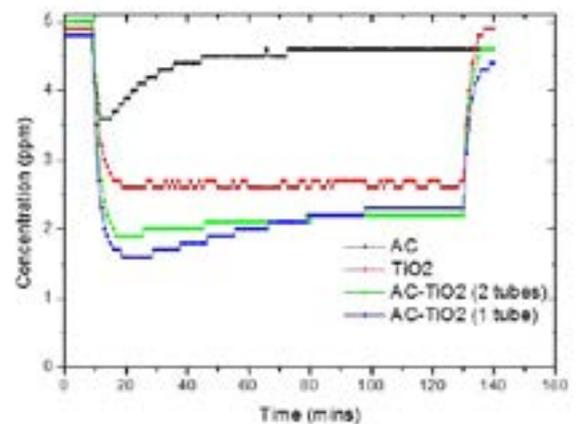
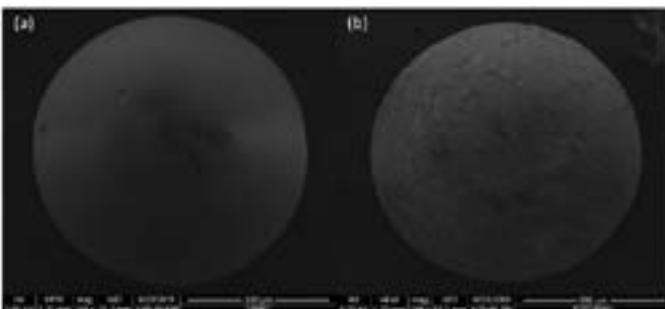
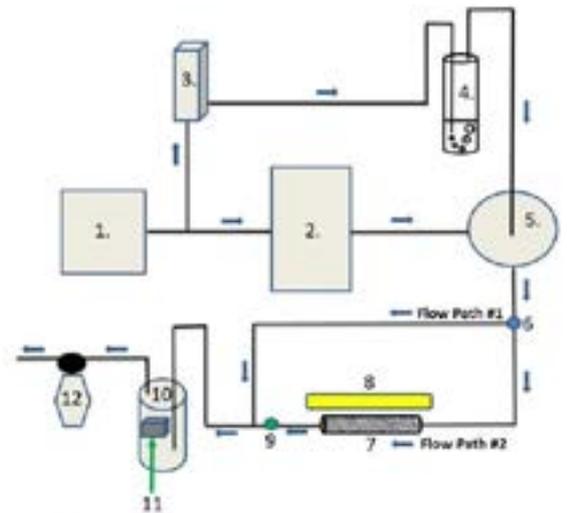
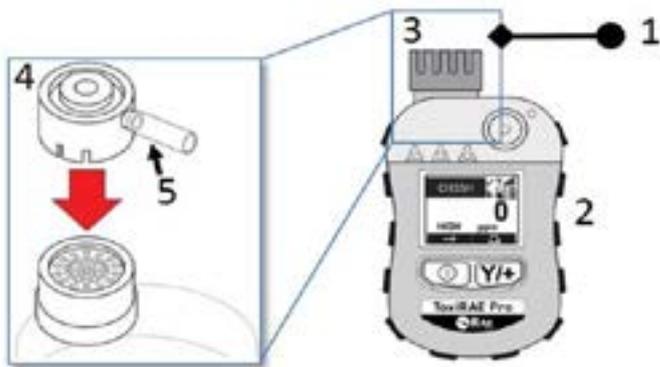


An Investigation into Air Purification of Malodorous Methyl Mercaptan by Photocatalysis and Adsorption

Authors: Donal Keane, Suresh Pillai, Lorraine Gibson, Justin Holmes and Michael Morris



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- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

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EPA RESEARCH PROGRAMME 2014–2020

**An Investigation into Air Purification of
Malodorous Methyl Mercaptan by Photocatalysis
and Adsorption**

(2014-RE-MS-3)

EPA Research Report

Prepared for the Environmental Protection Agency

by

Environmental Research Institute, University College Cork

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Cover image: The cover shows the experimental setup and materials used to investigate malodorous air purification by photocatalytic methods.

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Executive Summary

This research report describes efforts to investigate synergistic effects between adsorption and photocatalysis in the removal of a malodorous pollutant (methyl mercaptan) from air. A brief overview of odour and odour treatment technologies is provided. An experimental test setup was built based on International Organization for Standardization (ISO) photocatalysis air purification standards with certain differences; one of them was the gas detection method. In this study, an off-the-shelf gas monitor was used and its accuracy, advantages and disadvantages were compared with standard methods. Adsorbent–photocatalyst (activated carbon–titanium dioxide) composites were prepared and a method was developed to investigate and quantitatively measure synergy between the two odour treatment technologies.

Synergy was not found to exist for simple adsorbent–photocatalyst mixtures in this study. The methods used to measure synergy in the literature are inconsistent and an inter-laboratory standardised method is strongly recommended if test materials are to find commercialisation. The development of such a method based on the existing standards is not straightforward and for more complex composites (e.g. nanomaterials) further study is required.

The use of a gas detector proved low cost and easy to use compared with existing gas chromatography-based methods. Gas detectors could prove to be a useful method for proof of concept work, preliminary rapid prototyping and academic/educational purposes.

Feedback was obtained from industry on the applicability and potential of photocatalysis in air and odour purification. In general, it is well understood that many odour treatment technologies exist and perform well. For photocatalysis to compete, it will require clear advantages such as lower cost, higher performance and integration into existing infrastructure.

Combination with existing methods (such as adsorption–photocatalysis) or lower energy utilisation (e.g. solar light utilisation) could allow photocatalysis to become a disruptive technology in the odour or air purification market. In the case of photocatalytic odour purification in waste treatment facilities, a pilot plant demonstration would be required for the method to gain traction and compete with existing methods. However, based on the laboratory methods and results shown in this study, potential exists for development of a laboratory photocatalytic air/odour purification prototype unit for use in the fields of indoor air quality, heating, ventilation and air conditioning, and aerospace applications.

1 Introduction

1.1 Odour

Odour can be defined (EC, 2011) as a perception involving a set of complex processes (neurosensory process, cognitive process and amnesic process). This perception results from interactions between the olfactory mucosa (located in the nasal cavity) and gaseous substances, particularly volatile organic compounds (VOCs). The sources of odour emissions arise in both industrial and non-industrial sectors and thus consist of a large number of chemical compounds, which can be categorised as sulfur compounds (e.g. hydrogen sulfide), nitrogen compounds (e.g. ammonia), oxygen compounds (e.g. aldehydes) and hydrocarbon compounds (e.g. alkanes).

According to the Irish Environmental Protection Agency (EPA), odour accounted for 75% of all air emission complaints in Ireland in 2014 (EPA, 2014a). The negative environmental impact of odour has been described (EPA, 2010, 2014b). The health and well-being of individuals are affected as a result of exposure to odour at a sufficient concentration or during a sufficient time period. The following specific complaints were reported as responsible:

- vomiting;
- headaches;
- nausea;
- stress, anxiety and frustration;
- having to leave home and stay with family/friends or incur the expense of a hotel;
- inability to open windows during summer time;
- being unwilling to host guests as a result of embarrassment;
- keeping children indoors during summer holidays;
- inability to enjoy the garden for occasions (such as barbecues or birthday parties);
- inability to hang laundry out to dry;
- children being unable to sleep as a result of odour in bedrooms;
- additional discomfort for infirm elderly people.

Such phenomena are manifested in official complaints to the EPA; the majority relate to nuisance odour from licensed Integrated Pollution Prevention and Control

(IPPC) and waste sites. More specific examples have been provided, such as landfill sites, rendering facilities, composting and intensive agriculture activity (pigs and poultry).

However, in practice, odour is often extremely complicated to define, as it involves the impacts of many substances at extremely low concentrations (EPA, 2010, 2014b). Furthermore, odour has a number of inherent peculiarities (EC, 2011). Just one example of many is that odour from a substance or mixture of substances can be pleasant when diluted or offensive when concentrated.

This complexity makes finding a suitable odour control system (measurement, treatment, etc.) equally complicated. Nevertheless, a number of proven measurement and treatment methods exist (see Table 1.1) and general odour management systems have been strategised (Schlegelmilch *et al.*, 2005).

