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Three-phase photocatalysis using suspended titania and titania supported on a reticulated foam monolith for water purification

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Abstract

This paper presents the first results on the performance of a pilot-scale photocatalytic oxidation reactor having a TiO_2-coated 15 pores-per-inch (15 PPI) alumina reticulated foam monolith installed in the annular space between a centrally installed 1 kW UV lamp and the internal wall of the reactor. Photocatalytic oxidation of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in water was chosen as a test reaction to evaluate the performance of the new reticulated foam photocatalytic reactor and to compare its photocatalytic efficiency with that of the same reactor but with the same mass concentration of TiO_2 suspended in water as slurry catalyst. The reticulated foam monoliths were spray-coated with 10 and 12 wt.% Degussa P25 TiO_2 (equivalent to 18.58 and 21.78 g/L of water, respectively, in suspension). Results were analyzed in terms of overall DBU conversion, TOC conversion, initial reaction rates per unit reactor volume, photonic efficiency and overall process economics. For the test reaction above, results indicate that the 12 wt.% TiO_2-coated reticulated foam photocatalytic reactor was more efficient compared to the reactor using equivalent TiO_2 slurry, with DBU conversion of 100%, TOC conversion of approximately 23% and quantum yield of 3.8 (–) achieved in 60 min. The results clearly suggest that immobilised TiO_2 could be a cost-effective method that should be taken further to large-scale water purification using heterogeneous photocatalysis.

Keywords: Cocurrent downflow contactor; Photocatalysis; Kinetics; Reticulated foam monolith; TiO_2; Photocatalytic reactor

1. Introduction

The purification or treatment of contaminated or waste water by heterogeneous photocatalytic oxidation has been an increasingly interesting subject of research for the last 20 years due to its potential as a viable alternative to other advanced oxidation processes [1–6]. Titanium dioxide (TiO_2) Degussa P25 is the most commonly used photocatalyst due to its advantages over other known photocatalysts and has often been proposed for the degradation of pollutants in water or air [7].

The majority of published work on heterogeneous liquid phase photocatalysis has reported the use and efficiency of aqueous suspensions of TiO_2. However, downstream separation of the nano-size Degussa P25 TiO_2 from the treated water and the recycling of the photocatalyst have proved very difficult and uneconomical, especially with waste waters [8].

Due to the problems mentioned above, there has been an increase in research into immobilisation of TiO_2 on solid supports to eliminate the difficult separation and recycling of catalyst, thus improving the process economics. A literature review of reactor configurations tabulating photocatalytic research using slurry reactors and immobilised catalyst reactors can be found in [9], while a literature review tabulating methods of immobilisation of TiO_2 and support substrates coated can be found in [10,11]. Some researchers have reported that the efficiency of the slurried photocatalyst is larger than the supported form [8,10,12] while others have reported that the catalytic activity of TiO_2 is not affected when it is immobilised [13]. A direct and precise comparative assessment of the performance of reactors using suspended TiO_2 and

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immobilised TiO_2 particularly on the basis of actual mass concentration of TiO_2 immobilised on the support or in suspension is often hard to find in the open literature.

This work was carried out to develop an efficient photocatalytic support that can be used to eliminate persistent, non-biodegradable and toxic pollutants contained in waste or contaminated waters. The aim is to precisely compare the efficiencies of TiO_2 Degussa P25 in aqueous suspension and the same TiO_2 Degussa P25 immobilised on an inexpensive, custom-made 15 PPI reticulated foam monolith as a new photocatalytic support for pilot-scale water treatment. Only a few researchers [14–18] have carried out related photocatalytic studies using 10, 20 and 30 PPI reticulated foams but only for the gas phase oxidation of volatile organic compounds on a bench scale. This paper presents the first data on the use and precise assessment of the performance of a 15 PPI reticulated foam monolith for water treatment on a pilot-scale. The study was carried out using 1,8-diazabicyclo[5.4.0]undec-7-ene, also known as DBU, as a model substrate. DBU, a nitrogen-containing compound and a tertiary amine, is a recalcitrant compound present in waste water produced from pharmaceutical processes. The release into the environment as well as into surface water is possible during manufacturing processes; hence it is very important to develop the treatment technology for DBU urgently [19].

Reticulated foam monoliths are a family of materials whose light weight, flow through properties are easily customised to meet design requirements of reactor catalyst support. They exhibit a three-dimensional pore structure with versatility of shape, pore size, permeability, surface area and chemistry. A desirable property of reticulated foams is their high bed porosity which results in a much lower pressure drop in a reactor. In addition, and unlike honeycomb monoliths, reticulated foam monoliths have a tortuous pore structure which enhances intense turbulence and mixing [20]. The aim of this work, in addition to comparing the efficiency of TiO_2-coated reticulated foams with suspended TiO_2, is to show how randomly structured catalysts can improve the efficiency of a photocatalytic reactor and minimise or remove waste or by-products.

