



OpenAIR@RGU

The Open Access Institutional Repository at Robert Gordon University

<http://openair.rgu.ac.uk>

This is an author produced version of a paper published in

Applied Catalysis B: Environmental (ISSN 0926-3373)

This version may not include final proof corrections and does not include published layout or pagination.

Citation Details

Citation for the version of the work held in 'OpenAIR@RGU':

ADAMS, M., SKILLEN, N., MCCULLAGH, C. and AL-KHATIB, S. and ROBERTSON, P. K. J., 2013. Development of a doped titania immobilised thin film multi tubular photoreactor. Available from *OpenAIR@RGU*. [online]. Available from: <http://openair.rgu.ac.uk>

Citation for the publisher's version:

ADAMS, M., SKILLEN, N., MCCULLAGH, C. and AL-KHATIB, S. and ROBERTSON, P. K. J., 2013. Development of a doped titania immobilised thin film multi tubular photoreactor. *Applied Catalysis B: Environmental*, 130, pp. 99-105.

Copyright

Items in 'OpenAIR@RGU', Robert Gordon University Open Access Institutional Repository, are protected by copyright and intellectual property law. If you believe that any material held in 'OpenAIR@RGU' infringes copyright, please contact openair-help@rgu.ac.uk with details. The item will be removed from the repository while the claim is investigated.

“NOTICE: this is the author’s version of a work that was accepted for publication in Applied Catalysis B: Environmental. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in APPLIED CATALYSIS B: ENVIRONMENTAL, [VOL 130, (2013)] DOI <http://dx.doi.org/10.1016/j.apcatb.2012.10.008>

Development of a doped titania immobilised thin film multi tubular photoreactor

Morgan Adams*, Nathan Skillen, Cathy McCullagh and Peter K.J. Robertson.

IDEAS, Institute for Innovation, Design and Sustainability Research, CREE, Centre for Research in Energy and the Environment, The Robert Gordon University, School of Engineering, Aberdeen, AB10 1FR, UK

*Corresponding author. Tel.: +44 1224 262840; Fax.: +44 1224 262444. E-mail address: m.adams1@rgu.ac.uk (Morgan Adams)

ABSTRACT

This paper describes a novel doped titania immobilised thin film tubular photoreactor which has been developed for use with liquid, vapour or gas phase media. The current approach to photocatalyst and photoreactor development is firmly based on the principles of surface area. This dictate greatly limits the applicability of any semi-conductor photocatalyst in industrial applications, as a large surface area equates to a powder catalyst. This work aims to show that the development of a thin film coating, doped with a rare earth element, and a novel photoreactor design produces a photocatalytic degradation of a model pollutant (Methyl Orange) equal to that of P25 TiO₂. It will show that doped thin film tubes in a novel reactor configuration can produce a degradation rate of 95 % after 90 minutes under UV irradiation and 70 % under visible irradiation with no downstream processing required. The use of lanthanide doping is reported here in the titania sol gel as it is thought to increase the electron hole separation therefore widening the potential useful wavelengths within the electromagnetic spectrum. Increasing doping from 0.5 % to 1.0 % increased photocatalytic degradation by ~17 % under visible irradiation. A linear relationship has been seen between increasing reactor volume and degradation which would not normally be observed in a typical suspended reactor system.

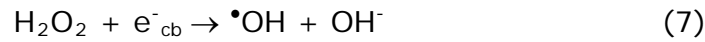
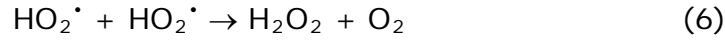
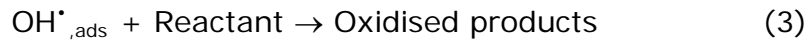
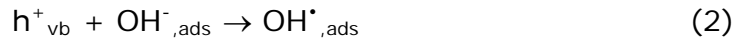
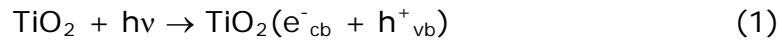
Keywords: *thin film, photocatalysis, titanium dioxide (TiO₂), lanthanides, surface area.*

1. INTRODUCTION

Semiconductor photocatalysis is an important area of research and is an ever growing industrial tool which is applicable to a wide range of fields. Semiconductor photocatalysis has grown significantly in the last three decades, and has been applied to a diverse array of environmental problems including air [1, 2], potable and wastewater treatment [3, 4], as well as photo-splitting of water to produce hydrogen gas [5-7], nitrogen fixation[8-10], microbe destruction [11, 12] and the remediation of oily waste [13-15].

TiO₂ acts as a photocatalyst due to its electronic structure, characterised by an electronically filled valence band and empty conduction band[16] separated by a band gap. If a photon of energy greater than or equal to the bandgap energy, E_g , is absorbed by TiO₂, an electron is promoted from the valence band to the conduction band. This generates a reducing electron in the conductance band and an oxidising hole in the valence band. The excited conduction band electrons may recombine with the valence band holes generating heat energy. Alternatively they may be trapped in surface states, undergo reactions with electron donating or accepting species that are adsorbed on the TiO₂ surface. The electron and holes formed are highly charged and result in redox reactions, which can ultimately result in the mineralisation of aqueous pollutants.

Hydroxyl radicals are believed to be generated on the surface of TiO₂ through a reaction of the valence band holes with adsorbed water, hydroxide or surface titanol groups (Eq 2). The photogenerated conductance band electrons react with electron acceptors such as oxygen which generates superoxide (O₂⁻) (Eq 4). Thermodynamically the redox potential of the TiO₂ electron/hole pair should enable the production of hydrogen peroxide, primarily via the reduction of adsorbed oxygen[17, 18] (Eqn 1-7).



While the field of photocatalysis has become diverse and extensive there remain 3 key areas of consideration: light wavelength, environment (reactor) and photocatalyst.

TiO₂, specifically P25, is well known as an efficient photocatalyst however has been shown to have limitations. Recent literature has shown a trend shift from ultra-violet (UV) to visible light driven photocatalysis with a view towards industrial applications [19-22]. TiO₂ is restricted to UV light due to its band gap energy of ~3.2eV. In an attempt to overcome this limitation metal doping has been successfully utilised to move the band gap of TiO₂ into the visible region. Lanthanide doping has been reported in the literature, primarily in conjunction with TiO₂ to produce nano-composites [23-25]. The addition of lanthanide ions to TiO₂ is thought to increase the electron hole separation [26, 27].

With light playing a key role in the process of photocatalysis it is essential the illumination provided is appropriate for the requirements. A high power and energy demanding light source is no longer suitable for an increasingly energy efficient world. Much of the literature has shown experimental designs which utilise ≥500W medium/high pressure lamps [28-31]. These lamps are impractical for industrial applications due to their fragility and are not essential for high efficiency photocatalysis. This raises concern over the true photocatalytic activity of a catalyst when used in conjunction with high powered lamps.

The use of P25 is also restricted in relation to downstream processing, particularly separation and filtration which can be problematic in industries such as water purification. The micrometric particle size of P25 results in

filtration becoming a labour intensive and expensive procedure. Methods have been proposed to overcome these obstacles including the use of the pelletised form of P25 [32, 33] [34] and immobilising catalysts onto a solid support [35-37]. Pelletised P25 has been known to 'crumble' due to mechanical abrasion, which again raises filtration problems. The immobilisation of catalysts presents an alternative process which yields a highly recyclable and cost effective method of catalyst production. A number of different coating methods have been published [38-41] along with a number of different solid supports including steel, titanium, activated carbon, zeolites, glass, quartz, glass fibres, optical fibres and silica[32, 42-47]. The ability to coat a wide variety of materials is an attractive prospect for industrial application.

The coating of a photocatalyst onto a solid support reduces the overall efficiency of the catalyst primarily due to the reduced surface area and mass transport limitations. The immobilised catalyst will not have the same porous structure observed with powder photocatalysts, thus the available surface area for photocatalytic transformation will be reduced.

