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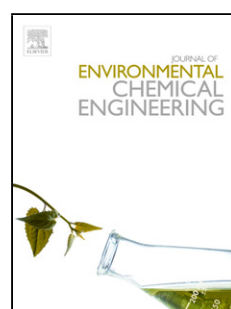
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Comparison of the photoactivity of TiO_2 coatings using a flat panel reactor and FTIR to monitor the CO_2 evolution rate

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Abstract

A system designed to continuously monitor the gas phase for the UV irradiation of flat panels of organic coatings has been modified to compare the photocatalytic degradation of organic pollutants using TiO_2 functional coatings. TiO_2 was formulated into pastes and was coated onto various stainless steel and glass fibre meshes. The photoactivity was determined by monitoring the photodegradation of acetone and following the rate of CO_2 evolution using FTIR spectroscopy. The kinetics were compared to the photoinduced degradation of indigo carmine, followed by UV-Vis spectroscopy to determine whether the CO_2 evolution method is a viable, rapid alternative to photodegradation monitoring. A correlation was established between the two methods by determining the rate constants of the decolourisation of indigo carmine and CO_2 evolution, demonstrating that such a method can be used as a rapid assessment of the photoactivity of photocatalytic coatings.

Keywords: Photocatalysis, Titanium dioxide, FTIR, Decolourisation

Introduction

TiO_2 based photocatalysts have been widely studied as potential materials for applications in wastewater treatment due to their photochemical stability, non-toxicity, low cost and strong oxidative potential. [1][2][3][4][5][6] Due to its ability to oxidise organic materials directly, TiO_2 can be used in paints, glass coatings and cements to give them sterilising, anti-fouling and photocatalytic properties. TiO_2 based coatings for applications in photocatalytic degradation of organic pollutants in wastewater have been extensively researched due to the advantages of avoiding costly filtering techniques required when TiO_2 suspensions are utilised [7]. TiO_2 immobilised onto porous membranes or support materials can not only be used for the decomposition of organic pollutants; but also for the

destruction of biological toxins and the inactivation of microorganisms, making TiO_2 films highly suitable for wastewater treatment systems. [8][9][10][11]

Many different methods exist to study the photocatalytic activity of a film or coating, however expensive analytical equipment and prolonged analysis periods are often required. [12][13] There are many compounds that serve to evaluate photocatalytic activity, with organic dyes being most commonly used. [14] In recent years, the methylene blue ISO test for assessing the activity of photocatalytic films has been scrutinised, due a number of assumptions required in the testing, along with poor repeatability and reproducibility. [15][16][17] The photocatalytic degradation of organics by irradiated TiO_2 has been shown to lead to the complete mineralisation, eventually degrading them to CO_2 and water (Eq. 1- 4). [18] [19] A simple, rapid method to compare the photoactivity of various TiO_2 functional coatings immobilised onto glass fibre and steel substrates has been developed which uses the rate of CO_2 evolved. This technique has been used to determine the degradation of acetone in the gas phase using a flat panel reactor and FTIR continuous monitoring. Previous studies using this technique were performed to monitor the photodegradation of polymers and polymer-based coatings containing TiO_2 [20] [21] Polymer coatings containing TiO_2 pigments are extensively used to coat steel products to protect against corrosion. However, the photoactivity of TiO_2 can lead to degradation of the organic components in the coating under high intensity UV conditions, leading to changes in the flexibility and appearance of the coating. Using a similar in-house designed test method, the photoactivity of TiO_2 functional coatings could be rapidly determined. The photoactivity of functional TiO_2 coatings immobilised onto various glass and steel substrates were studied by performing kinetic experiments; whereby the CO_2 evolution from the photodegradation of acetone was measured. The photodegradation of acetone has been used as a method to study photoactivity as it represents an organic indoor air pollutant and the absence of intermediates in the mineralization to CO_2 and water allow facile analysis of reactant and product. [22][23][24] The system here is designed to test photoactive coatings on various substrates in an airtight reactor irradiated with a UV light source. The results could then be compared to the photocatalytic degradation of indigo carmine using the same coatings to determine the feasibility of using simple CO_2 evolution monitoring to investigate photoactivity of functional coatings.

$$TiO_2 + h\nu \text{ (<387 nm)} \rightarrow e_{CB}^{-} + h_{VB}^{+} \qquad (1)$$

$$h_{VB}^{+} + R \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \qquad (2)$$

$$H_2O + h_{VB}^{+} \rightarrow {}^{\bullet}OH + H^{+} \qquad (3)$$

$${}^{\bullet}OH + R \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \qquad (4)$$
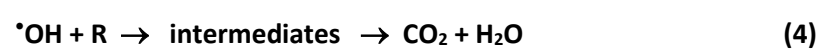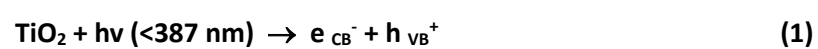
Experimental

