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The application of oscillatory flow mixing to photocatalytic wet oxidation

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Abstract

The photocatalysed mineralisation of methylene blue, a common organic dye, has been carried out in a novel Pulsed Baffled Tube Photochemical Reactor (PBTPR). The fluid hydrodynamics of the PBTPR is based on oscillatory flow mixing, which essentially exploits the phenomenon of flow separation resulting from fluid flow past sharp edges. The PBTPR has excellent solids handling capacity, and is capable of effecting complete dispersion and mixing of the photocatalyst slurry. The effects of oscillatory flow mixing are reported on properties such as adsorption and the reaction rate. A kinetic study has also been undertaken and kinetic parameters are reported for this system. A catalyst loading of 0.143 g/l has been found to be optimal for this system. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Oscillatory flow; Heterogeneous photocatalysis

1. Introduction

Much has been said and studied about the phenomenon of photocatalysis as a tool for air and water remediation. Such is the attraction that heterogeneous photocatalysis has generated that it has been applied to fields ranging from the mineralisation of organic pollutants in wastewater [1,2], to the sterilisation of microbial cells [3]. Novel applications have involved the demonstration of oil spill clean up by photocatalytic oxidation of crude oil, where the semi-conductor photocatalyst is coated onto buoyant cenospheres. Photocatalytic oxidation has been successfully applied for the treatment of a wide number of organic materials and the list is rapidly expanding. Titanium dioxide has emerged as the semi-conductor of choice amongst several alternatives that include ZnO, CdS, WO_3, CdSe, ZnS and $SrTiO_3$. Its high activity, when combined with its cheapness, photostability and inertness (biologically and chemically) explains the emergence of TiO_2 as the most widely utilised semi-conductor photocatalyst. Of the several types of TiO_2 available, Degussa P25 has emerged as a research standard due to its well defined nature and substantially higher photocatalytic activity than the other readily available samples of TiO_2 [3].

Several studies have been carried out in the area of photoreactor design [4–6]. It is however widely acknowledged that this field of research has not developed at the same pace, as there have been advancements in the understanding of the photochemistry of the photooxidative process. The complexity of developing suitably descriptive models of the heterogeneous photocatalytic process to aid in the design of photochemical reactor systems cannot be overemphasised. It has even been suggested that the photon flux, a feature which sets photocatalytic systems apart from their conventional catalytic counterparts, might itself constitute a special fluid phase, the so-called ‘electromagnetic phase’ with the efficient photon being considered a reactant [7]. Despite these complexities, several workers have proposed models and methodology for the design of photoreactors [5].

There has, however, been what can essentially be referred to as the ‘associated problem’ which has up to the present moment constituted a major problem for the commercialisation of the TiO_2 photocatalytic oxidation process, and that has to do with the problem of catalyst removal, post-treatment. It must be recalled that the primary application, to which photocatalytic oxidation has been applied thus far, is in the re-mediation of wastewater streams [1]. TiO_2 is made up of very fine powders of average particle sizes 0.3 μm, which essentially form a slurry in water. Thus before these treated wastewater streams can be re-circulated for re-use or discharge, there is a need for the removal of the semi-conductor from solution. This need for an extra post-oxidative filtration step introduces an un-favourable economic balance against the photocatalytic oxidation route for wastewater treatment. It has in fact been suggested that the energy costs for this separation step might altogether negate the energy savings derived from a solar induced

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decontamination process [8]. Several methods have been proposed and applied for dealing with this problem, the most commonly applied of which has been the use of fixed or fluidised bed reactors with supported catalysts. Thus while some workers have used reactors whose interior surfaces have been coated with the semiconductor photocatalyst [1], others have utilised catalyst particles coated onto supports which are more readily separable than the semi-conductor particles. The most widely used supports have been beads of several types although other materials such as fly-ash, hollow tubes, vycor glass, woven fabric, silica gel, sand and optical fibre bundles have been utilised [9,10].

2. Background

The problem that eventually led to the concept and development of the Pulsed Baffled Tube Photochemical Reactor (PBTPR) was the need for a photochemical reactor that could be utilised in the treatment of organic material in radioactive waste prior to storage [9]. The nuclear industry makes use of a wide range of organic materials which include solvents (such as are used in reprocessing plants), lubricating oils and greases, ion-exchange resins, PVC, butyl rubber, polythene, cellulose and chelating and decontamination agents. The presence of organic material in radioactive waste is often problematic since organic materials tend to be more chemically active than inorganic ones, and have a tendency to deterioration by various chemical interactions under storage or disposal conditions [11]. Contamination may result when radiolytic gases are released in storage causing waste containers to be breached by pressurisation or corrosion. Organic materials are known to increase the mobility of radio-nuclides, especially actinides with which they can form complexes that have higher solubility than inorganic actinide species, resulting in the release of radioactive organic species into ground water. Organic materials are also known to cause setting problems in cement, calling into question the traditional method of radioactive waste encapsulation. Thus, the removal of organic material in radioactive waste prior to encapsulation is beneficial.