2. Experimental work

2.1. Experimental set-up: the cocurrent downflow contactor reticulated foam photocatalytic reactor (CDC-RFPR)

All experimental work was carried out using a pilot-scale cocurrent downflow contactor reticulated foam photocatalytic reactor (CDC-RFPR) having a total system volume of 15 L. However, in comparative experiments using suspended TiO_2 the reticulated foam monolith was removed from the reactor converting it to a ‘slurry mode’ photocatalytic reactor. In all cases, the outer wall of the photocatalytic reactor consists of a standard QVF glass tube with internal diameter 0.1 m while the inner wall is a replaceable Pyrex sleeve (external diameter 0.0465 m, length approximately 0.5 m) mounted axially at the centre of the reactor. The annular photocatalytic reaction zone was 0.5 m long and the irradiated volume was 4.0 L. A TiO_2-coated custom-made 15 pores-per-inch (15 PPI) alumina reticulated foam monolith was installed in the annular space between a centrally installed 1 kW UV lamp and the internal wall of the reactor. The schematic diagram of the CDC-RFPR is shown in Fig. 1A while Fig. 1B is the photographic illustration of the photocatalytic reactor. UV radiation was provided by a UVA 1 kW Hanovia medium pressure lamp, which provides a maximum emission at 365 nm. Oxygen and liquid streams are introduced co-currently and downwards through an orifice in the entry zone at the top of an oxygen/air absorption column (QVF glass tube, diameter 0.05 m and length 0.5 m). A 5 mm orifice plate is attached to the underside of a metal cap fitted to the top of this glass column. In this column, the energy and turbulence due to a high-velocity gas–liquid jet causes efficient mass transfer of oxygen into the liquid phase and a close approach to equilibrium of the gas and liquid phase (approximately 97%) is typical of this section of the reactor [21]. The reactor was operated in a recirculation batch mode, where liquid stream containing reactants is re-circulated back into a well mixed recirculation reservoir with the aid of a centrifugal pump. A thermocouple inserted into the reaction zone through the CDC cap monitors the reaction temperature while a cooling coil inserted into the reservoir controls the reaction temperature, keeping it at 50 °C.

TiO_2 Degussa P25 (80% anatase, 21 nm primary particle size and $55 \pm 15\ m^2/g$ specific surface area) was used for all photocatalytic reactions.

2.2. The reticulated foam monoliths and preparation of the coatings

Two 15 PPI (15 pores per inch) alumina reticulated foam monoliths were custom fabricated by Vesuvius (Hi-Tech Ceramics), Alfred, NY, USA. The annular shaped monoliths, with external diameter of 86 mm, internal diameter of 66 and 450 mm high, were designed to fit perfectly into the annular space between the vertically and centrally positioned UV lamp and the internal wall of the photocatalytic reaction zone. This allows the gas and liquid stream to flow downwards through the irradiated annular space between the internal wall of the monolith and the external wall of the UV lamp. The reticulated foam monoliths were coated by Johnson Matthey Catalysts using a customised spray-coating technology. This method was chosen to ensure uniform anchoring of the catalyst (TiO_2) onto the surface of the reticulated foam monoliths. TiO_2 Degussa P25 was made into slurry with ultra pure (Millipore) water (18.58 or 21.78 g of TiO_2 per litre of water corresponding to 10 or 12% solids). Prior to coating, the foams were dried at 105 °C for 2 h and weighed. The wash coat slurry was then sprayed onto the foams to achieve a uniform coating and a loading of 10 or 12 wt.% TiO_2 on the foams. The foams were then dried at 120 °C for 2 h and then calcined at 500 °C overnight. The catalyst loading was determined by calculating the difference in weight before and after coating.

