論文 / 著書情報
Article / Book Information

題目(和文)	マイクロ構造された反応空間を用いた光誘起酸化処理の強化
Title(English)	Intensification of photo-induced oxidation processes by using microstructured reaction spaces
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出典(和文)	学位:博士（工学）, 学位授与機関:東京工業大学, 報告番号:甲第9623号, 授与年月日:2014年9月25日, 学位の種別:課程博士, 審査員:吉川　史郎,太田口　和久,Wiwut Tanthapanichakoon,関口　秀俊,日野出　洋文,森　伸介,大川原　真一
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第9623号, Conferred date:2014/9/25, Degree Type:Course doctor, Examiner:,,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

Intensification of photo-induced oxidation processes by using micro-structured reaction spaces

This research was proposed with the main objectives of *(i)* assessing the possibility of using microreactor technology for intensifying photochemical/photocatalytic water/wastewater treatment processes, and *(ii)* applying such technologies into new reactor concepts that would make possible to carry out light-induced treatments in an economical and efficient way. First, the photochemical decolourisation of a dye (methylene blue) under ultraviolet irradiation, and how it was affected by the miniaturisation of the reaction space was investigated. Then the effect of the presence of a photocatalyst (TiO_2) on its decolourisation and what differences are brought about when the photocatalytic process is carried out in microscale were evaluated. Building up on these experiences and considering the specific requirements for artificial (lamp) and natural (solar) light photoreactors, two different types of microreactor concepts are proposed and had their effectiveness investigated for the photocatalytic removal one of the most common class of organic contaminants (aromatics) by using phenol as a model pollutant. The aforementioned four steps of the research, together with the *introduction*, the *research background* and the *concluding remarks* sections, which make up the six chapters of the presented thesis, are briefly summarised below.

1. INTRODUCTION

This chapter contains an overall introduction to the works developed in this thesis, presenting the motivations guiding the research, the central tenets upon which it was carried out, the novel aspects unfolded over its course, and a general outline of the thesis structure

2. THEORETICAL BACKGROUND

This chapter presents a review on the theoretical background of the works developed in the thesis, briefly introducing the fundamentals of Advanced Oxidation Processes (AOP) (section 2.1), with a particular focus on photocatalysis (2.2). The issues regarding the engineering of photochemical reactors are introduced in section 2.3, followed by a presentation of the main concepts of the micro-reaction technology (2.4), in which the merits and demerits of microreactors for photocatalytic applications are discussed.

3. PHOTODECOLOURISATION OF METHYLENE BLUE (MB)

The first step in our study was the investigation of *the role of the reactor dimension* on the interaction of light with an absorbing species in solution (*i.e.* homogeneous photochemical reaction). A commercial microchannel reactor consisting of a 3 x 7 cm rectangular borosilicate glass plate, in which a semi-elliptic channel of 40 μm depth, 100 μm width and 50 cm length is engraved, was selected for this study. Illumination was provided by a UV-LED bundle with a monochromatic emission at 365 nm with adjustable intensity. The effect of MB concentration, light intensity and pH was investigated. The results showed that MB is decolourised to a larger extent in the microreactor, versus a larger scale batch reactor. We also found out an intricate relationship between the dye and the glass surface, especially when pH is high. The main conclusions from this step were that *(i)* photochemical reactions can be intensified in microreactors, and *(ii)* surface effects, like adsorption and surface reactions, are much stronger than in conventional scale reactors and, therefore, the observed behaviour of the chemical system can differ greatly between both scales.

4. PHOTODECOLOURISATION OF METHYLENE BLUE WITH TIO_2

Following the conclusions from the previous investigation, it was suggested that the immobilisation of a photocatalyst on the walls of the microchannel would enhance greatly the decolourisation process of MB. Thus a sol-gel method was used to immobilise a layer of TiO_2 onto the microreactor walls. The effects of pH and flow rate on conversion were investigated, and the microreactor performance was compared with a suspended slurry reactor. Results reinforced our previous findings about the strong adsorbability of the model pollutant and the observed trend in conversion with respect to the pH of the reaction medium. The main conclusions from this step were that *(i)* microreactors can circumvent the disadvantages of immobilising the catalyst particles: faster reaction rates were achieved in comparison with slurry reactors; and *(ii)* MB adsorbs strongly also to the photocatalytic layer, but *(iii)* a fast flow rate is able to desorb the adsorbed MB layer due to the strong shear stress experienced by the reactor walls.

5. DEVELOPMENT OF A LOW-COST PHOTOCATALYTIC MICROREACTOR FOR LOW-POWER LIGHT SOURCES

Considering the knowledge acquired from the previous studies, in particular (i) the importance of the interaction between the reactor walls and the reaction media, and (ii) the capacity of microreactors to achieve good conversions even at low irradiance levels; and combining these observations with four desirable traits for lamp-driven photocatalytic processes (*viz.* low manufacturing and operational cost, straightforward change in throughput, compactness, and maximum light harnessing), the reactor design discussed in this chapter was conceived. It consists of a microtube (inner diameter ranging from 0.25 to 1.00 mm) made of a UV-transparent and chemically inert fluoropolymer (PFA). The effects of the catalyst precursor suspension and the rounds of immobilisation procedure on the resulting photocatalytic layer were examined. The photocatalytic performance of the reactor as well as the effects of the reactor inner diameter, the solution pH, and the catalytic layer on it, were investigated by comparing the degradation rates of phenol. The main results for this investigation showed that *(i)* it is possible to immobilise the photocatalyst onto the tubings by using a low cost and simple thermal method; *(ii)* the resulting catalytic layer was robust to long-hour operations; and *(iii)* the reactor showed conversion comparable to the commercial glass microreactor, for about 1/100 of its cost, while also *(iv)* showing a reaction rate superior to the observed in a larger scale slurry reactor.

