PHOTOCATALYTIC NANOMATERIALS FOR AIR PURIFICATION

Benoît Kartheuser
CERTECH asbl, Rue Jules Bordet, zone industrielle C, 7180 Seneffe, Belgium,
benoit.kartheuser@certech.be

Abstract

Indoor air quality is becoming today a serious concern for the population of Western Countries. People spend generally 80 to 90 % of their time in confined spaces. They are exposed to a very large variety of pollutants (volatile organic compounds : VOC) coming from human activities, heating, chemicals released by furniture, building materials etc ... Odours problems encountered in such places are related to the presence of these VOCs sometimes in sub ppmv concentration.

Photocatalysis can be a good solution for air remediation.

We will be presenting some results on active air purifier testing.

1. INTRODUCTION

Today, most people living in industrial regions, particularly during the colder months, spend more than 80 % of their time in confined spaces (buildings, cars, planes …) with only short airing periods. Indoor pollution sources that release gases or particles into the air are the primary cause of atmosphere quality problems in homes. Efficient insulation combined with inadequate ventilation represents particularly aggravating conditions. Sometimes, indoor pollutant concentration can exceed the outdoor ones and generate discomfort if not health threatening effects.

Sources of indoor air pollution may originate from the combustion of oil, gas, coal, wood, tobacco ; building materials and furniture ; products for household cleaning and maintenance, personal care or hobbies and outdoor air pollution. In addition, many health problems are caused by biological agents such as fungi, moulds, bacteria and other micro-organism.

Their occurrence is often favoured by the use of inadequate materials and poor air treatment conditions.

Table 1 summarizes results obtained by Krause in 230 selected German houses. These results were confirmed by other studies.

Table 1. VOC concentrations measured in 230 German residences.

<table>
<thead>
<tr>
<th>Chemical family</th>
<th>Average concentration ($\mu$g/m$^3$)</th>
<th>Range ($\mu$g/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic hydrocarbons</td>
<td>166</td>
<td>16-1260</td>
</tr>
<tr>
<td>Alkanes</td>
<td>97</td>
<td>8.7-432</td>
</tr>
<tr>
<td>Chlorinated Hydrocarbons</td>
<td>48</td>
<td>3.5-1630</td>
</tr>
<tr>
<td>Terpenes</td>
<td>42</td>
<td>2.1-362</td>
</tr>
<tr>
<td>Carbonyl Compounds</td>
<td>29</td>
<td>5.2-347</td>
</tr>
<tr>
<td>Cyclohexanes</td>
<td>15</td>
<td>2.1-79</td>
</tr>
<tr>
<td>Alcohols</td>
<td>7</td>
<td>1-25</td>
</tr>
</tbody>
</table>

$^1$ includes ketones, aldehydes and esters.
One effective way to improve indoor air quality is to eliminate individual sources of pollutants. Another approach is dilution of the contaminated air, by increasing the inflow of outdoor air as long as that air is less contaminated than indoor air. Finally, the use of air purifiers can decrease indoor air contamination. The long-term performance of an air purifier depends on maintenance. Usually, these air purifiers are made up of different filters and collectors, which can remove most particulate materials including, biological and chemicals contaminants.

Organic contaminants are usually present at very low concentrations often less than 1 ppmv. A promising approach for VOC removal is to combine a suitably designed photocatalytic reactor in combination with particle filters.

Photocatalysis is a promising technology for air purification. Photodegradation occurs at room temperature and atmospheric pressure and oxidizes most pollutants to H\textsubscript{2}O and CO\textsubscript{2}. Most papers involving air treatment via photocatalysis report operations at ppmv (part per million) concentration with single or binary mixture of model molecules. Few studies have been carried out in the ppb range, eventually coupled with odour characterisation\textsuperscript{5,6,7,8}.

Air treatment by photocatalytic materials can be divided in two main categories: passive and active processes.

In the first group we can find paints, plastic flowers, textiles ... Those materials can degrade harmful substances, leading to VOC reduction. Due to the large surface that those materials can cover, the cleaning potential is high. One main condition for them to be effective is the need to work under artificial lighting, where the UV irradiation is very low.

The second group is composed of air purifiers: either standalone or in combination with an air conditioning system. They have the advantage of using UV lamps to activate the photocatalyst and to force VOC through the purifying surfaces.