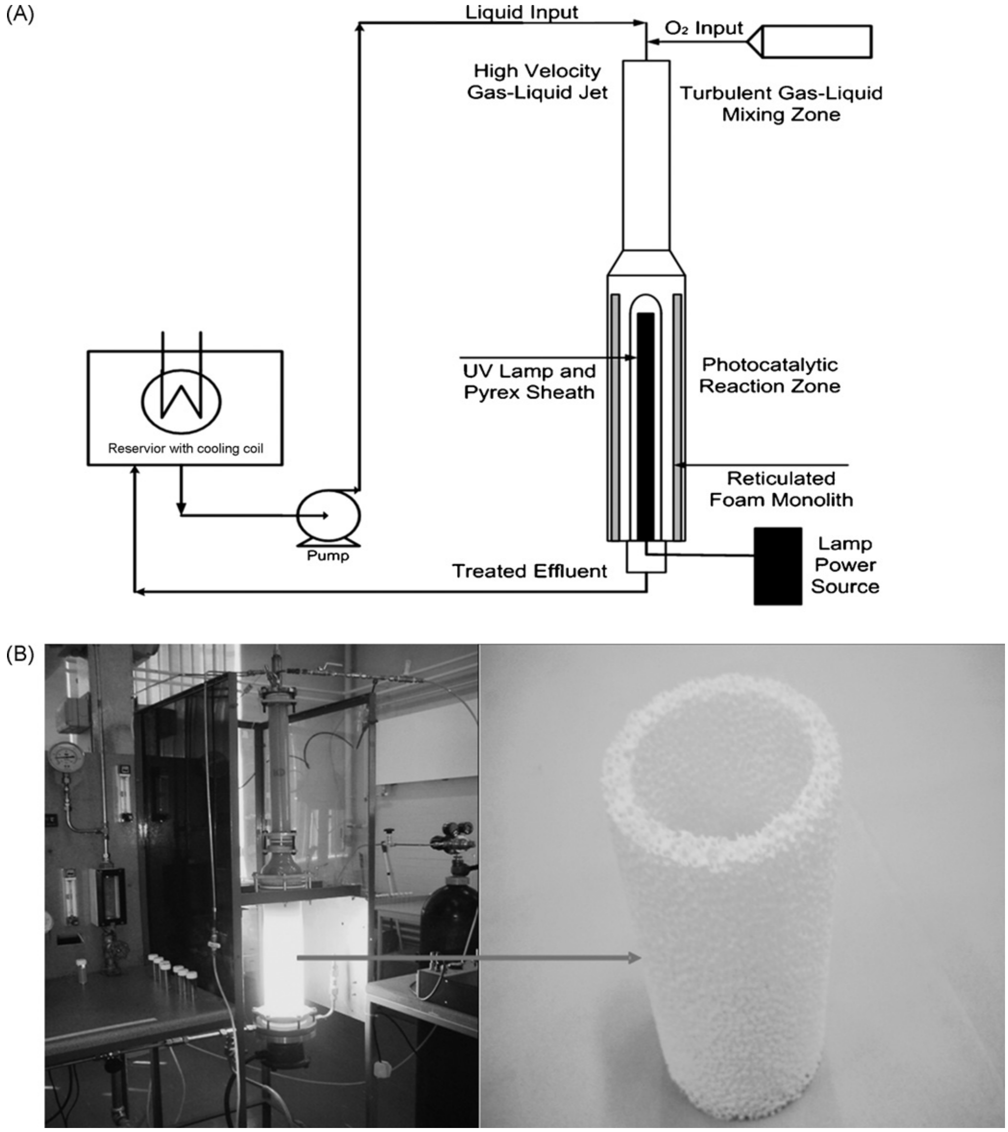

Fig. 1. (A) Process scheme of the experimental set-up used for the photocatalytic work and (B) photograph of the photocatalytic reactor showing the 15 PPI reticulated foam monolith.

2.3. Experimental procedure-reactions with suspended TiO_2

TiO_2 suspensions with equivalent weight of catalyst as loaded on the reticulated foams were prepared in deionised water by mixing TiO_2 with 15 L solution containing about 100 mg/L (0.6×10^{-3} mol/L) of DBU. The equivalent catalyst weight to the reticulated foams was selected to provide a scientific basis for comparison of the two cases. Further investigation of the effect of catalyst concentration in the slurry reactor including optimisation of photocatalyst concentration for DBU oxidation has already been published [19]. In the current study irradiation was started after the suspensions had been equilibrated in the dark for 30 min with constant mixing and oxygen sparging. The time, temperature, pH, initial concentration and total organic carbon (TOC) of initial suspension were recorded. Samples were also taken from the reactor effluent subsequently (0.02 L) at 15 min interval for analysis. The pH of the solution was unaltered; no buffer was added to control the pH. Temperature was kept constant at 50 °C using cooling water flowing through the cooling coil inserted into the reservoir. The samples were filtered using 0.45 μm nylon filters to remove the catalyst prior to analysis.

2.4. Reactions with immobilised TiO_2

For the reactions using immobilised TiO_2, the TiO_2-coated foams were installed in the photocatalytic reaction zone instead of using slurried TiO_2. The mass concentration of the TiO_2 on the foams was the same as the mass concentration of TiO_2 used for the slurry reactions. This was to ensure direct and precise comparative assessment of the performances of the reactions with immobilised or suspended photocatalyst. All reaction conditions, protocols, and analysis observed for the slurry reaction were repeated for the reactions with immobilised TiO_2. The only difference was the TiO_2 fixed on the foams instead of

TiO_2 in suspension. Experiments were repeated under the same conditions after 10 working days and deactivation or stripping of TiO_2 from the support was found to be negligible. The influence of photocatalyst weight deposited on the reticulated foam monoliths on DBU conversion (primary degradation and mineralisation) was investigated.

