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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

Adsorption process is one of the most widely applied technologies for water reuse and wastewater treatment. It plays an important role in determining the distribution, migration, transformation and fate of water pollutants. Adsorption has long been favored by many researchers because of its low cost, fast kinetics, low energy for regeneration, insensitivity to toxic substances and complete removal of pollutants even from dilute solution. In the practical operation of full-scale adsorption process, a fixed-bed adsorption system is preferred. In such a system, adsorption of the solutes is a time- and distance-dependent process. The curvature and symmetry of the breakthrough curve are usually subjected to different adsorbent-adsorbate systems and operating conditions. How to accurately describe the breakthrough curve is still a problem to be addressed urgently. The author tried to address the following problems: (i) Mathematical characteristics of the breakthrough curves by adjusting model parameters; (ii) Description of the heterogeneous diffusion-limited process based on the fractal-like kinetics and (iii) Establishment of empirical breakthrough models using hyperbolic tangent and double exponential functions. This study may help readers to better understand the adsorption process in a fixed-bed column and provide useful information for the design of adsorption systems.

The dissertation is divided into 5 chapters. In Chapter 1, the author introduced the research background, objectives and significance based on literature review. In this part, the author narrated adsorption principles, including mass transfer, adsorption types, breakthrough curve, and pointed out some defects of traditional breakthrough models, and provided corresponding feasible strategies, and then arrived at the objectives and framework of the thesis. In Chapter 2, the author defined four parameters including maximum specific breakthrough rate μ_{max}, lag time λ, inflection point t_i and half-operating time t_{50} to reflect the curvature and symmetry of the breakthrough curves: Bohart–Adams, Thomas and Yoon–Nelson models represented the same symmetric breakthrough curve; Clark and dose-response models showed an asymmetric breakthrough curve;

and Wolborska model was not a sigmoidal curve. The physical meaning of q_0m/vc_0 and a_0x/uc_0 was the operating time required to reach 50% breakthrough. The graphic description of the breakthrough curves and rate profiles contributed to selecting the optimal model. In Chapter 3, the author introduced the fractal-like kinetics or time-dependent rate coefficient into Bohart–Adams, Thomas and Yoon–Nelson models to describe the heterogeneous diffusion-limited process in a fixed-bed column. The fitting performance of fractal-like breakthrough models was validated by nitrate adsorption on chitosan-Fe(III) composite. Compared with the Bohart–Adams and Yoon–Nelson models (Adj. $R^2 = 0.9878$ and $\chi^2 = 1.37 \times 10^{-3}$), the fractal-like Bohart–Adams (Adj. $R^2 = 0.9989$ and $\chi^2 = 1.25 \times 10^{-4}$) and fractal-like Yoon–Nelson (Adj. $R^2 = 0.9992$ and $\chi^2 = 8.86 \times 10^{-5}$) models could better describe nitrate adsorption on chitosan-Fe (III) composite. The fractal-like breakthrough models could describe asymmetric breakthrough curves due to introduction of the fractal-like exponent h, which extended application scope of Bohart–Adams, Thomas and Yoon–Nelson models. In Chapter 4, the author proposed hyperbolic tangent and double exponential models to simulate the dynamic behaviors in a fixed-bed column for a wide range of water pollutants. The parameters n, $\mu_{\max}$ and λ were introduced to hyperbolic tangent and double exponential models to better express the curvature and symmetry of the breakthrough curve. The hyperbolic tangent and double exponential models represented symmetric and asymmetric breakthrough curves, respectively. The fitting performance of empirical breakthrough models was evaluated by nitrate adsorption on chitosan-Fe (III) composite. It was found that the double exponential model had best fitting performance with largest adjusted determination factor (Adj. $R^2 = 0.9977$) and smallest reduced chi-squared value ($\chi^2 = 2.54 \times 10^{-4}$). The maximum specific breakthrough rate $\mu_{\max}$, lag time λ, inflection point t_i and half-operating time t_{50} predicted by the double exponential model were 3.99×10^{-3} min^{-1}, 29.7 min, 121.9 min and 155.7 min, respectively. Finally, in Chapter 5, the author summarized the major conclusions of the thesis, and also pointed out the future research directions.

審 査 の 要 旨
Abstract of assessment result

This study developed new breakthrough models to simulate continuous-flow fixed-bed adsorption systems. The fractal-like kinetics or time-dependent rate coefficient was introduced into Bohart–Adams, Thomas and Yoon–Nelson models to describe the heterogeneous diffusion-limited adsorption process. The empirical breakthrough models such as hyperbolic tangent and double exponential models could simulate the dynamic behaviors in a fixed-bed column for a wide range of water pollutants. The fractal-like and empirical breakthrough models provided alternative methods for the modeling of continuous-flow fixed-bed adsorption. Moreover, the graphic description of effects of model parameters on the breakthrough curves and rate profiles intuitively revealed the physical meanings of model parameters, which was beneficial to understand the dynamic behaviors in a fixed-bed column. The revelation of mathematical relationships between breakthrough models significantly reduced the calculated amount instead of complex curve fitting. This study provided useful information for the design and optimization of adsorption systems.

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.