Journal of Photochemistry and Photobiology A: Chemistry 290 (2014) 63–71

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photocatalytic activity indicator inks for probing a wide range of surfaces

Andrew Mills[a,*], James Hepburn[a], David Hazafy[a], Christopher O'Rourke[a], Nathan Wells[a], Josef Krysa[b], Michal Baudys[b], Martin Zlamal[b], Hana Bartkova[b], Claire E. Hill[c], Kim R. Winn[c], Morten E. Simonsen[d], Erik G. Søgaard[d], Swagata Banerjee[e], Rachel Fagan[e,f], Suresh C. Pillai[e,g]

[a] School of Chemistry & Chemical Engineering, Queen's University Belfast (QUB), Northern Ireland, UK
[b] Department of Inorganic Technology, Institute of Chemical Technology Prague (ICT), Technická 5, Prague 166 28, Czech Republic
[c] Cristal Pigment UK Ltd., Laporte Road, Stallingborough, Grimsby, North East Lincolnshire, UK
[d] Section of Chemical Engineering, Department of Chemistry and Biotechnology, Aalborg University, Denmark
[e] Centre for Research in Engineering Surface Technology (CREST), FOCAS Institute, Dublin Institute of Technology, Kevin St., Dublin 8, Ireland
[f] School of Chemical and Pharmaceutical Sciences, Dublin Institute of Technology, Kevin St., Dublin 8, Ireland
[g] Department of Environmental Science, Institute of Technology Sligo, Sligo, Ireland

ARTICLE INFO

Article history:
Received 14 April 2014
Received in revised form 6 June 2014
Accepted 13 June 2014
Available online 21 June 2014

Keywords:
Photocatalysis
Inks
Standards
Resazurin
Acid Violet 7
Basic Blue 66

ABSTRACT

Three photocatalyst inks based on the redox dyes, Resazurin (Rz), Basic Blue 66 (BB66) and Acid Violet 7 (AV7), are used to assess the photocatalytic activities of a variety of different materials, such as commercial paint, tiles and glass and laboratory made samples of sol–gel coated glass and paint, which collectively exhibit a wide range of activities that cannot currently be probed by any one of the existing ISO tests. Unlike the ISO tests, the ink tests are fast (typically <10 min), simple to employ and inexpensive. Previous work indicates that the Rz ink test at least correlates linearly with other photocatalytic tests such as the photomineralisation of stearic acid. The average time to bleach 90% of the key RGB colour component of the ink, red for Rz and BB66 inks and green for AV7 ink, is determined, *ttb*(90), for eight samples of each of the different materials tested. Five laboratories conducted the tests and the results revealed an average repeatability and reproducibility of: ca. 11% and ca 21%, respectively, which compare well with those reported for the current ISO tests. Additional work on commercial self-cleaning glass using an Rz ink showed that the change in the red component of the RGB image of the ink correlated linearly with that of the change of absorbance at 608 nm, as measured using UV/vis spectroscopy, and the change in the a* component of the Lab colour analysis of the ink, as measured using diffuse reflectance spectroscopy. As a consequence, all three methods generate the same *ttb*(90). The advantages of the RGB digital image analysis method are discussed briefly.

1. Introduction

A number of different ISO tests have been developed to date to assess the activities of photocatalytic surfaces, however, most, if not all, are only able to probe a limited range of activities [1]. For example, the methylene blue (MB) test, ISO 10678:2010, is appropriate for moderately active materials, like most examples of commercial self-cleaning/easy clean glass, but is of little use for assessing the high activity, materials, like thick sol–gel titania films on glass, or photocatalyst paper and paints, due to the low diffusion coefficient of MB in solution [1,2]. Nor is the MB test effective in probing the efficacy of low activity materials, such as most commercial photocatalytic tiles, due to the low, but measurable UV photo-instability of MB [2]. The ISO air purification tests, such as the ones based on the removal of: NO*x* (ISO 22197-1), acetaldehyde (ISO22197-2) or toluene (ISO 22197-3:2011), are very good for assessing high (but not very high) activity, flat, non-porous materials [1], but poor for exploring the activities of moderately active flat, non-porous materials, such as self-cleaning glass, due to the high flow rates and low pollutant concentrations used [1]. In addition to the above, all of the ISO tests are slow (typically of 3–5 h duration) and require expensive analytical equipment and technical support [1]. Clearly, it would be desirable if a test method could be identified which was able to probe, simply, rapidly and cheaply, the wide range of

* Corresponding author. Tel.: +44 02890974339.
E-mail address: andrew.mills@qub.ac.uk (A. Mills).

http://dx.doi.org/10.1016/j.jphotochem.2014.06.007
1010-6030/

activities exhibited by the many different photocatalytic surfaces that are available currently, such as those found in the areas of commercial tiles, paints and glass.

In a recent paper we reported on a simple, inexpensive method for the rapid testing of the photocatalyst activity of self-cleaning surfaces of moderate activity, such as commercial self-cleaning glass [3]. In that paper, a photocatalyst activity indicator ink was used, comprising a dye, Resazurin (Rz), a sacrificial electron donor (i.e. SED, e.g. glycerol) and a polymer, hydroxyl ethyl cellulose (HEC) to encapsulate the dye and SED, when the ink had dried. This ink functions via a photo-reductive mechanism summarised by reactions (1)–(3), where SC is the underlying semiconductor photocatalyst film onto which the ink film is placed and allowed to dry, D_{ox} is the dye in its original, and usually highly coloured (oxidised) form (blue in the case of Rz) and D_{red} is the reduced, and differently coloured, form of the dye (pink in the case of Rz, but colourless for the other dyes used in this work).

$$SC \xrightarrow{hv>E_{bg}} SC*(h^+, e^-) \quad (1)$$

$$SED + SC*(h^+, e^-) \rightarrow SED_{ox} + SC(e^-) \quad (2)$$

$$SC(e^-) + D_{ox} \rightarrow D_{red} \quad (3)$$

E_{bg} is the band gap energy of the semiconductor, which is almost always titania, often in its anatase form (and so E_{bg} =ca. 3.2 eV), and SED and SED_{ox} are glycerol and glyceric acid/glyceraldehyde, respectively. Previous work reveals that the rate of the above, Rz ink-based, photocatalyst driven process, is directly correlated with the much slower destruction of a film of stearic acid (SA) on photocatalyst films on glass [4].

