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## 論 文 の 要 旨 Abstract of thesis

Phosphorous is an essential nutrient and plays a critical role in the development of agriculture and industry. Phosphorus recovery from phosphate-rich wastewater has been recognized as a key strategy to prevent eutrophication, which can simultaneously solve the phosphorus shortage issue. Recently, carbon-based adsorbents are becoming increasingly attractive as they can be derived from a wide range of agricultural waste feedstocks and has been claimed to possess potentials as cost-effective and environmentally sustainable adsorbents for pollutants management. This research aimed to synthesize innovative, cost-effective and sustainable carbon-based adsorbents from agricultural waste (tobacco stalks), which can remove excessive phosphate from aquatic systems effectively and further realize phosphorus recycling by application of phosphate loaded carbon-based adsorbents as fertilizer in agriculture for food production. This dissertation is divided into five chapters.

In chapter 1, the author stated the world's phosphorus issue relating to water eutrophication and shortage of phosphorus as well as the control policies of aqueous phosphate. Based on the comparison of the current technologies for phosphorus removal/recovery, the author pointed out the main advantages of adsorption process. Further, the author conducted some reviews on the literatures with respect to metal loading and thermal modification of agricultural waste for enhanced phosphate removal.

In chapter 2, the author prepared three novel iron-modified biochars through the pyrolysis of waste tobacco stalk and then decorated them by different ion modification. Results of batch adsorption experiments showed that the three novel biochars possessed remarkably higher phosphate adsorption capacity than the raw biochar. Specifically, the maximum adsorption capacities of FeCl<sub>2</sub>-modified, Fe<sup>2+</sup>/Fe<sup>3+</sup>-modified and FeCl<sub>3</sub>-modified biochar calculated from Langmuir equation were 7.24 mg/g, 7.50 mg/g and 17.4 mg/g, respectively. The pseudo n-order model ( $R^2 > 0.96$ ) fitted the adsorption process better than the pseudo first-order and second-order model. FeCl<sub>3</sub>-modified biochar exhibited a rapid and acid favorable phosphate removal, and the existence of other anions could hardly compete with phosphate species. In addition, the

author interpreted the main mechanism as ligand exchange and electrostatic attraction.

In chapter 3, the author prepared the MgAl-LDHs modified hydrochar composite through carbonization of tobacco stalk feedstock in solution under hydrothermal conditions. The author elucidated that the adsorption capacity of per unit weight of MgAl-LDHs in hydrochar was higher than that of pure MgAl-LDHs, demonstrating the synergetic effect between hydrochar and MgAl-LDHs. The adsorption results showed that the prepared composites were very fast and efficient in phosphate adsorption in a wide pH range or under the coexistence of high level of competing anions. The adsorption kinetic and isotherm data followed the pseudo-second-order equation and the Freundlich model ( $R^2 > 0.99$ ), respectively. The maximum adsorption capacity acquired by the Langmuir model were 30.7, 31.4 and 41.2 mg P/ g at 25, 35 and 45 °C, respectively, much higher than many adsorbents. The author also revealed that the adsorption mechanisms are ion exchange, ligand exchange and electrostatic attraction.

In chapter 4, the author studied the potential applications of FeCl<sub>3</sub>-modified biochar and MgAl-LDHs modified hydrochar. MgAl-LDHs modified hydrochar was comparatively recommended as a potential phosphatic fertilizer substitute, with the high content of non-apatite inorganic and apatite phosphorus (> 93%) after adsorption. While, based on the obvious enhancement of sludge dewaterability and phosphate removal ability, the author suggested that FeCl<sub>3</sub>-modified biochar could be a promising carbon-based composite for anaerobically digested sludge treatment.

In chapter 5, the author summarized the main conclusions of the whole study and pointed out the future research to fulfill the requirements for practical applications.

## 審査の要旨

### Abstract of assessment result

This study proposed an efficient alternative to utilize abundant agricultural organic solid wastes to produce promising adsorbents for phosphate removal from wastewater. In addition, phosphorus can be retained in soils by reutilization of the spent composites as a slow-release fertilizer. This multipurpose technology will not only contribute to phosphate-rich wastewater management, but also be propitious to maintain agricultural sustainability. In this dissertation, low-cost adsorbents were prepared through hydrothermal carbonization or pyrolysis of agricultural waste for the goals of efficient phosphate removal and reuse of the abundant agricultural lignocellulose wastes. The author proved that the iron-modified biochar, with low-cost, good selectivity, and high adsorption capacity, could be an attractive adsorbent for phosphorus-rich wastewater remediation. In addition, functionalized hydrochar with effective phosphate removal capability was developed through one-step hydrothermal preparation, which was propitious to decrease the complexity and cost of the carbon-based adsorbents production. Furthermore, obvious enhancement of sludge dewaterability and phosphate removal ability suggested that carbon-based adsorbents is promising for simultaneously phosphorus removal and sludge conditioning. After adsorption, the synthesized carbon-based adsorbents containing highly bioavailable phosphorus contents reflected high potential for being used as fertilizer, in which phosphorus can be retained in soils and have positive effects on the restoration of soil ecosystem and carbon sequestration.

The final examination committee conducted a meeting as a final examination on 14<sup>th</sup> January, 2020. 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.