Photodegradation monitoring using a closed loop flow reactor

The photocatalyst slurry used on all substrates contained titanium dioxide (P25, Degussa) and polyethylene glycol (average M_v 20,000, 10 % in H_2O) (Sigma-Aldrich) which were used without further treatment. The TiO_2 slurry was prepared by adding P25 nanoparticles to polyethylene glycol and water with constant stirring. The TiO_2 films were coated using a draw down method onto borosilicate glass, woven glass fabric (Fibreglass Direct, 270 g/m^2) and stainless steel mesh (Mesh Direct, aperture 0.31 and 0.026 mm). Sintering was carried out in a convection oven for 30 min at 450 °C for all samples. Previous studies have confirmed that this sintering temperature is suitable in removing all residue of the binder and STA data confirmed all the binder was removed. [25][26]

A full description of the design and workings of the flat panel reactor and FTIR continuous monitoring technique are described elsewhere [21] Briefly, the reactor consisted of a single aluminium block from which the cell is machined from, containing a bonded window which forms an airtight seal and allows the coated substrates to be irradiated. A narrow slit, which can be sealed, allows the introduction of the sample and 25 0.5 mm holes were drilled through the sample stage into the air outlet. The flat panel was incorporated into a closed loop flow system to monitor the photodegradation of acetone. The UV irradiation source consisted of 6 x 8 W UV lamps (λ_{max} 365 nm) and was placed 5 cm above the flat panel. The flat panel was connected to a diaphragm pump which circulated the gas in the sealed system via an infrared flow cell (path length 10 cm) mounted inside a Fourier transform

infrared spectrometer (FTIR Perkin Elmer System 2000). X-ray diffraction (XRD) was recorded on a Brüker d8 DISCOVER diffractometer with a Cu K$\propto$ X-Ray source (λ = 0.15418 nm) and analysed using Match 2 software.

Photocatalytic dye degradation

Adsorption experiments

Adsorption experiments were performed by immersing a 64 cm^2 glass substrate, coated in TiO$_2$ photocatalyst in 50 mL dye solution. The adsorption isotherms were obtained by using different concentrations of dye solutions between 4 and 20 mg/L. The amount of dye adsorbed was calculated by measuring the concentration of the solution before and after, using a Perkin Elmer Lambda 750S high performance UV/Vis spectrometer.

Photocatalytic degradation of indigo carmine

A laboratory bench test rig was used to determine the photoactivity of the different TiO$_2$ coatings using UV light from an 8 W UV lamp array. The spectral output of the UV lamps is shown in **Fig. 1.**

500 mL of a 10 mg/L solution of indigo carmine was used to monitor the photoactivity. This dye was chosen as a model pollutant as it has been studied widely in literature and the breakdown pathway and kinetics are well established. [27] It is still used as a vat dye and commonly used in the textile industry for polyester and denim dying. The use of indigo carmine as a model pollutant was also chosen as the λ_{max} is well defined, and the breaking of the central chromophore gives a rapid decolourisation. The UV lamp was switched on for thirty minutes and then placed over the test solution at t=0s, for the UV intensity to be achieved.

To quantify the degradation of the organic dyes, a UV-Vis spectrometer was used. The HR2000+ High Resolution UV-Vis Spectrometer was obtained from Ocean Optics, with the data analysed using SpectraSuite software. The UV-Vis probe was set up using deionised water as the background control. By setting the spectrum to the wavelength of the dye, the degradation could be recorded as a decrease in the absorbance over time.

Four coated substrates were tested in total using the flat panel reactor and dye degradation set-up. Acetone was chosen as a model organic contaminant as the carbonyl functional group could be easily monitored and integrated using the FTIR software.
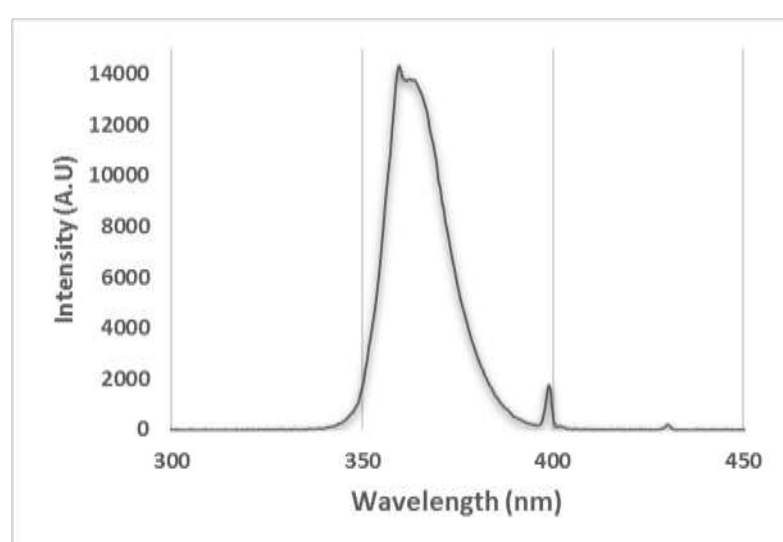

Fig. 1. Spectral output of UV lamp array used for photodegradation of indigo carmine and acetone

Flow cell calibration

CO_2 was the primary gas studied in this work, which is naturally present in the atmosphere. Background subtraction was therefore performed to ensure the change in CO_2 concentration within the system was correctly measured. To measure the CO_2 concentration, area integration of the FTIR peak in the region 2200 -2500 cm^{-1} was measured. The response of the cell to the increase in CO_2 was calibrated by injecting known volumes of acetone at regular intervals and the signal from the FTIR was recorded.