The development of the PBTPR arose out of the specific problem of finding a suitable treatment method for dealing with ion-exchange resins and chelating agents. These classes of compounds are especially problematic as they bind to radioactive metal ions and are therefore associated with higher amounts of radioactivity than most other organic materials. Sulphonated polystyrene ion-exchange resins (d_p, 0.5 mm) are utilised for the removal of radioactive cations from effluents. For reasons already outlined, it is desirable to remove these resin beads from the radioactive waste before encapsulation and subsequent storage. The wet oxidation of the resins takes place in two distinct stages.

1. The dissolution of the ion exchange resins in hydrogen peroxide to form a solution of complex organic molecules.
2. The eventual oxidation of the resulting molecules to carbon dioxide and water and/or the resulting mineral acids.

The application of photochemical oxidation to the resin treatment problem using conventional photoreactor configurations was found to be unsuitable for this particular system. The problem with conventional photoreactors lay in their inability to adequately handle aqueous streams containing solid particles. Though it is possible with conventional cylindrical photoreactors to ‘fluidise’ particles by selecting suitably high flow rates, the increased flow rates reduce the residence times for the reaction and the system becomes inefficient [9].

For this process the reactor needed to possess the capacity to provide the necessary process conditions for the first step of resin dissolution. To achieve this, the reactor had to possess the capacity to provide uniform solids distribution, efficient multi-phase mixing and control of residence time distribution (RTD) in continuous flow operation. The reactor also had to possess the capacity to generate sufficient turbulence to aid the dissolution of the resin beads. The mixing mechanism to be utilised also had to be non-invasive. Because the dissolution stage of the resin treatment process led to the formation of a dark opaque solution it was desirable to have radial fluid mixing profiles which would ensure that all parcels of fluid are periodically exposed to the narrow band close to the lamp. The PBTPR was developed in response to these specific process needs and was successfully applied to the solution of the resin treatment problem [9,12]. However, it soon became apparent that the solids handling capability of the PBTPR could be applied to the case of photocatalytic oxidation, specifically to aid in the suspension of supported catalyst particles. The basic fluid dynamical principles upon which the PBTPR is based will be described in the following section.

3. Oscillatory flow mixing

Studies have shown that fluid oscillation in the presence of baffles within the flow geometry leads to vigorous eddy mixing [13,14]. Mackley and co-workers [12–14] have carried out extensive research on pulsatile flow (Oscillatory Flow Mixing, OFM) and have successfully established the fundamental principles upon which its hydrodynamics is established. Drawing directly from this knowledge base, OFM reactors have been designed and have been shown to provide excellent solids handling capabilities, efficient multiphase mixing and plug flow RTD with high turbulence. The oscillatory flow mixing cycle can be explained with the aid of Fig. 1 which shows typical flow patterns in a pulsed baffled tube.

It can be seen that as the fluid flows past the sharp edges (the baffles), vortices are generated downstream of the baffles. There is a brief moment of flow cessation at the position of maximum fluid amplitude, during which time the

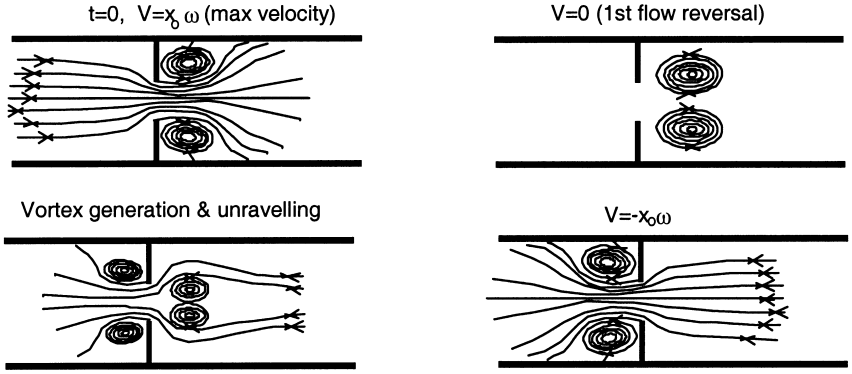

Fig. 1. Oscillatory flow patterns.

vortices detach from the baffle edge and expand. Upon flow reversal the vortices are shed into the bulk of the fluid. The cycle is repeated in the opposite direction and the behaviour is thus characterised by periodically repeating cycles of vortex generation, ejection and unravelling. This leads on a time-averaged basis to a uniformly mixed regime in each inter-baffle region.