2.5. Materials characterisation

The photocatalyst, TiO_2 Degussa P25, was supplied by Degussa. Characterisation was performed using Dynamic Vapour Sorption (DVS-1 automated gravimetric vapour sorption analyser, Surface Measurement Systems Ltd.). To determine the surface morphologies of the reticulated foam monoliths, the uncoated and coated foams were sputter coated with platinum and viewed in a Jeol 7000F field emission SEM using 10 kV acceleration voltages. The foams were also studied for internal defects using Skyscan X-ray micro-tomography (Skyscan 1072 software). Image analysis of the reticulated foams was also carried out to study the pore structure of the foams, using a Sony DSC-T9 digital camera with an optical magnification of 4 and a 640 × 480 VGA image size. The procedure reported by Richardson et al. [20] was followed for the image analysis using Jandel SigmaScan software to detect individual pore areas.

2.6. Reagents

All chemicals for the experiments and analysis were used as received without further purification. DBU (98%) was supplied by Aldrich. Oxygen (99.5%) and helium were supplied by BOC gases. HPLC grade acetonitrile, water and trifluoroacetic acid (TFA) were supplied by Fisher. Deionised water (Millipore) was used to prepare all chemical solutions.

2.7. Analysis

Samples collected at 15 min time intervals were promptly analyzed to follow the degradation of DBU, using an Agilent 1100 series High Performance Liquid Chromatograph (HPLC) system fitted with a UV detector and autosampler. The HPLC system was operated in isocratic mode using the following analytical method: acetonitrile–water (20–80%) as a mobile phase, mobile phase flow rate of 1 mL/min, column temperature of 40 °C, phenomenex Luna 10μ Phenyl-Hexyl, 4.6 mm × 250 mm column, UV detector at 230 nm and an injection volume of 5 μL. The course of mineralisation of DBU to carbon dioxide was followed using a Shimadzu Total Organic Carbon analyser (TOC-5050A with ASI-5000A auto-sampler).

2.8. Light intensity and photon flux

The UV radiation flux from the lamp was measured with a spectrometer (Horiba Jobin Yvon, Edison, NJ, SPEX 1680 double spectrometer with 5 nm bandwidth) fitted with a 365 nm UV detector. With the Pyrex tube in the reactor cutting off radiation below 300 nm, 365 nm was detected as the most effective wavelength.

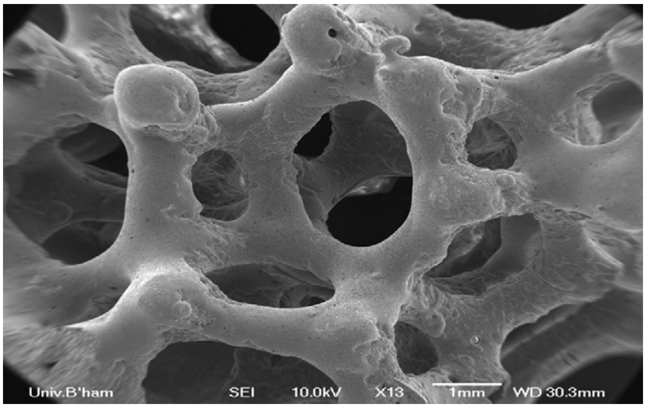

Fig. 2. SEM micrograph of a selected area of an uncoated reticulated foam monolith showing the unique pore structure of a 15 PPI, 99.5 wt.% α-Al_2O_3 reticulated foam monolith.

3. Results and discussion

3.1. Characterisation of the TiO_2-coated reticulated foam monoliths—SEM

Fig. 2 shows an SEM micrograph of a selected area of an uncoated reticulated foam monolith showing the unique pore structure of a 15 PPI, 99.5 wt.% α-Al_2O_3 reticulated foam monolith while Fig. 3 shows the surface morphology of the TiO_2-coated and uncoated reticulated foam monoliths as revealed by scanning electron microscopic examination. The spray coating resulted in uniform wash coat loading, as indicated by visual and microscopic analysis. To determine the long-term stability of the coating, liquid recirculation was also carried out for 1 h prior to reactions using the TiO_2-coated reticulates, to check for TiO_2 stripping. This was found to be negligible as TiO_2 particles were not found in samples withdrawn from the reactor. The spray-coated monoliths resulted in a uniform, non-fractured appearance and a large surface area for efficient photocatalytic reaction (Fig. 3). Characteristic properties of the reticulated foam monoliths studied here are as follows: 99.5 wt.% α-Al_2O_3 reticulated foam monolith without washcoat (BET surface area 0.2 m^2/g, pore diameter d_p 1.2 mm, bulk density 0.6 g/cm^3, bulk porosity 0.871); reticulated foam monolith with 10 wt.% TiO_2-washcoat (BET surface area 0.5 m^2/g, pore diameter d_p 0.85 mm, bulk density 0.613 g/cm^3, bulk porosity 0.893); reticulated foam monolith with 12 wt.% TiO_2-washcoat (pore diameter d_p 0.79 mm, bulk density 0.635 g/cm^3, bulk porosity 0.887).

