Photocatalytic Oxidation Performance to Removal of Volatile Organic Compounds in Indoor Environment

Arafa Awadalla Bakheet, Muhammad Fauzi Mohd Zain, Abdul Amir Kadhum and Zeinab Abdalla
Department of Architecture Engineering, Faculty of Engineering and Built of Environment, University Kebangsaan Malaysia

crossref http://dx.doi.org/10.5755/j01.erem.58.4.308

(received in April, 2011, accepted in December, 2011)

Volatile organic compounds (VOCs) exist widely in both the indoor and outdoor environment. Some of (VOCs) are toxic and effecting to human health, such as benzene and toluene. A study was carried out to investigate the use of Panels concrete coated with Titanium dioxide (TiO₂) catalyst in a fixed-bed reactor installed with a UV light lamp. The samples were studied using the GC (FID) multi-analyser for measuring the performance of photocatalytic active concrete products. Experiments were conducted to compare their efficiencies in degrading the Benzene. When the benzene loaded and passed through the photocatalytic reactor, the removal efficiencies were determined by GC (FID). The experimental results show the high benzene removal was achieved.

Keywords: Photocatalysis; Volatile organic compounds (VOCs); Air-cleaning; Concrete composite panels.

1. Introduction

Air pollution caused by road traffic and industry is one of the major problems in metropolitan and urban areas. Environmental contamination, which is growing around the world or in our daily home life, is a serious social problem not to be ignored. Indoor air pollutants impact human health, comfort and efficiency. The health effects of organic chemicals are eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Some organics can cause cancer in animals; some are suspected or known to cause cancer in humans (chiura 2003a).

Volatile organic compounds (VOCs) are among the most abundant chemical pollutants in the indoor air that we breathe (Jo & Park 1999, USEPA 1990). Since the 1970s, a lot of investigations have been carried out for measurement of the indoor air concentrations of VOCs all around the world. It is found that indoor air typically contains a greater number of VOCs at higher concentrations than outdoor air. The concentrations of VOCs are dependent on the environment. The mean concentrations of VOCs and total VOCs in established buildings are generally greater than those established public buildings and VOC concentrations in new buildings are much greater than those in established buildings (Jones 1998). Benzene, Toluene, and Formaldehyde and benzene are typical indoor pollutants (Lee & Chang 2000, Nagda & Rector 2003, Wolkoff 1998a, Yu & Crump 1998) and these materials, which are discharged mainly from plywood, particle board and adhesives for wallpapers. The emission of volatile organic compounds from building materials has been recognised as the largest
source of indoor air pollutants (Namiesnik 1999a). Table 1 shows some specific indoor sources of organic vapours. The table shows that the construction coverings and household cleaning products make the significant contribution to the air pollutants in indoor environment.

Photocatalytic oxidation (PCO) (Carp 2004a, Linsebigler & L.u.Yates 1995) is promising technologies for air purification because the pollutants can be oxidised to H2O and CO2. However, thermally catalytic oxidation requires high temperatures of 200–1200 °C for efficient operation and hence expensive. Furthermore, thermally catalytic oxidation is not economically feasible at low pollutant concentrations. Titanium dioxide has been used as a catalyst for the UV induced photocatalysis of pollutants in recent years.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source material(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paradichlorobenzene</td>
<td>Moth crystals, room deodorants</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>Paint removers, solvent usage</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Pressed wood products, foam</td>
</tr>
<tr>
<td>Styrene</td>
<td>Insulation, textiles, disinfectants, plastics, paints</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>Glues, deodorants, fuels, preventives, mold growth on leathers</td>
</tr>
<tr>
<td>Acrolein and cotton</td>
<td>Component of oak-wood, by-product of the combustions of wood, kerosene</td>
</tr>
<tr>
<td>Toluene disocyanate</td>
<td>Polyurethane foam, aerosols</td>
</tr>
<tr>
<td>Benzyl chloride</td>
<td>Vinyl tiles plasticized with butyl benzyl phthalate</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>Sterilizers (hospitals)</td>
</tr>
<tr>
<td>Volatile amines</td>
<td>Putrefactive degradation of casein-containing building materials</td>
</tr>
<tr>
<td>Benzene</td>
<td>Smoking</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>Wearing or storing dry-cleaned clothes</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Chlorinated water (showering, washing clothes, and dishes)</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>Industrial strength cleaners</td>
</tr>
<tr>
<td>Aromatic hydrocarbons (toluene,</td>
<td>Paints, adhesives, gasoline, combustion sources</td>
</tr>
<tr>
<td>ethylbenzene, trimethylbenzenes)</td>
<td></td>
</tr>
<tr>
<td>Aliphatic hydrocarbons (Octane,</td>
<td>Paints, adhesives, gasoline, combustion products</td>
</tr>
<tr>
<td>decane, undecane)</td>
<td></td>
</tr>
</tbody>
</table>

