A Modified Belter Model for Correlating Asymmetric Breakthrough Curves of Water Pollutants

*Water, Air, & Soil Pollution*  https://doi.org/10.1007/s11270-021-05399-3

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**Abstract**

Several theoretical and empirical models are available to correlate experimental breakthrough curves of water pollutants, one of which is the two-parameter Belter model. Although not as well known as the century-old Bohart–Adams model, the Belter model is being used with sufficient frequency to merit wider awareness of its strengths and weaknesses. Through a systematic analysis, it is shown that the two adjustable parameters of the Belter model are analogous to the equilibrium capacity and rate parameters of the Bohart–Adams model. Breakthrough curves predicted by the Belter model are perfectly symmetric because their inflection points are invariant and always correspond to the midpoint of the curves. As a consequence, the Belter model provides poor fits to asymmetric breakthrough curves. In this work, an improved version of the Belter model is introduced. The new model with a floating inflection point manifests excellent conformity with mildly and, more importantly, severely asymmetric breakthrough curves.

**Keywords:** Adsorption modeling; Asymmetric breakthrough curve; Fixed bed adsorption; Inflection point; Sigmoid curve.

**1 Introduction**

The modeling of water pollutant adsorption in fixed bed adsorbers is of continuing interest to researchers working in the area of water decontamination. Many articles and books have been written on the topic of fixed bed adsorption modeling. As a consequence, several theoretical and empirical models have been developed for describing the dynamics of fixed bed adsorbers. The simplest representation of fixed bed adsorption is based on the assumptions of plug flow and local interphase equilibrium. This model predicts that the breakthrough curve of a fixed
bed adsorber with a Langmuir isotherm subject to a step change in feed concentration consists of a shock or perfectly sharp step function profile. In this limiting case, the performance of the fixed bed is at its maximum. However, breakthrough curves for real-life adsorption systems will tend to spread because of dispersive effects such as convective dispersion, fluid-to-particle mass transfer, and intraparticle diffusion, resulting in sigmoid or S-shaped profiles. Mechanistic models accounting for axial dispersion and finite resistance to mass transfer can be found in the book by Ruthven (1984), the solution of which depends on the nature of the equilibrium isotherm. If the isotherm is linear analytical expressions may be derived. If the equilibrium relationship is of nonlinear form numerical solution is generally required.

Although models based on axial dispersion and diffusional mass transport provide a realistic description of fixed bed dynamics, they are computationally complex. A simpler, commonly used fixed bed model employs a linear driving force (LDF) approximation, which lumps all dispersive effects into a single rate coefficient. This simplified modeling approach predicts a sigmoid breakthrough curve using the LDF rate coefficient as the sole curve-broadening factor and the equilibrium isotherm to shift the position of the curve on the time coordinate. A model with the correct functional form, together with an equilibrium parameter and a rate parameter, provides all that is needed to predict a sigmoid breakthrough curve. Indeed, several two-parameter models used in adsorptive water remediation research are of this type. Notable examples include the models of Bohart and Adams (1920) and Thomas (1944), both of which predict sigmoid curves with the help of an equilibrium capacity parameter and a rate parameter based on reaction kinetics. Empirical models proposed by Yoon and Nelson (1984) and Belter et al. (1988) have a scale parameter, which acts like an equilibrium parameter, and a shape parameter, which behaves like a rate parameter. A major drawback of models of this type is that empirical relationships between model parameters and operational conditions (e.g., feed concentration, flow rate) must be established if they are to be used for process design.

The Bohart–Adams, Thomas, and Yoon–Nelson models, which are mathematically analogous (Chatterjee and Schiewer, 2011; Chu, 2020; Lee et al., 2015), have been widely used to correlate breakthrough curves of water contaminants. Their popularity owes much to the fact that the model equations can be easily linearized to allow parameter estimation by linear regression. However, the data fitting ability of the three models is rather limited. Restricted by their functional form, the three models are confined to describing symmetric breakthrough curves. Some attempts have been made to improve their ability to represent asymmetric breakthrough curves, as discussed by Apiratikul and Chu (2021). The model of Belter et al., by comparison, has attracted much less attention. Part of the reason for its obscurity lies in the
mistaken belief that the model equation containing the error function cannot be linearized. (A linear version is given and tested in the present study.)

