing apparatus was connected to an Onga –Riva Flow, 0.33HP pump by clear chemical resistant hosing.

The pump was set to a flow rate of 3L/min and was checked before each trial. Before each test 1 litre of deionised water was reticulated through the system to flush it clean and to ensure that the system was running correctly. After set up and flushing, the Naphthalene sample was poured into the apparatus, sealed and allowed to run for 5 minutes. The initial sample was then taken and the pump was turned off. A concrete sample was then placed inside the apparatus, the lid was sealed, the pump turned back on and finally the UV light was turned on. The apparatus was not turned off during any of the testing runs.

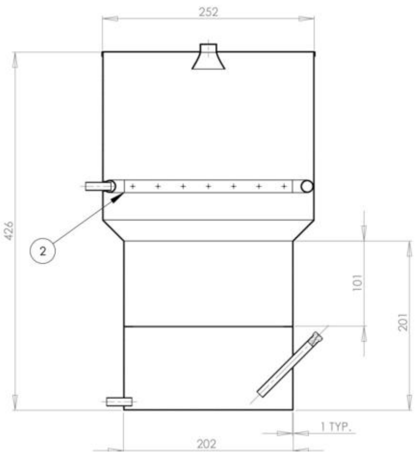


Figure 2: Testing Apparatus

Performance Liquid Chromatography

The samples were tested using the USEPA 8270D "Semi Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS)" method. This method is designed to extract samples of semi volatile organic compounds from various solid waste matrices, soils, air sampling media and water samples.

TEST RESULTS AND DISCUSSIONS

The mechanical properties of the photocatalytic permeable concrete are shown in Table 1. The test methods used for the analysis of the mechanical and hydraulic properties have been described in previous work (Bolt et al. 2011). The results on degradation of naphthalene of permeable concrete are discussed in the following sections.

Table 1. Overview of Mechanical and Hydraulic results

Trial	% TiO_2	W/C	Mechanical Testing				
			Standard test	Permeability Falling Head (k)	Permeability Constant Head (k)	Compressive Strength	Density
			% Void	mm/s	mm/s	MPa	Kg/m^3
1	0	0.32	31	15.9	6.12	8.3	1757
2	0	0.32	26	12.4	5.0	10.0	1839
3	0	0.32	22	7.1	3.94	12.5	1944
13	0	0.41	0	0	0	15.8	2181
4	5	0.33	31	21.0	6.66	5.7	1713
7	5	0.33	29	11.8	6.50	6.5	1711
10	5	0.35	24	10.0	5.0	8.2	1754
14	5	0.42	0	0	0	11.0	2152
5	10	0.33	30	15.5	5.37	4.0	1687
8	10	0.34	33	13.8	5.59	5.6	1569
11	10	0.39	21	4.8	3.71	9.6	1924
15	10	0.43	0	0	0	13.0	2247
6	15	0.34	33	7.3	3.38	3.3	1603
9	15	0.38	26	3.4	3.55	7.7	1807
12	15	0.41	17	2.2	1.4	14.0	1979
16	15	0.48	0	0	0	12.3	2047

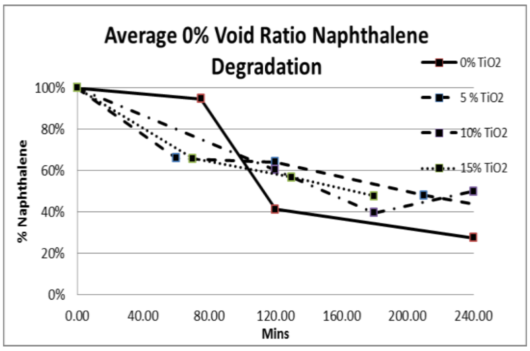
Four groups of samples with varying void ratio (0, 20, 25 and 30%) and percentages of T_iO_2 (0, 5, 10 and 15%) were tested, the result are shown in Figure 3. The 0% void ratio concrete (Trials 13,14, 15 and 16) was used to simulate a normal structural concrete pavement to establish a benchmark for measuring whether permeable concrete is more effective for degradation than normal concrete. Four tests were conducted with 0%, 5%, 10%, and 15% T_iO_2 with samples taken every hour for 4 hours. As it can be seen in Figure 3a, the addition of T_iO_2 reduced the presence of Naphthalene by approximately 30% for all T_iO_2 addition percentages. The sample which had no T_iO_2 added (Trial 13) did not change until after 70 minutes. However, Figure 3a depicts that there is a significant decrease of Naphthalene at the 120 minute interval for the Trial 13. The decrease of Naphthalene at 120 minutes for the 0% T_iO_2 (Trial 13) may have been caused by the vaporisation of Naphthalene at temperatures greater than 308K, 35℃ (Faundez et al. 2007). At 120 minutes the temperature of the sample was 40℃. The volatility of Naphthalene could cause it to vaporise and reduce the quantity present in the water sample.

The results for 20% void ratio were shown in Figure 3b. It is evident from the figure that the two additions of T_iO_2 reduced the concentration of Naphthalene significantly, compared to the control mix. The 10% and 15% additions of T_iO_2 had almost identical degradation rates at 60 minutes, reducing the naphthalene concentration by 50%. At the same time interval, the control mix which contained no T_iO_2 had a reduction of 3%. After 240 minutes of testing, the 10% and 15% additions of T_iO_2 samples had reduced the concentration of Naphthalene by more than 85%. The control mix had reduced the concentration by 16%. However, the temperature had already achieved 35℃ at 180 minutes and any degradation would have likely been caused by vaporisation and not by the permeable concrete.

