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論　文　の　要　旨
Abstract of thesis

The water issues around the world have been focused on water body contamination. On the other hand, it is attractive and meaningful to recover useful chemicals from wastewater or seawater for reutilization and to save treatment cost. There are already several methods that have been applied in wastewater treatment and resource recovery, including precipitation, coagulation, biological method, air stripping, adsorption and so on. Adsorption process is a good means for easing environmental pollution and resource shortage at the same time, while development of high-efficiency adsorbent is essential for the real application. This dissertation described the synthesis of functional adsorbent materials based on modified zeolite and metal hexacyanoferrate (MHCF) and their applications for pollution control and element recovery in wastewater / seawater. This dissertation is divided into 5 parts.

In chapter 1, the author introduced the currently existing problems concerning water contamination and compared several treatment methods for solving the problems. Specifically, in this chapter the author made literature reviews on synthesis and properties of zeolite / MHCF adsorbents, treatment methods used in nutrients containing wastewater and examples of decontamination / metal recovery in seawater to reflect the advantages of applying zeolite / MHCF adsorbents in the given systems.

In chapter 2, the author investigated the treatment of excess nutrients containing wastewater. High concentrations of ammonium and phosphate may not only cause eutrophication once being flushed into natural water bodies, but also inhibit the biogas production efficiency at a high ammonium concentration. The author prepared the bead-like zeolite-chitosan-$FeCl_3$ (ZCFe) adsorbent and applied in NH_4^+ / PO_4^{3-} mixed solutions with a N:P mass ratio of 4:1 to simulate the anaerobic digestion liquid. Results showed that the maximum adsorption capacity was 7.7 mg-P $\cdot g^{-1}$ and 25.1 mgN $\cdot g^{-1}$ when the initial phosphate and ammonium concentration were 25-300 mg-P $\cdot g^{-1}$ and 100-1200 mgN $\cdot g^{-1}$, respectively. In addition, the author also found that the adsorbents after adsorption can be recycled by treatment with 0.025 mol $\cdot L^{-1}$ HCl.

In chapter 3, the author researched the decontamination of radioisotope and nutrient substance by cobalt hexacyanoferrate (CoHCF) adsorbent for monovalent cations Cs^+ and NH_4^+ adsorption. CoHCF has been proven to be effective for Cs^+ and NH_4^+ adsorption, while it is still unclear how to increase the adsorption amount for each adsorbate. Therefore, in this study, the author examined the adsorption behaviour of Cs^+ and NH_4^+ by varying the composition of CoHCF to shed light on choosing suitable adsorbents. The author synthesized CoHCF with a vacancy ratio ranging from 0.014 to 0.47 by mixing the reactants $Na_4[Fe(CN)_6] \cdot 10H_2O$ and $CoCl_2 \cdot 6H_2O$ with a flow method. The adsorption amounts of Cs^+ and NH_4^+ were tested in batch mode and the author found that NH_4^+ adsorption onto CoHCF was advantageous for CoHCF with higher Na content, with the highest adsorption amount of 53.12 mg-N $\cdot g^{-1}$. However, the author still found that the adsorption trend of Cs^+ was opposite to that of NH_4^+ with the highest Cs^+ adsorption amount of 268.32 mg-Cs $\cdot g^{-1}$. The author further interpreted the principles of selecting adsorbents for Cs^+ and NH_4^+ adsorption as follows: CoHCF with higher vacancy ratio is suitable for adsorption of larger cations such as Cs^+, while it is beneficial to use CoHCF of more condensed lattice but higher Na content for adsorption of smaller cations such as NH_4^+.

In chapter 4, the author focused on the recovery of K^+ from seawater by CoHCF thin film coated electrode with a natural adsorption and an electrochemical desorption / regeneration process. K^+ is an essential element for life with increasing demand by industry and it is attractive to recover K^+ from seawater considering its huge K^+ stock. Results of batch adsorption experiments showed that the powder-form CoHCF-0.67 had a good K^+ adsorption amount of 7.22 mmol $\cdot g^{-1}$ (282.30 mg-K $\cdot g^{-1}$) from 10 mmol $\cdot L^{-1}$ KCl solution, far beyond the adsorption amount of CuHCF-0.67, NiHCF-0.67 and FeHCF-0.67. K^+ adsorption from seawater by CoHCF was verified to be a fast process reaching equilibrium within 20 min. The author pointed out that that the K^+ recovery system can work for at least 4 cycles without serious loss of K^+ adsorption ability by desorption / regeneration using the electrochemical process.

In chapter 5, the author gave the major conclusions for the whole study and prospected the future researches for the fulfill of applying this study in real cases.

This study offered an opportunity to realize wastewater decontamination and resource recovery at the same time using adsorption method. Nutrient components (NH_4^+ and PO_4^{3-}), radioisotope Cs^+ and life essential element K^+ can be removed or recovered from wastewaters / seawater with a perfect efficiency using the modified zeolite or MHCF adsorbent. The development and application of the new adsorbents would not only ease the wastewater treatment difficulty but also realize reutilization of the adsorbed substances.

審 査 の 要 旨

Abstract of assessment result

In this dissertation, functional adsorbents were synthesized based on modified zeolite and MHCF for the goal of efficient wastewater treatment and resource recovery at the same time. ZCFe adsorbent was prepared and used for simultaneous removal of NH_4^+ and PO_4^{3-} from synthetic wastewater. The author proved the adsorbent to be feasible in the real application for treating high nutrient-containing wastewater considering its convenient preparation and recycling ability. In addition, the strategy of increasing the adsorption amount of Cs^+ / NH_4^+ by CoHCF was established by varying the vacancy ratio of the adsorbent. Through rational adjustment of the CoHCF adsorbent's composition, this study provided a solution for the effective treatment of radioisotope or nutrient containing wastewater. Furthermore, K^+ recovery from seawater was realized by dipping a CoHCF thin film electrode in seawater for adsorption and then conducting desorption / regeneration through electrochemical process. This study showed the great potential of retrieving K^+ element from seawater without complicated separation.

The final examination committee conducted a meeting as a final examination on 18th July, 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.