The two-parameter model of Belter et al. was first used by Brady et al. (1999) to describe fixed bed adsorption of copper ions. Since that time, it has been used to fit breakthrough data of several classes of water contaminants including metal ions (Faisal et al., 2020; Ghasemi et al., 2011; Lodeiro et al., 2006; Naji et al., 2020; Ramirez et al., 2007; Riazi et al., 2016; Saldaña-Robles et al., 2018; Stanley and Ogden, 2003; Sulaymon et al., 2010, 2015; Wong et al., 2003), ammonia (Faisal et al., 2020; Naji et al., 2020), organic compounds (Faisal et al., 2020, 2021; Knapik et al., 2020; Naji et al., 2020), dyes (Fernandez et al., 2014; Khoo et al., 2012; Lee et al., 2008; Teng and Lin, 2006), and oils (Srinivasan and Viraraghavan, 2014). However, there has been surprisingly little research on the data fitting properties of the Belter et al. model. As a result, we know very little about its strengths and weaknesses as a model of fixed bed adsorption.

This paper focuses on a detailed analysis of the model presented by Belter et al. Specifically, the objectives of the present study are twofold: (1) to investigate the ability of the Belter et al. model to correlate previously published breakthrough curves of water contaminants with varying degrees of asymmetry; and (2) to develop a new version of the Belter et al. model capable of tracking severely asymmetric breakthrough curves.

2 The Belter Model

Eq. 1 is the empirical model of fixed bed adsorption presented by Belter et al. (1988). In this equation, \( c \) is the effluent concentration at the bed outlet, \( c_0 \) is the feed concentration at the bed inlet, \( \text{erf} \) denotes the error function, \( t \) is time, and \( \tau \) and \( \sigma \) are two adjustable parameters.

\[
\frac{c}{c_0} = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{t - \tau}{\sigma \tau \sqrt{2}} \right) \right]
\]  

(1)

Eq. 1 is known as the Belter model although that seems slightly unfair to Cussler and Hu. The Belter model uses two fitting parameters to predict a sigmoid curve with \( \tau \) acting as a scale parameter and \( \sigma \tau \) performing as a shape parameter. It should be noted that the \( \tau \) term in the product \( \sigma \tau \) is superfluous and can be removed.

The Belter model and its modified version were fit to published breakthrough data using a nonlinear least-squares regression procedure. Model performance was evaluated by two statistical metrics: the coefficient of determination \((R^2)\) and the residual root mean square error \((\text{RRMSE})\) given by Eqs. 2 and 3 respectively. In these two equations, \( n \) is the number of data
points, \( M_j \) is the \( j \)-th model value of \( c/c_0 \), \( E_j \) is the \( j \)-th experimental value of \( c/c_0 \), \( E_m \) is the mean of experimental values, and \( p \) is the number of adjustable parameters.

\[
R^2 = 1 - \frac{\sum_{j=1}^{n} (M_j - E_j)^2}{\sum_{j=1}^{n} (M_j - E_m)^2} \quad (2)
\]

\[
\text{RRMSE} = \sqrt{\frac{\sum_{j=1}^{n} (M_j - E_j)^2}{n - p}} \quad (3)
\]

The Belter model can be linearized to facilitate parameter estimation by linear regression. Eq. 4 is a linear form of the Belter model, where \( \text{erf}^{-1} \) stands for the inverse error function. Excel provides the error function but not the inverse error function. The latter can be approximated using the inverse normal cumulative distribution \([\text{erf}^{-1}(x) = \text{NORM.S.INV}((x+1)/2)/\text{SQRT}(2)]\).

\[
\text{erf}^{-1}\left(2 \frac{c}{c_0} - 1\right) = -\frac{1}{\sigma \sqrt{2}} + \frac{1}{\sigma \tau \sqrt{2}} t \quad (4)
\]

3 Results and Discussion

Three sets of previously published breakthrough curves with different curve characteristics are used to evaluate and compare the data fitting ability of the Belter model and its modified version.

3.1 Data Correlation Using the Belter Model

3.1.1 Copper Breakthrough Data

Da Costa Rocha et al. (2020) have used two different adsorbents, geopolymer and zeolite, to remove copper from water. The adsorbent was loaded into a glass column with a diameter of 1.5 cm and a packed length of 15 cm. Fig. 1A shows a set of breakthrough data obtained with a fixed bed of geopolymer, which was used to treat a synthetic copper solution of 2 mmol L\(^{-1}\). The flow rate used was 3 cm\(^3\) min\(^{-1}\), giving an empty bed contact time (EBCT) of 8.8 min.

