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審査研究科	生命環境科学研究科
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論　文　の　要　旨
Abstract of thesis

Nowadays, the serious environmental issues such as water eutrophication, soil acidification and particulate matter ($PM_{2.5}$) are becoming the major human survival crisis. In addition, discharge of wastewater containing high dissolved ammonia concentration and gaseous NH_3 emission are the two main contributors to the above problems relating to nitrogen. Among all the available technologies, adsorption with the advantages of easy control, low cost and high efficiency was applied in this study to remove/recover ammonia by using the newly developed adsorbents, especially under the high concentration of dissolved ammonia together with high sodium salt concentration and gaseous NH_3 sorption at high working temperature (~250 °C) conditions. The dissertation is divided into 5 chapters.

In Chapter 1, the author gave a literature review on current treatment methods for dissolved ammonia and gaseous ammonia removal. By comparing the advantages and disadvantages of the available technologies from previous studies, the author focused on the development of adsorbents for ammonia, and addressed the current problems for adsorbents if being used to deal with high sodium salt concentration and high working temperature conditions. At last, the author pointed out the main objectives of this research.

In Chapter 2, the author investigated and compared the removal of NH_4^+ from aqueous NH_4Cl solutions and salty water. For NH_4^+ sorption, a new Prussian blue (PB) analogue, namely sodium cobalt (II) hexacyanoferrate (II) (NaCoHCF), $Na_yCo(II)[Fe^{2+}(CN)_6]_x \cdot zH_2O$ with high capacity and selectivity was prepared. Even in a salty solution prepared by using NaCl at a Na^+ concentration of 9,350 mg/L, this newly developed adsorbent could maintain the maximum adsorption capacity (q_{max}) at 4.28 mol/kg, about 40 times higher than zeolite under the similar condition. The selectivity factor (α) defined by the ratio of equilibrium constant for NH_4^+ to that for Na^+ was calculated to be 96.2. The high selectivity of the prepared NaCoHCF achieved good NH_4^+ adsorption performance, even in the synthetic seawater with a high Na^+ concentration of 9,350 mg/L.

In Chapter 3, the author investigated gaseous NH_3 sorption/capture under a wide range of temperature

using PB analogues, among which cobalt hexacyanocobaltate (CoHCCo) was prepared and evaluated when operation temperature varied from 20 to 250 °C. The results showed that this newly prepared adsorbent can be applied in the temperature swing adsorption (TSA). The highest NH_3 sorption capacities of CoHCCo were 25.2, 18.6, 8.6, and 2.1 mmol/g at 20, 100, 150, and 250 °C, respectively. Also, the prepared adsorbent can maintain its stable structure during the sorption-desorption cycles by injecting 8 vol% NH_3 gas mixed with room air.

In Chapter 4, to compare with CoHCCo used in Chapter 3, another new adsorbent named zinc hexacynanocobaltate (ZnHCCo) was developed. Results indicated that ZnHCCo exhibited the same sorption capacity as CoHCCo did; moreover, the adsorbed NH_3 could be desorbed by pressure swing adsorption (PSA) process at moderate high working temperature (100 °C). In this chapter, the effect of air at a moderate humidity (RH: 76%) on the NH_3 sorption performance of ZnHCCo and CoHCCo was also evaluated.

In Chapter 5, the author briefly summarized the major conclusions and prospected the future research works in order to realize the practical application of the above technologies. These conclusions are meaningful regarding ammonia removal/recovery from wastewater containing high sodium salt concentration and under a humid atmosphere at working temperature ranging from room temperature to 250 °C. Based on the results from this study, pilot- and industrial- scale systems for ammonia removal/recovery could be established to provide more scientific data for commercialization.

Results from this work imply that the new adsorbents, PB analogues, could provide an effective solution for NH_4^+ removal from wastewater or for ammonia recovery from exhaust gas containing NH_3 due to their much higher sorption capacity and selectivity, and for NH_3 capture/recovery in the field of wastewater treatment and air pollution control. As NH_3 can be used as fuels and H_2 carrier, the developed adsorbents can be very promising in the hydrogen energy field. This study also provides a cost-effective method to alleviate ammonia pollution caused by excessive use of fertilizer and large-scale ammonia production. Further research efforts are still necessary for recycling and re-utilization of the adsorbents and confirmation of NH_3 recovery efficiency in the presence of other trace gases and humidity.

審 査 の 要 旨
Abstract of assessment result

In this research, PB-based adsorbents were developed targeting ammonia removal/recovery from wastewater and NH_3-containing atmosphere. The results from the effect of high sodium salt concentration on NH_4^+ sorption indicated, the developed adsorbent NaCoHCF has the highest sorption capacity (q_{max}) of 4.36 mol/kg compared to other commercial adsorbents. This is attributable to its higher selectivity to NH_4^+, providing important references for NH_4^+ removal/recovery from the sea water. New adsorbents were also developed for gaseous NH_3 capture/recovery from 8 vol% NH_3 atmosphere. The decomposition temperature of ZnHCCo can reach around 350 °C even under pure air and room air conditions. On the other hand, CoHCCo could keep its stable structure even after adsorbing 8 vol% NH_3 atmosphere at a wide working temperature (~250 °C). CoHCCo and ZnHCCo have good recyclability during the sorption-desorption process by TSA, indicating both sorbents could be recycled and reused after being adsorbed for industrial application. Furthermore, ZnHCCo can also be recycled by PSA at high working temperature (100 °C), indicating ZnHCCo has unique sorption properties at moderate high working temperature. It is very meaningful to utilize TSA or PSA process to desorb the adsorbed NH_3 as the desorbed NH_3 can be easily used as fuels or clean energy H_2 carrier. Thereby, this study not only contributed to amelioration of NH_4^+/NH_3 pollution problem but also to hydrogen energy field. Besides, as the author mentioned, CoHCCo and ZnHCCo have higher sorption capacity compared to other NH_3 sorbents developed from previous studies, showing their great potential for ammonia removal/recovery in the real world of wastewater treatment and air pollution control.

The final examination committee conducted a meeting as a final examination on 18th Jan. 2019. The applicant provided an overview of dissertation, addressed questions and comments raised during Q&A session. All of the committee members reached a final decision that the applicant has passed the final examination.

Therefore, the final examination committee approved that the applicant is qualified to be awarded the degree of Doctor of Philosophy in Environmental Studies.