1.2 State-of-the-art Odour Treatment Technology

A wide range of odour treatment techniques exist and have been subject to academic and policy review (Schlegelmilch *et al.*, 2005; EC, 2011). The key features and disadvantages of these so-called end-of-pipe odour treatment techniques have been assessed and are described in Table 1.1.

1.3 Photocatalysis and ISO Air Purification Tests

Photocatalysts are materials that can accelerate chemical reactions by absorbing light quanta of suitable wavelengths depending on the band structure (Dong *et al.*, 2013, 2014; Banerjee *et al.*, 2014, 2015; Schneider *et al.*, 2014; Etacheri *et al.*, 2015; Rahna *et al.*, 2016). Photocatalysts have a wide range of industrial applications ranging from self-cleaning materials to water purification (Banerjee *et al.*, 2015). For an overview of gas phase photocatalytic air purification, the reader is referred to the recent review by Verbruggen (2015). Various International Organization for Standardization (ISO) methods

Table 1.1. Common odour treatment technologies

Technique	Key feature	Disadvantages
Adsorption	Molecules of odorous compounds attach to solid surfaces	Regeneration required
Absorption	Desorption compounds are dissolved in a scrubbing liquid	Scrubbing liquid requires disposal
Biological treatment	Organic contaminants degraded by microorganisms	Drying of media Acidification by inorganic compounds
Incineration	Thermal treatment of odour compounds	Secondary emissions Pre-concentration required High cost
Photo/UV oxidation	UV-induced formation of highly reactive radicals and ions, which can lead to oxidation of odorous compounds	Very high energy demand UV radiation required

UV, ultraviolet.

have been implemented to analyse the effectiveness of various types of photocatalysts, which can be employed by industries to test the products, thereby ensuring the quality of the product (Banerjee *et al.*, 2015).

To date, there are five ISO photocatalytic air purification test standards for the following test gases: nitric oxide (NO) (ISO, 2007), acetaldehyde (CH₃CHO) (ISO, 2011a), toluene (C₆H₅O) (ISO, 2011b), formaldehyde (CH₂O) (ISO, 2013a) and methyl mercaptan (CH₃SH) (ISO, 2013b). In 2012, Mills *et al.* (2012) reviewed the first three standards available at the time. The fifth, and most recent, standard uses CH₃SH as the test gas, chosen as a “typical malodorous substance”. Of the five test standards, it was chosen as the ideal test gas for odour purification tests by photocatalytic methods. The ISO standards were followed closely (although not identically – this investigation was not a development or quality/reliability study) in terms of experimental setup, test conditions and data generation.

1.4 Adsorption–Photocatalysis Synergy

In simple terms, synergy between adsorption and photocatalysis in pollutant removal occurs if the combined material adsorbs and photocatalyses pollutants better than the two materials acting separately. As part of a review on carbon-based nanomaterials for photocatalytic enhancement, Leary and Westwood (2011) described synergy and its quantification via the synergy factor. The synergy

factor was first defined by Matos *et al.* (1998) as follows:

$$R = \frac{k_{app}(TiO_2 + C)}{k_{app}(TiO_2)} \quad (1.1)$$

where k_{app} is the apparent first order rate constant, TiO₂ is titanium dioxide and C is carbon.

Since this much-cited publication, many studies have employed the synergy factor to measure synergy effects (usually degrading water pollutants) between adsorption and photocatalysis, typically employing Evonik P25 as a standard reference material. A review of the findings is beyond the scope of this report, but has been completed by Leary and Westwood (2011). In short, the review findings on synergy studies show inconsistency in how the synergy factor is calculated. Leary and Westwood (2011) pointed out that sometimes the synergy factor is used and at other times it is absent. Furthermore, the authors noted that the mass fractions and overall masses can be different or unspecified depending on the study. Such crucial discrepancies make data comparisons difficult or impossible. Furthermore, differences in experimental setup and methods between laboratories is thought to affect kinetic parameters, as they depend on volume, mass fractions, area of irradiated photocatalyst, etc.

These findings point towards the necessity of a standardised test method to establish if synergy is occurring (and, if so, to quantify it) in adsorbent–photocatalyst composites. In this study, a robust and simple experimental test method is developed to investigate if synergy occurs for simple granular mixtures of activated carbon (AC) and TiO₂ for the

gas phase removal of odorous CH_3SH . Although the test setup and test conditions were not the same as the ISO standard, the data interpretation of the ISO standards to quantify the pollutant removal amount was followed carefully (i.e. catalyst/adsorbent performance is measured by quantity of CH_3SH removed rather than kinetics).

1.5 Gas Detection in ISO Photocatalysis Tests

As Mills *et al.* (2012) pointed out, one of the disadvantages of the ISO standards is that each individual sub-test requires expensive and different analytical equipment (listed in Table 1.2). Other analytical methods such as ion chromatography (NO_3) and an infrared analyser (CO_2) are recommended in the first two standards (ISO, 2007, 2011a) to measure photocatalytic by-products. Interestingly, the final three standards (ISO, 2011b, 2013a,b) describe measurement of just the pollutant test gas. It was also pointed out that technical support and training are often needed for operation and maintenance of these analytical methods (Mills *et al.*, 2012). Although the gas chromatographic methods are powerful and can quantitatively identify and measure photocatalytic by-products, the expense in terms of cost and experimental person-hours can cause researchers to struggle to build the apparatus and they can also lose focus and time spent on the original goal of the standards (to test photocatalytic performance). Concerns such as these were described as “possibly unavoidable” (Mills *et al.*, 2012). In this

study, we address the issue by employing a low-cost, commercially available “off-the-shelf” gas monitor as an alternative gas analyser for measurement of the fifth ISO standard test gas (CH_3SH) (ISO, 2013b) in photocatalytic air purification tests.

Although gas detectors used in photocatalytic experimental setups have been reported in the literature [a good example of a fixed CH_3SH detector is by Li *et al.* (2006)], such instances are rare and not the primary purpose of the studies. Emerging analytical methods have also recently been proposed as alternatives to the ubiquitous gas chromatography (GC) methods described in Table 1.2 in photocatalytic air purification. Ireland and Ducati (2015) employed field asymmetric ion mobility spectrometry (FAIMS) to analyse the photo-oxidation of indoor VOC air pollutants. Yao and Feilberg (2015) used proton-transfer-reaction mass spectrometry (PTR-MS) to characterise the photocatalytic degradation of odorous compounds associated with livestock. Both of these new analytical methods rival the standardised GC methods in terms of specification, but do not address the principal concern of Mills *et al.* (2012) regarding cost and ease of use. In another interesting study, Stefanov *et al.* (2015) employed commercially available semiconductor gas sensors in a 3D-printed photocatalysis reactor. However, using such sensors requires supporting electronics for digital readout and is not a “ready-to-use” gas detection system. The low-cost detector used in this study (Honeywell ToxiRae Pro) is portable, has online data-logging capability and is inherently user-friendly, as its primary purpose is chemical site safety.

Table 1.2. Analytical methods employed in ISO air purification tests

Test gas	Analytical method
NO	CA
CH_3CHO	GC-FID/PID DNPH/HPLC
$\text{C}_6\text{H}_5\text{O}$	GC-FID/PID
CH_2O	DNPH/HPLC
CH_3SH	GC-FID/FPD

CA, chemiluminescent analyser; DNPH/HPLC, 2,4-dinitrophenylhydrazine-derivatised high-performance liquid chromatography; FID, flame ionisation detector; FPD, flame photometric detector; GC, gas chromatography; PID, photoionisation detector.

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1.6 Objectives

The primary objective of the project is to investigate the existence of synergy between photocatalysis and adsorption for CH_3SH removal. This includes experimental design allowing measurement of synergy. Other objectives are:

- to evaluate the highest performing adsorbent for CH_3SH removal;
- to investigate the feasibility of using a low-cost, easy-to-use gas detector as an alternative to standard GC for measurement of CH_3SH concentration;
- to explore the real-world application of photocatalytic odour removal.

2 Experimental Procedures

Note: the analytical methods described here have been recently reported by the authors (Keane *et al.*, 2017).