As illustrated in Fig. 1A, the experimental breakthrough curve is fairly symmetric; the initial and saturation segments are of similar length. Fig. 1A shows that the nonlinear fit of the Belter model is in satisfactory conformity with the experimental data, returning good fit statistics \((R^2 > 0.99, \text{Table 1})\). Plotting the copper data according to the linear form of the Belter model (Eq. 4) yields an apparent linear trend, as illustrated in Fig. 1B. The \(R^2\) score for the linear regression analysis is 0.964. The Belter model curve computed using the parameter
estimates of the linear fit ($\tau = 3403.8$ min and $\sigma = 0.104$) is depicted in Fig. 1A. It is apparent from Fig. 1A that the nonlinear fit is superior to the linear fit.

![Image](A)

**Fig. 1** (A) Nonlinear and linear fits of the Belter model compared to observed copper breakthrough data reported by da Costa Rocha et al. (2020). (B) Linear regression of copper breakthrough data according to Eq. 4

**Table 1** Parameter estimates and fit statistics for nonlinear fits of copper, reactive red 141, and fluoride breakthrough data

| Parameter and statistical metric | Contaminant          |               |               |
|---------------------------------|----------------------|---------------|---------------|
|                                 | Copper               | Reactive red  | Fluoride      |
| Belter                          | 3320                 | 540           | 2452          |
| $\tau$ (min)                    | 0.11                 | 0.265         | 0.911         |
| $\sigma$                        | 0.993                | 0.985         | 0.925         |
| $R^2$                           | 0.033                | 0.043         | 0.084         |
| RRMSE                           | 8.11                 | 6.28          | 7.61          |
| $\sigma^2$                      | 0.014                | 0.044         | 0.126         |
| $R^2$                           | 0.995                | 0.995         | 0.994         |
| RRMSE                           | 0.027                | 0.025         | 0.024         |
3.1.2 Reactive Red 141 Breakthrough Data

The uptake of the dye reactive red 141 by pyrrhotite ash in a fixed bed adsorber has been studied by Mouldar et al. (2020). In Fig. 2, a set of breakthrough data taken from the work of Mouldar et al. (2020) is shown. The breakthrough data were measured using a glass column with a diameter of 1.5 cm and a packed length of 4.7 cm. The feed concentration and flow rate used were 100 mg L\(^{-1}\) and \(1.66 \text{ cm}^3\text{ min}^{-1}\), respectively. The EBCT calculated from the bed volume and flow rate was 5 min.

Because the initial segment (e.g., \(t = 300-400\) min) is noticeably shorter than the saturation segment (e.g., \(t = 700-1100\) min), the breakthrough curve depicted in Fig. 2 exhibits a moderate degree of asymmetry. This type of curve shape is known as tailing, which refers to a phenomenon in which the effluent exhibits a slow approach toward the influent concentration near column saturation. Various reasons have been put forward to explain the tailing phenomenon, including flow nonuniformity, nonspecific adsorption, heterogeneous particle size distribution, and gradual reduction in the intraparticle diffusion rate. The Belter model was fit to the Fig. 2 data. As can be seen, the predicted values of \(c/c_0\) do not agree well with the experimental data. In particular, the initial and saturation stages of the observed breakthrough curve are poorly described by the Belter model. Table 1 shows that the \(R^2\) and RRMSE scores for the dye fit are inferior to those for the copper fit, suggesting that the dye breakthrough curve is more asymmetric than the copper breakthrough curve.

![Fig. 2 Belter model fit compared to observed reactive red 141 breakthrough data reported by Mouldar et al. (2020)](image)

3.1.3 Fluoride Breakthrough Data

Fixed bed experiments have been performed by Tovar-Gómez et al. (2013) to study the adsorption of fluoride on bone char. Fig. 3 shows a data set taken from the work of Tovar-Gómez et al. (2013).
Gómez et al. (2013). A column with an internal diameter of 2.5 cm and a packed length of 7.5 cm was used. The feed concentration and flow rate used were 9 mg L\(^{-1}\) and 3.3 cm\(^3\) min\(^{-1}\), respectively. Based on the bed volume and flow rate, the EBCT was found to be approximately 11 min.