It is extremely important to have standards to assess the activity of what it is advertising, mainly on the web. The available standard at the ISO level concerns mainly the activity of the photocatalytic substrate exposed to only one component.

Such standards are not sufficient to assess the activity of the air purification device.

All systems (active or passive) are exposed in real life conditions to combinations of numerous volatile compounds.

For the passive systems, it is important to run the evaluations under lighting condition close to the normal indoor environment where the amount of activating UV light is very low.

We shall review a laboratory test method to assess the photocatalytic air purifier performance that has been validated in real life conditions, as well as some results on the performance of commercial system. Finally, an example of problem that can be faced during testing will be shown.

2. EXPERIMENTS

The photocatalytic material/system is tested in a airtight chamber simulating a confined space of about 1m\textsuperscript{3}. The figure 1 presents a schematic view of the test chamber.
The chamber is equipped with a fan to homogenize the air, some septa for sampling air on special cartridges and for online analysis by gaz chromatography, a temperature and humidity probe, electrical connections and a septum to introduce the VOC mixture to be tested.

Prior to running a test, the chamber, with the device to be tested in operation, is flushed with clean humidified air. The device is stopped before the VOC introduction.

The VOC mixture is introduced in the test chamber with a syringe and homogenised by the fan. Once the VOC concentration is stable, the device is switched on.

The chemical evolution is followed using online gas chromatograph with a photo ionisation detector (GC-PID) and CO₂ with a micro gas chromatograph equipped with thermal conductivity detector (μGC-TCD).

Reaction by-products can be monitored by sampling air through special cartridges then analysed by thermal desorption coupled with a gas chromatograph combined with a mass spectrometer (GC-MS) or, for aldehydes by chemical desorption followed by high performance liquid chromatography (HPLC).

Depending on the UV lamp wavelength, ozone can be produced. This compound is detected with a specific sensor.

Initial test conditions were 50% ± 5% RH and 22 °C ± 2°C.

The humidity and temperature were measured and recorded with a humidity/temperature probe.

Four devices were tested:

The device A is a commercial system composed of a particle filter, followed by an activated carbon filter then a photocatalytic material illuminated with a UVA lamp.

The device B is a prototype with similar combination of filters.

Devices C and D are also commercial systems but without any particle and activated carbon filters.

Due to the presence of activated carbon, device A and B were tested at high concentrations.

Devices C and D were tested at low concentrations.
Finally, a device E was used in real condition for the removal of ethylene. Its activity was assessed before and after the test.

3. RESULTS

Graph 1 and 2 presents the results of the devices A and B for the degradation of a VOC mixture composed of acetone, acetaldehyde, heptane, toluene and o-xylene at concentration near 20 ppmv each.

Graph 1: Chemical evolution with device A

Graph 2: Chemical evolution with device B

Clearly, both devices behaved differently. In the case of the commercial system, only toluene, o-xylene, and heptane were removed quickly from the gas phase, but they are still present at low concentration after 1200 min of test. We can also observe that acetone and acetaldehyde are difficult to be removed. Finally, there is almost no CO$_2$ produced. CO$_2$ results typically from the mineralization of VOC’s. In this case, we can conclude that this commercial device has a very low photocatalytic action. The removal of toluene, n-heptane and o-xylene is due to the presence of the activated carbon filter. This filter has a very low activity vs acetaldehyde and acetone.

The device B shows a production of CO$_2$ indicating an oxidation of VOC due to the photocatalytic surface action. Unlike device A, acetone and acetaldehyde are removed from the gas phase and after 1200 min, all residual chemicals are below the detection limit of the equipment.

As for device A, toluene, n-heptane and o-xylene are mainly removed through the presence of the activated carbon. But the amount of CO$_2$ produced is higher than the expected one if only acetone and acetaldehyde are oxidized by the photocatalytic system. This indicates that chemicals which are released by the activated carbon are also oxidized to produce CO$_2$.

In this case, the device B has both actions: chemical trapping by the activated carbon filter and VOC oxidation by the photocatalytic surface under UVA illumination.

This combination is interesting in case of pollutant peaks. Photocatalysis is efficient in treating low VOC concentrations. In case of a significant surge of pollution which would overwhelm the catalytic surfaces, the activated carbon can act as a buffer and moderate an excessive contamination of the equipment.

