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学位の種類	博　士（環　境　学）
学位記番号	博　甲　第　　８８３８　　号
学位授与年月日	平成　３０年　９月　２５日
学位授与の要件	学位規則第４条第１項該当
審査研究科	生命環境科学研究科
学位論文題目	Study of Adsorption-based Technology for Removal/Detection of Trace Inorganic Contaminants in Water （吸着技術に基づく水中の微量無機物汚染物質の除去・検出技術開発に関する研究）

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論　文　の　要　旨
Abstract of thesis

Porous materials-based adsorption technology has been extensively studied for the removal and/or sensing of trace inorganic contaminants, especially those with high toxicity and low biodegradability (like arsenic, copper, and cyanide, etc.). However, up to the present, their industrial-scale application, or their scaling up application from laboratory research to the real world is still lacking, mainly due to the discrepancy between the ideal conditions in theory and the real water environment in practice, which resulted in the overstated effect of many newly reported materials. Another reason is possibly owing to the powdery shape of the most developed materials, which is inconvenient for practical application. This research developed three novel porous materials which are more realistic to the practical application, i.e. Zeolitic Imidazolate Frameworks-8 (ZIF-8), Metal-Organic Framework-76(Tb) (MOF-76(Tb)), and Powdered Activated Carbon (PAC) modified with polyamidoamine (PAMAM) dendrimer. Research results show that these three newly-developed materials can be used for effective trace arsenate, Cu^{2+} and CN^- removal and/or sensing in practice.

The thesis is divided into 5 chapters. In Chapter 1, the author introduced the research background, significance, and literature review. The author also addressed the major inorganic contaminants (arsenate, copper, and cyanide) concerned and the major reasons why so many newly reported porous materials have not been applied in practice, and then arrived at the objectives and framework of the thesis. In Chapter 2, the author investigated arsenate removal from raw water, especially for trace (ppb, μg/L) arsenate in a more realistic water environment by the novel porous material (ZIF-8). Results showed that ZIF-8 outperformed some other adsorbents, achieving the first and highest reported adsorption capacity (76.5 mg/g) at a low equilibrium

concentration (9.8 μg/L). Efforts were also made to shed light on the mechanisms involved in the enhanced arsenate adsorption performance. In Chapter 3, the author researched the feasibility of depositing a typical powdered fluorescent porous material (MOF-76(Tb)) onto the domestic silk fiber to realize feasible copper detection in the practice of water quality monitoring. By comparing the products from hydrothermal, microwave assisted, and layer-by-layer methods, the layer-by-layer method could produce the desirable and controllable coating of MOF-76 onto the silk fiber. The resultant composite demonstrated a high selectivity and sensitivity on Cu^{2+}(i.e. a linear detection concentration range of 10^{-3}–10^{-5} M with a low detection limit up to 0.5 mg/L, K_{SV} of 1192 M^{-1} at 293 K), and rapid response time (5 min), making the composite a good candidate for colorimetric and fluorescent detection of aquatic Cu^{2+}. The quenching effect of this composite was first reported and its mechanism was proposed to associate with the interaction between Cu^{2+} and benzene-tricarboxylate (BTC) ligand, leading to the decrease of energy transfer efficiency. In Chapter 4, the author focused on the feasibility of preparing a disposable composite material using PAC modified with PAMAM for the advanced treatment of coking wastewater (cyanide removal). Results from the laboratory, pilot, and industrial-scale experiments indicate that this one-step novel process could efficiently remove bio-refractory pollutants, achieving the maximum chemical oxygen demand (COD) and cyanide removals of around 85.3% and 99.4%, respectively. Its effluent could meet the corresponding discharge standards without any further treatment, i.e., COD < 30 mg/L, cyanide < 0.1 mg/L, and improved effluent safety (lower toxicity). The easy operation and high efficiency of this method reflect its great potential for engineering application in the tertiary treatment of coking wastewater. Finally, in Chapter 5 the author summarized the major conclusions of the thesis, and proposed the future research directions.

審　査　の　要　旨
Abstract of assessment result

This research explored three novel porous materials which are more realistic to practical application: (1) a novel porous material (Zeolitic Imidazolate Frameworks-8, ZIF-8) for the removal of arsenate, especially from the trace level (ppb, μg/L) arsenate contaminated water environment; (2) a typical fluorescent porous material (Metal-Organic Framework-76(Tb), MOF-76(Tb)) coated onto silk fiber so as to realize the easy separation and prevent the loss of the powdered material during its further usage in copper ion detection; and (3) powdered activated carbon modified with polyamidoamine (PAMAM) to be used as disposable material for high efficacy COD and cyanide removals. Kinetics and mechanisms were also investigated regarding their enhanced efficiency or functionality. In order to manifest their feasibility in the real practice, the author not only carried out their laboratory experiments, but also did the pilot- and industrial- scale tests, reflecting their applicability in the real world of water and/or wastewater treatment. Results from this research are expected to provide new concepts and useful information for the application of porous materials-based adsorption technology in the real practice of water/wastewater treatment and water quality monitoring.

The final examination committee conducted a meeting as a final examination on 20 July, 2018. The applicant provided an overview of the 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.