2.1 Materials and Methods

The calibration CH_3SH gas is generated using a standard gas generator (Kin-Tek 491 MB). The generator employs National Institute of Standards and Technology (NIST) traceable permeation tubes as the span gas source. Both the generator and permeation tubes were supplied by Eco-Scientific Limited. The variable area flow controller and all tubing were supplied by Fischer Scientific. The mass flow controller (Alicat) was supplied by Carl-Stuart. All valves were supplied by Swagelok. The gas chambers, Dreschel bottle and photoreactor tubes (90 mm length, 8 mm outer diameter, 5 mm inner diameter) were made by an in-house glassblower. Aeroxide P25 TiO_2 powder, glass beads (710–1180 μm) and glass wool were supplied by Sigma-Aldrich. The ToxiRae Pro (Honeywell, Rae Systems) gas monitor with CH_3SH electrochemical sensor [range, 0–10 parts per million (ppm); resolution, 0.1 ppm] was supplied by Envirosafe Ireland. The humidity/temperature logger (Onset HOBO MX1101) was supplied by Tempcon Instrumentation Limited. The ultraviolet (UV) lamp

(Uvitec LI206BL Black-Light unfiltered UV longwave lamp) was purchased from Accuscience.

2.2 Gas Detector Calibration and Validation

A CH_3SH gas detector (ToxiRae Pro) was employed as a test detector. Prior to each use, the detector was calibrated by connection via an adapter supplied with the detector to a gas standards generator as shown in Figure 2.1. The detector head is purged with calibration gas for 30 minutes prior to internal instrument detector calibration (1 min). The linearity validation test was performed by supplying the calibration span gas over a range indicated by the ISO standard (ISO, 2013b) (0–5 ppm) by changing the flow rate using a mass flow controller housed within the gas standard generator. The measured detector concentration was recorded at 1-minute intervals.

2.3 Preparation of Photocatalytic Tubes

Photocatalytic test materials were prepared by coating glass beads with Aeroxide P25 TiO_2 powder (Sigma Aldrich) using methods similar to those reported by Basha *et al.* (2010). Six grams of glass beads, 0.6 g

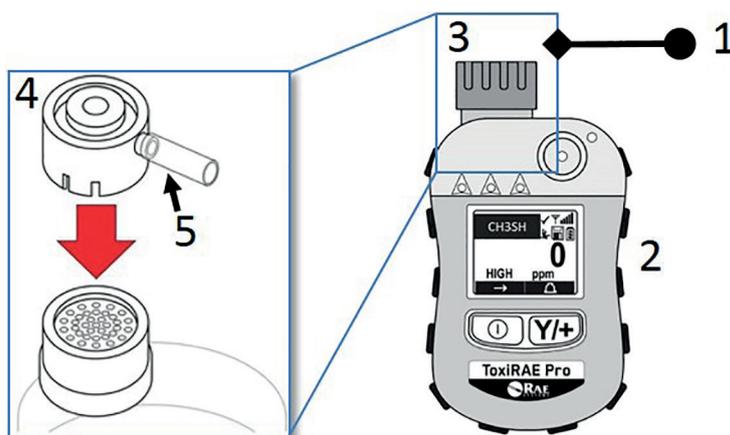


Figure 2.1. Schematic of ToxiRae Pro gas monitor connection. (1) Gas standard generator in validation test or gas detection chamber in photocatalytic test; (2) ToxiRae Pro CH_3SH detector; (3) ToxiRae Pro detector head; (4) ToxiRae Pro calibration cover; (5) Tygon soft tubing ($\frac{1}{4}$ inch outer diameter, $\frac{5}{8}$ inch inner diameter) over the calibration cover nozzle. Reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

of P25 powder and 240 cm³ of deionised water were placed in a sealed 250-cm³ Schott glass bottle and sonicated in a bath for 1 hour at room temperature. The top of the bottle was removed and the bottle was placed in an oven at 110°C overnight. The dried and coated beads were removed, and the excess TiO₂ powder was removed by repeated washing with deionised water and sieving through a Test Sieve (Fisherbrand 200 mm diameter × 500 μm). The coated and uncoated beads are imaged by scanning electron microscopy (SEM) (JEOL model FEI FP 2031/11 Inspect F field emission scanning electron microscope). Fixed quantities of the powder-coated beads from the same batch are packed into glass photoreactor tubes between glass wool (Sigma Aldrich) and retaining springs (Markes International) for the photocatalytic air purification tests.

2.4 Experimental Test Setup

The photocatalytic air purification test setup shown schematically in Figure 2.2 has features from different reported setups including the ISO standards (ISO, 2007, 2011a,b, 2013a,b; Yu and Brouwers, 2009; Idris

et al., 2010; Kibanova *et al.*, 2012). A photograph of the setup is shown in Figure 2.3. Compressed air is supplied to both the gas standards generator and the Drechsel bottle. The span gas is humidified in a gas-mixing chamber and flows directly (flow path 1) to the humidity detector in the gas detection chamber, followed by the gas detector. The flow rate of the span gas and diluent humidified air are adjusted in the gas standards generator and variable area flow controller/mass flow controller, respectively, such that stable readings of 5.0 ± 0.3 ppm CH₃SH and 50 ± 5% relative humidity are observed by the detectors. The plug valve and three-way valve are then opened, allowing the test gas to flow through the photoreactor tube to both detectors (flow path 2). Adsorption is observed by reduction in the CH₃SH reading on the detector. Once the reading returns to 5 ppm, the UV lamp is turned on to test the photocatalytic performance of the powder-coated sample over a 3-hour period, after which the lamp is turned off to ensure a return of the test gas to within 10% of the test concentration.

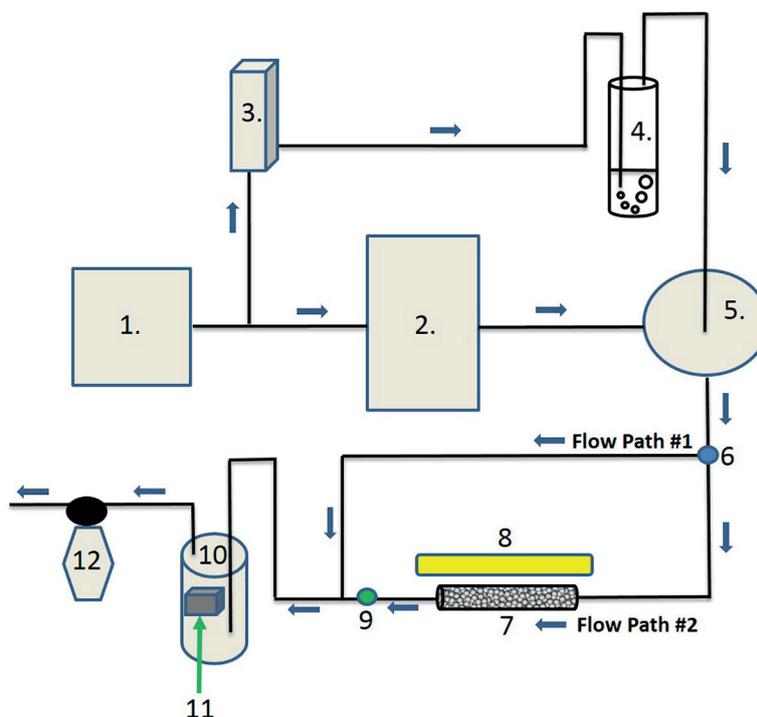


Figure 2.2. Schematic of test setup for photocatalytic air purification. (1) Air compressor; (2) Kin-tek standard gas generator; (3) variable area flow controller or mass flow controller; (4) Drechsel bottle (humidifier); (5) gas-mixing chamber; (6) three-way ball valve; (7) photoreactor tube; (8) UV lamp; (9) quarter-turn plug valve; (10) gas-detection chamber; (11) temperature and humidity detector; (12) gas detector. Reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