The hydrodynamics within a pulsed baffled tube is characterised by two dimensionless groups, the oscillatory Reynolds number, Re_o, and the Strouhal number, St; as well as by the geometrical configuration of the baffles. The oscillatory Reynolds number, Re_o, and the Strouhal number, St, are defined below.

$$Re_o = \frac{x_o \omega D}{\nu} \tag{1}$$

$$St = \frac{D}{4\pi x_o} \tag{2}$$

For the case where there is an additional net flow along the tube, a net flow Reynolds number, Re_n, becomes relevant. This is given as:

$$Re_n = \frac{DU}{\nu} \tag{3}$$

Where U is the superficial net flow velocity through the tube (m/s).

4. Particle suspension in oscillatory flow

Mackley et al. [14] investigated the dissolution and suspension of ion exchange resins in a Pulsed Baffled Tube Reactor, PBTR (OFM reactor) and found that the resin beads could be kept in suspension beyond certain threshold oscillatory flow conditions and that varying the oscillatory flow conditions would lead to a population distribution of the beads in the reactor. By considering a model based on the concept that set fractions of particles are advected up or down from each baffled cell per stroke, and by assuming that these fractions are constant for all cells in the column, they created a series of first order ODEs of the cell concentrations as a function of time. Upwards and downwards advection are considered to be able to occur simultaneously. They have developed a model for predicting the particle distribution profile in an OFM device. The model is presented below.

$$\gamma = 1 - \exp\left\{-R\frac{V_{\text{oscillatory}}}{V_{\text{terminal}}}\right\} \tag{4}$$

Where γ is the ratio of the concentrations of particles in adjacent cells. $V_{\text{oscillatory}}$ and V_{terminal} are the oscillatory velocity and particle terminal velocity, respectively. The value of R for the resin beads was found to be 0.8. This correlation has been tested for a range of baffle spacings and orifice diameters, and it has been found to hold true, provided the fluid mechanics generated by the presence of baffles and an oscillatory flow could generate chaotic flow.

5. Experimental section

The PBTPR is essentially an annular photoreactor. It is a baffled cylindrical vessel, with an UV lamp running along the entire length of its central axis. For the experiments reported in this work a PBTPR of 87.4 mm OD, 75.6 mm ID and 910 mm length was utilised (see Fig. 2). The radiation source was a 30 W HERAUS low-pressure mercury lamp emitting at 254 nm. Radiation is monochromatic at this wavelength as determined by radiometric studies using a Macam UV radiometer. The reactor vessel is made of borosilicate glass, which cuts off light below 300 nm, and can adequately contain stray radiation from the UV lamp. The base of the vessel is flanged to an aluminium alloy diaphragm retainer, with a Perspex adapter housing a Teflon diaphragm. The stainless steel baffles separated at a spacing of $0.5D_o$, are held in place by three threaded stainless steel rods. The pulsing unit uses an anti-phase displacement cam to impart fluid oscillations to the diaphragm via on oil filled cylinder. Pulsing was carried out over conditions ranging from 0 to 11 Hz frequencies and 0–4.5 mm amplitudes, corresponding to oscillatory Reynolds numbers in the range of up to 24,000 in the top scale. All experiments were performed in batch mode. A constant supply of air was applied to the system at a flowrate of 200 cm^3/min.