The proposed photocatalytic degradation of acetone to give CO_2 is given in **eq. 5.** In the degradation studies, 10 μL acetone was injected into the cell, (0.001 mol dm^{-3}) it is expected that around 0.003 mol dm^{-3} CO_2 would be evolved when complete degradation was achieved. The photocatalytic degradation of acetone does produce intermediates through its reaction pathway, reported by Stengl et al. [28] [29] [30] In this study however, only the CO_2 evolution will be monitored as full mineralisation to CO_2 can be achieved. It

was expected that a fast decrease in acetone and fast increase in CO_2 would be observed using all the different coatings. One molecule of acetone would yield three molecules of CO_2 if full mineralisation is achieved. [31]

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O \quad (5)$$
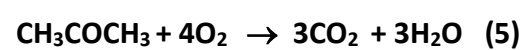
Results and discussion

Calibration of Flow Cell

The FTIR gas cell used has a volume of 140 cm^3. Using this volume, known amounts of CO_2 were injected into the flow cell and the concentration of gas was calculated. A calibration curve, shown in Fig 2, was then constructed using the FTIR absorption units against the concentration. A second calibration was then performed for acetone using the same method. These injections were performed in the dark to avoid any degradation. Although the FTIR apparatus is not as sensitive as other analytical techniques, it allows for continuous monitoring and can detect the differences in the rate of CO_2 evolution from coatings having relatively low photoactivity. Before each test was performed, the system was run with the pump and UV lamps on for 30 min to ensure all traces of acetone were degraded. Studies were also performed in the dark to investigate the adsorption of acetone on TiO_2.
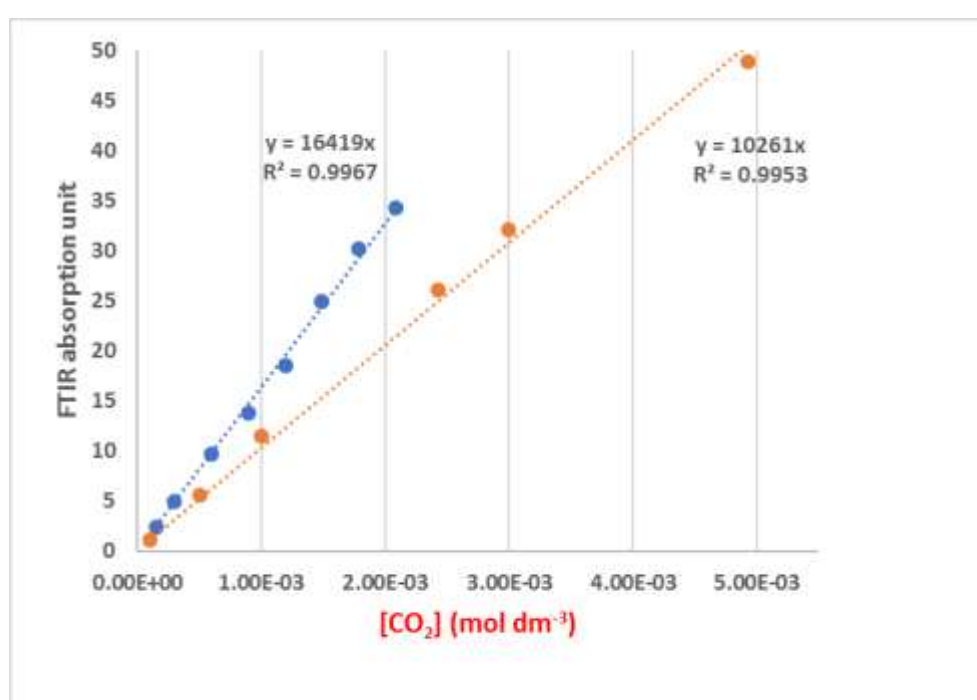
Fig. 2: Calibration plot showing the FTIR signal response vs. concentration of injected CO_2 (Blue) and acetone (orange)

Kinetics of the evolution of CO_2 from the photodegradation of acetone

Table 1 details the substrates used and the amount of TiO_2 per m^2 immobilised onto each substrate as determined by gravimetric analysis. The results were expressed as photoactivity of the various coated substrates and were then normalised in relation to the amount of TiO_2. **Fig. 3** illustrates the CO_2 evolution obtained from the four different coatings. A commercially available photocatalytic felt (Quartzel®) was also tested using the same methods for comparison of photoactivity of coatings.