3.2. Comparative photocatalytic transformation rates and photonic efficiencies of DBU on suspended TiO_2 and TiO_2 immobilised on reticulated foam monoliths

In order to evaluate the photocatalytic efficiency of TiO_2 immobilised on a reticulated foam monolith, photocatalytic transformation of solutions of the same concentration (6.801×10^{-4} mol/L) of DBU were carried out using 10 and 12 wt.% TiO_2-coated reticulated foam monoliths and the equivalent mass concentration of TiO_2 (18.58 and 21.78 g/L,

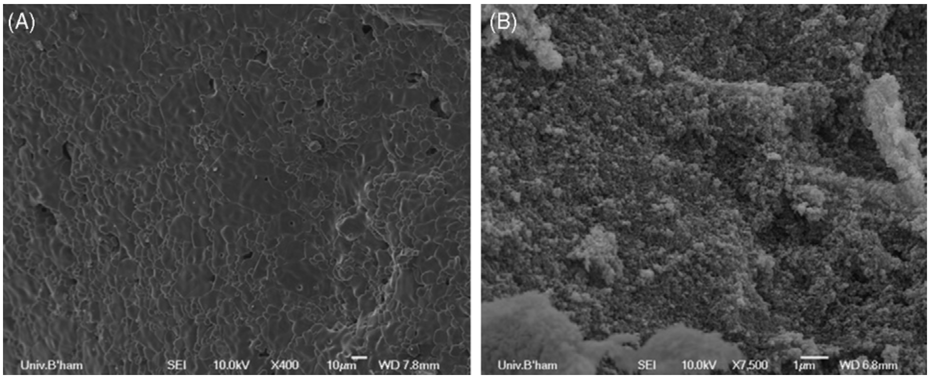

Fig. 3. SEM micrographs of selected areas of (A) uncoated 15 PPI reticulated foam monolith and (B) coated 15 PPI reticulated foam monolith.

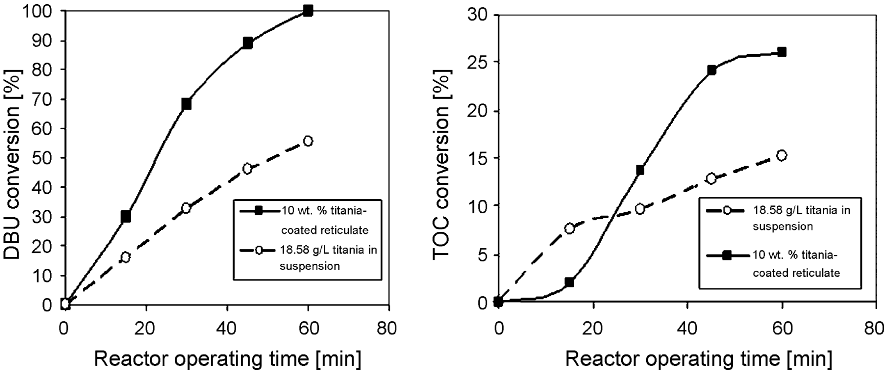

Fig. 4. Comparative photocatalytic conversion of DBU and TOC with TiO_2 P25 (18.58 g/L suspension) and 10 wt.% TiO_2-coated reticulated foam monolith. Experimental conditions: 50 °C, liquid circulation rate 10 L/min, O_2 flow rate 0.1 L/min, initial DBU concentration 0.6801×10^{-3} mol/L.

respectively) used in slurry mode. Results for all cases were evaluated in terms of percentage conversion for the primary degradation of DBU, TOC mineralisation and photonic efficiency. From the results shown in Figs. 4 and 5, complete conversion of DBU was achieved from reactions using the 10 and 12 wt.% TiO_2-coated reticulates in 60 min compared with 56 and 41% conversion of DBU in the same time from reactions using 18.58 and 21.78 g/L of TiO_2 in suspension, respectively. Also, TOC conversion for the 10 and 12 wt.% TiO_2-coated reticulates were 26 and 23%, respectively, after 60 min compared with TOC conversion of 15 and 10% for reactions using 18.58 and 21.78 g/L of TiO_2 in suspension, respectively.

