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Research Paper

A photocatalytic impeller reactor for gas phase heterogeneous photocatalysis

Oluwatosin Tokode[a,*], Radhakrishna Prabhu[b], Linda A. Lawton[c], Peter K.J. Robertson[d]

[a] Department of Engineering, CU Coventry, CV1 5FB, United Kingdom
[b] School of Engineering, Sir Ian Wood Building, Robert Gordon University, Aberdeen, AB10 7GJ, United Kingdom
[c] School of Pharmacy and Life sciences, Sir Ian Wood Building, Robert Gordon University, Garthdee Road, Aberdeen AB10 7GJ, United Kingdom
[d] School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, United Kingdom

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ABSTRACT

A novel photocatalytic reactor based on a stirred tank configuration has been described. This reactor employs the use of photocatalytic impellers to aid the mass transport of gaseous organic compounds during photocatalytic reactions. Experiments involving toluene vapour photo-oxidation showed the reactor configuration is susceptible to catalyst deactivation even at low concentrations if treated for prolonged periods. For this reactor, the reactive time scale exceeds the diffusive time scale hence, toluene photo-oxidation was reaction limited. The dependency of photonic efficiency of the reaction on mass transfer and catalyst deactivation was observed when correlated with the Damköhler number and deactivation induced reduction reaction rates respectively. The results show an inverse variation with Damköhler number and proportionality to reaction rates.

1. Introduction

Heterogeneous photocatalysis using semiconductor catalysts is an advanced oxidation process [1,2] with environmental applications in air remediation [3], hydrogen generation [4], corrosion prevention [5] and water purification [6–9]. Its application in environmental remediation is of significant importance because of its capability for complete degradation of organic and inorganic hazardous compounds [10,11]. The process is initiated when the catalyst particle absorbs photons having energy equal to or greater than the bandgap of the semiconductor catalysts. Upon band gap excitation, highly reactive holes (h^+) and electrons (e^-) are generated, these two go on to generate highly oxidizing hydroxyl radical ($OH\cdot$) and reductive superoxide (O_2^-) [10,12,13]. The photo-generated species take part in redox reactions either on the surface or in the bulk with a characteristic low efficiency because of the recombination of electrons and holes. Heterogeneous photocatalytic reactions require the adequate interaction of photons, semiconductor catalyst and the pollutant molecule to achieve complete degradation of pollutants. As a result, special attention must be paid to the design of photocatalytic reactors to facilitate these processes. In recent years, there have been a concentration of efforts on the synthesis of highly active titanium dioxide catalysts [14–17] and more importantly, design of reactors for heterogeneous photocatalysis. This has led to different reactor configurations being reported in the research literature [18–21].

Photocatalytic reactors in heterogeneous photocatalysis bring together all components required for the photocatalytic reaction process to take place. These components such as photons, pollutant and catalyst that are required for the transformations of reactants interact when brought together into a single unit. Their interactions in a single unit reactor enables the monitoring and/or regulation of parameters such as mass transfer, temperature and concentration. This ensures that photons are adequately utilized, intermediate products can be identified and kinetics of the photocatalytic process can be studied. Therefore, the aim of reactor design is to optimize these elements and parameters to neutralise the pollutant completely and achieve the greatest possible yield. In order to achieve this, a large catalyst surface area is essential. Catalysts in the powdered form provide a larger surface area than immobilized catalysts which have significantly reduced surface area. The use of immobilized catalysts has however, now been widely reported in the literature [22] because it eliminates the cost of separating powdered catalysts from liquid in solid-liquid treatment processes. They also provide numerous reactor design possibilities in gas-solid treatment. Different reactor configurations exist for gas-solid heterogeneous photocatalysis; Cassano and Alfano [23] identified the four most widely reported configurations in the photocatalytic literature to be monoliths [24], packed bed [25], catalytic walls [26] and fluidised bed [27] reactors. Previous studies employing these reactor configurations failed to

* Corresponding author.
E-mail addresses: olu.tokode@cuc.coventry.ac.uk, oluizrel@gmail.com, ac0221@coventry.ac.uk (O. Tokode).

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bring together all reactor components required for transformations of reactants into a single unit. Li Puma and Yue [28] used a pilot plant falling film reactor to compare effectiveness of photon-based oxidation processes. The reactor was designed for optimal light absorption however, the feed tank which supplied the pollutant and the collector tank which collects treated fluids were external to the reaction chamber which housed the UV lamp. Adams et al. [29] designed a single pass, continuous flow drum reactor for wastewater treatment. The reactor employed three separate but connected drum reactors with paddles positioned on the inside of the reactor drum to allow the mixing of wastewater with catalysts pellets. UV lamps were in each drum to illuminate the catalyst. Residence time in each drum was 3 min hence, three drums were required to increase the overall residence time and consequently, the treatment time of pollutants. This led to a separation of the reactor unit into sub-units. For slurry reactors where the catalyst is a separate unit within the reactor, mass transfer limitations are not of great concern. Martin et al. [30] however, reported a decrease in reactor efficiency at high catalyst loading. This was as a result of restrictions in radiation transport when optical thickness of the catalyst suspension exceeded the optimum level. Fluidised bed reactors use an upward air stream to bring powdered catalysts into contact with gas phase pollutants suffer a similar limitation. Kuo et al. [31] reported the limitations of fluidised bed reactors to include powdered catalyst drifting away from the main reaction area of the reactor. This is due to the powdered catalyst being a separate unit within the reactor. The fine structure of the TiO_2 powder may also lead to losses through trapping of the powder in reactor crevices.