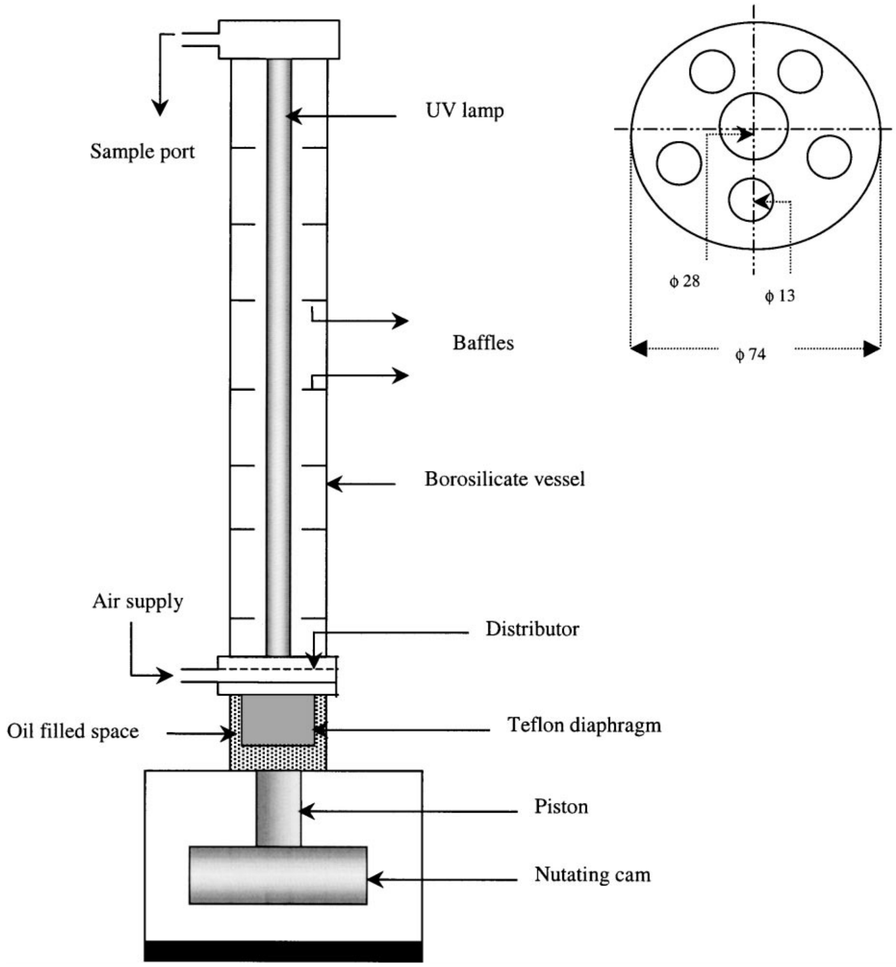

Fig. 2. Schematic view of the Pulsed Baffled Tube Photochemical Reactor (PBTPR). Planar view of baffles is shown.

The study investigated the photocatalysed decolourisation of methylene blue. Methylene blue is a brightly coloured commonly available water-soluble dye. TiO_2 is known to be effective for catalysing the complete oxidative mineralisation of methylene blue [1,2,9]. Degussa P25 titanium dioxide was utilised as the photocatalyst. The material is known to have a BET surface area of $50\,m^2/g$ and is mostly in the anatase form with a mean particle size of $0.3\,\mu m$ [1]. The experiments reported in this study were all performed with TiO_2 in the slurry phase. The methylene blue used was obtained from Aldrich. All solutions were prepared using Reverse osmosis water. The initial methylene blue solution had maximum optical absorbance at 661 nm.

Changes in the concentration of methylene blue were followed using a Unicam UV1 spectrophotometer. Initial calibration studies showed that within the range 0–14 $\mu mol/dm^3$ the Beer-Lambert law was obeyed with great precision. At the start of each run, 3.5 l of methylene blue solution was charged to the reactor vessel and airflow activated. The required catalyst loading would then be applied and the pulsing unit activated. The set-up is allowed to remain in this ‘dark reaction’ state for 20 min, during which time, there is some adsorption of the solute onto the catalyst and the system reaches adsorptive equilibrium. The lamp is then switched on. In addition to the fluid pulsing, the air bubbles generated by the air supply were also observed to aid in the mixing. Samples are drawn every other minute and are returned to the vessel after spectrophotometric readings are taken.

6. Results and discussion

6.1. Effect of oscillations on reaction rates

These series of experiments were carried out for oscillatory conditions ranging from 0 to 11 hz and 0–4.5 mm. Airflow of $200\,cm^3$/min was supplied throughout the duration of each run. Reaction rates are observed to decrease as the mixing intensity increases for catalyst concentrations of 29 mg/l and 140 mg/l Fig. 3. This is due to the increase in the ‘apparent scattering’ centres with increasing oscillatory Reynolds number. However, for the case of high catalyst loading at 570 mg/l, the reaction rate is observed to remain