Fig. 6 displays the TOC conversion over a longer reaction time of 120 min; final TOC conversions for the 10 and 12 wt.% TiO_2-coated reticulates were 55.64 and 53.58%, respectively, demonstrating that higher TOC conversions were obtained by extending the reaction time further than 60 min. The complete oxidation of organic carbon to CO_2 is a slow process in comparison with primary degradation of the initial DBU [19] and this is illustrated by the longer time taken to achieve over 50% TOC conversion using both TiO_2-coated reticulates. From this precise assessment and comparison in terms of actual DBU conversion and TOC conversion, it is clear that for the reactions carried out using TiO_2 immobilised on reticulated foam

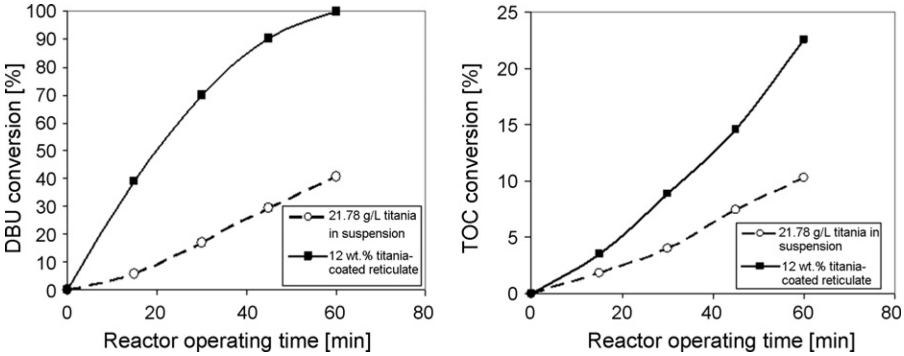

Fig. 5. Comparative photocatalytic conversion of DBU and TOC with TiO_2 P25 (21.78 g/L suspension) and 12 wt.% TiO_2-coated reticulated foam monolith. Experimental conditions: 50 °C, liquid circulation rate 10 L/min, O_2 flow rate 0.1 L/min, initial DBU concentration 0.6801×10^{-3} mol/L.

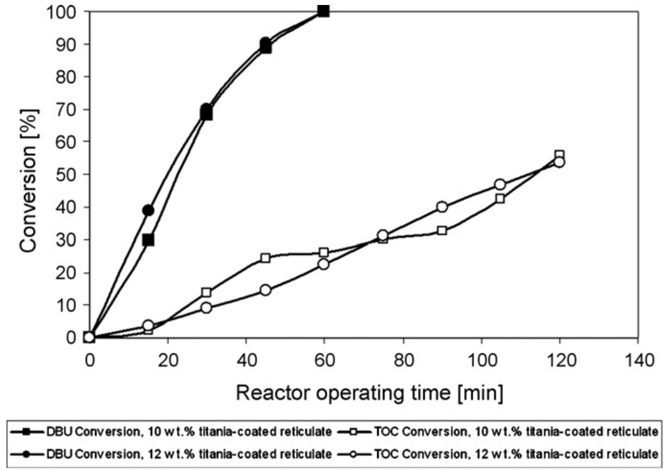

Fig. 6. Comparative photocatalytic conversion of DBU and TOC with 10 and 12 wt.% TiO_2-coated reticulated foam monolith. Experimental conditions: 50 °C, liquid circulation rate 10 L/min, O_2 flow rate 0.1 L/min, initial DBU concentration 0.6801×10^{-3} mol/L.

monoliths DBU was destroyed more quickly than the reactions carried out using the same mass concentration of TiO_2 in suspension. Comparing the performance of the 10 and 12 wt.% TiO_2-coated reticulated foam monoliths, Fig. 6 shows complete conversion of DBU was achieved from reactions using both 10 and 12 wt.% TiO_2-coated reticulated foam monolith in 60 min while TOC conversions from both reactions were 10 and 23%, respectively. Therefore, the 12 wt.% TiO_2-coated reticulated foam monolith was more effective.

It is noted here that the performance of the slurry reactor may be improved if the catalyst concentration is optimised. The effect of slurry catalyst concentration was studied, and it was found that 100% DBU conversion occurred after 45 min for the optimal catalyst loading of 0.5 g/L TiO_2. Although the optimal catalyst loading in slurry mode leads to a faster conversion than the reticulated foam catalysts, the slurry process suffers from the considerable additional cost of downstream catalyst separation, which is avoided by the use of reticulated foams.