Table 1. Selected support materials and weight of TiO_2 per m^2/g

Sample	Abbreviation	Details	Weight of TiO_2 per m^2 (g)
Fibreglass	GFM	$270g/m^2$	34.2
Stainless steel mesh	SSM	0.31 aperture	65
Fine Stainless steel mesh	Fine Mesh	0.026 aperture	20.1
Quartzel® mat	Quartzel	Quartz fibres modified with TiO_2	-
Glass	Glass	Borosilicate (6mm)	31.3

Fig. 3 shows the CO_2 evolution results from the five coated substrates used to degrade acetone. Two blank studies were also performed using the coated glass substrate. A set of degradation studies were carried out under non-illuminated conditions, to confirm degradation of acetone occurred using UV irradiation only. No observable photodegradation was measured in the dark. The curves show there are differences in the rate of degradation of acetone for each of the different coatings on support materials. The CO_2 evolution rates for the different coated supports are shown in **table 2.** Stainless steel mesh coated support showed the highest photoactivity, with a CO_2 evolution rate of 0.065 mmol m^3/min. The results for the photoactive felt, Quartzel®, showed the photoactivity to be greater than that of all other samples and only slightly less than that of the stainless steel mesh support. The support with the lowest photoactivity was the coated glass. Quartzel is a product designed to be used inside equipment and used with a UV-A or UV-C light source. The products high photoactivity is attributed to its specific texture, high surface area (9 μm fibres) and the optical properties of silica for a maximum activation by UV radiation. [30] The stainless steel mesh showed a higher level of photoactivity than all other samples tested, which is attributed to a higher surface area of the active coating being available.

An XRD diffraction pattern of the coated stainless mesh is shown in **Fig. 4**. Diffraction peaks at 25.3, 36.9, 37.8, 38.6, 48.1, 53.9, 55.1 and 62.7°, 2θ anatase (COD7206075) and 27.4, 36.1, 41.2, 54.3, 56.7, 62.8, 64.1, 69.1 69.8° 2θ rutile (COD9009083), confirm the thermal stability of the TiO_2 coating at sintering temperatures of 500°C. Diffraction peaks corresponding to the stainless steel mesh are also visible on the XRD patterns, at 43.4 and 50.6° 2θ suggesting the thickness of the coating is less than 5 μm.
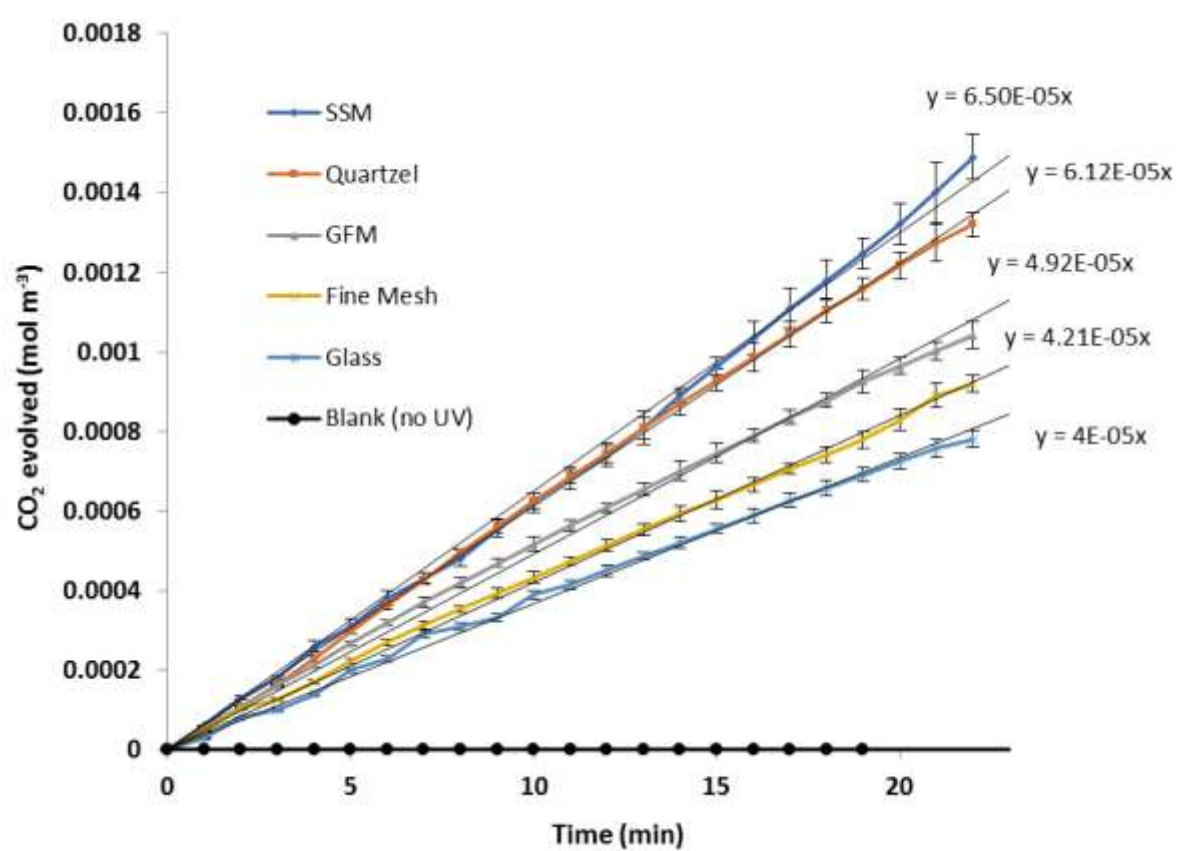
Fig. 3: Photocatalytic mineralisation of acetone over TiO$_2$ coated supports under UV irradiation
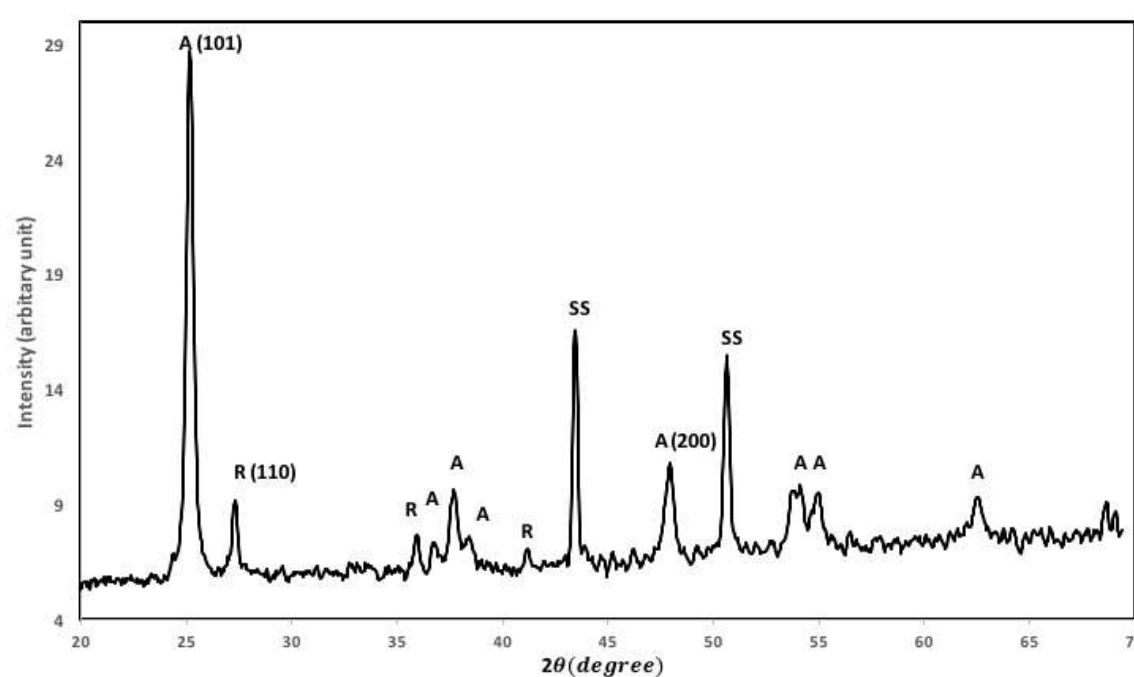
Fig. 4: XRD patterns of stainless steel mesh coated with TiO$_2$, sintered at 500°C