Following on from the above work, in this paper this same simple method has been expanded, and now uses not only the Rz ink but also two other different photocatalyst activity inks, so as to be able to assess the activity of a number of different flat, smooth, largely non-porous photocatalytic materials, such as glass, paint and tiles, which collectively exhibit a wide range of photocatalytic activities.

2. Experimental

2.1. Chemicals and materials

All chemicals were purchased from Sigma–Aldrich and, unless otherwise stated, were used as received. The water used to produce all inks was double distilled and deionised. The commercial self-cleaning glass used to test the ink was BioClean® supplied by Saint-Gobain, the commercial photocatalytic tiles were from Deutsche Steinzeug and the commercial, fast, photocatalytic paint (StoClimasan Color) was purchased from Sto Ltd. The 'fast' glass photocatalyst samples were prepared, by ICT, using a sol–gel technique according to a previously reported method [5] and the medium activity paint was prepared by QUB, by mixing 5% (by volume) of a highly active photocatalytic paint based on PC50 anatase titania, with one that exhibits no activity, with both paints being provided by Cristal. Coated samples of these medium and high activity paints were made using a No. 4 K-bar – a wire-wound rod – (delivering a wet coating of 40 μm) to draw-down a layer of paint to cover a glass microscope slide, 26 mm × 76 mm. All paint-coated samples were then left to dry in the dark under ambient conditions for 30 min and used without any further treatment.

2.2. Preparation of the photocatalyst medium activity indicator ink: the Resazurin ink (Rz)

The Rz ink was made by dissolving 0.15 g HEC (CAS No.: 9004-62-0; viscosity: 145 mPa s for 1 wt% solution in water) into 9.85 g high purity (conductivity ≤2 μS cm^{-1}) water to give a solution of 1.5 wt%. 1 g of glycerol was then added to this polymer solution, followed by 10 mg of Rz, (CAS No.: 62758-13-8; purity 75%) and 20 mg of the surfactant, polysorbate 20 (CAS No.: 9005-64-5). The ink was stirred with a magnetic stirrer for a minimum of 8 h and then stored in a fridge. The ink was used within 2 weeks of its preparation but, each time, before its application, it was removed from the fridge and stirred on a magnetic stirrer at room temperature for 1 h.

2.3. Preparation of the photocatalyst low activity indicator ink: the Basic Blue 66 ink (BB66)

The procedure for making the BB66 ink was identical to that for the Rz ink, except 50 mg of BB66 (CAS No.: 94233-04-2; purity 20%) were used in place of the Rz.

2.4. Preparation of the photocatalyst high activity indicator ink: the Acid Violet 7 ink (AV7)

The procedure for making the AV7 ink was identical to that for the Rz ink, except 25 mg of AV7 (CAS No.: 4321-69-1; purity: 40%) were used in place of the Rz.

The structures of the three redox dyes, i.e. Rz, BB66 and AV7 are illustrated in Fig. 1.

2.5. Sample size, number and pre-treatment

The materials under test were cut into ca. 25 mm × 25 mm squares and 8 samples used for each test. The ink tests are ideal for testing samples in almost any condition although, usually, this will be preferably in a pristine (i.e. usually very clean) form. In order to achieve the latter state, a cleaning protocol will usually have been performed, such as: a thorough wiping with a water-soaked cloth (to remove any dirt) followed by 15–24 h irradiation with UVA light, as is recommended by most of the existing ISO photocatalyst test methods [1]. However, the ink tests can also be used to probe the activities of samples in a variety of different states, such as: contaminated, aged or weathered. As a consequence, in order to assess correctly the activities associated with such samples, of what is otherwise the same material, little or no pre-treatment is recommended to form part of the test per se, although details of the sample, its source and any pre-conditioning applied to the sample before the test, should form part of any report made by the tester on the photocatalytic activity of the sample of the material tested. Thus, in this work, most of the materials were cleaned only by wiping lightly with a water-soaked, silicone-free, tissue and then allowed to dry for 60 min in the dark under ambient conditions. In the case of the paint samples, however, which had surfaces that were more easily damaged than those of the tile and glass samples, no pre-treatment was used.

2.6. Coating the sample with the ink

In order to coat a ca. 25 mm × 25 mm sample with a photocatalyst activity indicator ink, it was secured to an impression bed (i.e. a clipboard) and a line of ink ca. 2.5 cm long deposited along the length of the top (but ca. 3 mm from the top) of the sample, using a pipette. The typical amount of ink delivered in this way was ca. 65 μL. A wire wound rod (K-bar No. 3) was then used to spread/coat the ink onto the sample by drawing the bar down from the top of the sample (just above where the line of ink was deposited) to the bottom, using sufficient pressure on the bar to ensure the spiral wire remains in contact with the sample throughout the drawdown process, but not so much that the K-bar is bowed during the drawdown process, which produces an uneven coating. This process was then repeated for the other seven samples of the material under test and