In order to demonstrate the viability of semiconductor photocatalysis for industrial applications, reactor design is an equally critical factor. Effective reactor design research and development aims to scale up laboratory bench scale processes to industrially feasible applications. Photo reactor scale up is achievable via two processes; conventional enlargement of laboratory reactors to pilot and then industrial scale or through mathematical modelling which utilise the fundamentals of chemical engineering and small scale experimentation [28, 48-50]. Scaling up photocatalytic reactors is, however a complex process with many factors needing consideration to yield a technically and economically efficient process. These factors include distribution of target species and photocatalyst, mass transfer, reaction kinetics and irradiation characteristics. The issue of effective photocatalyst illumination is particularly important as this essentially determines the amount of fluid or gas that may be treated per effective unit area of deployed photocatalyst.

Photocatalytic activity can be significantly affected by the surface area of a catalyst. A number of investigations have been reported which aim to increase photocatalytic efficiency by increasing surface area. Surface areas of photocatalysts in the range of $27.5 \text{ m}^2 \text{ g}^{-1}$ through to $400 \text{ m}^2 \text{ g}^{-1}$ have been reported [51, 52]. The literature generally states that increasing surface area will improve photocatalytic activity as an increased number of sites for photocatalytic reactions will be present. This was the focus of an investigation by Amano *et al* [53] where CO_2 evolution from acetaldehyde decomposition increased with an increasing specific surface area from 10 to $\sim 33 \text{ m}^2 \text{ g}^{-1}$. Furthermore, investigations have attempted to increase the already high surface area of TiO_2 ($50 \text{ m}^2 \text{ g}^{-1}$) in an attempt to improve photocatalytic transformations. Phonthammachai *et al* produced TiO_2 with a high surface area of $163 \text{ m}^2 \text{ g}^{-1}$ for inclusion into a membrane for the degradation of 4-nitrophenol [54].

Presented in this study is an investigation into the development of a novel thin film multi tubular photoreactor consisting of a lanthanide doped titania sol gel coating. The performance of the reactor shall be assessed as a catalyst platform by methyl orange degradation. The application of low powered (36W) visible and UV lamps with a view to large scale industrial applications were examined. As a means of catalyst platform appraisal, experiments were conducted with titania sol gel coated silica beads and P25 (the main default titanium dioxide formation for photocatalysis). Furthermore, experiments were conducted to determine if a linear relationship exists in the scaling up process of the coated glass columns. This investigation aims to show that a significantly large surface area is not essential to achieve efficient photocatalytic activity, which in turn can allow for more practical photoreactor developments for industrial applications.

2.0 Experimental

2.1 Titania Sol Gel

The sol–gel formulations were produced following a modified method by Mills *et al* [55]. 4.65 g (4.43 mL) of glacial acetic acid (Sigma Aldrich) was added to 20 mL of titanium isopropoxide (Sigma Aldrich). To this solution 120 mL of 0.1 mol L⁻¹ nitric acid (Fisher Scientific) was added before heating the mixture at 80 °C for 8 h in a water bath. The resulting opaque solution was then filtered through a 0.45 µm filter (Whatman) to remove any aggregated particles.

2.1.1 Doped Titania Sol Gel

To produce the doped titania films, Nd(NO₃)₃·6H₂O (Fisher Scientific), was dissolved in the 120 mL of 0.1 mol L⁻¹ nitric acid before adding the solution to the titanium isopropoxide and acetic acid. Two concentrations of 0.5 wt% (0.6 g) and 1 wt% (1.6 g) were examined. The sol was completed by heating in a water bath as detailed in 2.1.

2.2 Coated Silica Particles

Coated silica particles were produced by saturating a beaker of 50 – 100 µm particles with the titania sol. The coated particles were then transferred to a clean flat surface where they were spread thinly and allowed to dry at room temperature before calcination at 450 °C for 30 minutes.

The coated and uncoated silica particles were analysed under SEM (Leo S430) to determine the quality of coating and also to perform EDAX analysis to determine elemental distribution.

2.3 Multi Tubular Photoreactor

The multi tubular photoreactors were produced by dip coating glass tubes in the titania sol gel solution. The glass tubes (Fisher Scientific) were cut into 65 mm lengths, prior to coating. These tubes were allowed to dry at room temperature before being calcined in a high temperature chamber furnace (Carbolite, UK) at 450 °C for 30 min.

The reactor vessel, (Supelco), was coated on the inside with the sol gel solution and allowed to dry at room temperature before calcination at 450 °C for 30 min.

32 glass tubes were placed into the glass reactor vessel producing the unit, (Fig. 1).

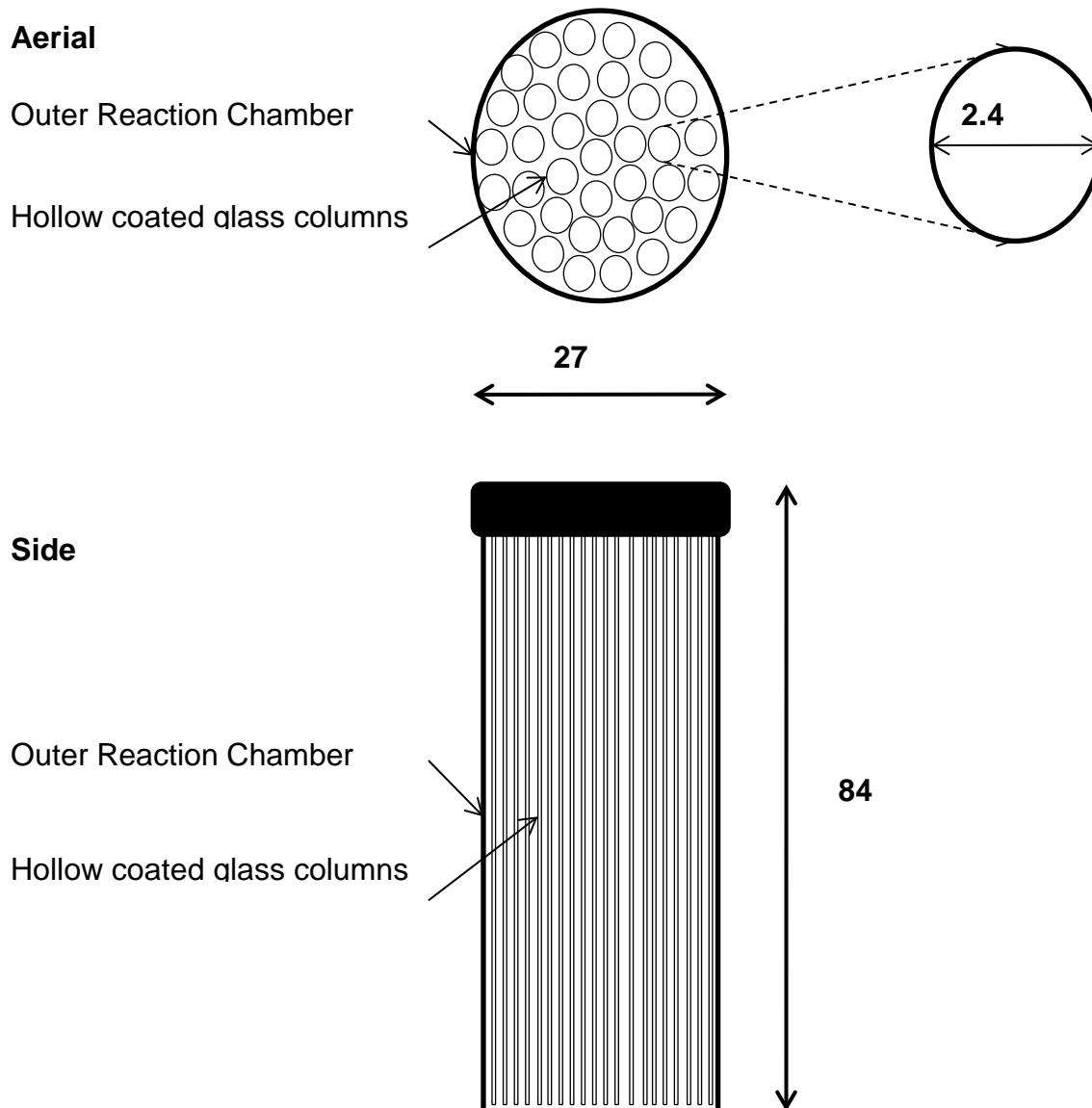
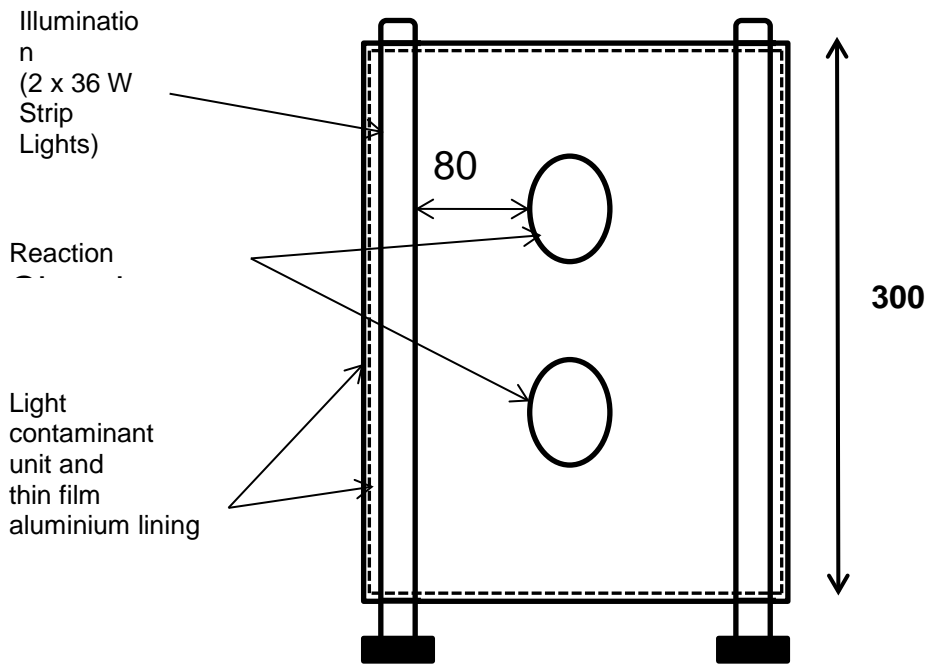