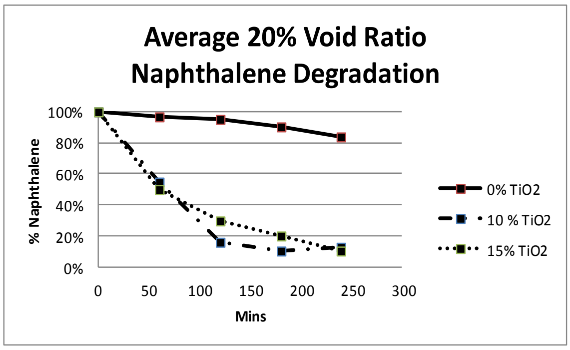
The control mix for the 25% void ratio (Trial 2) achieved 28% reduction of Naphthalene, which was the highest degradation recorded of all the control mixes. However, the temperature at 180 minutes was greater than 35℃ and hence, vaporisation likely caused the reduction in Naphthalene. Figure 3c reveals that the 15% addition of T_iO_2 achieved slightly better results than the 5% addition and reduced the concentration of naphthalene by 50% at 60 minutes, compared to a 34% reduction with the 5% addition of T_iO_2 at the same time.

However, at 240 minutes the 15% addition had reduced the concentration by 80%, which was only 8% higher than the 5% addition. This supports previous findings of Husken et al. (2009), where the increase in T_iO_2 had less effect on the degradation rate than increasing the surface area. The research indicates that it would be uneconomical to add the extra 10% T_iO_2 to permeable concrete for such a small gain in degradation rate.

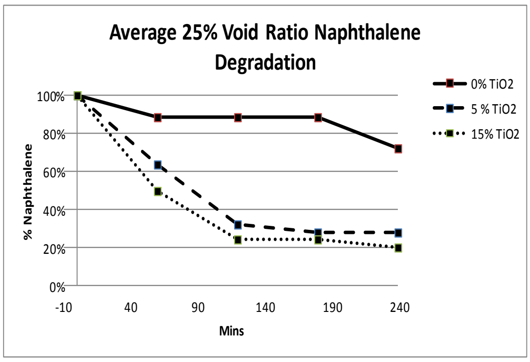
The 30% void ratio degradation results (Figure 3d), showed that the 5% addition of T_iO_2 reduced the Naphthalene concentration by 87% at 240 minutes. This result was significantly higher than the 10% and 15% T_iO_2 additions at the same time interval. Once again this supports the conclusion that increasing the addition of T_iO_2 does not necessarily increase the degradation rate.



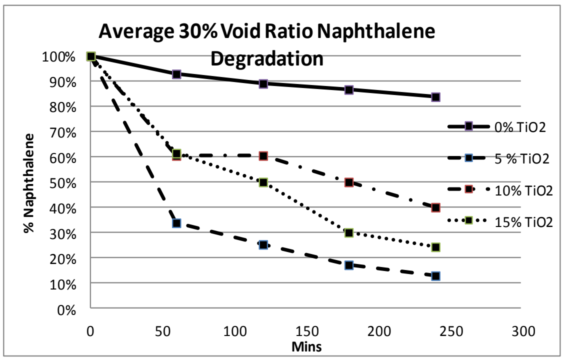
(a) 0% Void Ratio



(b) 20% Void Ratio



(c) 25% Void Ratio



(d) 30% Void Ratio

Figure 3. Naphthalene Degradation Over 90 Minutes

As the 30% void ratio had the largest surface area, it was expected that it would have the highest degradation rate. However, when comparing the degradation results to other void ratios, it is seen that the 30% void ratio with 15% T_iO_2 did not perform as well as the other void ratios with 15% T_iO_2 addition. It was noted previously that the 30% void ratio permeable concrete achieved the highest rate of permeability for both permeability test methods (Bolt et al. 2011). The reduction in degradation may have been caused by the increase of fluid flow rate through the permeable concrete, which effectively reduced the H_2O contact time with the H^+ ions present on the surface of photocatalytic concrete and therefore, reduced the formation of the hydroxyl radicals. The testing results indicated that the 20% void ratio photocatalytic permeable concrete was most effective for the degradation of poly-aromatic hydrocarbons presented in water samples.

It was noted during the testing that the temperature of the samples were generally higher for the normal concrete (0% voids) than for permeable concrete. This was likely caused by the surface of the concrete heating up under the UV lamp and not cooling as effectively as the permeable concrete samples. Nakayama & Fujita’s (2010) research collaborates this theory, their research concluded that permeable concrete has a surface temperature significantly lower than traditional concrete, due to its reduction in thermal conductivity. Therefore, the results for the normal concrete can only be compared up to the 90 minute time interval, as after this, the temperature rises above 40 ℃ and significant vaporisation has likely occurred. The data shows (Figure 3a) that before vaporisation occurs, Naphthalene does not experience degradation in normal concrete (0% voids, 0% T_iO_2). Therefore, standard road, driveway and footpath pavement dense concrete would not experience degradation of PAH under normal conditions.

CONCLUSIONS

The use of photocatalytic permeable concrete in urban environments for waste water management systems provides a unique approach to the harnessing and detoxification of urban runoff waters. However, little or no research had been conducted on the application of photocatalytic permeable concrete and the degradation of organic pollutants in water. The photocatalytic permeable concrete manufactured for this research significantly reduced the concentration of PAH for all three void ratios and achieved much higher reduction than the photocatalytic standard concrete. It is also found that an increased dose rate of T_iO_2 had little effect on the overall degradation. The different void ratios produced varying results and the 20% void ratio was the most effective, allowing more time for the reaction to take place. The research showed that photocatalytic permeable concrete is superior for the degradation of organic compounds, compared to standard photocatalytic concrete. This is due to the increased surface area created by the void allowing more reaction sites on the surface of the concrete.

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