6. DEVELOPMENT OF A HIGH-THROUGHPUT SOLAR PHOTOCATALYTIC REACTOR WITH MICROS-TRUCTURED REACTION SPACE

The most costly part of a photocatalytic treatment is the light source, not only operationally but also capitally if highly specialised UV lamps are used. To tackle this drawback, several groups have proposed using natural sunlight as a light source. This chapter presents a brief review on the engineering of solar reactors and discusses its merits and drawbacks. Based on the experience acquired with the previous studies, two packed bed reactors (PBR), designed to provide high specific surface area, micro-structured reaction spaces, and with geometry suitable for coupling with parabolic trough or compound parabolic collectors, were conceived. The PBR body consists of a UV-transparent glass cylinder with inlets and outlets perpendicular to its axis. In one concept, both ends of the reactor body are closed and packed with glass beads coated with TiO_2 layers. In the other concept, an inner tube (SUS or porous PVC, depending on the operation conditions) is installed concentrically with the reactor body, and the annular space between them is then packed with the catalyst-covered glass beads. The reactor was applied to the degradation of phenol using a solar simulator as light source. Results showed that *(i)* the design with an inner tube achieved faster reaction rates than the design without the inner tube, while *(ii)* both reactors performed better than a slurry batch. *(iii)* Oxygen input improved the reaction rate only slightly, but allowed for the mineralisation to proceed further than without a gas feed.

7. CONCLUDING REMARKS

Throughout the thesis, the feasibility of utilising the micro-structuring approach to improve the current photocatalytic reactor technology, particularly for water and wastewater treatment, was examined. It involved combined efforts to tackle the drawbacks of immobilised photocatalysis and the drawbacks of microreactors, while keeping in mind economic constraints. In this chapter, an overview of the importance of the findings reported in this thesis (7.1) is presented along with discussion of some possible guidelines for the advancement of this research field (7.2).

業績一覧

本研究に基づく査読論文

1. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. **2014**. Intensification of Photochemical Wastewater Decolorization Process Using Microreactors. *Journal of Chemical Engineering of Japan*, v. **47**, p. 136-140.（3 章）

2. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. **2014**. Photocatalytic decolorization of methylene blue in a glass channel microreactor. *Journal of Chemical Engineering of Japan* (in press).（4 章）

3. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. **2014**. On the use of fluoropolymer tubes as photocatalytic microreactors: catalyst deposition and performance evaluation. *Journal of Environmental Chemical Engineering* (in press).（5 章）

4. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. Novel micro-structured packed-bed reactors for intensification of solar photocatalysis. (under preparation)（6 章）

国際会議

1. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. *Intensification of photochemical wastewater decolorization process by using microreactors*. International Workshop in Process Intensification 2012: Seoul, **2012**.（3 章）

2. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. *Enhancing dye decolourisation by using photocatalytic microreactors*. 9th World Congress of Chemical Engineering: Seoul, **2013**.（4 章）

3. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. *Influence of channel material and size on the photodegradation of organic compounds in microreactors*. 9th World Congress of Chemical Engineering: Seoul, **2013**.（5 章）

国内会議

1. Ramos, B., Ookawara, S., Matsushita, Y., Yoshikawa, S. マイクロリアクターを用いた光触媒排水処理のプロセス強化。第 32 回光がかかわる触媒化学シンポジウム：東京、**2013**.

参考

1. Ramos, B., Ookawara, S., Matsushita, Y., Yoshikawa, S. *Using microreactors for intensifying water treatment processes*. 5th Multidisciplinary International Students Workshop: Tokyo, **2013**.

2. Ramos, B.; Ookawara, S.; Matsushita, Y.; Yoshikawa, S. *Improving the efficiency of photocatalytic water treatment using microreactor technology*. 8th Asia-Oceania Top University League on Engineering (AOTULE): Bangkok, **2013**.

本研究以外の査読論文

1. Ramos, B.; Farah, J. P. S.; Teixeira, A. C. S. C. **2012**. Estimating reaction constants by ab initio molecular modeling: a study on the oxidation of phenol to catechol and hydroquinone in advanced oxidation processes. *Brazilian Journal of Chemical Engineering*, v. **29**, p. 113-120.

2. Ramos, B.; Teixeira, A. C. S. C. **2009**. Molecular-Scale Modeling of the Degradation of Phenol in Advanced Oxidation Processes Reaction Media. *Computer Aided Chemical Engineering*, v. **27**, p. 285-290.