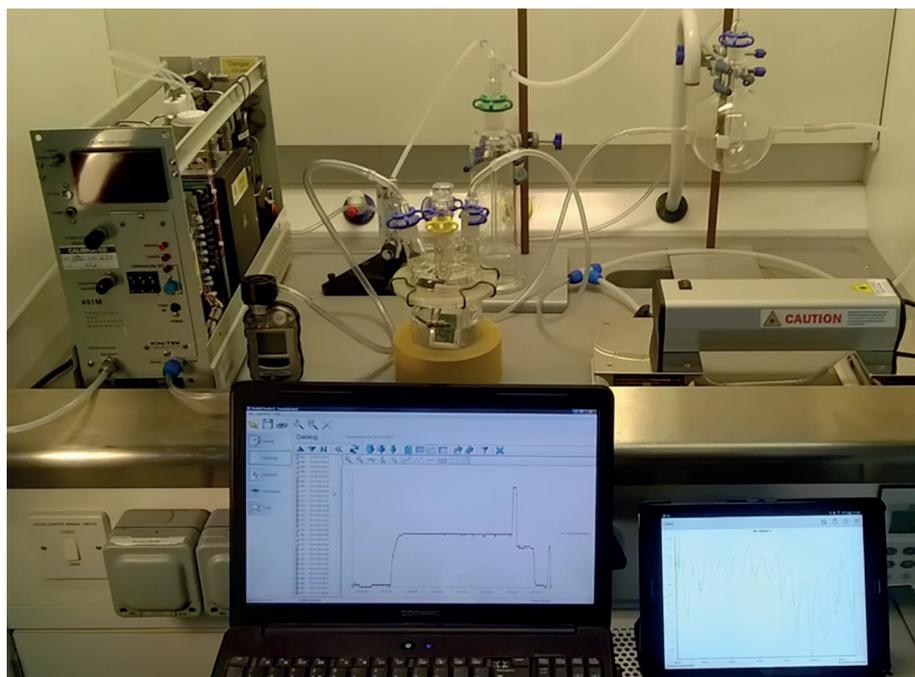


Figure 2.3. Photograph of experimental setup.

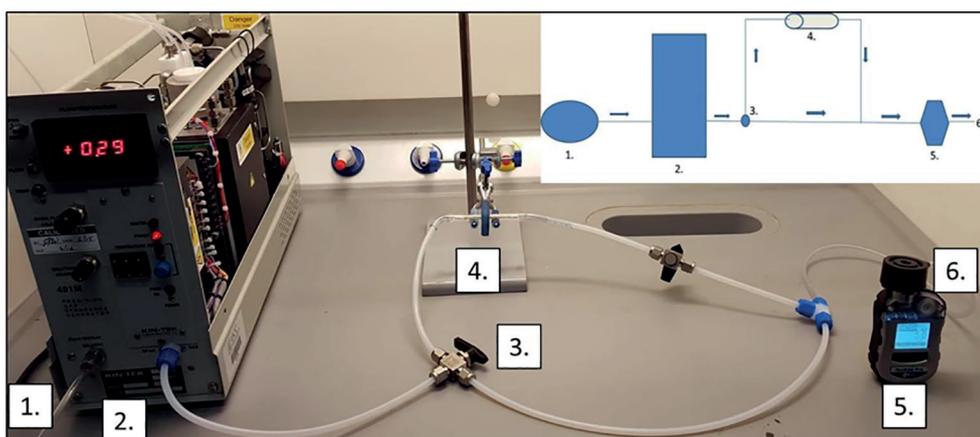


Figure 2.4. Photograph with schematic inset of experimental setup for evaluation of adsorbent performance. (1) Compressed air; (2) gas standards generator; (3) three-way valve; (4) adsorbent tube; (5) gas detector; (6) vent.

2.5 Evaluation of Adsorbents

Prepared adsorbent tubes were connected to the apparatus, allowing evaluation of various adsorbents for removal of the test odorous gas. A photograph and schematic of the overall apparatus is shown in Figure 2.4. A number of common commercial adsorbents were evaluated for treatment of 5 ppm CH_3SH .

2.6 Synergy Experiments

As it was desired to carry out the synergy evaluation tests in the same span of pollutant gas concentrations

as ISO standard (5 ppm) and a reasonable experiment time (3 hours), a number of experiments were carried out to provide a mass of AC and TiO_2 , such that equilibrium gas concentration would not go below zero in the measured time. For example, if a typical mass of AC (100 mg) was used, the effects of synergy could not be evaluated in the 120-minute timeframe, as the concentration would be at zero and the integrated areas (as per ISO) would be the same for differing masses of photocatalyst. These preliminary tests showed that a sample mass of 0.0040 g of AC and 0.5 g of TiO_2 would result in CH_3SH removal quantities in which synergy could be both observed and measured.

TiO₂-coated beads were prepared similarly to those described in section 2.3. The only difference is that the beads were not washed with water and as a result contained loosely adhered TiO₂. This resulted in an increase in the amount of CH₃SH removed (~2.4 ppm as opposed to ~1.3 ppm for 0.5g of coated beads). All

coated beads in the samples in Table 2.1 were taken from the same 6-g batch.

Four experiments were undertaken with different samples and configurations to collate data for measurement as shown in Table 2.1.

Table 2.1. Adsorption–photocatalysis synergy experiments

Experiment	Sample tube(s)	Mass of TiO ₂ coated beads (g)	Mass of AC (g)	Mass of glass beads (uncoated) (g)
1	AC	0.0040	0	0.5
2	TiO ₂	0.5	0	0
3 ^a	TiO ₂ and AC ^a	0.5	0.0040	0.5
4	TiO ₂ and AC	0.5	0.0040	0

^aIn experiment 3, two sample tubes were employed in series. The AC adsorbent tube was placed in line and before the photocatalytic tube. The tube containing AC also contained 0.5g of uncoated glass beads, which had a negligible effect on the removal of CH₃SH.

3 Results and Discussion

3.1 Gas Detector Validation

The span gas target concentration was reduced from 5 ppm to 0.9 ppm at 1-minute intervals by modifying the flow rate across the permeation tube from 0.29 L/min to 1.72 L/min with 80 data points. Figure 3.1 shows that the CH₃SH detector gives a highly linear response with an R^2 value of 0.999 and y -intercept of 0.11881. Both of these values can be considered good linearity fits as part of a general analytical method validation (Harris, 2007), and it is thus fit for purpose as a detector in the photocatalytic air purification test setup.

3.2 Adsorbent Air Purification Tests

A number of adsorbents were tested to evaluate the highest performing material to combine with TiO₂ photocatalysis in synergy investigations. Although such adsorbents have been tested before for air purification, it is important to re-test for specific target pollutants as a result of a potentially different performance. Furthermore, adsorbents with optical transparency (aerogel, porous glass) would be ideal as supports in a photocatalytic reactor.

In these experiments, AC was found to be the highest performing adsorbent by a significant margin. The performance can be summarised by the following:

AC >>> Zeolite 13X > Zeolite 4A > Silica gel > Aerogel > Controlled pore glass

Although it was predicted from the literature review that AC would be superior, the significant gap in performance (as measured by test gas breakthrough, defined as the point at which 5% of the analyte is measured by the detector after the test start) was noteworthy. The key finding is shown graphically in Figure 3.2. As shown, breakthrough occurs after 143 minutes. From this, it was concluded that AC is currently the highest performing adsorbent support for the photocatalyst. The finding is similar to previous academic evaluations for AC and also is historically well known in general odour treatment adsorbents. To illustrate, breakthrough for Zeolite 13X occurred after 6 minutes. Indeed, the other adsorbents did not succeed in removing the test gas to 0 ppm. Nevertheless, such evaluations are necessary to evaluate the highest performing adsorbent for specific test pollutant gases and also the potential trade-off in optical properties (transparency), which would be