Adsorption studies of indigo carmine

Indigo carmine solution was used to study the photocatalytic activity of the TiO$_2$ coatings. The kinetics of the degradation are shown in **Fig. 5**. The absorption maximum of indigo carmine was observed at λ_{max} 610 nm so this was used to follow the degradation. A calibration was performed to determine the concentration of indigo carmine in the solution.

The observed degradation rate for the UV catalysed reaction was found to be different for each TiO$_2$ coated substrate. Photolysis and adsorption experiments confirmed that no degradation took place in the absence of TiO$_2$. A small reduction in dye concentration occurred in the absence of UV, suggesting that the dye adsorbed onto the surface of the catalyst. The adsorption of the dye onto the photocatalyst is an important parameter in determining the degradation rate. When dye molecules adsorb onto the surface of photocatalysts, they act as electron donors, injecting electrons from their excited state to the conduction band of the photocatalyst under UV irradiation. Adsorption tests were carried out in a dark box to study the equilibrium constants of indigo carmine on the surface of the catalyst. q$_e$ (adsorption capacity at equilibrium) is the quantity of dye

adsorbed in mg per unit surface area at equilibrium. The plotted isotherm and the reciprocal are shown in **Fig. 5** showed a Langmuir distribution, which assumes there is a monolayer coverage, all adsorption sites are equally probable, and it is a second order reaction. The shape of the isotherm suggests there is no real competition between the solvent and the adsorbate to occupy the catalyst surface sites. The Langmuir Equation was used to explain the adsorption of indigo carmine onto the coating. The linear form was used to calculate the maximum amount of dye adsorbed per unit surface (qm (mg / m $^{-2}$)) and the Langmuir equilibrium constant (K (dm3 mg-1)). These were determined to be 42.02 mg / m^{-2} and 0.025 dm^3 mg^{-1}