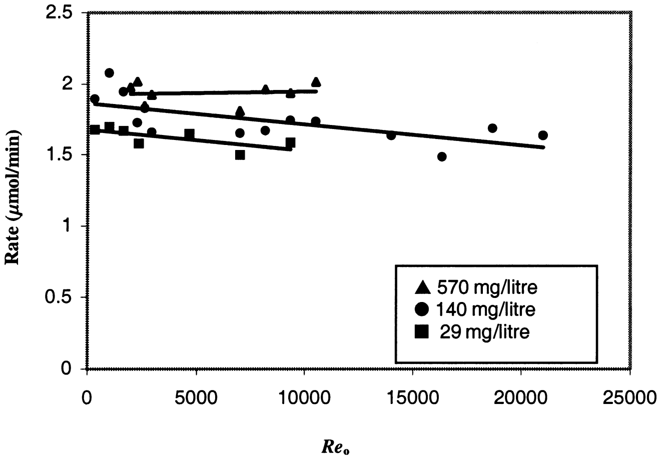

Fig. 3. Plot of reaction rates (µmol/min) as a function of the Oscillatory Reynolds number for various catalyst concentrations. Airflowrate 200 cm^3/min.

fairly constant over the entire range of mixing intensities studied. In this case, the system is already very ‘optically dense’ and as such there is very little change in the optical properties of the system with increasing mixing intensity. A run without catalyst was also carried out but no reaction was observed.

It therefore becomes obvious that the PBTPR is most efficiently utilised at the threshold of conditions necessary to successfully suspend and uniformly disperse the photocatalyst particles. Our work indicates that conversion in a well-mixed heterogeneous photochemical system decreases with increasing turbulence. These effects have been observed by other workers [5,6]. In particular, Cassano et al. [5] report that the addition of scattering centres to a very well mixed photochemical system always produces a diminishing in the average reaction rate compared to the case where there is no scattering. The effect of increasing the oscillatory Reynolds number is an increase in the mixing intensity, which quite expectedly leads to even greater scattering due to the chaotic particle trajectories generated.

6.2. The effect of catalyst loading on reaction rate

When the catalyst loading was increased from 0 to 140 mg/l there was an observed increase in the average reaction rate determined over the entire range of pulsing conditions. However, beyond a catalyst loading of 140 mg/l average reaction rates were observed to reach a ‘plateau’.

The observed optimum catalyst concentration occurs at a loading of ~140 mg/l. Fig. 4 is a plot of the average reaction rates at three different catalyst loading rates, and shows the initially observed increase in rates, and the limiting ‘plateau’ that delineates the location of the critical (optimal) catalyst concentration for the system.

Many workers consistently utilise significantly higher catalyst concentrations for photocatalytic oxidation using TiO_2 as catalyst and there is very little agreement on the sort of catalyst concentrations that can be deemed optimal. Chen and Chou [15], while treating the TiO_2 photocatalysed decolourisation of methylene orange have reported that increases in rate occurred for catalyst loading from 0 to 8 g/l. The rates remained constant for loading of between 8 and 24 g/l and were observed to decrease for catalyst loading from 24 to 40 g/l. Hermann [7] has also reported the limiting value for the catalyst concentration to be 2.5 mg of TiO_2 per cubic centimetre of suspension, which corresponds to a value of 2.5 g/l, but states that for actual tetraphasic (Gas–solid–liquid organic phase-UV light systems) an optimised slurry suspension was comprised of 3.5 g/l of TiO_2. Herman suggests that this limit i.e. the optimal catalyst concentration depends on the geometry as well as the on the

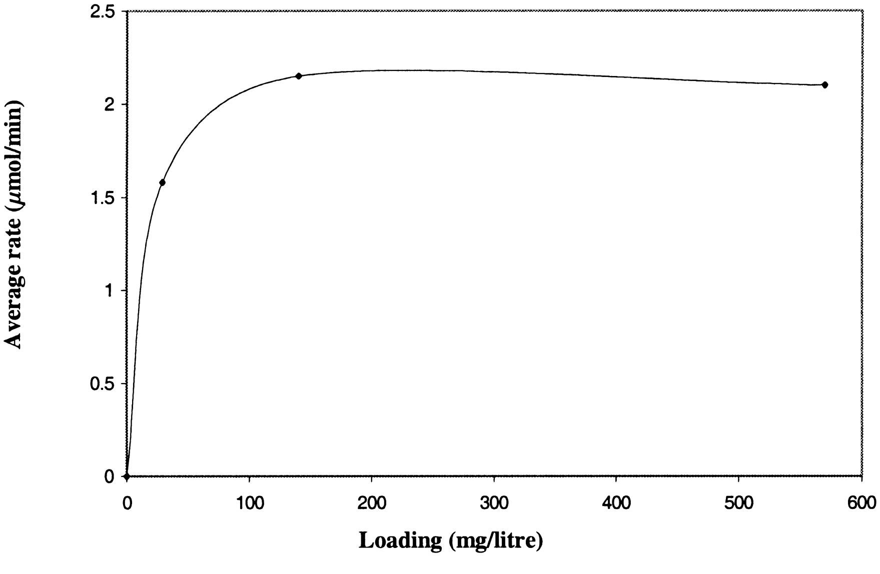

Fig. 4. Plot of average reaction rates (µmol/min) as a function of the catalyst loading.