Devices C and D were tested at lower concentration.
The mixture used is composed of acetaldehyde, propionaldehyde, heptane, toluene and styrene at concentration near 1000 ppbv each.

The chemical evolutions are shown in graph 3 and 4.

The device C shows a poor activity, except for styrene. No CO$_2$ is produced indicating that the VOC oxidation did not occur. But ozone was produced linearly as a function of time, to reach a concentration above the analyser limit of 1000 ppbv. This was probably produced by the UV light source.

Graph 3: Chemical evolution with device C  
Graph 4: Chemical evolution with device D

The device D was tested with the same mixture. All of the VOC are removed quite rapidly with production of CO$_2$. This device shows a good photocatalytic behaviour.

These four experiments indicates clearly that claims of photocatalytic activity need to be properly validated.

Two of the commercial system did not present any photocatalytic activity eventhough UV lamps were present. More important depending on the UV wavelength used, ozone can be produce. Ozone is a harmful compounds.

The described test chamber is well adapted to carry out such of experiments. It is flexible and many parameters can be controled.

Finally, a device E was used in real life condition for the removal of ethylene. Its activity was assessed before and after the test in the test chamber. Results are shown in graph 5.

Graph 5 : Ethylene degradation before and after test under real condition
Many aromatics compounds were detected in the gas phase. They were desorbed from the surface when the reactor was switched ON.

**Table 2.** GC-MS analysis of the air sampling.

<table>
<thead>
<tr>
<th>Temps de rétention (min)</th>
<th>Composé</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,57</td>
<td>Acétaldéhyde</td>
</tr>
<tr>
<td>2,93</td>
<td>Acétone</td>
</tr>
<tr>
<td>9,31</td>
<td>Toluène</td>
</tr>
<tr>
<td>11,33</td>
<td>Hexanal</td>
</tr>
<tr>
<td>12,4</td>
<td>Hexamethyl cyclotrisiloxane</td>
</tr>
<tr>
<td>14,03</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>14,32</td>
<td>Xylène</td>
</tr>
<tr>
<td>14,37</td>
<td>Hexanol/4 methyl pentanone</td>
</tr>
<tr>
<td>15,16</td>
<td>Dimethyl benzene</td>
</tr>
<tr>
<td>16,45</td>
<td>Alpha pinene</td>
</tr>
<tr>
<td>17,82</td>
<td>Alpha methylstyrene</td>
</tr>
<tr>
<td>17,90</td>
<td>Dimethyl hexane</td>
</tr>
<tr>
<td>18,45</td>
<td>Hexyl ester acétique</td>
</tr>
<tr>
<td>19,89</td>
<td>Acetophenone</td>
</tr>
<tr>
<td>22,82</td>
<td>Acide Butanoïque, 2 methyl, hexyl ester</td>
</tr>
</tbody>
</table>

After the test under real conditions, the photocatalytic surface had a heterogeneous aspect as shown in photo 1. Before the test, the surface has a homogeneous white colour. After the test, it presents a lot of grey spots. The FTIR analysis on areas with and without defect did not give useful information.

But the chemical analysis carry out during the electronic microscopy observation points out the presence of sulphur. Photo 2 is an electronic photography of a defect and photo 3 is a zoom of part of the photo 2.

**Photo 1.** photocatalytic surface after test

**Photo 2.** Electronic microscopy observation of a defect  
**Photo 3.** zoom of photo 2.
The crystalline phase is very rich on sulphur, probably under titanium sulphate. Many other parts of the coating show similar rich sulphur area.

Sulphur is known to poison the active phase. It is important in this application to avoid a poisoning of the photocatalytic active phase by trapping components which are responsible for the deactivation.

4. CONCLUSIONS

We presented in this paper a simple test setup to assess the photocatalytic activity of commercial or prototype devices.

Results on commercial systems indicate that it is very important to have a validated standard test method to assess photocatalytic activity.

Even if we try to be as close as possible to the real indoor environment, tests under real life condition are needed and necessary. They can inform us on the photocatalytic behaviour against complex air matrix to be treated and to adapt the air cleaning purifier to the considered application.

LITERATURE REFERENCES