$$\frac{q_e}{q_m} = \frac{K\,C_e}{1 + K\,C_e}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K\,q_m}\,\frac{1}{C_e}$$
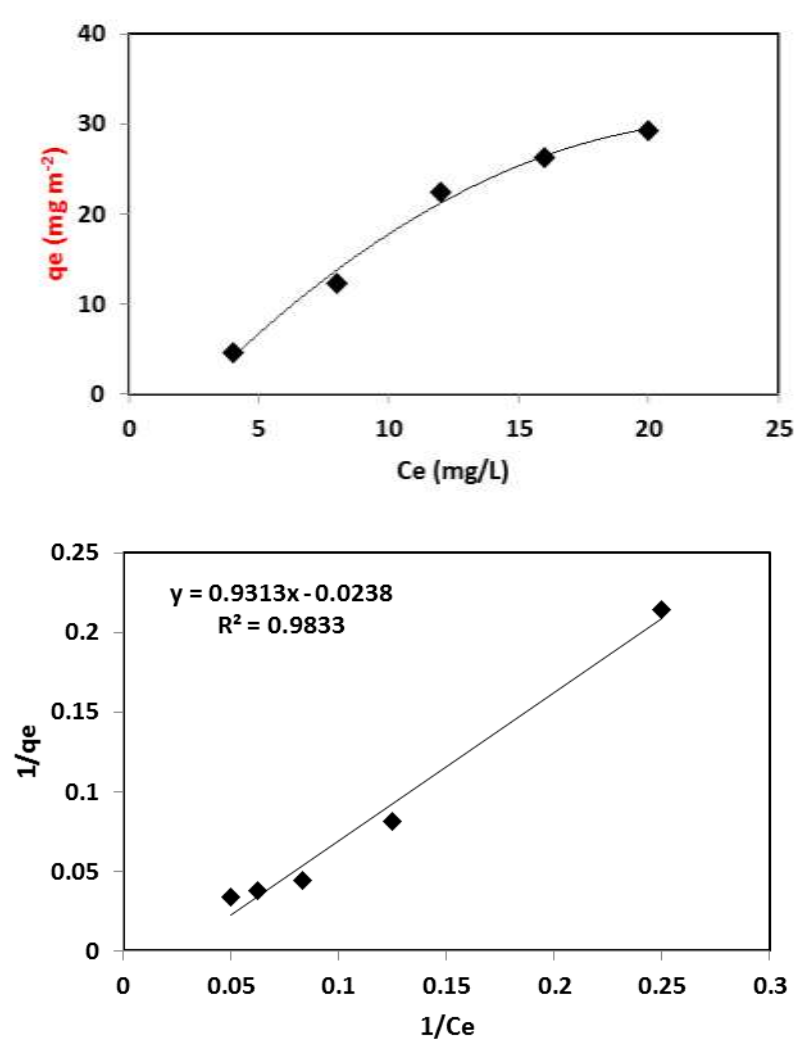
Fig. 5: Adsorption isotherm of indigo carmine on TiO₂ coating

Photocatalytic degradation of indigo carmine

As has been presented in a number of studies, the kinetics of the photocatalytic degradation of organic dyes is described by pseudo-first order kinetics. [32][33]

$$\ln C_0 / C_t = kt$$

where C_0 is the initial concentration, C_t is the concentration at any time (t) and K is the rate constant. **Fig. 6** shows the degradation curves as a function of time for the four different coated substrates. Each test was run in the dark for 30 min as the adsorption equilibrium

was reached within a 30 minute period. The photocatalytic degradation of indigo carmine followed the first order kinetic model, explained in terms of the Langmuir-Hinshelwood mechanism [34]. The reaction rate constant (K) was used to compare the photocatalytic activity of the TiO_2 coatings. **Fig. 7** displays the plot of Ln C_0/C_t for the different coated substrates. The rate constants for the different substrates were found to be between 0.0078 and 0.0403 min^{-1}. The dye degradation used as a measure of the photocatalytic activity was found to be fastest using the stainless steel coated mesh (SSM).

The rates of degradation varied significantly when the different coated substrates were used and were found to be: stainless steel mesh (0.0403) > glass fibre mesh (0.0176) > fine stainless steel mesh (0.0142) > glass (0.0078). The surface area and thickness of the coatings on each of the substrates varied so to compare the different substrates, the photoactivity was calculated per g of TiO_2. This then enabled a comparison of the photoactivity to be made using both methods.

Gravimetric analysis was performed on each of the coated substrates to determine the weight of TiO_2 immobilised onto each of the different materials. The results were then used to determine the rate of degradation per g of TiO_2.