working conditions of the photoreactor. Mazarrino et al. [16] have carried out studies on the degradation of glycolic acid using TiO_2 photocatalysis and have observed that for the system which they studied, the concentration of the catalyst seemed to play a secondary role with only minor improvements in yield being observed when the catalyst loading was varied from 10 to 100 mg/l. Hone et al. [3] investigated the effects of catalyst concentration on photocatalytic sterilisation rates of microbial cells and found that the optimum catalyst loading for these systems was 0.1 g/l. Wang and Adesina [17] have investigated the photocatalytic causticisation of sodium oxalate using TiO_2 and have reported an optimal catalyst loading of 0.5 g/l for their system. Alfano et al. [6] have investigated both theoretically and experimentally, the effects of scattering in photochemical systems. They posit that an increase in the particle concentration at constant concentration of the absorbing species produces an increase in the optical thickness and an increase in the scattering albedo, thereby leading to a diminishing in the average reaction rate with respect to the case with no scattering.

Brucatto and Rizzuti [18] have developed a simplified model (Zero Reflectance Model, ZRM) for the estimation of the radiant flow field in heterogeneous photoreactors, which also allows for the a-priori determination of the critical catalyst concentration. The ZRM when applied to our reactor system predicts a critical catalyst concentration of ~0.36 g/l, which is about 2–3 times larger than the values we have obtained experimentally. However, as earlier stated the ZRM is at best a useful first approximation to the range of catalyst loading that will make for optimal concentrations in the system. The conservative catalyst concentrations predicted in the ZRM model are however quite instructive, as they present in the clear logic that the model formulation is based upon, a theoretical rationale in support of the argument for low to moderate catalyst loading. This is, however, not to underplay the fact that each heterogeneous photocatalytic system is unique to itself, in the nature of the absorbing species, the specific sample population of particle size distributions of photocatalyst utilised in the experiments, the reactor geometry, nature of light source, fluid hydrodynamics, mass transfer characteristics and other related phenomena.

What our work clearly shows however, is the existence of an optimum catalyst loading at moderate catalyst concentrations, for a situation of high fluid mixing. The results presented in the earlier sections also show that the effect of increasing the pulsing intensity for a fixed catalyst concentration is a fall in reaction rates. This is due to the fact that the increase in mixing increases the 'apparent' scattering centres within the reactor since the particle dispersion profiles are modified. Particle dispersions in oscillatory flow systems are known to be dependent on the pulsing intensity. Thus we might expect that for the case of slurry type photoreactors, for any particular concentration of catalyst, there is a certain minimum fluid flow condition at which reaction rates are highest and beyond which rates either remain constant, or depending on the particular systems under investigation, might even be observed to fall notwithstanding the fact that mass transfer is improved by increased mixing. Within this range of conditions rates clearly are optically limited, since the optical characteristics of the system pre-dominate to the exclusion of the mass transfer properties.

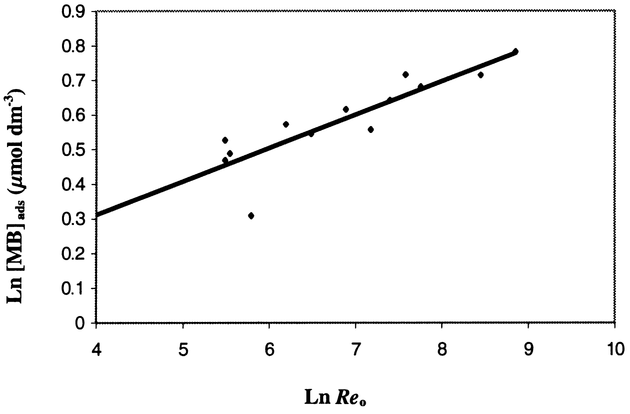

Fig. 5. Plot of the logarithms of the amount of solute adsorbed (μmol/dm^3) as a function of the oscillatory Reynolds number.

6.3. Effect of pulsing conditions on adsorption

It is well known that in the TiO_2 photo-catalysed oxidation of methylene blue some methylene blue is adsorbed onto the catalyst to be desorbed and oxidised later.