The fluoride breakthrough profile presented in Fig. 3 is very different from those of copper and reactive red 141 depicted in Figs. 1A and 2. The zero effluent concentration period was very brief; a sharp increase in the effluent concentration emerged quickly, reaching \(c/c_0 \approx 60\%\). The subsequent tailing in the breakthrough data was very long. This severely asymmetric breakthrough curve resembles a hyperbolic profile rather than a sigmoid curve. From the results presented in Fig. 3, it is evident that the fit of the fluoride data by the Belter model is a failure. The level of agreement between the experimental and predicted values of \(c/c_0\) is very low. In addition, the predicted curve intersected the vertical axis at \(t = 0\), giving a conspicuous nonzero effluent concentration at time zero. Table 1 shows that the \(R^2\) and RRMSE scores for this case are far inferior to those for the copper and reactive red 141 cases.

![Belter model fit compared to observed fluoride breakthrough data reported by Tovar-Gómez et al. (2013)](image)

**Fig. 3** Belter model fit compared to observed fluoride breakthrough data reported by Tovar-Gómez et al. (2013)

### 3.1.4 Properties of the Belter Model

The results presented above reveal that the Belter model could handle the copper data with a slight degree of asymmetry but was practically useless when challenged with the fluoride data with a pronounced degree of asymmetry. Before we discuss possible reasons for the poor performance, it is instructive to first explore how the two parameters \(\tau\) and \(\sigma\) control the behavior of the Belter model.

The nonlinear fit of Fig. 1A is used as an example, which was calculated using \(\tau = 3320\) min and \(\sigma = 0.11\). Fig. 4A depicts three curves generated with different values of \(\tau\) while
holding $\sigma$ constant at 0.11. Curve 2 corresponds to the original nonlinear fit of Fig. 1A. Decreasing $\tau$ (3320 min) by 50% yields curve 1; increasing $\tau$ by 50% produces curve 3. It is clear that the smaller $\tau$ value shifts curve 2 to the left while the bigger $\tau$ value moves it to the right. So, the parameter $\tau$ functions very much like the equilibrium capacity parameters of the Bohart–Adams and Thomas models, which control the position of a breakthrough curve on the time coordinate.

![Fig. 4 Breakthrough curves predicted by the Belter model. Curve 2 corresponds to the original nonlinear fit of Fig. 1A, calculated using $\tau = 3320$ min and $\sigma = 0.11$. (A) Effect of $\tau$ at constant $\sigma$. (B) Effect of $\sigma$ at constant $\tau$.](image)

The effect of $\sigma$ is illustrated in Fig. 4B. As in Fig. 4A, curve 2 in Fig. 4B corresponds to the original nonlinear fit of Fig. 1A. Curves 1 and 3 were calculated by holding $\tau$ constant at 3320 min and changing $\sigma$ (0.11) by $\pm$50%. Curve 1, produced by the smaller $\sigma$ value, is much sharper than curve 2. Curve 3, generated by the bigger $\sigma$ value, is a more spread-out profile compared to curve 2. The parameter $\sigma$ is therefore similar to the rate parameters of the Bohart–Adams and Thomas models, which control the spread of a breakthrough curve.
However, in contrast to $\sigma$, the value of the Bohart–Adams/Thomas rate parameter needs to be increased in order to obtain a sharper curve.

The unsatisfactory fits of the reactive red 141 and fluoride breakthrough curves are due to an inflexible mathematical property of the Belter model. Every sigmoid curve predicted by the Belter model contains a single inflection point. A sigmoid curve is perfectly symmetric if its inflection point is located at the midpoint, and asymmetric if it does not. A three-step procedure may be used to find the location of the inflection point for a Belter sigmoid curve. First, the second derivative of the Belter model is derived, given here by Eq. 5. Next, the left-hand member of Eq. 5 is set equal to zero and the resulting equation is solved for $t$. The result is $t = \tau$. Finally, substitution of this $t$ value into the Belter model (Eq. 1) leads to Eq. 6.

$$\frac{\partial^2 \left( \frac{c}{c_0} \right)}{\partial t^2} = \frac{(\tau - t) \exp\left[ -\left( \frac{\tau - t}{2\sigma^2} \right)^2 \right]}{\sigma^3 \tau^3 \sqrt{2\pi}}$$