The immobilized reactor configuration has been reported to be effective in providing adequate interaction between photons, catalyst and pollutant within the reactor. The supports on which these catalysts are immobilized vary greatly. Supports reported in the literature include but are not limited to glass, silica and optical fibre [22]. An ideal support should exhibit strong affinity for the pollutants, high specific surface area and strong binding with the catalyst without reduction in catalyst activity. Peill and Hoffmann [32] reported the design of an optical fibre reactor (OFR) which employed optical fibre cables as a means of light transmission to the catalyst. The TiO_2 catalyst was immobilized on the fibre cores. UV illumination from an external lamp was transmitted through the optical fibre into the reaction chamber hence, pollutant, photons and catalyst were a single unit in the reactor. The OFR reactor configuration reduced mass transport limitations however, stiffer fibres with separators were recommended to prevent delamination of the catalyst coating. In immobilized photoreactor development, the major challenges encountered are complications of reactor scale-up such as mixing, mass transport, reactant-catalyst contact and installation of catalysts and achieving a high ratio of activated catalyst to illuminated surface through efficient light intensity distribution inside the reactor [33]. These challenges can be adequately addressed through innovative reactor design using design concepts from various reactor configurations.

In this study, the development of a photocatalytic impeller reactor (PIR) for gas phase photocatalysis with a potential to overcome the aforementioned challenges is reported. This is the first heterogeneous photocatalysis study in the gas phase to investigate the use of the PIR reactor configuration. It is designed to have the catalyst, UV source, reactor chamber and mixing impellers as a single unit while overcoming mass transport limitations of an immobilized catalyst. The catalyst was supported on modified rushton impellers to make them photoactive and improve reactant-catalyst contact. This reactor configuration's potential to overcome mass transport limitations by the mixing action of the impellers while under constant illumination by a UV LED array surrounding the reaction chamber was evaluated. Toluene vapour was used as a model pollutant and its photo-oxidation was used to evaluate the reactor performance.

2. Materials and methods

2.1. Immobilized TiO_2 catalyst preparation

Titania sol-gel was synthesized through the polymeric route [34] using a titanium tetraisopropoxide (TTIP, Sigma Aldrich) precursor. 5 mL of TTIP was added to 65 mL of 2-propanol (Fisher) and stirred vigorously for 2 h. Subsequently, a mixture of 51 µL of 15.7 M nitric acid, 349 µL distilled water and 5 mL 2-propanol was added dropwise and stirred for 15 min. The resulting titania sol-gel was sonicated for 2 min and left standing for 24 h. Thick layers of TiO_2 were immobilized on glass slides (38 × 12 × 6 mm, Fisher) by dip coating, the glass slides were wholly submerged in the sol-gel for 60 s and slowly withdrawn. The coated slides were allowed to air dry for an hour before undergoing heat treatment in a furnace at 500 °C for an hour.

2.2. Photocatalytic impeller reactor (PIR)

The photocatalytic impeller reactor (PIR) is a gas phase reactor which operates in principle as a stirred tank reactor. The reactor system consists of an ultra-band UV LED (FoxUV™) array. Each UV LED was 5 mm round with wavelength peak at 360 nm, viewing angle of 15° and typical radiant power maintenance of > 90% past 1200 h. The UV LED array was wrapped around the reaction chamber as the illumination source. The reaction chamber was made of a transparent PMMA tubing (Plexiglas® XT) with 92% UV transmission hence, virtually all UV irradiation from the light source is incident in the reaction chamber. A vertically aligned stainless steel (316) shaft running through the centre of the chamber supports the impellers in the reactor. The impellers consist of glass slides (Fisherbrand FB58620) coated with TiO_2 and the coated slides are inclined at 30° and arranged perpendicularly to each other on circular discs. The immobilized TiO_2 film makes the impellers photoactive. A schematic of the designed reactor is shown in Fig. 1.

The shaft is supported at the top and bottom by ball bearings which make its rotation possible and sealed at the bottom with a double lip Viton rubber shaft seal where it exits the chamber and connects to a reversible synchronous motor (Crouzet). The reactor is sealed at the bottom with Viton gaskets as well as the top where three ports are located. The ports are an outlet sealed with propylene 2-way ball valves having Viton seals, an inert septum sealed inlet and a sampling port fitted with a filter and valve.

2.3. Experimental operating conditions

The PIR reactor was operated in batch mode, the inlet and outlet were sealed during operation while sampling took place through the

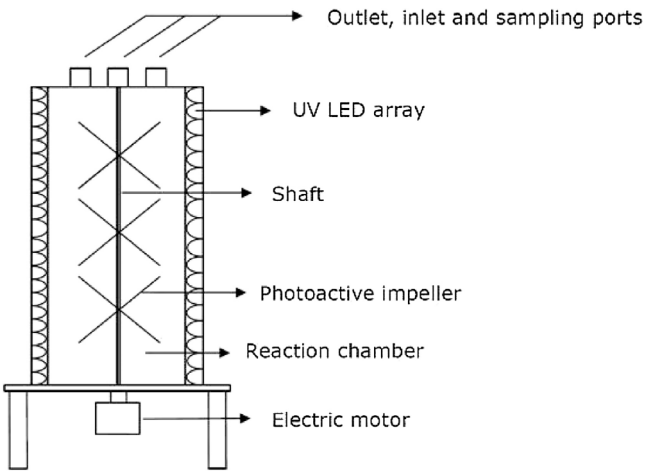

Fig. 1. Schematic of photocatalytic impeller reactor.