Table 2: Photocatalytic rate constants for different coated supports

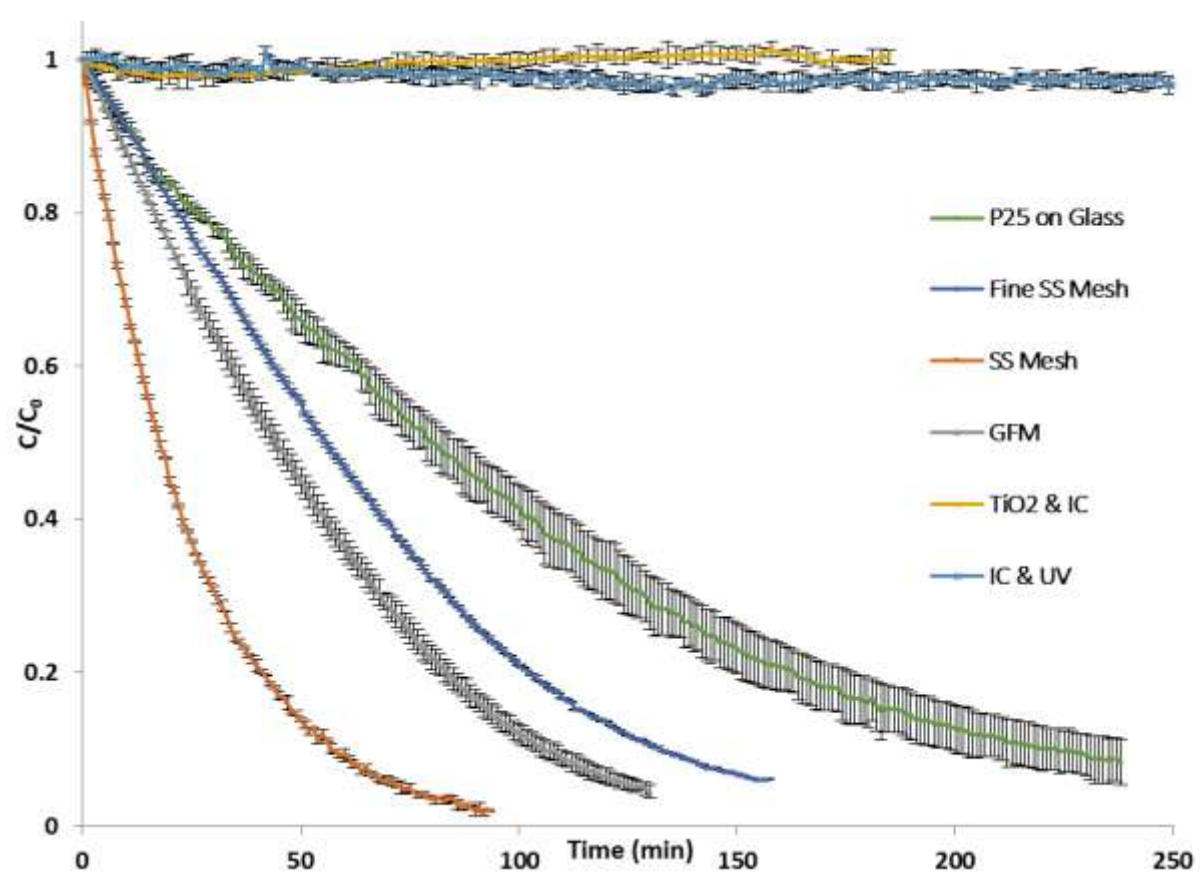| Substrate	Rate constant K (min^{-1})	Rate constant K(min^{-1})/g	CO_2 evolution [mol/dm^{-3}]
Glass	0.0078	0.0597	3.7×10^{-5}
Glass fibre mesh	0.0176	0.0742	4.92×10^{-5}
Stainless steel mesh	0.0403	0.0967	6.5×10^{-5}
Fine stainless mesh	0.0142	0.065	4.21×10^{-5}
Quartzel	-	-	6.12×10^{-5}

Fig.6. Degradation kinetics of indigo carmine (10 mg/L aqueous solution) including photolysis, adsorption and the four different TiO₂ coated substrates
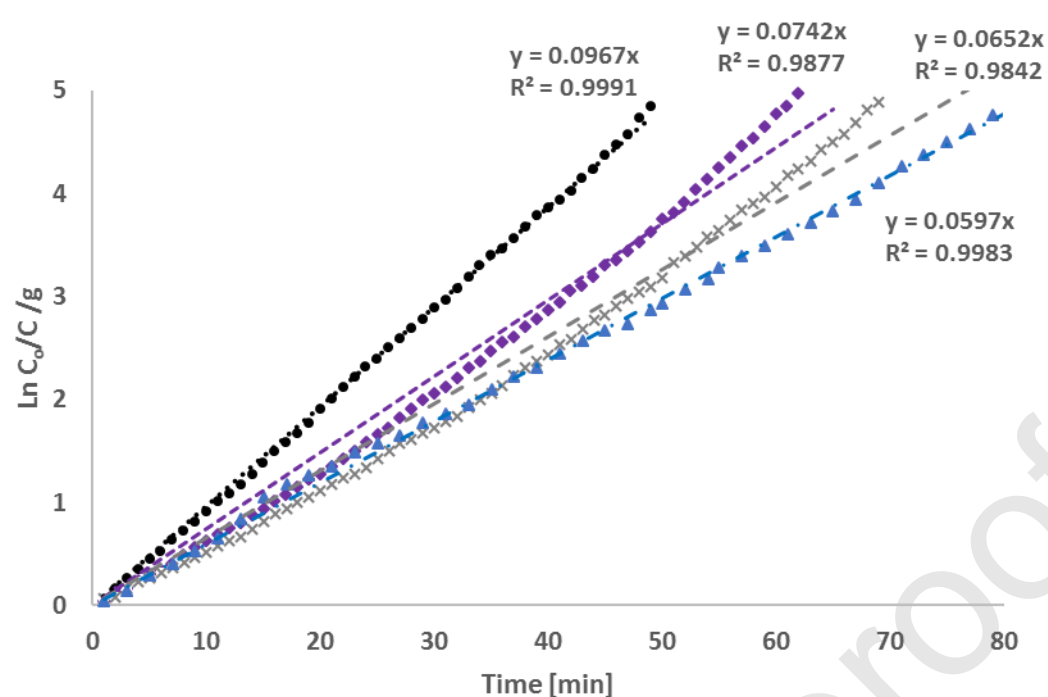
Fig: 7 Plot of Ln C_0/C_t vs time for four TiO_2 coatings immobilised on various substrates per g of TiO_2 – Glass (blue), FSS (grey), GFM (purple) SSM (black)