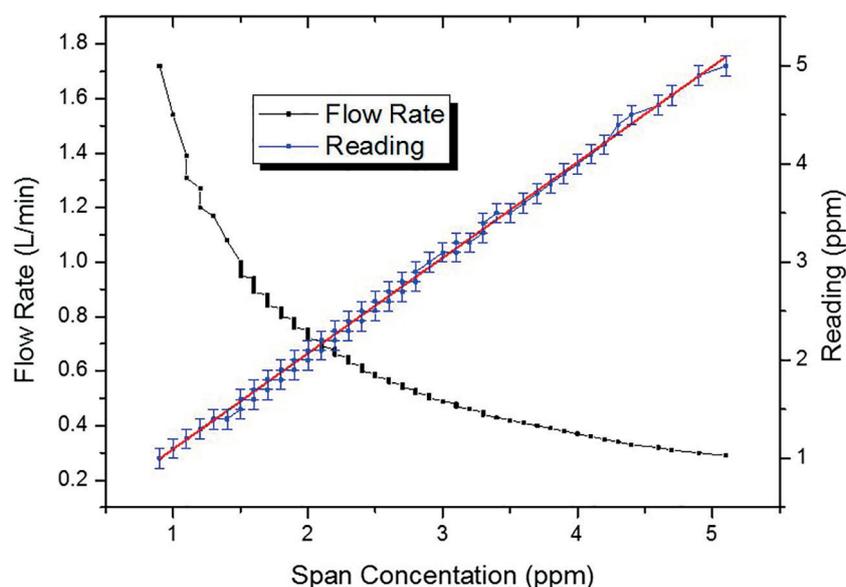


Figure 3.1. Linearity of ToxiRae Pro CH₃SH gas monitor. Reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

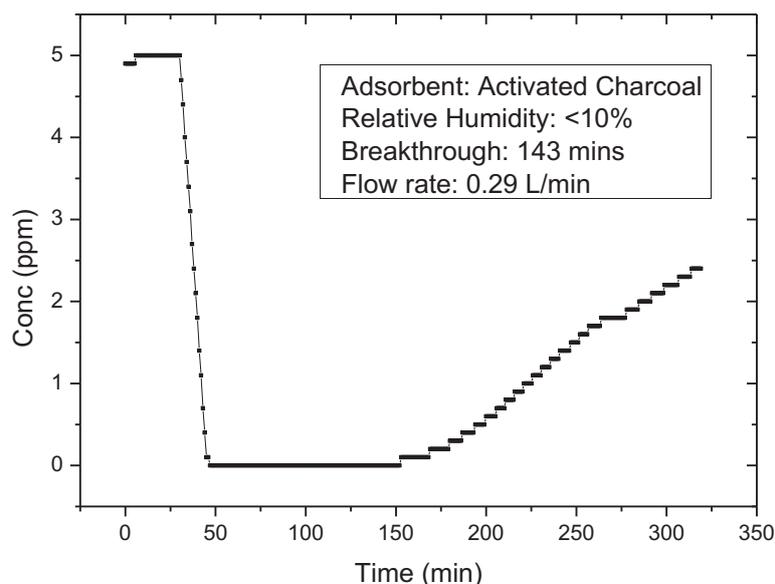


Figure 3.2. Adsorption of CH_3SH by AC.

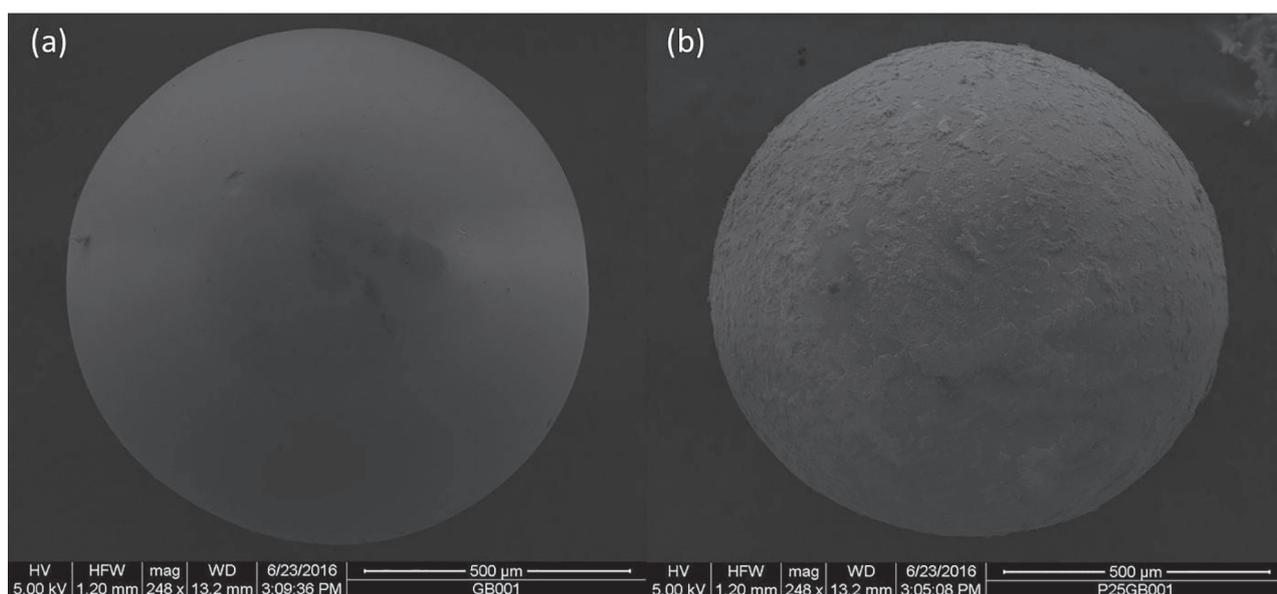


Figure 3.3. Equal magnification SEM images of (a) uncoated and (b) TiO_2 -coated glass beads. Reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

expected to increase performance in a photocatalysis-adsorbent composite.

3.3 Photocatalytic Air Purification Tests

Four samples with different quantities (2, 1.5, 1.0 and 0.5 g) of TiO_2 -coated glass beads from the same batch were tested in the photocatalytic test setup to demonstrate the applicability of the gas detector, i.e. that the “method can differentiate [...] samples with

different photocatalytic performance” (ISO, 2007, 2011a,b). The coating method produced a thin film of TiO_2 as shown by equal magnification SEM in Figure 3.3. As opposed to TiO_2 in powder form, the coated beads showed minimal adsorption satisfying the ISO adsorption requirement: that the gas concentration at the outlet of the reactor returns to supply gas concentration within 30 minutes. To the naked eye, the coated beads in the glass photoreactor tubes were semi-transparent, allowing adequate UV illumination of the photocatalyst surface. Quantities of coated

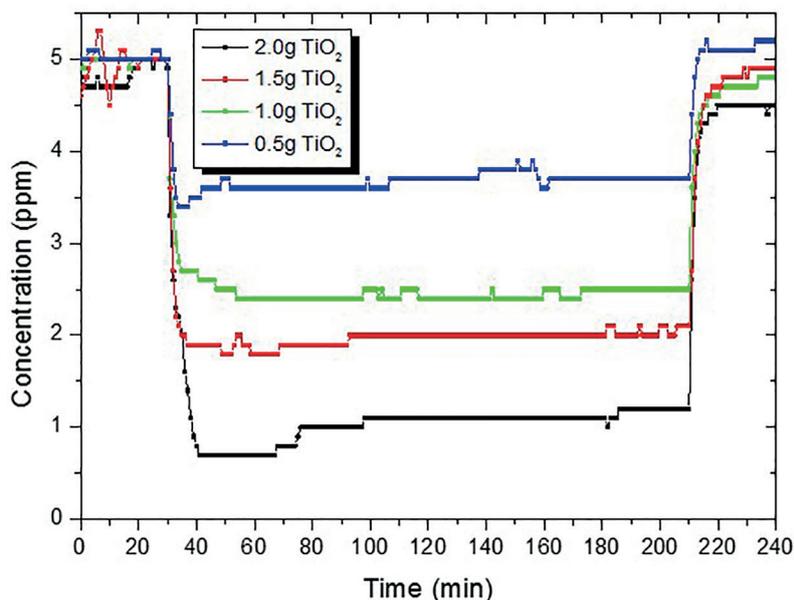


Figure 3.4. Concentration vs time data profile of CH_3SH during the test operation using differing quantities of TiO_2 -coated glass beads. Reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

Table 3.1. Removal (R_M) of CH_3SH by test sample

Sample (g TiO_2)	Number of data points ^a	ϕ_{M0} ^b	ϕ_M ^c	R_M ^d (%)
2.0	60	5.0	1.1	78
1.5	60	5.0	2.0	60
1.0	60	5.0	2.5	50
0.5	60	5.0	3.7	26

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^aData points extracted from ToxiRae Pro monitor to personal computer via USB.

^b ϕ_{M0} is the supply concentration of CH_3SH (ppm).