Previous studies have established that oscillatory flow mixing improves mass transfer [12]. This series of experiments was carried out to determine the effect of oscillatory flow conditions on the amount of solute adsorbed. The plot of adsorption versus pulsing conditions could be modelled by a power law relationship between the amount of solute adsorbed and the oscillatory Reynolds number.

$$[MB]_{\mathrm{ads}} = kRe_{\mathrm{o}}^{\mathrm{n}} \qquad (5)$$

A log–log plot yielded a straight-line graph (see Fig. 5), whose slope was the index of the power law expression. The index of the power law was found to be 0.0962 while a value of 0.9289 was obtained for the constant term K.

The final form of the model is therefore given as,

$$[MB]_{\mathrm{ads}} = 0.9289Re_{\mathrm{o}}^{0.0962} \qquad (6)$$

The model holds for values of $Re_{\mathrm{o}} > 0$ Fig. 6.

These results indicate that the PBTPR, like other pulsatile fluid mixing devices, can provide for improved mass transfer, simply by increasing the intensity of the pulsing conditions.

6.4. Determination of the kinetic parameters

Several kinetic models have been proposed for the photocatalytic mineralisation of organic pollutants. Numerous studies have reported that the initial rate of disappearance of

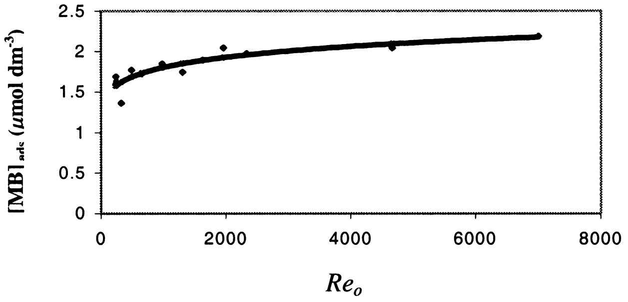

Fig. 6. Plot of the amount of solute adsorbed as a function of the oscillatory Reynolds number. The solid dark line represents the power law model to which the data is fitted.

the organic pollutants fits a Langmuir-Hinshelwood kinetic scheme, given as:

$$r_\mathrm{i} = \frac{-\mathrm{d}[S]_\mathrm{i}}{\mathrm{d}t} = \frac{k(S)K(S)[S]_\mathrm{i}}{1 + K(S)[S]_\mathrm{i}} \tag{7}$$

Where $[S]_\mathrm{i}$ the initial concentration of the pollutant S and $K(S)$ is taken to represent the Langmuir adsorption constant of the species S on the surface of TiO_2, and $k(S)$ is a proportionality constant which provides a measure of the intrinsic reactivity of the photoactivated surface with S [2].

Initial rates of the TiO_2 photocatalysed mineralisation of methylene blue were obtained over a range of concentrations (0–25 μmol/dm^3). Assuming that the rates could be fitted to a Langmuir-Hinshelwood kinetic scheme, we can rearrange Eq. (7) to obtain the standard reciprocal form shown in Eq. (8).

$$\frac{1}{r_\mathrm{i}} = \frac{1}{k(S)K(S)[S]_\mathrm{i}} + \frac{1}{k(S)} \tag{8}$$

Fig. 7 represents a plot of the reciprocals of the initial rates and the initial methylene blue concentrations. As is expected, the data give a straight line fit, from which the kinetic parameters can be determined. From regression analysis of the data represented in the plot in Fig. 7, $k(S)$ which is a measure of the intrinsic reactivity of the photoactivated surface with the solute was found to be 8.8933 ± 2.01 μmol/min. The value of $K(S)$ obtained was 0.0206 ± 0.004 dm^3/μmol. The value of $K(S)$ obtained in this study is comparable to the value of 0.0258 ± 0.0013 dm^3/μmol obtained by Matthews [1] for a similarly defined parameter.

7. Discussion

Our work has shown that the improvements in mass transfer in the PBTPR, do not necessarily translate into improvements in conversion, or in reaction rates, for the case of heterogeneous, slurry phase photocatalysis [9]. Although this would at first glance seem to run contrary to conventional wisdom, the effect of diminishing reaction rates with improved mixing in heterogeneous (slurry) photochemical systems, has been observed by other workers [5,6].