Fig. 1. Arrangement of Multi Tubular Photoreactor

2.4 Experimental Setup

Reaction vessels were placed in a light containment reactor which was lined with thin film aluminium and illuminated by two 36 W non integrated compact fluorescent lamps. A range of visible and UV spectral output lamps were utilised, (Fig. 2). The light containment reactor was capable of running two reaction vessels simultaneously per experiment. During the experiments with the silica coated beads and P25 agitation of the reaction mixture was achieved by magnetic plates and stirrers. There was no agitation during experiments with the coated glass columns.

Aerial



Side

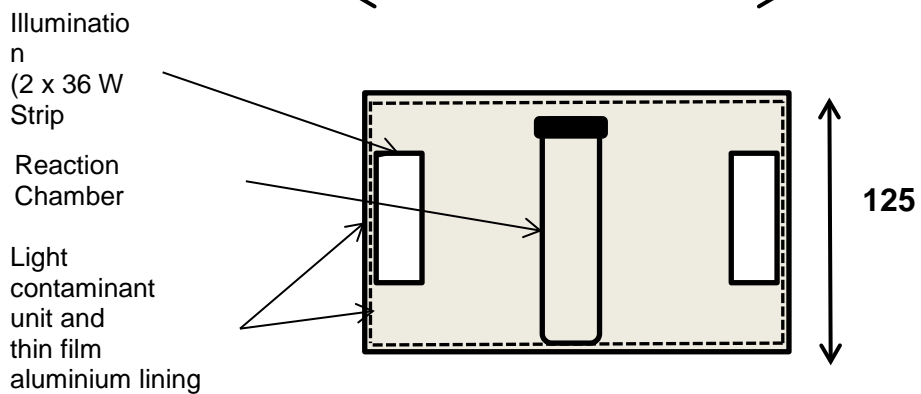


Fig. 2. Configuration of illumination box

Methyl orange (MO, 1×10^{-5} M) was used as a model pollutant to compare the photocatalytic activity of the coated silica beads and the multi-tubular photoreactor. Experiments were also performed using Degussa P25 as a base comparison. Reaction volumes of 20 ml were withdrawn from the stock solution for each individual experiment. Each experiment was allowed an equilibrium time of 20 mins in the dark prior

to illumination for 90 mins. Samples (1 ml) were taken, by syringe extraction, before and after the equilibrium period to allow the dark absorbance to be calculated. During the 90 min illumination period samples were taken every 30 mins in triplicate. In addition to triplicate samples, experiments were also run in triplicate. A syringe filter (0.45 μm) was utilised to filter samples during P25 experiments. No filtration was required for the silica coated beads and immobilised coated glass columns. Analysis of samples was done by UV-VIS spectrometry, monitoring absorbance of MO at 462nm. Absorbance readings were normalised to 1.

2.4.1 Illumination Sources

The two different illumination lamps used were spectrally analysed using a Stellarnet EPP2000 Spectrometer to determine their exact emissions. Fig. 3. (a) shows the emission spectra of the Philips CLEO PL-L UV lamp (blue plot), which displays a large UV peak at 350 nm and a sharp shoulder peak at 353 nm. The other visible emissions can be seen at 404, 436, 546 and 578 nm.

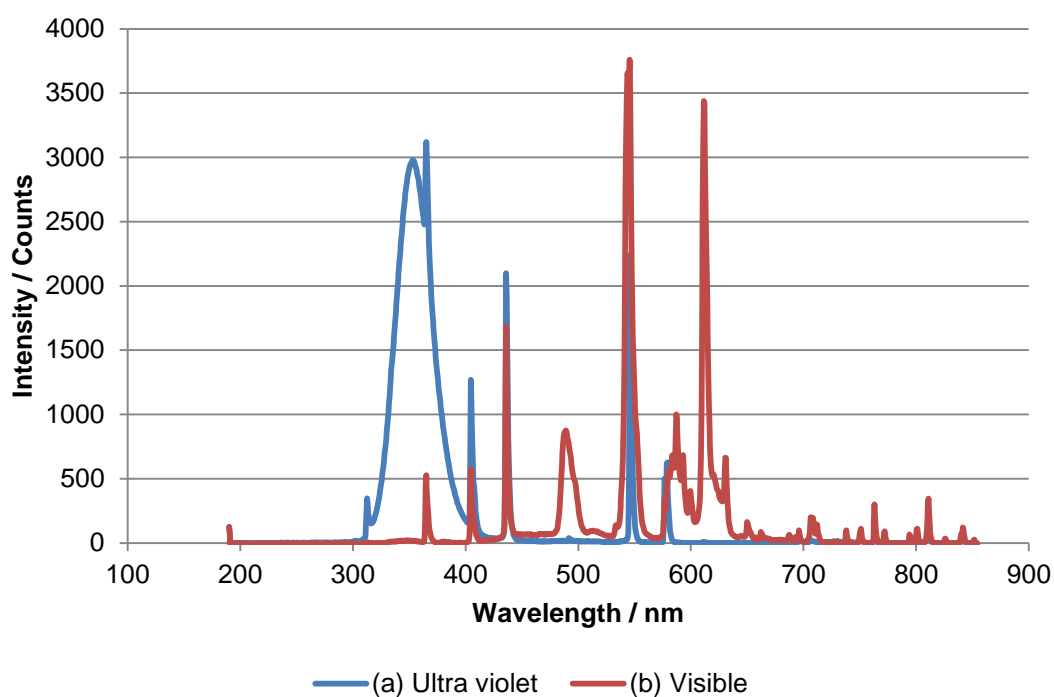


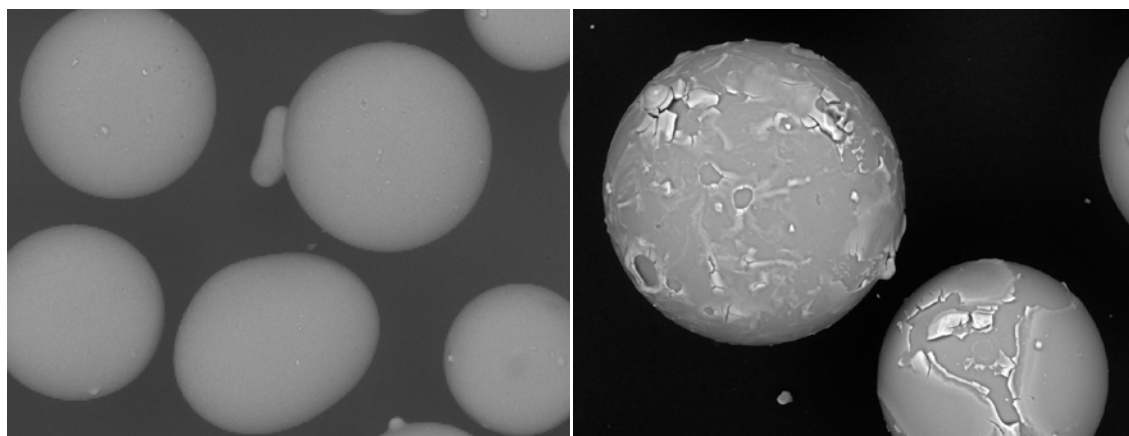
Fig. 3. Emission spectrum for UV and Visible Lamps