^c ϕ_M is the average (60 data points) concentration of CH_3SH at reactor exit (ppm).

^d R_M is the percentage of CH_3SH removed, calculated as $R_M = (\phi_{M0} - \phi_M) / \phi_{M0}$.

beads were tested allowing removal of CH_3SH within the range of that reported in the ISO standard (ISO, 2013b) (0–5 ppm).

As shown in Figure 3.4 and Table 3.1, the gas detector was able to quantify the removal of the test CH_3SH pollutant gas by differently performing photocatalytic coatings in a satisfactory manner, which is the primary goal of the ISO standard. Greater accuracy is obtained as a result of the data-logging capability of the detector in which 60 data points in the last hour of the test can be averaged to obtain ϕ_M (averaged

concentration at reactor exit). This is in comparison with the ISO standards, which recommend that ϕ_M should be the average of at least three or more measurements. Without an automatic sampling system connecting the photoreactor outlet to the detector, the manual sampling of >3 ϕ_M measurements would prove to be laborious and prone to irreproducibility on account of human error. For these reasons, the typical concentration versus time trace in some of the ISO standards can have a low number of data points per hour as a result of manual sampling [e.g. three data points per hour in the CH_3SH standard (ISO, 2013b)]. The other standards that have automatic sampling to the gas analyser (ISO, 2007, 2011a,b) have graphical data sets similar to those shown in Figure 3.4.

3.4 Gas Detectors as “Pollutant Measurement Equipment”

At a first glance at the schematic diagram of the overall test equipment in the ISO standards, the “pollutant-measurement equipment” appears straightforward (Figure 3.5a), with a basic setup in which the test gas line is connected to an “analyser” followed by a sampling pump. However, further information on the analyser reveals a more complicated gas-sampling system in which a six-way valve is recommended for reproducible and automatic sampling (Figure 3.5b).

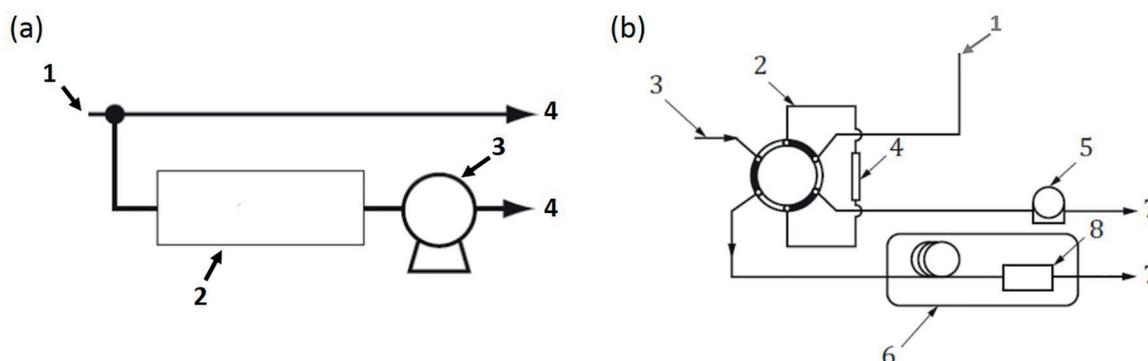


Figure 3.5. (a) Analytical system in ISO 22197-5 test equipment: (1) from photoreactor; (2) analyser; (3) sampling pump; (4) vent. (b) Gas sampling system in ISO 22197-5 test equipment: (1) from photoreactor; (2) six-way valve; (3) carrier gas; (4) metering tube; (5) sampling pump; (6) gas chromatograph; (7) vent; (8) flame ionisation detector. Figures modified from ISO 22197-5 (ISO, 2013b). Copyright (2013) with permission from the National Standards Authority of Ireland (NSAI). Modified figure reproduced from Keane *et al.* (2017) with permission from the Royal Society of Chemistry.

Table 3.2. Advantages and disadvantages of using ToxiRae Pro gas detector in CH₃SH air purification photocatalytic tests

Advantages	Disadvantages
<ul style="list-style-type: none"> • Low cost • Real-time data logging • Compact, portable and user friendly 	<ul style="list-style-type: none"> • Not fully standardised and requires further validation • Not possible to measure by-products • Detection limit of 0.1 ppm

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The use of a portable gas monitor, as used in this study, greatly simplifies the measurement of the test gas at the reactor outlet. The detector can be directly connected to the photoreactor outlet without the need for a sampling pump (Figure 2.1), or, alternatively, as a result of its compact size, it could be placed within a small detection chamber. Overall, the advantages and disadvantages of using such a detector are described in Table 3.2. The disadvantages could be overcome by complete validation of the detector compared with the GC standard methods, use of a multi-gas detector that measures by-product and use of a detector with higher specification that has lower detection limit of parts per billion (ppb). Such detectors would incur further cost, but would still remain low relative to GC analytical methods, and could provide a satisfactory “middle ground”. With advances in miniaturisation of detectors and sensors, the acquirement of commercially viable products with increasing sensitivity is emerging (Liu *et al.*, 2012).

As an aside, it is interesting to note that, in the CH₂O photocatalytic standard (ISO, 2013a) published

after the review by Mills *et al.* (2012), it is stated that other analytical methods that give equivalent or better performances can be used. This statement is not in any of the other four standards and can only be assumed to have been included as a result of concerns over the use of the 2,4-dinitrophenylhydrazine-derivatised high-performance liquid chromatography (DNPH/HPLC) method as an analytical method that provides an accurate data set. No information is provided on whether the alternative analytical methods need to follow industrial standards. Indeed, in the case of the standard for the removal of CH₂O, chosen as a typical pollutant responsible for sick building syndrome, there is scope to employ a low-cost gas detector similar to the example in this study, as a large number of instruments are on the market.

Despite the successful demonstration described in this study, the use of gas detectors is not standardised so they cannot be recommended as alternatives to the standardised analytical methods used in the ISO photocatalytic standards. What is

required is a full validation study directly comparing the detectors with the existing analytical methods shown in Table 2.1. For example, Mills *et al.* (2013, 2014) demonstrated photocatalytic indicator inks as an alternative to existing ISO tests for rapidly assessing the activities of photocatalytic surfaces. An inter-laboratory test was completed to establish repeatability and reproducibility (Mills *et al.*, 2014) and thus the precision (ASTM, 2013) of their proposed test method. Similar “round-robin” tests were undertaken in the first three photocatalytic gas purification test standards (ISO, 2007, 2011a,b). In this respect, whereas the ISO photocatalytic standards are used for the development, quality assurance and design data generation of photocatalytic materials (ISO, 2007, 2011a,b, 2013a,b), we suggest that the use of a gas detector is currently more suitable for academic research and proof of concept evaluations. Indeed, it could be envisaged that the detectors could be used in undergraduate or secondary (high school) education to demonstrate photocatalytic air purification. For example, universities could include the method in an environmental outreach programme similar to the “spectroscopy in a suitcase” programme funded by the Royal Society of Chemistry (RSC) and Science Foundation Ireland (SFI). Details of the highly successful programme provided by the Chemistry Department at University College Cork can be found at www.ucc.ie/en/chemistry/outreach/sias/. This would expose younger scientists to the

air purification method, which is currently somewhat inaccessible as a result of the complexity and cost of the test setup. The construction of an inexpensive, easy-to-use overall test setup (including gas detectors) for educational/proof of concept purposes is worthy of future work. Even in these proposed applications, it is important that preliminary validation, such as linearity, is carried out prior to testing. As a case in point, early findings have shown that the ToxiRae Pro employing the formaldehyde electrochemical sensor (resolution: 0.01 ppm) did not perform as well as the CH₃SH sensor did in this study.