Eq. 6 states that the location of the inflection point for a Belter breakthrough curve corresponds to the midpoint of the curve, that is, $c/c_0 = 0.5$. As demonstrated in Fig. 4B, all three simulated curves with different $\sigma$ values pass through the midpoint at $c/c_0 = 0.5$ and $t = \tau = 3320$ min, which is indicated by the intersection point of the two dashed lines. It is clear that the location of the inflection point for a Belter breakthrough curve is invariant and always matches the midpoint. This means that it is impossible to alter the inflection point location ($c/c_0$) by changing $\tau$ or $\sigma$. This is the reason why the Belter model was unable to track the strongly asymmetric fluoride data (Fig. 3) and the moderately asymmetric reactive red 141 data (Fig. 2). To fit such breakthrough curves, the Belter model must shift the location of the inflection point away from the midpoint. We describe in the next section a modification procedure that can convert the invariant inflection point of the Belter model to a floating one, allowing the Belter model so modified to track asymmetric breakthrough curves to a significant degree of precision.

### 3.2 Modified Belter Model

#### 3.2.1 Logarithmic Transformation

A logarithmic transformation method (Apiratikul and Chu, 2021) is used to modify the Belter model. The main idea is to convert the parameter $t$ in the Belter model to $\ln(t)$. Since we can take the logarithm only of dimensionless numbers, the parameter $t$, which has the dimension of
time (min), must be made dimensionless. To this end, we define a new entity, $T$, which is equal to 1 min. Next, we multiply each term having the dimension of time in the argument of the error function by $(T/T)$, as shown in Eq. 7. We simplify Eq. 7 to Eq. 8. Finally, taking the logarithm of the dimensionless term $(t/T)$ in Eq. 8 yields Eq. 9. Since $T$ is equal to 1 min, it may be omitted from Eq. 9. Eq. 10 is the final form of the modified Belter model. It should be noted that $t$ and $\tau$ in Eq. 10 are now dimensionless quantities. A linear form of the modified Belter model is given by Eq. 11.

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \text{erf} \left( \frac{t(T/T) - \tau(T/T)}{\sigma(T/T)\sqrt{2}} \right) \right\}$$  \hspace{1cm} (7)$$

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \text{erf} \left( \frac{(t/T) - (\tau/T)}{\sigma(T/T)\sqrt{2}} \right) \right\}$$  \hspace{1cm} (8)$$

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \text{erf} \left( \frac{\ln(t/T) - (\tau/T)}{\sigma(T/T)\sqrt{2}} \right) \right\}$$  \hspace{1cm} (9)$$

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \text{erf} \left( \frac{\ln(t) - \tau}{\sigma(T/T)\sqrt{2}} \right) \right\}$$  \hspace{1cm} (10)$$

$$\text{erf}^{-1} \left( 2 \frac{c}{c_0} - 1 \right) = -\frac{1}{\sigma\sqrt{2}} + \frac{1}{\sigma\tau\sqrt{2}} \ln(t)$$  \hspace{1cm} (11)$$

As an aside, we note that the functional form of the modified Belter model defined by Eq. 10 is consistent with an analytical solution for a phenomenological model of fixed bed adsorption, given here by Eq. 12 (Sigrist et al., 2011; Xiu et al., 1997). The symbols in Eq. 12 are defined by Eqs. 13–21, where $R_p$ is the adsorbent radius, $\rho_p$ is the adsorbent density, $L$ is the length of packed bed, $\varepsilon$ is the bed voidage, $v$ is the interstitial velocity, $K$ is the Henry’s law equilibrium constant, $k_f$ is the external film mass transfer coefficient, $D_s$ is the surface diffusion coefficient, and $D_a$ is the axial dispersion coefficient. The empirical parameters of the modified Belter model may thus be interpreted in terms of these physical parameters. It is important to note that Eq. 12 is valid for linear adsorption. Fixed bed adsorbers designed for water remediation are generally operated under nonlinear conditions.

