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主 論 文 の 要 旨

論文題目　**FABRICATION OF INNOVATIVE MATERIALS FOR WASTEWATER TREATMENT**
(廃水処理のための革新材料の作製)

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論 文 内 容 の 要 旨

Nowadays, wastewater contaminated by numerous organic substances, produced from both human activities and industries, is one of the most important problems of the world. These contaminated waters are known to have an adverse effect on human health as well as aquatic livings who consume them. Several countries have already developed the purification technologies, especially for the places that generate a large amount of wastewater. However, the technologies to apply in small to medium wastewater production are still in-adequate. Therefore, new and easy-to-apply wastewater purification technologies to eliminate the organic substances contaminated in wastewater before discharge to the nature is necessary for realizing a sustainable society.

Among various conventional processes, which have been employed to get rid of the contaminants from wastewater; such as coagulation-flocculation, chlorination, adsorption, advanced oxidation processes (AOPs), adsorption and AOPs seem more promising owing to their low energy and toxic solvent consumptions, high performance and convenient operation systems. In addition, they do not generate secondary waste, thus, the disposal or post-treatment are not required in comparison with other treatment processes. Considering the adsorption process, activated carbon (AC) and zeolites are extensively used as an adsorbent. Although their powdery form presents a good adsorption performance because of the high specific surface area, it lacks in separation ability and reusability after treatment process. Moreover, the saturated adsorption on the adsorbent was found to limit their performance. In case of AOPs, especially in the photocatalytic degradation process using TiO_2 as a photocatalyst, the organic molecules were degraded by the reactive radical oxidizing species (e.g. OH•) generated in the system. However, the sinking of TiO_2 powder leads to the low light illumination on the TiO_2 surface resulting in an insufficient energy for exciting the electron-hole separation during the photocatalytic reaction.

In order to overcome the aforementioned problems, the development of new materials for rectifying the limitations of conventional materials are considered. This dissertation presents the study on fabrication of three innovative materials for wastewater treatment application. The structure of this dissertation and the brief details of each study are explained as follows.

Chapter 1 provides a brief overview of the research conducted in this dissertation, including the objective and introduction of developed materials.

Chapter 2 introduces the background of this study and the importance of the present research. Information on the current wastewater problems of the world and on the conventional technologies are reviewed. In addition, the objective of this research is clarified.

Chapter 3 reports the synthesis of magnetic activated carbons based on a magnetite/epoxy resin system. Magnetic properties have been embedded to the well-known adsorbent, ACs, have been studied to overcome their lack in separation ability after use. Conventionally, the fabrication of the magnetic activated carbons (MACs) are performed by the introduction of magnetic precursor, such as magnetic nanoparticles, into the as-synthesized activated carbons (ACs). However, the introduced magnetic particles were found to clog or narrow the generated pores of the ACs resulting in the lower adsorption performance. In order to solve this issue, we report a new method to synthesize the MACs which can prevent the pore clogging and modified its synthesis conditions. The important three main steps are; (i) the embedding of Fe_3O_4 particles into the epoxy resins, (ii) the carbonization of Fe_3O_4-embedded epoxy resins having the main agent to hardener of 9:1 at the temperature of 500 °C for 40 min with the heating rate of 300°C/h, and (iii) KOH activation at 700°C for 1 h. From the pore structure characterization, the mixed structure of micropores and mesopores with relatively high pore volume and surface area was obtained. Moreover, the synthesized MACs present the high adsorption performance with a high maximum adsorption amount of 650 mg/g against methylene blue (MB), which is equivalent to that of ACs synthesized with the same condition. Additionally, the MACs could be quickly and easily separated from the solution using a neodymium magnet by their enhanced magnetic properties.

Chapter 4 deals with the synthesis of a floating photocatalyst *via* electroless Ni-P-TiO_2 composite plating on polypropylene (PP) balls (ENP-TiO_2-PP balls). TiO_2 is a well-known broad-band gap semiconductor, which is extensively applied as a photocatalyst in photocatalytic degradation of organic molecules. However, the sinking of TiO_2 powder at the bottom of the container during the non-stirring reaction make the UV irradiation on their surface insufficient. In addition, they also lack in the separation and reusability after treatment process. Here, the floating TiO_2 was synthesized to overcome the aforementioned problems using polypropylene (PP) hollow ball as a floating substrate. Conventionally, the photocatalytic reaction occurring on the TiO_2 surface was reported to degrade the PP properties. From this point, the electroless Ni-P-TiO_2 composite plating technique (ENP) was applied to deposit TiO_2 on PP ball. The ENP-TiO_2 composite layer was expected to act as the barrier for protecting the PP surface from TiO_2 photocatalytic degradation. Several important parameters have been studied and the optimum condition was found to be the pre-treatment of PP ball surface by hot xylene and H_2CrO_4 followed by ENP plating with the Ni-P solution containing 45.0 g/L of P25 TiO_2 powder at pH 9.0 under stirring at 80 °C for 20 min. From the morphology characterization, the good adhesion between the ENP-TiO_2 composite coatings and PP substrate were confirmed. An ENP layer with amorphous Ni-P structure and high P concentration, which is previously reported to provide the good material properties as well as high resistance to severe environment, have been obtained. Additionally, the synthesized ENP-TiO_2-PP balls could maintain the good floatability and exhibited the enhanced photocatalytic activity against MB solution.

Chapter 5 challenges on the synthesis of floating adsorbent/photocatalyst fabricated through a TiO_2 deposited hydrophobic pure-silica zeolite crystallized on hollow glass microsphere. The previous two materials were synthesized in order to overcome the lacks of conventional materials but the third material was designed considering the present issues, leading to a new material structure. As mention previously, the adsorption performance of adsorbent is limited by the saturated adsorption, meanwhile, the photocatalytic efficiency of the photocatalyst is influenced by the sufficient photon excitation as well as the adsorption of the targeted molecule on its surface. In addition, both lacks the ability to be easily separated from the media. From the above factors, the tri-layer floating adsorbent/photocatalyst was designed and synthesized through the deposition of TiO_2 on the pure-silica MFI-type zeolites (PSZ), which were crystallized on the hollow glass microsphere (TiO_2-deposited PSZ-HGMs). The adsorption of organic substances on the hydrophilic TiO_2 surface was improved by the hydrophobic PSZ crystals. In the same moment, the saturation of the organic substances adsorbed on the PSZ was also relieved by the photocatalytic reaction taken place on the adjacent TiO_2 surface. Furthermore, the UV irradiation on the TiO_2 surface including the difficulty in the separation of the material after usage were solved by maintaining the floatability using the floating substrate (i.e. HGMs). The synthesized TiO_2-deposited PSZ-HGMs with distributed mixed phase of anatase-rutile TiO_2 with high coverage, continuous, random orientation and well attachment of coffin-like shaped PSZ crystals on the HGM surface were successfully synthesized. The synthesized TiO_2-deposited PSZ-HGMs exhibited the high MB removal performance, the ability to continuously degrade MB and rapid floatation ability.

Chapter 6 summarizes the finding of this dissertation. Three innovative materials showing good properties and performance for removing organic substances contaminated in wastewater were successfully synthesized. Their characteristics and performances are promising to apply, especially for limited area, due to their low production and operation cost, environmental friendliness, and easy separation.