The efficiencies of all cases above were also compared in terms of photonic efficiency, ϕ. Photonic efficiency, an efficiency indicator for photocatalytic processes, has been calculated for the experiments above, using [22]:

$$\phi = \frac{(\mathrm{d}C_0/\mathrm{d}t)V_\mathrm{T}}{I_0} \tag{1}$$

where $\mathrm{d}C_0/\mathrm{d}t$ is the initial DBU transformation rate (3.1365×10^{-7} mol/(L s) for the reaction using 10 wt.% TiO_2-coated reticulate, 3.3205×10^{-7} mol/(L s) for the 12 wt.% TiO_2-coated reticulate, 1.4266×10^{-7} mol/(L s) for the reaction using 18.58 g/L TiO_2 in suspension and 5.2768×10^{-8} mol/(L s) for the reaction using 21.78 g/L TiO_2 in suspension). V_T is the total system volume (13.92 and 13.73 L, respectively, for the reactors fitted with the TiO_2-coated reticulates and 15 L for reactors using TiO_2 in suspension). I_0 is the amount of incident active photons per unit of time (einstein s^{-1}). I_0 is the same for all reactions reported in this work because it is related to a standard process where the same UV lamp was used for all experiments. The value of I_0 (1.20×10^{-6} einstein s^{-1}) was determined using a spectrometer reported under Section 2. From the results, the photonic efficiency for reactions carried out using 10 and 12 wt.% TiO_2-coated reticulates are 3.6 and 3.8, respectively, while the photonic efficiency for the reactions carried out using 18.58 and 21.78 g/L TiO_2 slurries are 1.8 and 0.7 (–), respectively, confirming that the reactions using the TiO_2-coated reticulates outperformed the reactions using equivalent mass concentration of TiO_2 in suspension. The photonic efficiency for the reaction using 10 wt.% TiO_2-coated reticulate was two times the value for the reaction using 18.58 g/L TiO_2 slurry while the value for the 12 wt.% TiO_2-coated reticulate was five times the value for the reaction carried out using 21.78 g/L TiO_2 slurry, showing significant differences which will impact on the economics of the photocatalytic treatment method as well as the reactor configuration (slurry mode or immobilised photocatalyst mode). However, there was no significant difference between the values calculated for reactions carried out using the TiO_2-coated reticulates.

3.3. DBU reactivity, kinetics analysis and kinetic models using the reticulated foam monoliths

Fig. 7 shows the comparative degradation of DBU using 10 and 12 wt.% TiO_2-coated reticulated foam monoliths and their equivalent mass concentration in suspension. The higher DBU conversion by the 12 wt.% TiO_2-coated reticulate suggests an increased reaction rate due to higher TiO_2 load on the reticulate as compared to the performance of the 10 wt.% reticulate. Expectedly, the performance of the reticulate in DBU degradation increases with increased catalyst weight. The reticulated foam photocatalytic reactor uses a batch of catalyst (fixed bed) to treat a batch of fluid. In this system, we follow the degradation of organics (DBU) with time and interpret the

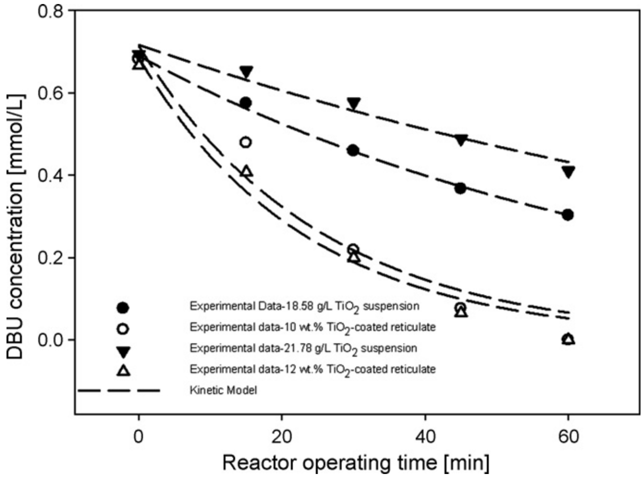

Fig. 7. Experimental validation of first-order kinetic model for suspended TiO_2 and reticulated foam monolith reactions. Experimental conditions: 50 °C, liquid circulation rate 10 L/min, O_2 flow rate 0.1 L/min, initial DBU concentration 0.6801×10^{-3} mol/L.

Table 1
Photocatalytic transformation rates of DBU on suspended and immobilised TiO_2 P25

Catalyst	Initial transformation rate, r_0 (mol/(L min))	Kinetic constant, k (L/($g_{cat.}$ min))
TiO_2 P25 slurry (18.58 g/L)	8.5597×10^{-6}	2.7658×10^{-3}
Immobilised TiO_2 (10 wt.% coated reticulate)	1.8819×10^{-5}	7.4243×10^{-3}
TiO_2 P25 slurry (21.78 g/L)	3.1661×10^{-6}	1.4466×10^{-3}
Immobilised TiO_2 (12 wt.% coated reticulate)	1.9923×10^{-5}	6.7625×10^{-3}

results with the batch reactor performance equation:

$$\frac{t}{C_{A_0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{V}{W}\int \frac{dX_A}{-r'_A} \tag{2}$$

where t is the reactor operating time in minute, r_A the reaction rate, C_{A_0} the initial concentration of DBU, X_A the conversion, V the volume of reacting solution and W is the weight of TiO_2 catalyst. From this expression and assuming that the photocatalytic degradation of DBU follows a first-order kinetic with respect to the concentration of DBU, the following expression is derived:

$$C_A = C_{A_0}\exp\left(-\left(\frac{W}{V}\right)kt\right) \tag{3}$$

where C_{A_0} is the initial concentration of DBU, k the first-order kinetic constant, V the volume of reacting solution and t is the reactor operating time. Fig. 7 shows a satisfactory least square fitting of the experimental data to the equation above (r = 0.99–0.97). These results indicate clearly that the heterogeneous photocatalytic degradation of DBU on these TiO_2-coated reticulated monoliths can be satisfactorily modelled assuming first-order kinetics. Sanchez et al. [23] also reported a first-order kinetic model for trichloroethylene (TCE) photocatalytic degradation using a polyethylene terephthalate (PET) monolith. From Fig. 7, the kinetic constant, k, obtained from least square fitting of experimental data to the first-order kinetic model is calculated for all reactions and shown in Table 1. The kinetic constant from the reaction using 12 wt.% TiO_2-coated reticulate was approximately three times larger than the value obtained when equivalent mass concentration of TiO_2 (21.78 g/L) was used in suspension while the kinetic constant calculated from the reaction using 10 wt.% TiO_2-coated reticulate was approximately five times larger than the value calculated for the reaction when an equivalent mass concentration of TiO_2 (18.58 g/L) was used in suspension showing that TiO_2-coated reticulates outperformed the slurry catalysts contrary to observations from other reports using TiO_2 immobilised on other types of supports like steel and glass.

Table 1 shows the kinetic constants of photocatalytic transformation of DBU using immobilised TiO_2 in comparison with similar reactions using equivalent mass concentration of TiO_2 in suspension. From the table, the initial reaction rate when 10 wt.% titania-coated reticulate was used was approximately two times the initial reaction rate when the equivalent mass concentration of TiO_2 (18.58 g/L) was used in suspension. While the initial reaction rate when the 12 wt.% titania-coated reticulate was used was approximately six times the rate when the equivalent mass concentration of TiO_2 (21.78 g/L) was used in suspension. This shows that adding more TiO_2 to the slurry system caused a decrease in photocatalytic efficiency possibly due to an increased extinction coefficient. Comparing the initial reaction rates when both 10 and 12 wt.% titania-coated reticulates were employed for the photocatalytic transformation of DBU, the 12 wt.% titania-coated reticulate slightly outperformed the 10 wt.% titania-coated reticulate by about 1.06 times.

Assuming complete mineralization of all organics in the system and an excess of oxygen, the equation for the heterogeneous photocatalytic oxidation of DBU is proposed as

$$C_9H_{16}N_2 + (25/2)O_2 \xrightarrow{h\nu,TiO_2} \text{Intermediates} \rightarrow 9CO_2 + H_2O + 2H^+ + 2NO_3{}^- \tag{4}$$

Five intermediate products of the photocatalytic degradation of DBU were detected and identified by Ochuma et al. [19] using HPLC and GC–MS analysis. These intermediate products are caprolactam, 3-methyl-adenine, 2,6-dimethyl-4-hydroxybenzaldehyde, 3-methoxy-4,5,6-trimethylphenol and 4-amino-5-formamidomethyl-2-methylpyrimidine. However, under optimised degradation conditions (temperature, PH, catalyst loading or weight of catalyst deposited on reticulate, initial concentration of DBU), complete conversion of DBU and all intermediates is possible since over 90% mineralisation of DBU using a cocurrent downflow contactor photocatalytic reactor is possible and has been reported [19].

4. Conclusion

Results have shown that the pilot-scale reticulated foam monolith photocatalytic reactor fitted with 15 PPI TiO_2-coated reticulates and equipped with a 1.0 kW UV lamp is capable of compete conversion of DBU in 60 min showing great promise for industrial scale water purification using heterogeneous photocatalytic oxidation. From the results, DBU conversion for the reactions carried out using the 10 and 12 wt.% TiO_2-coated reticulates were 100% after 60 min while the corresponding TOC conversions were 26 and 23%, respectively. The reactions carried out using the TiO_2-coated reticulates were more efficient compared with the reactions carried out using TiO_2 in suspension, under these experimental conditions. A reverse situation may however occur should the foam be compared with optimum TiO_2 concentration in a slurry reaction. For the reactions carried out using TiO_2 in suspension, increasing the TiO_2 loading caused a decrease in the reaction efficiency due to an increased extinction coefficient, while increasing the weight of TiO_2 deposited on the reticulates only slightly increased the reaction efficiency. Optimum TiO_2 concentration for studies using DBU has been reported as 0.5 g/L [19]. The performance of these TiO_2-coated reticulated foam monoliths shows great promise for the use of immobilised TiO_2 for large-scale application of photocatalytic treatment of contaminated water and for improving the overall process economics.

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