Fixed Bed Adsorption of Water Contaminants: A Cautionary Guide to Simple Analytical Models and Modeling Misconceptions

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ABSTRACT

This contribution is intended as a concise review of the modeling approaches used to describe breakthrough curves of water contaminants and as a cautionary guide to some common and persistent modeling misconceptions. Its intended audience is early career researchers working in the area of adsorptive water remediation. First, typical data- and mechanism-driven models are discussed. A brief description of numerical fixed bed models with multiple curve broadening mechanisms (axial dispersion; intraparticle diffusion; film mass transfer; reaction kinetics) is presented. Particular attention is paid to analytical fixed bed models constructed for linear and nonlinear trace systems. Because these models assume that a single curve broadening mechanism is operative, their functional forms are relatively simple. Examples of spreadsheet calculations with these models are provided. A summary describing several egregious misconceptions associated with the use of two phenomenological models based on reaction kinetics (Bohart–Adams and Thomas) and one empirical model (Yoon–Nelson) to fit breakthrough curves is presented. In many previous studies, the three models have been used blindly, resulting in meaningless findings. It is the author's hope that this article will help the early career researcher avoid repeating the same mistakes.

INTRODUCTION

The presence of trace amounts of contaminants in water and wastewater requires the use of highly efficient treatment technologies. Adsorption is often the best choice for water purification or decontamination owing to its unique ability to treat dilute solutions and to remove a vast array of organic and inorganic contaminants. It is normally carried out in a column packed with porous solid particles because a fixed bed gives much better contaminant removal efficiency than a batch stirred tank. Because it is rarely possible to predict the performance of a given contaminant-adsorbent system from first principles, the analysis of fixed bed adsorption relies on information extracted from experimental studies. Initial testing is usually performed on small-scale laboratory columns to generate breakthrough data. A breakthrough curve is a plot of effluent concentration as a function of time.

The information contained within an experimental breakthrough curve is most conveniently captured using mathematical models. Although a variety of fixed bed models with varying degrees of complexity have been used to process breakthrough data taken at small scales, the most commonly used ones are those proposed by Bohart and Adams, Thomas, and Yoon and Nelson. The popularity of the three models owes much to the fact that their model equations can be linearized to allow parameter estimation by linear regression. Because the three models are highly simplified, they cannot be used to probe the mechanistic nature of fixed bed adsorption dynamics. Instead, they are used as empirical tools to correlate breakthrough profiles. Empirical relationships between their fitting parameters and operational conditions (e.g., flow rate, feed concentration) must be established if they are to be used for process design or optimization. A prominent example ~~of~~ for such a modeling approach is the bed depth-service time (BDST) equation. The BDST equation uses breakthrough data acquired from multiple runs of fixed bed adsorption experiments to establish the relationship between bed depth and the time taken for breakthrough to occur, that is, the service or breakthrough time. According to the BDST equation, this relationship should be linear. The calibrated BDST equation can then be used to size full-scale adsorption columns. It is well known that the BDST equation is based on the Bohart–Adams model. It should be noted that the data analysis step in the BDST design methodology involves experimental data taken from the initial stage of a breakthrough curve where the service time resides. In contrast, in academic research, a model is often fitted to the entire profile of a breakthrough curve. Therefore, the modeling issues raised in this work have no direct bearing on the BDST design methodology.

Every year, scholarly journals churn out hundreds of research articles on the use of the Bohart–Adams, Thomas, and Yoon–Nelson models to fit fixed bed breakthrough data. Unfortunately, this substantial body of literature is marred by various modeling misconceptions and misapplications of the three seemingly simple models. This sad state of affairs reflects the collective failure of journal editors and manuscript reviewers to weed out low-quality modeling work. Despite repeated concerns raised by a handful of researchers,[1–4] the publication of such meaningless modeling results continues to grow unabated. This ever-growing body of fallacious literature is liable to mislead and confuse the interested researcher. Nonetheless, the previous efforts to sound the alarm bell have not been all in vain; the misuse of the three models is now slowly being recognized.

This article is intended to keep the faulty modeling practice in the spotlight and to help the early career researcher become a more competent user of simple fixed bed models. To this end, we firstly provide a concise review of the types of fixed bed models used in the field of adsorptive water decontamination. This introductory note puts the Bohart–Adams, Thomas, and Yoon–Nelson models in context and gives readers an appreciation for the diversity of fixed bed models so that they can better understand the modeling options available to them. Then, a comprehensive dissection of several persistent misconceptions associated with the use of the three models is presented. As background information on the Bohart–Adams, Thomas, and Yoon–Nelson models, the reader is referred to the books by Cooney[5] and Tien.[6] The books by Ruthven,[7] Suzuki,[8] Tien,[9] and Worch[10] provide comprehensive information on more advanced models of fixed bed adsorption, some of which are briefly elucidated here.