Photocatalytic reactions are attractive because they do not require high temperature operational conditions and they can be very selective in radiation absorption. photocatalysis has beneficial characteristics, such as its chemical and physical stability, as well as the oxidizing power of the photogenerated holes. It has become apparent that organic compounds can be oxidized to CO2 by hydroxyl radicals generated on the TiO2 surfaces (Hashimoto & Fujishima 1997). Multiple aspects of TiO2 photocatalytic oxidation of organic compounds in the gas phase have been addressed by a profuse scientific literature over the past 20 years. In heterogeneous TiO2 photocatalytic systems, after irradiation of the photocatalyst with UV Light increases the electron-hole generation (Matsubara 1995a): (a) After irradiation of UV light ranging from 300 to 400 NM, the photocatalytic reaction begins with the generation of electron-hole pairs:

\[
\text{TiO}_2 \xrightarrow{hv} h^+ + e^-
\]

(b) The \( h^+ \) reacts with \( OH \) dissociated from water to form the hydroxide radical;

\[
h^+ + OH^- \rightarrow OH^-
\]

(c) The \( e^- \) reacts with molecular oxygen to form the superoxide anion;

\[
e^- + O_2 \rightarrow O_2^-
\]

(d) The superoxide anion further reacts with \( H^+ \) dissociated from water to produce \( HO_2^- \) radicals;

\[
H^+ + O_2^- \rightarrow HO_2^-
\]

(e) \( NO \) diffuses to the surface of \( TiO_2 \) and is oxidized to \( NO_2 \) by \( HO^* \) radicals;

\[
NO + HO^* \rightarrow NO_2 + OH^*
\]

(f) Finally \( NO_2 \) reacts with hydroxyl radicals to form nitric acid.

\[
NO_2 + OH^* \rightarrow HNO_3
\]

The great redox power of the UV induced electron-hole pair of photocatalysts can also decompose the organic pollutants. An example of degradation of palmitic acid is shown:

\[
\text{TiO}_2 \xrightarrow{hv} h^+ + e^-
\]
After the release of the first carbon atom, the n-C_{15}H_{31}OH radicals are oxidized by \( \text{OH} \) radicals to an alcohol:

\[
\text{n-Cl}_{15}\text{H}_{31}\text{OH} + \text{h}^+ \rightarrow \text{n-Cl}_{15}\text{H}_{31}\text{COOH} + \text{H}^+ + \text{Cl}_{15}\text{H}_{29} - \text{COOH}.
\]

The produced n- \( \text{Cl}_{15}\text{H}_{29} - \text{COOH} \) undergoes oxidation into aldehyde, and then further to acid n- \( \text{Cl}_{15}\text{H}_{29} - \text{COOH} \). Subsequently, a second photo-Kolbe reaction takes place to release the second CO\(_2\). The chain reactions continue until the palmitic acid is completely mineralized to CO\(_2\) and H\(_2\)O. Some side reactions may also be induced to generate volatile compounds, accelerating the oxidation process.

Consequently, there have been many studies on TiO\(_2\) photocatalysis using TiO\(_2\) coated glass, and tiles, paper containing TiO\(_2\) etc, for the removal of toxic materials from the environment (Hodgson 2007, Matsubara 1995a, Sopyan 1994). Photocatalytic oxidation (PCO) is considered a promising technology, and has been investigated by many researchers in various fields. Several researchers appear there is ability to break down volatile organic compounds in the air and it has been proven in many instances (Ginestet 2005a, Obuchi 1999a, Tomida 2005, Zhao & Yang 2003). PCO reactors usually use pure titanium dioxide (TiO\(_2\)) with some metal ions to improve the PCO reactivity, and VOCs are removed through the repeated process of absorption and oxidation reactions of TiO\(_2\) (Kayabal & Bulus 2000).

Benzene brings about various problems at very low concentrations; the efficient adsorption of toxic substances onto TiO\(_2\) is an important factor determining its degradation ability. The current study was designed to investigate the efficiency and performance of photocatalytic materials such as Titanium dioxide (TiO\(_2\)) to the technique of producing concrete composite panels, using local waste materials for solving the problem of the increasing rates of Volatile Organic Compounds (Benzene) in indoor air buildings.