Fig. 3. (b) shows the emission spectra of the General Electric Biax L 830 (red plot) fluorescent tube which displays a single ultra violet emission of 364nm with the remaining strong emissions in the visible region, 404, 486, 543, 587, 611 being the predominant wavelengths.

3.0 Results and Discussion

3.1 SEM/EDAX of Coated and Uncoated Silica Particles

The SEM image, Fig. 4 (a) shows uncoated silica particles exhibiting a smooth textured surface. Image (b) shows titania sol gel coated silica particles which display a textured “cratered” and in parts slightly fracture surface. The surface effects observed are due to variation in sol gel thickness, drying and proximity of particles during furnace annealing. The thicker areas of coating tend to be more fragile and do not bond as well as to the surface. The process of manufacture can be greatly improved to eliminate the surface fracturing. The majority of particles exhibit a good surface to coating interface.



(a)

(b)

Fig. 4. (a) Uncoated silica particles and (b) titania coated silica particles

The EDAX analysis of the uncoated and coated particles are shown in Fig. 5 and Fig. 6. As expected the uncoated silica particle produces an EDAX spectrum of a typical silica glass composition. The coated particle displays the same silica glass composition with the addition of Ti which comes from the titania sol gel coating.

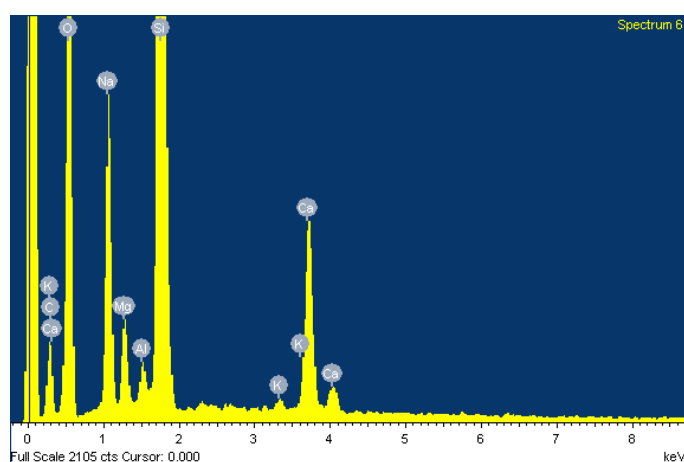


Fig. 5. EDAX spectrum of undoped silica particles

There was no elemental evidence of the neodymium doping, but this is potentially due to the level of doping, and therefore element concentration in a thin coating on a small particle. Further indepth analysis will be examined and reported later.

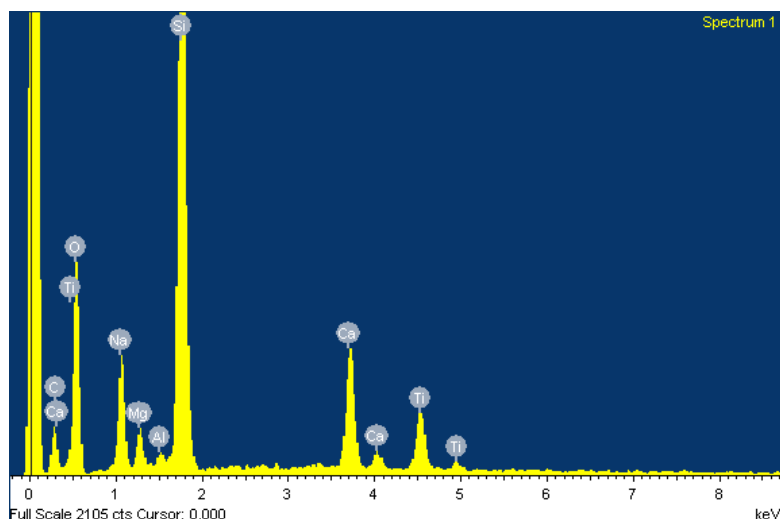


Fig. 6. EDAX spectrum of doped silica particles

3.2 MO degradation (UV irradiation)

The first photocatalyst examined was P25 TiO₂, the surface area of P25 is ~60 m²/g and was therefore expected to achieve a high level of degradation.

Fig. 7. shows the 3 plots for dark control, light control and TiO₂ experiments. The controls show no discernable variation throughout the duration of the experiment. Degradation of 97% for TiO₂ under UV irradiation was observed. A standard deviation of 0.0673 was calculated from triplicate experiments for the P25 experiments.

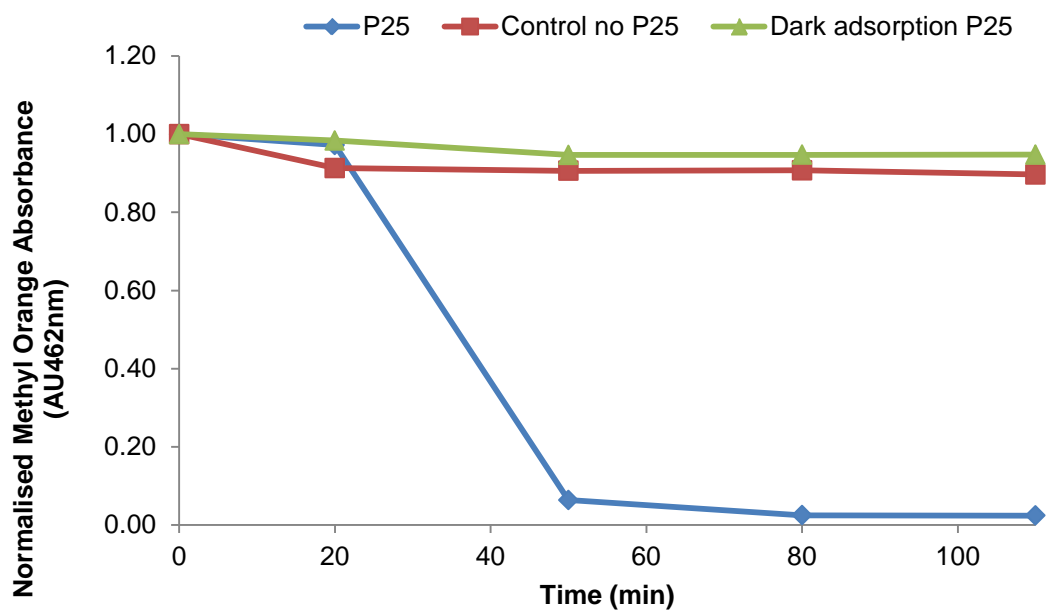


Fig. 7. Methyl Orange degradation by P25 TiO₂ – 72W UV Illumination

The second photocatalyst examined was the titania sol gel coated silica beads, the calculated surface area of coated particles is $\sim 0.024 \text{ m}^2/\text{g}$. A standard deviation of 0.0245 was calculated from triplicate experiments for the sol gel coated bead experiments.

Fig. 8. shows the 3 plots for dark control, light control and coated beads experiments. The controls show no discernable variation throughout the duration of the experiment and neither did the coated bead experiment.