3.5 Adsorption–Photocatalysis Synergy

Figure 3.6 shows concentration versus time profiles for CH₃SH removal in the four experiments carried out to observe and measure synergistic effects between photocatalysis and adsorption. Figures 3.7–3.10 show the integrated areas proportional to the amount of CH₃SH removed in each experiment. Table 3.3 shows the calculated removal amounts of CH₃SH over the entire time profile expressed as μmol (as recommended by ISO) and as a percentage. As shown, the difference between the three configurations is negligible, and it can be concluded that synergy between photocatalysis and adsorption for gas phase removal of CH₃SH is negligible for simple mixtures. On the other hand, the consistency of the data shows that

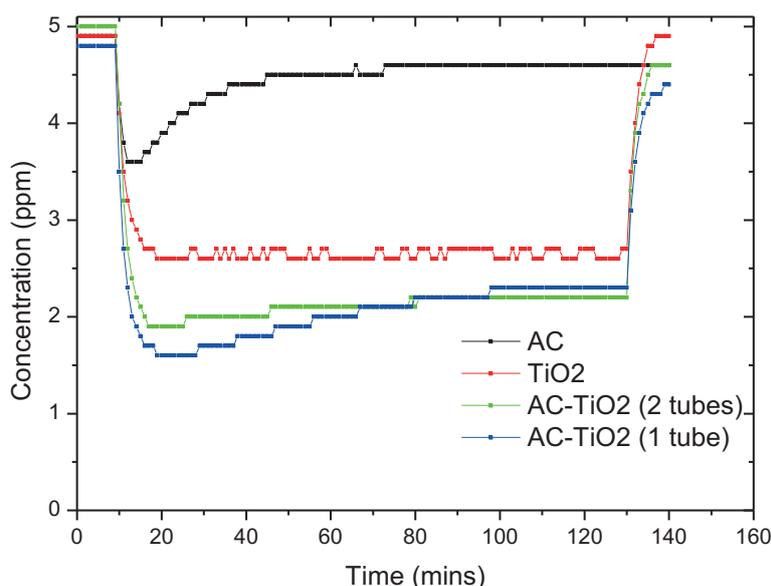


Figure 3.6. Concentration vs time profiles for synergy evaluation.

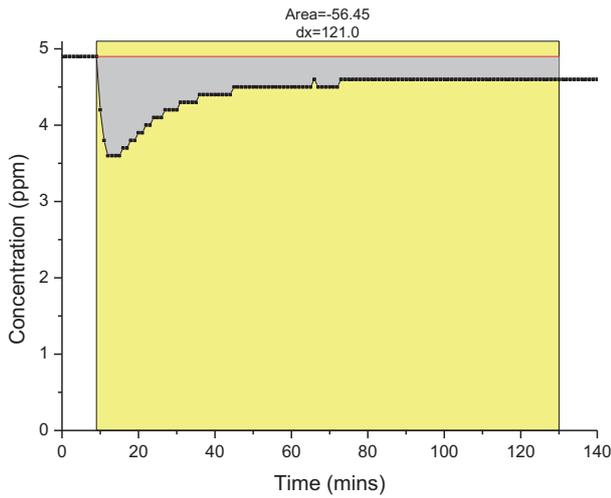


Figure 3.7. CH₃SH removal by AC adsorption (Table 2.1, experiment 1). The integrated area in grey is proportional to the amount of CH₃SH removed.

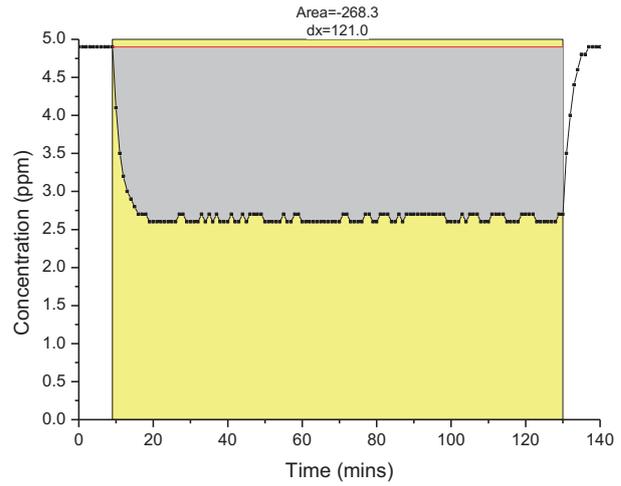


Figure 3.8. CH₃SH removal by photocatalysis (Table 2.1, experiment 2). The integrated area in grey is proportional to the amount of CH₃SH removed.

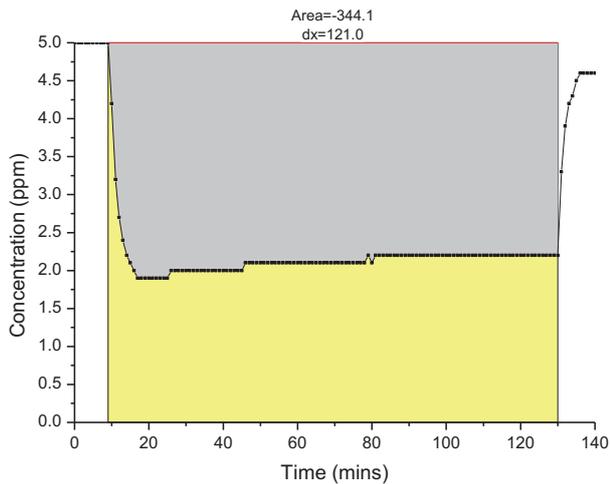


Figure 3.9. CH₃SH removal by photocatalysis and adsorption (Table 2.1, experiment 3). The integrated area in grey is proportional to the amount of CH₃SH removed.

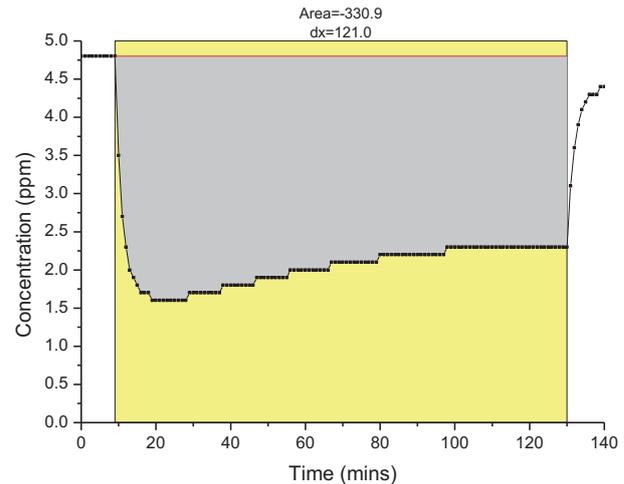


Figure 3.10. CH₃SH removal by photocatalysis and adsorption (Table 2.1, experiment 4). The integrated area in grey is proportional to the amount of CH₃SH removed.

the experimental design is robust and fit for purpose for other gas phase synergy experiments.

For real-world odour treatment facilities, there is no advantage in combining adsorption and photocatalysis. The two odour treatment technologies remain competitive and a cost analysis would be required to establish the most cost-effective method to achieve the required odour removal quantities. Until synergy is demonstrated, there is no reason to combine the two methods.

3.6 Adsorbent–Photocatalyst Synergy in ISO Testing

As a result of the inconsistent measurement of synergy in photocatalyst–adsorbent materials discussed above, there is a clear need to develop a standardised approach to evaluate if synergy exists and to measure the quantity for material comparisons. Development of such a test method, using materials and methods similar to the existing ISO photocatalysis air purification standards, is not straightforward. The

Table 3.3. Calculated removal amounts of CH₃SH over the entire time profile (μmol and %)

Sample	Flow rate (L/min)	Total pollutant load (μmol)	Integrated area	CH ₃ SH removed (μmol) ^a	CH ₃ SH removed (%)
AC	0.29	7.76	56.45	0.73	9.41 ^b
TiO ₂	0.29	7.76	268.3	3.47	44.72 ^b
AC TiO ₂ two tubes	0.29	7.83	344.1	4.45	56.83
AC TiO ₂ one tube	0.29	7.52	330.9	4.28	56.91

^aThe amount of pollutant removed from the test gas is calculated by the following formula:

$$n_M = (f/22.4) \int (\varphi_{Mi} - \varphi_M) dt$$

where:

n_M is the amount of CH₃SH removed by the test piece (μmol);

f is the air-flow rate (L/min);

φ_{Mi} is the supply volume fraction of CH₃SH (μ/L);

φ_M is the CH₃SH volume fraction at the reactor exit (μ/L).