2. Experimental Program

2.1. Preparation of Specimens

Cement material that is used in this study is an Ordinary Portland Cement (OPC) commercially available in Malaysia (Poon, Yu, and Ng 2001). The recycled aggregate (RA) is also used in this study. In the stand the recycled aggregate underwent a process of mechanized sorting; only the smaller fine aggregate proportion will use for making the basic layer of the samples in this study (Nagao & Suda 1989). The maximum size of the recycled aggregate that used was 300 mm. The sand that was used is fine natural river sand commercially available in Malaysia. The Chemical material used is titanium dioxide (TiO\(_2\)) Anatas, which is commercially available, and was used due to its high purity and accurate specifications (Nagao & Suda 1989).

2.2. Sample proportions

The samples were fabricated in steel moulds with internal dimensions of (20\(\times\)10\(\times\)5) cm. The wet mixed materials weighed between (700g to 800g) for each sample depending on the different materials. The steel forms were on hand-filled and then compressed with a compression machine with a speed of 500 KN / min for 1 min. After 1 day the samples have been removed their forms and cured in a chamber with a controlled Humidity (75%) and a temperature of (25 °C) until tested. The surface layers were tested for benzene photodegradation at 10, 20 and 30 days with GC (FID) equipment.

2.3. Mix proportions

Admixture prepared with cement, recycled aggregate (RA), and Titanium dioxide (TiO\(_2\)) were mixed with sand and water. A series of mixes proportion were prepared to find out the effects of titanium dioxide and its efficiency on benzene removal. The mixes were mixed with cement and aggregate in ration from (1:2, 1:2:5) and (1:3) were prepared. The sizes of aggregate from (2.50 to 3.50 mm) were used through all of the experiments. The content of Titanium dioxide in all mixes was in a range from (0.5% to 0.07%) as given in (Table 2).

<table>
<thead>
<tr>
<th>Table 2. Mixes prepared with different materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative proportions (by weight(g))</td>
</tr>
<tr>
<td>Ratio</td>
</tr>
<tr>
<td>1:2</td>
</tr>
<tr>
<td>1:2:5</td>
</tr>
<tr>
<td>1:3</td>
</tr>
<tr>
<td>1:2</td>
</tr>
<tr>
<td>1:2:5</td>
</tr>
<tr>
<td>1:3</td>
</tr>
</tbody>
</table>

2.4. Equipments

The essential part of the experimental setup used is a photocatalytic reactor allowing a sample of the size (10\(\times\)20 cm\(^2\)) to be fixed. The reactor is made
from materials which are non-absorbing to the applied pollutant and can hold up UV light source with wavelengths 366 nm. The UV light was used to supply photo irradiation to activate the photocatalyst. The reactor is tightly closed with a glass plate made from borosilicate glass allowing the UV rays to pass through with almost no restriction. The surface of the specimen is fixed parallel to the covering glass inside the reactor, leaving a hole of 0.5cm for the gas to pass through it; the gas taster only passes the reactor through the hole between the sample surface and the glass cover in longitudinal direction. All structural designed parts inside the box are to allow laminar flow of the gas along the sample surface and to put off distribution. Temperature and humidity sensor are two types of sensors were used. Benzene removal was observed by analyzing sample using GC (FID). Studies of the adsorption and photocatalytic decomposition of benzene carried out at room temperature (27°C). Benzene was injected into a 5 ml reaction vessel equipped using a micro syringe. The initial concentration of benzene was 12.5 ppm and 35 ppm, respectively. Specimens which was placed in the bed of a reaction vessel, was illuminated with an UV lamp from a distance of 10 cm for a fixed time. After irradiation, samples were withdrawn from a sampling port attached to the side of the vessel and injected into the gas chromatograph using a micro syringe. The concentration of benzene was measured using GC (FID).

![Fig. 1. Different concentration measured of benzene within 5 h under UV light for the photoactive panels](image)

3. Results and Discussion

When photocatalytic degradation occurs, organic compounds such as benzene will be formed. Measured values of benzene are clearly higher in the chamber than in the outdoor environment. In addition, the photocatalytic samples produce more absorption than the non-photocatalytic samples. The benzene in the gas phase was successfully decomposed by the photocatalytic reaction in a Photo reactor under UV irradiation conditions. It was already had a synergistic effect observed with the use of TiO$_2$ photocatalytic for degradation of benzene. This synergistic effect was attributed to the creation a common interface between the two at fixed Phases and by a transfer from benzene to adsorb TiO$_2$, where it immediately photocatalytic degraded.