Comparison of photoactivity monitoring methods

Fig. 8 shows a plot of the differences in rate constants of the breakdown of indigo carmine using the different coated substrates compared to the CO_2 evolution rates. The results are normalised to the results of the dye degradation and CO_2 evolution rates for TiO_2 coated on glass. Using the CO_2 evolution method, the difference in photoactivity of several different coated supports could be determined. Comparing the rates of IC degradation and rate of CO_2 evolution for the four different supports, it was possible to rank photoactivity using both methods, with less than a 5% difference in the compared results. Using P25 coated on glass (the sample which showed the lowest photoactivity), the increase in photoactivity for each of the coated supports increased by 9, 14 and 30 % for fine stainless mesh, glass fibre mesh and SS mesh respectively. Comparing this to the CO_2 evolution results, the photoactivity of the coatings increased by 13, 16 and 32 % for fine SS, glass fibre mesh and SS mesh.

Comparing the results from the standard dye degradation study to the CO_2 evolution test, it is well suited to study the photoactivity of photocatalytic coatings on various substrates. Comparing the commonly used standard stearic acid test (SA test) using the destruction of the acid to monitor self-cleaning surfaces, the degradation of acetone is more rapid, no intermediates are formed to interfere with the results and no thin films using solvents need to be produced on the photoactive surfaces. Compared to standard dye degradation experiments, which are well suited for studying photocatalysts for water purification, the method is less suited to study self-cleaning and superhydrophilic surfaces. The preferred method involves depositing a thin layer of stearic acid onto the films and monitoring the destruction over time using FTIR.

The degradation of acetone is an even simpler method that requires no deposition of SA, no extra solvents and the mineralisation of acetone is a simple, rapid proccess to monitor via FTIR.
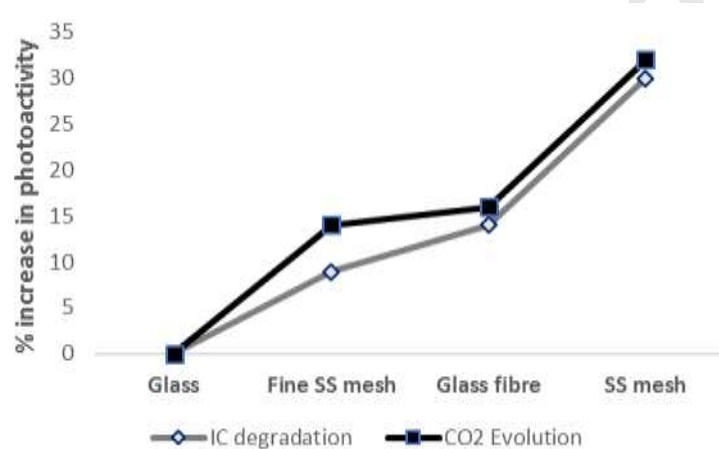

Fig: 8: Comparison of IC degradation and CO_2 evolution testing methods expressed in % increase in photoactivity relative to P25 on glass substrate

Conclusions

A photocatalytic coating containing P25 TiO_2 nanoparticles was successfully immobilised onto fibreglass and stainless steel substrates. *In situ* FTIR spectroscopy of the photogenerated CO_2 has been shown to provide reproducible and comparable results, demonstrating the potential for such a method to be used as a rapid monitoring technique for photoactivity of coatings. The results from the CO_2 evolution show a clear correlation to the more common method of organic dye degradation. Four substrates, including glass fibre and stainless steel mesh were used as supports for a TiO_2 based photocatalytic coating. The photoactivity of each of the immobilised coatings were evaluated by the photocatalytic degradation of an aqueous solution of indigo carmine under UV irradiation. The CO_2 evolution method was then evaluated as an alternative technique to monitor the photoactivity of coatings. The results of the CO_2 evolution demonstrate there is a potential for this method to be used as a standard testing approach. Using a borosilicate glass substrate as a standard support, the correlation of the level of photoactivity using both methods showed a trend of increasing photoactivity with fine stainless steel mesh, glass fibre mesh and stainless steel mesh.

Compared to the more traditional technique of standard dye degradation, the CO_2 evolution technique enables a rapid evaluation of photocatalytic films and coatings. With concerns raised over the use of the standard methylene blue test due to its reliability, a number of new methods for assessing photoactivity of films are being reported, which coincides with the continuing interest in commercial photocatalytic coatings which need to be verified.

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