^bAddition of these two values yields 54.13%.

current ISO photocatalytic air purification tests are designed for net removal of gas phase pollutants by photocatalysis. The simple adsorption and desorption of the gas phase pollutant by the test sample (not due to photocatalysis) is evaluated by tests in the dark. The standards also state that the standard cannot be applied to a test sample that does not give a stable concentration of the pollutant in the designated time.

From these principles, it is clear that method changes are required for measurement of synergy, i.e. adsorption measurement must also be taken into account. The following are some changes/challenges involved in incorporating adsorption or synergy measurements into the ISO tests:

- The test must be extended to powdered or granular materials. This would require changes to the apparatus (photoreactor, test piece setup, etc.) and possibly also to the test conditions (e.g. flow rate, starting concentrations).
- The test would require quantity of pollutant removed over the entire designated time as opposed to the final hour as a result of concentration variation.
- This would mean that the method of integrating the area over the curve as opposed to three data points in the final hour would be necessary.
- Testing the synergy of nanoparticles or composites using the method in this report is a challenge on account of difficulties in separately preparing adsorbent and photocatalysis samples. A potential solution would be to prepare identical samples and to allow one sample to reach “adsorption

equilibrium”, a common approach in literature tests. A higher initial concentration may be required to shorten testing time requirements.

- Because of the complex physio-chemical and optical processes involved, achieving the required repeatability and reproducibility in an inter-laboratory study could be a roadblock to successful implementation.

3.7 Photocatalysis for Odour Treatment: Feedback from Industry

As part of the research project, one of the objectives was to reach out to industry and policymakers working in odour treatment technologies in Ireland to get feedback on the application and potential (or lack thereof) of photocatalytic odour treatment. Following informal discussion, summarised feedback was as follows:

- Existing odour treatment technologies, of which there are several, work well. Each has its own advantages and disadvantages.
- Odour problems in industry or odour complaints from the public are unique and complex and must be taken on a case-by-case basis when considering odour abatement strategy.
- As an advanced oxidation process, photocatalysis is expected to have application at low concentrations rather than high concentrations of pollutant. The potential exists to have a photocatalytic module in line with another odour treatment technology.

- A working photoreactor prototype with significant cost savings would be required to gain traction with industry users. It would be beneficial if a modular system/skid could be incorporated and could easily replace existing units.
- Considering that recent air quality odour complaints in Ireland are mainly about composting facilities, a targeted demonstration of application would be beneficial. However, considering that no commercial photocatalytic air purification exists for waste treatment facilities (to the best of the authors' knowledge), the cost and technical difficulty of such a project should not be underestimated. Similar to the previous point, success and cost reduction would greatly depend on incorporation of a photoreactor and UV system into existing waste treatment units. Furthermore, as odour problems are on a case-by-case basis, an odour profile and analytical methods with the required sensitivity would need to be in place for a specific composting site.
- Photocatalysis could be a disruptive technology in a miniaturised system in indoor air quality; heating, ventilation and air conditioning; and aerospace applications. However, to prove the concept, purification of gaseous pollutant mixtures found in real air would need to be demonstrated as opposed to the single gas purification tested in this study, the ISO air purification photocatalysis standards and the majority of academic studies.

4 Conclusions and Future Work

4.1 Gas Detection

Through method validation (linearity) and differentiation of sample performance, the use of a commercial gas detector is shown to be a suitable analytical method for photocatalytic air purification of CH_3SH . The advantages, such as low cost, ease of use and data-logging capability, make it an attractive alternative to existing gas chromatographic methods. Similar studies with other detectors/sensors have demonstrated wider application to other pollutant gases. Full validation with an inter-laboratory study and comparison with existing standardised gas chromatographic methods would be necessary for use of such detectors in quality assurance and commercialisation of photocatalytic materials. Nevertheless, the data generated in this study show that gas detectors can have sufficient accuracy for use in academic photocatalytic air purification tests.

4.2 Adsorption–Photocatalysis Synergy

A simple and robust experimental test method was developed to investigate and quantify if synergistic effects are observed for the removal of CH_3SH by adsorption and photocatalysis. The data interpretation followed carefully those used in the ISO standard test method. In this study, no synergy was measured. It is important to note that only simple physical mixtures of industrially ubiquitous and low-cost granular AC

and powder-coated TiO_2 were employed. The use of more advanced materials such as graphene, carbon nanotubes, TiO_2 nanoparticles, consolidated (heat-treated) composites, etc., could result in the widely reported synergy effects found in the literature. This would, however, require a more complex test method design. As a result of the inconsistencies in synergy measurement found in the literature for adsorbent–photocatalyst materials that demonstrate synergy to find commercial application, there is an urgent need for an ISO-standardised test method (test setup, sample preparation and data interpretation) to measure synergy. Otherwise, adsorption and photocatalysis will remain competitive technologies for odour treatment (also for general air and water purification).

4.3 Real-world Application of Photocatalysis Technology

For photocatalysis to become widely used in industrial air or odour purification, it must compete with well-established and high-performing technologies. This may be achieved by proving it more cost-effective or by combining photocatalysis with existing methods. An example of the former is utilisation of visible/solar light to reduce electrical energy requirements (which has been a goal of photocatalysis researchers for a number of decades). An example of the latter is synergy between adsorption and photocatalysis (as was investigated in this study).

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Abbreviations

AC	Activated carbon
C₆H₅O	Toluene
CH₂O	Formaldehyde
CH₃CHO	Acetaldehyde
CH₃SH	Methyl mercaptan
EPA	Environmental Protection Agency
GC	Gas chromatography
ISO	International Organization for Standardization
NO	Nitric oxide
ppm	Parts per million
SEM	Scanning electron microscopy
TiO₂	Titanium dioxide
UV	Ultraviolet
VOC	Volatile organic compound

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL

Tá an Gníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaoil a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: Déanaimid córais éifeachtacha rialaithe agus comhlionta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.

Eolas: Soláthraimid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spríodhíre agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.

Tacaíocht: Bimid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaoil atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaoil inbhuanaithe.

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaoil:

- saoráidí dramhaíola (*m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistriúcháin dramhaíola*);
- gníomhaíochtaí tionsclaíoch a scála mór (*m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta*);
- an diantalmhaíocht (*m.sh. muca, éanlaith*);
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe (*OGM*);
- foinsí radaíochta ianúcháin (*m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíochta*);
- áiseanna móra stórála peitрил;
- scardadh dramhuisece;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdarás áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhírú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídionn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uisce idirchriosacha agus cósta na hÉireann, agus screamhuisecí; leibhéal uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaoil

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil (*m.sh. tuairisciú tréimhsiúil ar staid Chomhshaoil na hÉireann agus Tuarascálacha ar Tháscairí*).

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis ceaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainiú, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaoil in Éirinn (*m.sh. mórphleananna forbartha*).

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéal radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as tairmí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaoil ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinn-teoireacht i ndáil leis an gcomhshaoil (*m.sh. Timpeall an Tí, léarscáileanna radóin*).
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosaint agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord Iáinimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltáí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inné agus le comhairle a chur ar an mBord.

An Investigation into Air Purification of Malodorous Methyl Mercaptan by Photocatalysis and Adsorption



Authors: Donal Keane, Suresh Pillai,
Lorraine Gibson, Justin Holmes and Michael Morris

Identifying Pressures:

Odour accounts for 66% of all complaints received by the EPA regarding licensed sites (waste and industrial) in 2016. Exposure to offensive odours can cause stress and/or reduced quality of life. The resolution of odour problems at licensed sites continues to remain a key priority for the EPA.

Developing Solutions:

Odour is inherently difficult to define as it involves many chemical compounds at extremely low concentrations. A number of methods are available to successfully remove odour and best practices exist, although each method has certain disadvantages. Novel technologies include combining existing methods synergistically to improve performance and reduce operating costs. Future green solutions would most likely involve utilizing renewable energy, such as solar radiation (visible light photocatalysis), for odour abatement. Finally, as part of a future odour management plan, low-cost miniaturized odour sensors (electronic noses) would be integrated. This would replace on-site human olfactometry and off-site laboratory chemical analysis which is slow and expensive. Based on laboratory methods and results shown in this study, potential exists for development of a laboratory photocatalytic air/odour purification prototype unit. Based on the laboratory methods and results shown in this study, potential exists for development of a laboratory photocatalytic air/odour purification prototype unit.