3.1. Photocatalytic removal of benzene

The removal and degradation of benzene is commonly investigated on different TiO$_2$ surfaces. Benzene is one of many different indoor VOCs. It was injected into the chamber, and the concentrations were observed. Figure 1 shows the decomposition and removal of benzene. The removal of VOCs can be explained with adsorption onto a different surface of samples. A clear photocatalytic effect was observed for photoactive samples. These samples could decompose the injected pollutants more than the other non-photocatalytic samples. The results were also illustrated high concentrations of benzene absorption after five hours as (0.0.763 g/L). The measured concentrations from the photoactive panels within five hours were illustrated in (Fig.1.).

3.2. Influence of Titanium dioxide loading on benzene removal efficiency

TiO$_2$ was carried out a series of benzene adsorption in a continuous gas flow reactor with a titanium dioxide layer of doped on concrete panels. Figure 2 shows the chromatogram diameter of benzene with rotation time is about (5.827) min, which is calculated from the minimum equilibrium cross-sectional diameter, and can therefore be easily adsorbed on the surface of samples.

When initially using layer doped of TiO$_2$ as the adsorbent, the high slope of the advance curve indicates very fast adsorption under UV light (366 nm) transfer effect, (10%) of the relative benzene concentration was obtained on the first (15) minutes is bout (0.004 g/L) (fig.1.) adsorbed and then increased slightly after five hours to ( 0.0763 g/L). The evolution of specific surface area and adsorption capacity of benzene on TiO$_2$ are illustrated in (Fig.3.). In The (Fig.4.) the adsorption capacity increases under UV light until reaches a maximum concentration after five hours.
Fig. 2. The chromatogram diameter of benzene with rotation time

Fig. 3. Very fast adsorption of benzene reaches on the first 15 minutes by TiO₂ under UV light in the Photocatalytic reactor

Fig. 4. The maximum concentration of benzene removal reaches after five hours under UV light in the Photocatalytic reactor
3.3. Influence of porosity of the panel surface layer on benzene removal

Micropores areas increased averagely from (1.5 m² g⁻¹ to 5.5 m² g⁻¹) according to BET surface areas, as raising photocatalytic content up to (1 %mol). The samples showed the highest microporosity, (10.02 m² g⁻¹ and 10.55 m² g⁻¹), respectively. The higher framework microporosity leads to higher interaction adsorbsents between the TiO₂ and benzene molecules, therefore, resulting in the gradual enhancement in benzene-adsorbed amount up to the optimal capacity of (10%) every (15) minutes. These results are consistent with numerous reported literatures on bi-porous materials irrespective of light hydrocarbon, aliphatic or aromatic hydrocarbons (Li 2005a, Newalkar 2003a). The microporosity also influences on the adsorption behaviour for gaseous benzene via the relative diffusion control. However, once again, the microporous regions dominated the adsorb ability in view of the reduction in micropore areas, resulting in the faster diffusion and the corresponding lower benzene-adsorbed amounts than those of (5 %) doped materials. It obviously indicated that the framework microporosity plays an important role in controlling diffusion mechanism of the adsorbate molecules over photocatalytic materials directly relating to the adsorbability. Similar observations were also acknowledged by researchers in (Li 2005a). Associating several parameters, such as the largest external surface area and micropore area, high total pore volume and pore diameter, 10% photocatalytic doping content is the optimum amount for the adsorption conditions in the present study. The results shows that porosity of the surface layer is important which efficiently increased the area available to reacting with the pollutants. The porosity of the surface layer was affected by the type of materials with which they were prepared. Materials with a lower density led to a higher porosity of the panels. The particle size distributions of the materials used also affected the porosity of the panels.

4. Conclusion

A composite TiO₂ Panel is very effective for the photocatalytic decomposition of benzene, which is an indoor pollutant. Based on this study, the following conclusions can be drawn; a test was carried out in which adequate amount of benzene was injected every 60 minutes under UV-irradiation. In the case of the TiO₂ panel, the benzene concentration in the reaction liner, it was expressed as a percentage of the first quarterly added increased regularly through the sequential addition. The result also illustrates the enhanced photocatalytic activities of TiO₂ micropore for pollutant removal and the influence of the surface layer porosity on benzene adsorption was affected by the type of materials with which they were prepared.

The results show that titanium dioxides decreased with age, but the decrease stabilized at the age of 60 days. Titanium dioxide was used as the better form of source from a commercial source; hence, it be the best photocatalytic ability for improve indoor air quality.

Acknowledgment

The authors would like their sincere thanks to Prof. Mohd.Zain express sponsor of the research team and I offer my greetings and best wishes to all those who supported me in every aspect of my work

References


Photocatalytic Oxidation Performance to Removal of Volatile Organic Compounds in Indoor Environment


E-mail:  arafa_bakheet@yahoo.com

E-mail:  fauzi@eng.ukm.my

E-mail:  Amir@eng.ukm.my

E-mail:  Zeinab3007@yahoo.com