The increase/improvement in reaction rates is a function of the number of active (absorptive) sites available. In a photocatalytic system, the number of active sites available should strictly be proportional to the number of photocatalyst particles available. It should be recalled that it is the surface sites of the particles to which solute has been adsorbed that is primarily involved in the particle-photon interaction which the photo-oxidative process depends upon. It is however clear that the increase in the reaction rate with increasing catalyst concentration continues until a certain ‘critical’ mass of catalyst is reached.

One explanation for the observed effect suggests that at low catalyst concentrations, substantial amounts of radiant

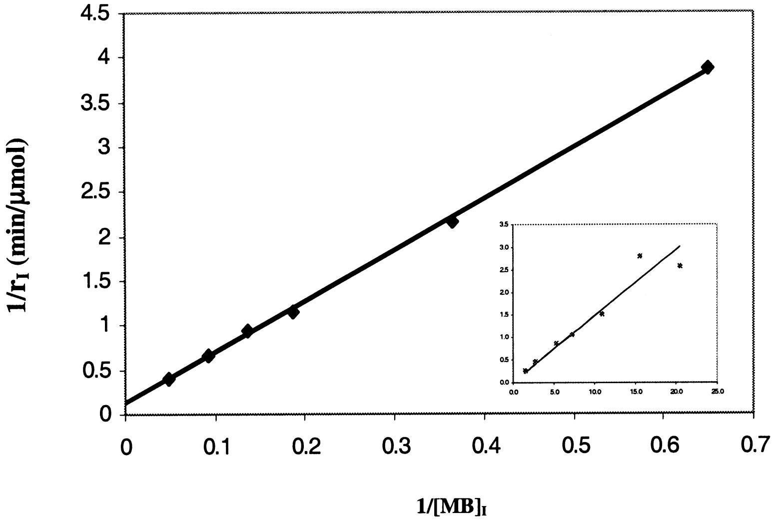

Fig. 7. Plot of the reciprocals of the initial rates as a function of the reciprocals of the initial concentrations. Insert: Plot of initial reaction rates as a function of the initial concentration of methylene blue. The solid line was calculated using the kinetic parameters obtained from the kinetic studies.

energy are lost through the walls of the reactor. These losses are reduced as the catalyst concentration increases leading to higher reaction rates since a greater amount of radiation is utilised. However, when the concentration becomes high enough to extinguish the radiation before reaching the wall, all the radiation is at this point being utilised and further increase of catalyst concentration does not result in an increase in photoconversion [18]. At higher catalyst concentrations, the layer in which light is extinguished becomes progressively smaller and it is believed that the mass transfer phenomena of reagents between the ‘dark’ layers and the active irradiated layers begins to limit the reactants concentration giving rise to an observed decrease of the photoconversion.

Brucatto and Rizzuti [18] suggest that this last effect would be strongly influenced by the mixing rates inside the photoreactor as well as the photoreactor thickness. Our work has shown that mixing rates do affect the photoconversion rates. We have also found that the improvements in mass transfer (adsorption) with increased pulsing conditions does not engender a corresponding improvement in the reaction rates, suggesting that the scattering effects which are caused by the apparent increase in ‘scattering centres’ as the pulsing intensity increases is the primary rate determining factor.

8. Conclusions

The PBTPR has been demonstrated to be viable as a photoreactor for the treatment of wastewater. When applied to heterogeneous photocatalysis its performance is limited only by the fact that the intense mixing conditions inevitably lead to an increase in the ‘apparent scattering centres’ and thus, a decrease in reaction rates. However, the capacity for controlled mixing, control of residence time distributions, simplicity of operation and its non-invasive mixing character makes it a particularly attractive photoreactor. The real strengths of the PBTPR will however be best exploited when applied to a homogeneous system for which the rate is mass transfer limited. Highly absorbing solutions for which it is essential that the reagent fluid be exposed to the narrow irradiance zone will equally better exploit the immense potentialities of this novel photoreactor. In addition to these will be heterogeneous photocatalytic systems, which utilise naturally buoyant catalyst supports. For such systems, oscillatory flow mixing can guarantee efficient catalyst dispersion and suspension.

9. Nomenclature

γ	Ratio of particle concentrations in adjacent cells
ω	Angular frequency of oscillation, radians/s
x_o	Centre to peak amplitude of oscillation, m
D	Tube diameter, m
ν	Kinematic viscosity, m^2/s
U	Superficial net flow velocity, m/s
Re_o	Oscillatory Reynolds number
Re_n	Net flow Reynolds number
St	Strouhal number
R	A constant
$V_{oscillatory}$	Oscillatory velocity, $2\pi\omega X_o$, m/s
$V_{terminal}$	Particle terminal velocity, m/s

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