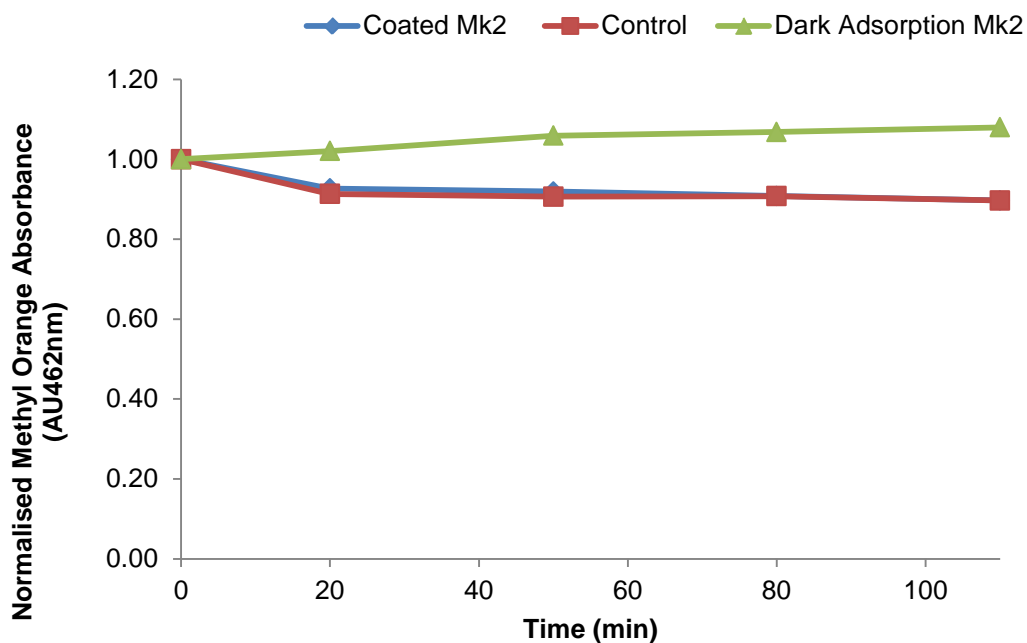


Fig. 8. Methyl Orange degradation by coated silica beads – 72W UV Illumination

The final photocatalyst examined was the thin film doped Titania sol gel coated tubes; the calculated surface area of coated tubes is $\sim 0.04 \text{ m}^2/\text{g}$. A standard deviation of 0.0157 was calculated from triplicate experiments for the sol gel coated tube experiments.

Fig. 9. shows the 3 plots for dark control, light control and coated tube experiments. The controls show no discernable variation throughout the duration of the experiment. Degradation of 95% for the coated tubes under UV lamps was observed.

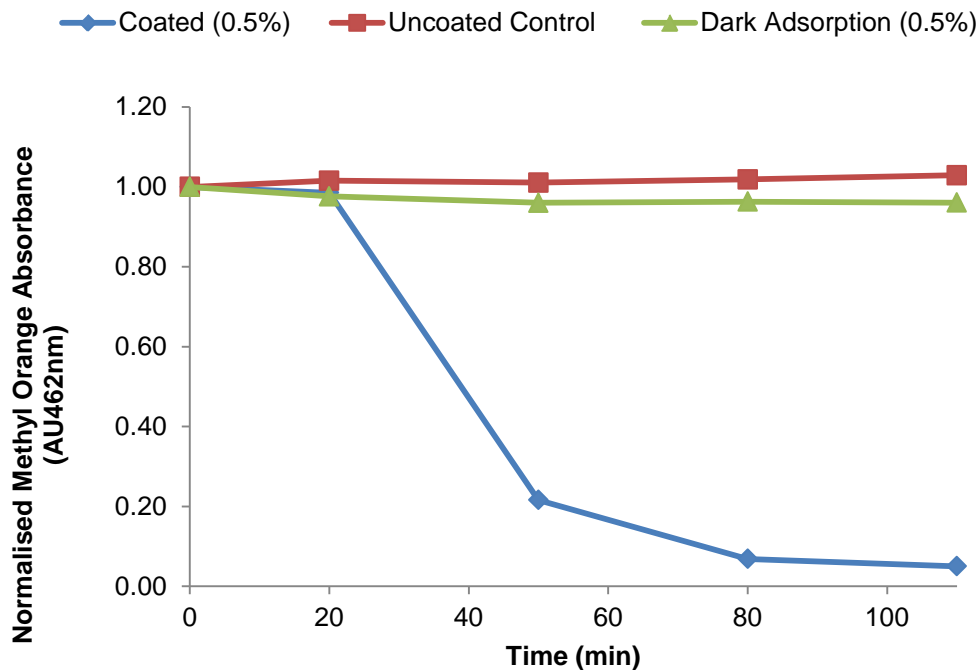


Fig. 9. Methyl Orange degradation by Immobilised Thin Film Catalyst Mini Reactor – 72W UV Illumination

It can be seen from the performance of the photocatalysts that the degradation of MO in the TFMCP was similar to the result when Deg P25 was employed, Fig. 5 & Fig. 7. In addition to a comparable overall degradation, similarities can be seen in the nature in which degradation occurs. Both the TFMCP and P25 suspended system showed a significant reduction in MO absorbance within the initial stage of illumination. After 30 min illumination 78 % and 93 % degradation was observed for TFMCP and P25 respectively. Conventional theory shows that the higher the surface area, the greater the photocatalytic activity. Recent research has shown [53] the relationship between photocatalytic activity and CO₂ reduction follows a linear path. If this were applied to this work it would be expected that in relation to P25 TiO₂ at 60 m²/g, coated beads would produce a degradation of 0.04 % and coated tubes would produce a degradation of 0.06 % using the same experimental parameters.

This is not the case, it was shown here that indeed the coated particles with a surface area of $0.24 \text{ m}^2/\text{g}$ did not produce any notable degradation, this is possibly due to the particle density. In the case of the coated tubes with a surface area of $0.04 \text{ m}^2/\text{g}$, they produced a degradation of 95 %, which compared favourable to that of P25 TiO_2 .

3.3 MO degradation (Visible irradiation)

The sol-gel coated silica beads and coated tubes were doped with the lanthanide neodymium which shifted the energy band gap into the visible light activated region while retaining the UV properties of TiO_2 .

As with the UV illumination, the first photocatalyst examined under visible irradiation, peak emissions 543 and 612 nm, was P25 TiO_2 . Figure 10 shows the 3 plots for dark control, light control and TiO_2 experiments. The controls show a 7 % variation throughout the duration of the experiment. MO degradation of 98 % in the presence of Deg P25 TiO_2 under visible light irradiation was observed.

