学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　朱 倩倩

学 位 論 文 題 名

Enhanced oxidation of brominated phenols using iron(III)-porphyrin catalysts immobilized on functionalized supports

(機能化された担体への鉄 (III)-ポルフィリン触媒の担持による臭素化フェノール類の促進酸化に関する研究)

Bromophenols, a class of brominated flame retardant (BFR), are widely used as reactive and additive BFRs in the production of electronic circuit boards and other electronic equipment. In particular, tetrabromobisphenol A (TBBPA), 2,4,6-tribromophenol (TrBP) and pentabromophenol (PBP), which have been reported to show endocrine disruption effects, are produced in high volumes. The high levels of bromophenols have been found in landfill leachates. Due to the potential environmental risks, bromophenols in landfill leachates must be degraded and detoxified. Iron(III)-porphyrins have been applied to the catalytic degradation of halogenated phenols as green catalysts in homogeneous conditions. Although Iron(III)-porphyrins show high catalytic activity in homogeneous conditions, the deactivation was caused by self-degradation in the presence of an oxygen donor such as $KHSO_5$ and H_2O_2. In addition, the presence of humic substances (HSs), which widely distribute in landfill leachates, inhibit the catalytic oxidation of bromophenols by iron(III)-porphyrins. To suppress the deactivation and enhance the reusability of iron-porphyrin catalyst, the immobilized iron-porphyrins were focused in the present study. In addition, to eliminate the inhibition by HSs and enhance the selectivity, iron(III)-porphyrin catalysts were immobilized to a variety of supporters that have some functions, such as large negative electrostatic filed and size selectivity. As a result, the catalytic activity in the presence of HSs was found to be effectively enhanced by the use of ionic liquid functionalized Fe_3O_4. The finding in the present study will provide useful immobilization strategies for the practical use of iron(III)-porphyrin catalysts in the waste water treatment.

Chapter 1 describes the application of bromophenols, potential environmental risks, previous techniques for treatment of bromophenols, and the influences of HS on the bromophenol degradation. In addition, the advantages and disadvantages of iron(III)-porphyrin catalysts for the catalytic oxidation of bromophenols were explained, based on the previous reports, and my strategy for the catalyst design was discussed.

In Chapter 2, to suppress the self-degradation of iron(III)-porphyrin, an iron(III)-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (FeTCPP) was immobilized on a functionalized silica gel (SiO_2-FeTCPP) for the catalytic degradation of TrBP, one of the widely used bromophenols, in the absence and presence of HS. More than 90% of the TrBP was degraded in the pH range of 3-8 in the absence of HS, while the optimal TrBP degradation was in the pH range of 5-7 in the presence of HS. Although the inhibition of HS was not sufficiently eliminated above 50 mg L^{-1} of HS, more than 90% of TrBP was finally degraded at HS concentrations below 50 mg L^{-1} and 10 times of catalyst recycles

were achieved even in the presence of HS.

In Chapter 3, the Fe(III) tetrakis(*p*-sulfonatephenyl)porphyrin (FeTPPS) was axially immobilized on imidazole functionalized silica (FeTPPS/IPS) to enhance the performance of iron(III)-porphyrin catalyst in the presence of HS. The catalytic activity of FeTPPS/IPS was examined to the catalytic degradation of TBBPA, a commonly used BFR and an endocrine disruptor. This catalytic system was pH independent in the absence of HS, and more than 95% of the TBBPA was degraded in the pH range from 3 to 8, while the optimal pH for the reaction was at pH 8 in the presence of HS. Although the TOF was decreased in the presence of HS, over 95% of the TBBPA was degraded within 12 h in the presence of 28 mg-C L^{-1} of HS. At pH 8, the FeTPPS/IPS catalyst could be reused up to 10 times without any detectable loss of activity for TBBPA degradation and debromination, even in the presence of HS.

In Chapter 4, to suppress the inhibition of HSs for the oxidative degradation effectively, a mesoporous molecular sieve SBA-15 supported FeTPyP (FeTPyP-SBA-15) was synthesized and applied to the degradation of PBP using $KHSO_5$ as an oxygen donor. The prepared FeTPyP-SBA-15 showed a high catalytic activity and 50 μM of PBP was efficiently degraded at pH 8 using 125 μM $KHSO_5$ even in the presence of 50 mg L^{-1} HS. The turnover frequency (TOF) for the FeTPyP-SBA-15 in the presence of 25 mg L^{-1} HS (58.3 h^{-1}) was larger than that for a control catalyst, FeTPyP-SiO_2 (16.7 h^{-1}). Thus, the FeTPyP-SBA-15 had a high selectivity for the catalytic degradation of PBP and the orderly porous structure of FeTPyP-SBA-15 played a key role in decreasing the adverse effect of the HS.

In Chapter 5, to overcome the disadvantages in the lower catalytic activities of heterogeneous catalysts, the " liquid phase " methodologies were introduced into the solid catalysts to " restore " homogeneous catalytic conditions. For facilitating separation of the used catalyst, FeTPPS was introduced to the ionic liquid (IL) coated Fe_3O_4 by ion-pair formation via electrostatic interaction. The prepared Fe_3O_4-IL-FeTPPS catalyst was examined to the catalytic oxidation of TrBP and the inhibition of HS was suppressed even in the presence of very high concentration (86 mg L^{-1}). Although mineralization of bromophenols had not been observed in other prepared catalysts (SiO_2-FeTCPP, FeTPPS/IPS and FeTPyP-SBA-15), the 55% of TrBP was mineralized, indicating that the catalytic activity of iron-porphyrin was largely enhanced by the ionic liquid.

Chapter 6 describes the conclusions of the present study.