学 位 論 文 審 査 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　ウアガセーム　ガサマー

審査担当者	主査	教授	増田 隆夫
	副査	教授	福岡 淳
	副査	准教授	荻野 勲
	副査	教授	向井 紳

学 位 論 文 題 名

Development of Monoliths with Introduced Straight Microchannels for Applications in Continuous Wastewater Treatment
（直状マイクロ流路を導入したモノリス体の開発と連続式廃水処理への応用）

Wastewater from many industries is contaminated with soluble aromatics. Due to their high impacts to health and the environment even at a ppm-level concentration, strict standards and regulations regarding their concentration in wastewater effluents are applied worldwide. Among the treatment techniques for water-soluble aromatics, adsorption by carbon materials and heterogeneous photocatalysis are the two techniques widely studied. Along with the development of new adsorbents and photocatalysts with improved properties, continuing research on how to integrate them into a fixed bed is required to efficiently use them in continuous operations. Structured adsorbents and catalysts potentially overcome mass transfer limitations often encountered in conventional packed beds, while enabling high flow rate and minimal pressure drop. In this work, the use of porous monoliths with introduced straight microchannels and thin channel walls were suggested to overcome mass transfer limitations and further increase the contact area in wastewater treatment systems. The thin walls of the monolith would facilitate rapid mass transfer, and the straight microchannels would minimize the pressure drop when fluid flow through the monoliths. The synthesis methods, and the applications of the monoliths were discussed to show their potentials to be used for continuous treatment of soluble aromatics in wastewater.

Part 1 (Chapter 2 and 3) describes the use of $TiO_2 - SiO_2$ monolithic microhoneycombs synthesized by the ice templating method for photocatalytic treatment of wastewater.

In Chapter 2, $TiO_2 - SiO_2$ microhoneycombs were synthesized using an inexpensive sodium silicate solution as a precursor for SiO_2, which is similar to the production of commercial silica gels. The use of reactive alkoxides of Ti could be avoided by using a commercial TiO_2 sol instead. Monolithic microhoneycombs with 25 mol% TiO_2 were successfully synthesized. The straight microchannels introduced by the ice templating method could minimize the pressure drop across the bed to less than a hundredth of that of beds packed with particles having the same diffusion path length. The samples also have high BET surface areas over 500 $m^2\ g^{-1}$, which could facilitate both radiative transport and adsorption of the substrate. This leads to improved photocatalytic activities compared with disk-type TiO_2 photocatalysts having lower surface area, both in batch and continuous flow systems. In addition, the effect of calcination temperature to photocatalytic activity was studied. Although TiO_2 could retain its anatase phase even after calcination at 1000 ℃, the decrease in specific surface area led to the decrease in photocatalytic activity. The results emphasize the importance of photocatalysts with high specific surface area, which the synthesis could be realized by the ice templating method.

In Chapter 3, the synthesis method of $TiO_2 - SiO_2$ microhoneycomb photocatalysts was further improved by using two sources of TiO_2 sols stabilized at different pHs, so that the morphology of the samples can be controlled independently from TiO_2 content. This synthesis method resulted in uniform distribution of TiO_2 inside SiO_2 matrix, so samples having 10 mol% TiO_2 synthesized by the improved method could show similar photocatalytic activity compared with the 25 mol% TiO_2 samples synthesized by the method introduced in Chapter 2. The effect of calcination temperature was studied again in this chapter. It was found that samples calcined at 600 − 800 ℃ had improved compressive strength and photocatalytic activity, while retaining the anatase phase of TiO_2 and high BET surface areas over 500 $m^2\ g^{-1}$. It was also found that the microhoneycomb morphology was not only effective in minimizing the pressure drop across the system, but also in uniform distribution of the feed flow, compared with systems with packed bed of particles having the same diffusion path length. The results further illustrate the potentials of microhoneycomb-shaped photocatalysts to be used to fulfill various process demands.

One of the limitations of larger honeycomb photoreactors (mm-order channels) is that the light intensity rapidly decreases along the length of the monolith, and the optimal aspect ratio of the monoliths must be determined. The design guidelines of monolithic adsorbents also stated that it is crucial to be able to make monoliths having optimal channel size and wall thickness. Therefore, the synthesis methods of monoliths with straight microchannels which allow independent control of channel size and wall thickness are preferred. However, it is difficult to do so in the ice templating method. Therefore, in Part 2 (Chapter 4 and 5), a new synthesis method of monoliths with introduced microchannels, which allows independent control of channel size and wall thickness, was developed.

In Chapter 4, a new synthesis method to synthesize monoliths with introduced straight microchannels was developed. The "fiber templating method" used polyester fibers, which decompose at high temperatures, leaving only a trace of them behind, to introduce microchannels to the monoliths. Carbon gels synthesized by the polycondensation of resorcinol and formaldehyde were selected due to the ability to tune the porosity during the synthesis, and monoliths made from these carbon gels were successfully synthesized by the fiber templating method. The channel size and the wall thickness of the monoliths could be independently adjusted by changing the size and the amount of the template fibers, respectively. The synthesized monoliths also had adequate mechanical strength to be activated, and samples with high BET surface area of over 1600 $m^2\ g^{-1}$ could be obtained at a burn-off ratio (B.O.) of 47%, without altering the overall morphology. The synthesized monolith also showed high adsorption capacities of phenol, both in batch and continuous flow systems. It was found that the monoliths with channel sizes of 60 − 93 μm and wall thickness of up to 70 μm could effectively adsorb phenol in continuous flow systems at the superficial velocity of 3 cm min^{-1}. In these cases, the lengths of unused bed (LUB) for 20-mm samples were 5 mm or less. The results show the potential of the fiber templating method and the synthesized monoliths to be used in continuous adsorption.

In Chapter 5, the optimal dimensions (channel size and wall thickness) of the monoliths were determined via the simulation of breakthrough curves. The parameters in mass transfer were obtained by fitting the breakthrough curves obtained from the experiments with theoretical equations. The concept of limiting diffusion time was introduced to determine the slowest mass transfer step, and to determine the optimal dimensions. The simulations predict the optimal channel size to be 93 − 115 μm, and optimal wall thickness to be 57 − 71 μm. These simulations could also be used to predict whether the continuous adsorption process with the monoliths would suffer from mass transfer for the systems using monoliths in which the dimensions were not included during the determination of limiting diffusion time, and also for the systems with different residence time. Therefore, guidelines to use the breakthrough curves to determine the optimal dimensions of the monoliths were established. Finally, the simulated breakthrough curve of the monolith having optimal dimensions was compared to those of beds packed of spherical particles, and the monolith performed better than the packed beds, both in terms of mass transfer and hydraulic resistance. The results show the advantages of using the monolithic adsorbents with introduced straight microchannels, which the channel size and wall thickness could be tuned to optimize the performance in continuous adsorption.

Finally, Chapter 6 shows the general conclusions of this work. It is shown that monoliths with introduced straight microchannels have high potentials for the applications in continuous treatment of soluble aromatics in wastewater to improve the performance of conventional treatment systems.

Considering these research achievements, we conclude that the author is eligible to receive a doctoral degree of engineering from Hokkaido University.