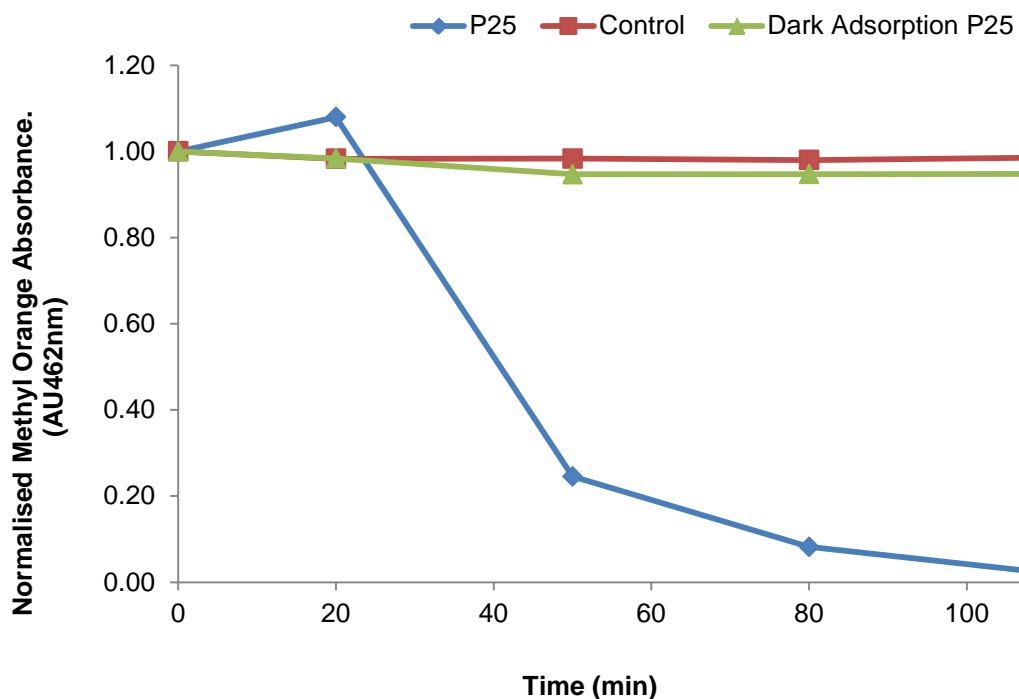


Fig. 10. Methyl Orange degradation by P25 TiO₂ – 72W Visible Illumination

As with the UV irradiation, Fig. 8, the visible irradiation of the titania sol gel coated silica beads, Fig. 11, showed little to no variation for the 3 plots of dark control, light control and coated beads experiments. The controls show no discernable variation throughout the duration of the experiment and the coated bead experiment showed a 3 % variation which is insufficient to be photocatalytic.

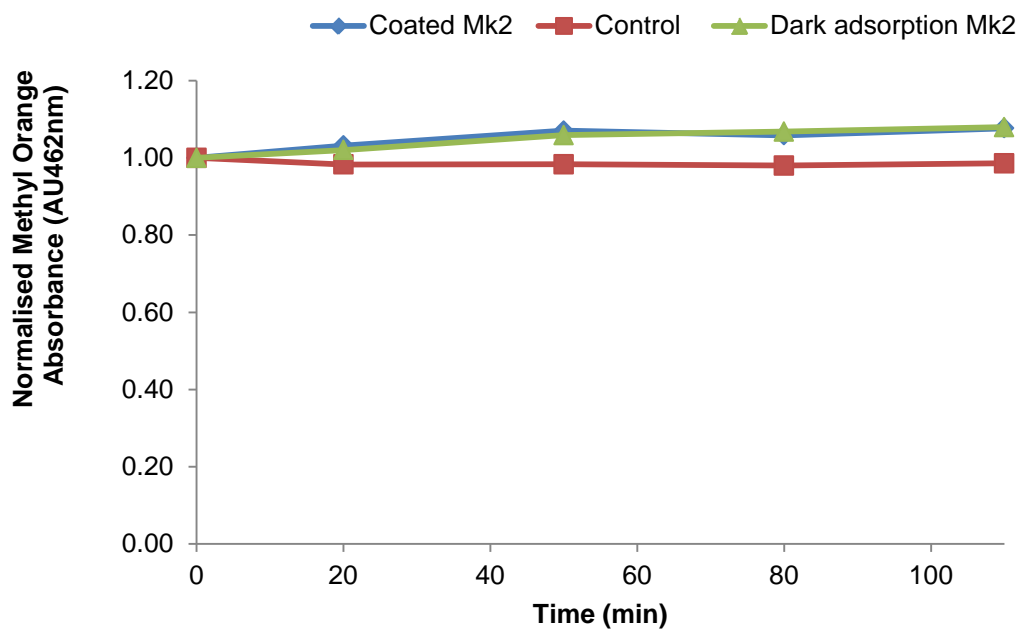


Fig. 11. Methyl Orange degradation by coated silica beads – 72W Visible Illumination

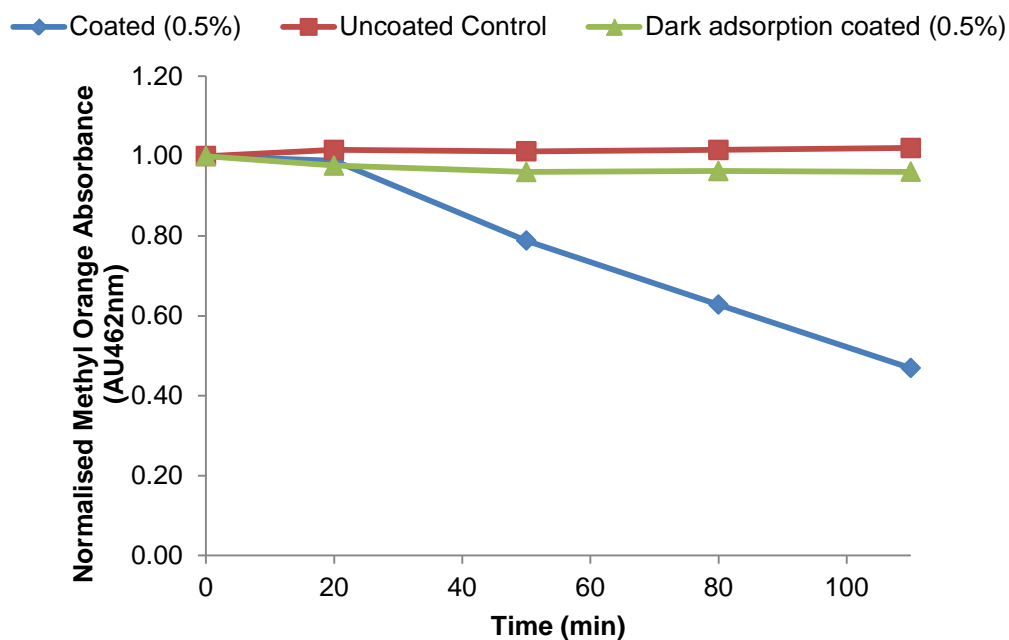


Fig. 12. Methyl Orange degradation by 0.5 % Doped Immobilised Thin Film Catalyst Mini Reactor – 72W Visible Illumination

The Titania sol gel tubes, Fig. 12, the controls show no discernable variation throughout the duration of the experiment. Degradation of 53 % for the coated tubes under visible irradiation was observed.

This experiment was repeated with 1.0 % doping, Fig. 13, the controls again show no discernable variation throughout the duration of the experiment. The observed degradation for the coated tubes under visible irradiation was 70 %. This is a ~17 % improvement over the 0.5 % doped sample and shows the improved absorbance of increasing the level of dopant. The exact same reactor configuration was employed, therefore any variation in methyl orange degradation is purely due to the catalyst and no other factor.

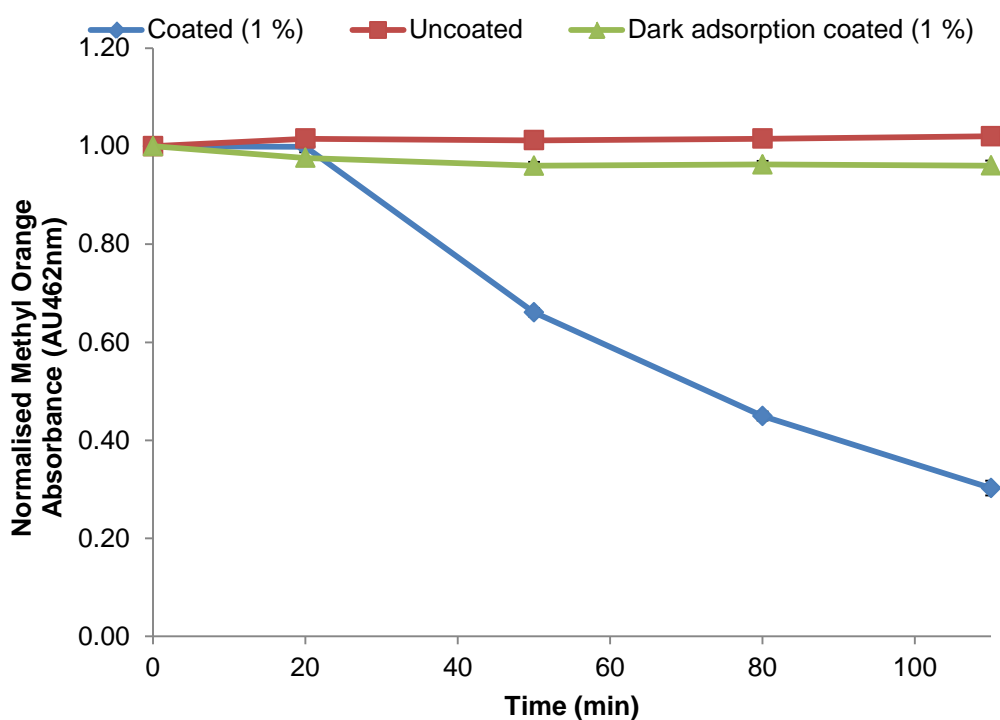


Fig. 13. Methyl Orange degradation by 1 % Doped Immobilised Thin Film Catalyst Mini Reactor – 72W Visible Illumination

It can be seen from the performance of the photocatalysts that the coated tubes produced a degradation rate slower than that of Deg P25 catalyst. Interestingly a comparable level of degradation was achieved with Deg P25 under visible light to UV light. Electrons will not be transported across the band gap of P25 by the energy provided by pure visible light [56-58]. The spectral output recorded for visible light used in this study show a low level of UV light activity thought to be sufficient to activate P25 particles, Fig. 3.

The downstream processing of the coated glass column reactor was minimal in comparison to the time consuming, expensive and unreliable downstream processing associated with P25. Prior to UV/Vis spectrometer analysis of the P25 samples filtration was performed. Separation of catalyst and reaction mixture was achieved by syringe filtration; however, this method can not provide 100 % separation due to the colloidal-like suspension created by P25. This was shown by the variation observed between standard deviation of replicates, 0.0673. This level of variation was not observed in the experimental data for experiments conducted with the coated glass tubes, standard deviation of 0.0157. Furthermore when comparing the catalyst platforms, the coated silica beads (3 %) showed minimal absorbance reduction suggesting no photocatalytic activity. Filtration of the silica beads was not required as they were large enough in size to fall out of suspension when agitation was stopped.

3.4 Surface Area Effect

Surface area is a controlling factor in photocatalysis and can significantly alter the rate of a reaction. The surface area of immobilised catalysts is often overlooked as powder provides a greater surface area for catalytic activity. However, immobilised reactor configurations which utilise the full catalyst coating and reduce mass transport limitations can be highly photocatalytically active. To achieve photocatalytic efficiency in an immobilised system mass transport limitations can be reduced via close contact of catalyst and pollutant or via the agitation of the model pollutant. The TFMCP in this investigation showed mass transport

limitations can be reduced by the use of closely packed coated columns. The configuration ensures the model pollutant is constantly in close contact with a coated surface. This increases the ease of reaction between catalyst and pollutant. Fig. 14 shows the level of degradation achieved by P25 (97 %) and the TFMCP (95 %) under UV light and the calculated surface area. Despite a significantly reduced surface area, in comparison to the suspended system, the immobilised catalyst performed within ~3 % of the P25 suspended system. For industrial applications the TFMCP can be considered to have outperformed the suspended system as no agitation or downstream processing of samples was required which reduced the overall energy consumption, cost and time frame of the reaction.

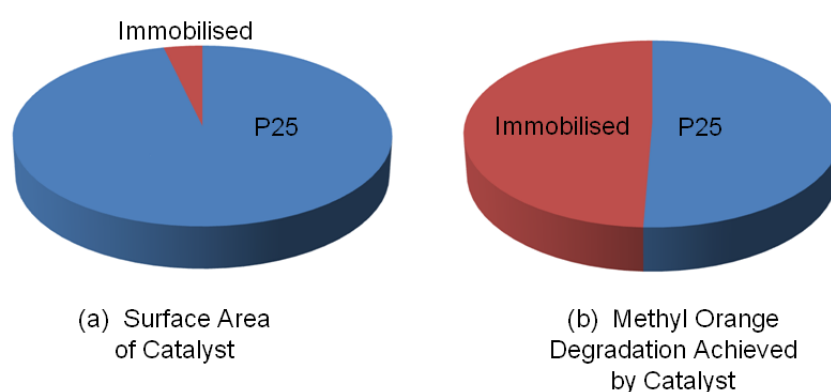


Fig. 14. Comparison of methyl orange degradation and catalyst surface area

4.0 Mini, Midi and Maxi Multi Tubular Scale Up

To examine the feasibility and ease of scale up for processing increased volumes of dye, two larger multi tubular photoreactors were created. From experience it was already known the issues relating to increasing catalyst loading, volume and energy required for agitation [32, 33, 59-

61]. Firstly a 200 mm tube reactor was created using a 250 ml measuring cylinder as the reactor vessel, secondly 260 mm tube reactor was created using a 350 ml hydrometer jar as a reactor vessel, due to the large size it was not possible to coat the inside of these vessels. The 260 mm tube size was the maximum permissible tube which could be processed in the furnace.

The results from these initial experiments into scale up are shown in Table 1, which displays the number of coated tubes, tube length, reactor volume, percentage degradation at 30 minutes and final percentage degradation at 90 minutes.

Table 1 Micro, Midi and Maxi reactor degradation rates, volume and tubes

Reactor	Reactor Volume / ml	Number of Tubes and Length/mm	Degradation at 30 mins/ %	Degradation at 90 mins/ %
Micro	20	32 x 65	78.0	94.97
Midi	120	61 x 200	53.88	91.78
Maxi	250	92 x 260	75.87	91.62

5.0 Conclusion

In conclusion it can be seen from the performance of the photocatalysts that the coated tubes produced a degradation rate similar to that of a powder catalyst under UV irradiation and a 70 % degradation under visible irradiation. The use of lanthanide doping has been investigated here in the Titania sol gel as it is thought to increase the electron hole separation. The addition of a lanthanide ion is likely to widen the absorption potential of a coating into the visible region. This was shown

to happen with 1.0 % doping and the observed 20 % improvement over the 0.5 % doped sample.

Conventional theory has shown that the higher the surface area, the greater the photocatalytic activity. The immobilised reactor configurations have shown utilisation of the full catalyst coating and therefore reduced mass transport limitations. The application of a powder catalyst in any reactor design generates sample handling issues, an inability to accurately monitor online degradation, the need to filter processed effluent streams, the possibility of introducing “super fine” TiO₂ particles to a water course. Also the environmental impact of increased energy consumption to run a suspended powder reactor unit increased the carbon footprint. These are removed completely by the development of thin film photoreactors. There is no limitation on sample monitoring, risk of suspended material discharge or unnecessary power wastage. With increased capacity it would be more than possible to compete with existing industrial scale photoreactors.

This work has demonstrated the potential to develop thin film coatings, when combined with intelligent reactor configuration, allowing a photocatalytic process comparable to that of a powdered catalyst.

6.0 Acknowledgements

The authors wish to thank the Engineering and Physical Sciences Research Council for funding project EP/H004130/1, titled International Collaboration in Chemistry Enhancing Direct Photoelectrochemical Conversion of CO₂.

Morgan Adams wishes to thank EPSRC for funding his post-doctoral post and Nathan Skillen wishes to thank EPSRC for funding his PhD research.

7.0 References

- [1] P. Yaron, *Applied Catalysis B: Environmental* 99 (2010) 448-460.
- [2] P. Pichat, J. Disdier, C. Hoang-Van, D. Mas, G. Goutailler, C. Gaysse, *Catalysis Today* 63 (2000) 363-369.
- [3] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, *Catalysis Today* 147 (2009) 1-59.
- [4] R. Dillert, Vollmer, S., Gross, E., Schober, M., Bahnemann, D., Wienefeld, J., Pahlmann, K., Schmedding, T., Arntz, H.-J., Sager, G., *Zeitschrift für Physikalische Chemie* 213 (1999) 141-147.
- [5] A. Fujishima, K. Honda, *Nature* 238 (1972) 37-38.
- [6] K.E. Karakitsou, X.E. Verykios, *J. Phys. Chem.* 97 (1993) 1184-1189.
- [7] Suzuki in, Eds. Ollis, David F., Al-Ekhabi, H. Elsevier (1993).
- [8] M.M. Taqui Khan, N. Nageswara Rao, *Journal of Photochemistry and Photobiology A: Chemistry* 56 (1991) 101-111.
- [9] M. Schiavello, *Electrochimica Acta* 38 (1993) 11-14.
- [10] M.M.T. Khan, D. Chatterjee, M. Krishnaratnam, M. Bala, *Journal of Molecular Catalysis* 72 (1992) 13-18.
- [11] C. McCullagh, J. Robertson, D. Bahnemann, P. Robertson, *Research on Chemical Intermediates* 33 (2007) 359-375.
- [12] J.C. Ireland, P. Klostermann, E.W. Rice, R.M. R M Clark, *Applied Environmental Microbiology* 59 (1993) 1668-1670.
- [13] M. Nair, Z. Luo, A. Heller, *Industrial & Engineering Chemistry Research* 32 (1993) 2318-2323.
- [14] O.R.S. da Rocha, R.F. Dantas, M.M.M.B. Duarte, M.M.L. Duarte, V.L. da Silva, *Chemical Engineering Journal* 157 80-85.
- [15] M. D'Auria, L. Emanuele, R. Racioppi, V. Velluzzi, *Journal of Hazardous Materials* 164 (2009) 32-38.
- [16] K.W. Boer, Van Nostrand, New York (1990) 1472.
- [17] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, *Environmental Science & Technology* 22 (1988) 798-806.
- [18] E.R. Carraway, A.J. Hoffman, M.R. Hoffmann, *Environmental Science & Technology* 28 (1994) 786-793.
- [19] H. Sun, S. Wang, H.M. Ang, M.O. Tade, Q. Li, *Chemical Engineering Journal* 162 (2010) 437-447.
- [20] W. Su, J. Chen, L. Wu, X. Wang, X. Wang, X. Fu, *Applied Catalysis B: Environmental* 77 (2008) 264-271.
- [21] J. Anotai, A. Jevprasesphant, Y.-M. Lin, M.-C. Lu, *Separation and Purification Technology* 84 (2012) 132-137.
- [22] Q. Chen, D. Jiang, W. Shi, D. Wu, Y. Xu, *Applied Surface Science* 255 (2009) 7918-7924.
- [23] X. Quan, Q. Zhao, H. Tan, X. Sang, F. Wang, Y. Dai, *Materials Chemistry and Physics* 114 (2009) 90-98.
- [24] Y. Zhang, H. Zhang, Y. Xu, Y. Wang, *Journal of Solid State Chemistry* 177 (2004) 3490-3498.
- [25] J.-w. Shi, J.-t. Zheng, P. Wu, *Journal of Hazardous Materials* 161 (2009) 416-422.
- [26] Q. Xiao, Z. Si, J. Zhang, C. Xiao, Z. Yu, G. Qiu, *Journal of Materials Science* 42 (2007) 9194-9199.
- [27] F.B. Li, X.Z. Li, C.H. Ao, S.C. Lee, M.F. Hou, *Chemosphere* 59 (2005) 787-800.
- [28] H.-Y. Shu, M.-C. Chang, *Journal of Hazardous Materials* 125 (2005) 244-251.
- [29] M.d.I.M. Ballari, O.M. Alfano, A.E. Cassano, *Chemical Engineering Science* 65 (2010) 4931-4942.

- [30] M. Sharma, T. Jain, S. Singh, O.P. Pandey, *Solar Energy* 86 (2012) 626-633.
- [31] S.-J. Kim, H.-G. Lee, S.-J. Kim, J.-K. Lee, E.G. Lee, *Applied Catalysis A: General* 242 (2003) 89-99.
- [32] M. Adams, Campbell, I., Robertson, P.K.J., *International Journal of Photoenergy* Volume 2008 (2008) 7 pages.
- [33] C. McCullagh, P.K.J. Robertson, M. Adams, P.M. Pollard, A. Mohammed, *Journal of Photochemistry and Photobiology A: Chemistry* 211 (2010) 42-46.
- [34] N. Bouazza, M.A. Lillo-Rodríguez, A. Linares-Solano, *Applied Catalysis B: Environmental* 77 (2008) 284-293.
- [35] N.M. Mahmoodi, M. Arami, *Journal of Photochemistry and Photobiology B: Biology* 94 (2009) 20-24.
- [36] N.M. Mahmoodi, M. Arami, J. Zhang, *Journal of Alloys and Compounds* 509 (2011) 4754-4764.
- [37] H.F. Lin, K.T. Valsaraj, *Journal of Hazardous Materials* 99 (2003) 203-219.
- [38] X. Ding, S. Zhou, L. Wu, G. Gu, J. Yang, *Surface and Coatings Technology* 205 2554-2561.
- [39] Y. Ao, J. Xu, D. Fu, C. Yuan, *Applied Surface Science* 255 (2008) 3137-3140.
- [40] R. Kavitha, S. Meghani, V. Jayaram, *Materials Science and Engineering: B* 139 (2007) 134-140.
- [41] S. Kumar, A.G. Fedorov, J.L. Gole, *Applied Catalysis B: Environmental* 57 (2005) 93-107.
- [42] M. Uzunova-Bujnova, R. Todorovska, D. Dimitrov, D. Todorovsky, *Applied Surface Science* 254 (2008) 7296-7302.
- [43] B. Zhu, L. Zou, *Journal of Environmental Management* 90 (2009) 3217-3225.
- [44] W. Zhang, Y. Li, C. Wang, P. Wang, *Desalination* 266 40-45.
- [45] T.P.T. Cushnie, P.K.J. Robertson, S. Officer, P.M. Pollard, R. Prabhu, C. McCullagh, J.M.C. Robertson, *Journal of Photochemistry and Photobiology A: Chemistry* 216 290-294.
- [46] G. Vella, G.E. Imoberdorf, A. Sclafani, A.E. Cassano, O.M. Alfano, L. Rizzuti, *Applied Catalysis B: Environmental* 96 399-407.
- [47] A. Danion, J. Disdier, C. Guillard, O. Paise, N. Jaffrezic-Renault, *Applied Catalysis B: Environmental* 62 (2006) 274-281.
- [48] V. Benz, Müller, M., Bahnemann, D.W., Weichgrebe, D., Brehm, M., *Deutsche Offenlegungsschrift DE 195 14 372 A1* (1996).
- [49] G.E. Imoberdorf, A.E. Cassano, H.A. Irazoqui, O.M. Alfano, *Catalysis Today* 129 (2007) 118-126.
- [50] M. van Well, R.H.G. Dillert, D.W. Bahnemann, V.W. Benz, M.A. Mueller, *Journal of Solar Energy Engineering* 119 (1997) 114-119.
- [51] H. Zhang, Y. Li, Q. Zhang, H. Wang, *Materials Letters* 62 (2008) 2729-2732.
- [52] H.C. Liang, X.Z. Li, J. Nowotny, *Solid State Phenomena* 162 (2010) 295-328.
- [53] F. Amano, K. Nogami, M. Tanaka, B. Ohtani, *Langmuir* 26 (2010) 7174-7180.
- [54] N. Phonthammachai, E. Gulari, A.M. Jamieson, S. Wongkasemjit, *Applied Organometallic Chemistry* 20 (2006) 499-504.
- [55] A. Mills, G. Hill, S. Bhopal, I. Parkin, S. O'Neill, *J. Photochem. Photobiol. A: Chem.* 160 (2003) 185-194.
- [56] T.A. Egerton, H. Purnama, J.A. Mattinson, *Journal of Photochemistry and Photobiology A: Chemistry* 224 31-37.
- [57] H.-x. Guo, K.-l. Lin, Z.-s. Zheng, F.-b. Xiao, S.-x. Li, *Dyes and Pigments* 92 1278-1284.
- [58] S.G. Kumar, L.G. Devi, *The Journal of Physical Chemistry A* 115 13211-13241.
- [59] P. Robertson, Campbell, I., Donnacher, R., *World Patent* (2006).
- [60] O.A. Salu, Adams, M., Robertson, P.K.J., Wong, L.S., and McCullagh, C., *Desalination and Water Treatment In Press* (2010).

[61] C. McCullagh, N. Skillen, M. Adams, P.K.J. Robertson, *Journal of Chemical Technology & Biotechnology* 86 1002-1017.