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \text{erf} \left( \frac{\ln(\lambda) - \alpha}{\beta\sqrt{2}} \right) \right\}$$  \hspace{1cm} (12)$$

$$\lambda = \frac{D_f t}{R_p^2}$$  \hspace{1cm} (13)
\[ \alpha = \ln \alpha - \frac{1}{2} \ln \left(1 + \frac{\alpha_2}{\alpha_1^2}\right) \]  

(14)

\[ \beta = \sqrt{\ln \left(1 + \frac{\alpha_2}{\alpha_1^2}\right)} \]  

(15)

\[ \alpha_i = \theta (1 + \delta) \]  

(16)

\[ \alpha_2 = \frac{2\theta\delta}{3} \left(1 + \frac{1}{Bi}\right) + \frac{2\theta^2}{Pe} (1 + \delta)^2 \]  

(17)

\[ \theta = \frac{D L}{v R_p} \]  

(18)

\[ \delta = K \rho_p \left(1 - \frac{\varepsilon}{\varepsilon}\right) \]  

(19)

\[ Bi = \frac{k_f R_p}{D s K \rho_p} \]  

(20)

\[ Pe = \frac{v L}{D_a} \]  

(21)

### 3.2.2 Floating Inflection Point

The advantage of the modified Belter model over the original model is that the former has a floating or variable inflection point. The location of the inflection point can be derived using the three-step procedure discussed earlier. Briefly, the second derivative of the modified Belter model, given here by Eq. 22, is set equal to zero and solved for \(\ln(t)\). The result is \(\ln(t) = \tau - (\sigma \tau)^2\). Substitution of the last result into Eq. 10 leads to Eq. 23, which defines the location of the inflection point. According to Eq. 23, the modified Belter model has a floating inflection point which varies with \(\sigma \tau\). The lower and upper limits of the inflection point location are \(c/c_0 = 0\) and \(c/c_0 = 0.5\), respectively.

\[ \frac{\partial^2 (c/c_0)}{\partial t^2} = \frac{\left[\tau - (\sigma \tau)^2 - \ln(t)\right] \exp\left\{-\left[\tau - \ln(t)\right]^2 / 2 (\sigma \tau)^2\right\}}{\left(\sigma \tau\right)^3 t^2 \sqrt{2\pi}} \]  

(22)

\[ \frac{c}{c_0} = \frac{1}{2} \left[1 - \text{erf}\left(\frac{\sigma \tau}{\sqrt{2}}\right)\right] \]  

(23)
3.3 Data Correlation Using the Modified Belter Model

The modified Belter model defined by Eq. 10 was fit to the copper data. Values of the parameters required to fit Eq. 10 to the experimental data are listed in Table 1, and a comparison of the fitted and experimental results is shown in Fig. 5A. As can be seen, the modified Belter model provides a quantitatively correct description of the experimental data. Table 1 shows that the fit statistics ($R^2$ and RRMSE) are slightly better than those for the original model fit. Because the copper breakthrough curve is only slightly asymmetric, the superiority of the modified model versus the original model is not obvious in this case. Fig. 5B reveals that the copper data can be regressed using the linear form of the modified Belter model (Eq. 11). Fig. 5A shows that the linear fit is marginally inferior to the nonlinear fit.

![Fig. 5](image)

**Fig. 5** (A) Nonlinear and linear fits of the modified Belter model compared to observed copper breakthrough data reported by da Costa Rocha et al. (2020). (B) Linear regression of copper breakthrough data according to Eq. 11

The fits of the modified Belter model to the reactive red 141 and fluoride data are presented in Figs. 6 and 7, respectively. The agreement between the fitted and experimental results is excellent in these two cases, demonstrating that the modified Belter model has the
ability to accurately track the two asymmetric breakthrough curves. The \( R^2 \) and RRMSE scores for these two fits are vastly superior to those for the original model fits, as can be seen in Table 1. Comparisons of Figs. 2 and 6 and Figs. 3 and 7 indicate that the modified Belter model is the best performing model.

![Modified Belter model fit compared to observed reactive red 141 breakthrough data reported by Mouldar et al. (2020)](image)

**Fig. 6** Modified Belter model fit compared to observed reactive red 141 breakthrough data reported by Mouldar et al. (2020)

![Modified Belter model fit compared to observed fluoride breakthrough data reported by Tovar-Gómez et al. (2013)](image)

**Fig. 7** Modified Belter model fit compared to observed fluoride breakthrough data reported by Tovar-Gómez et al. (2013)

As noted above, the modified Belter model has a floating inflection point, which allows it to track the shape of an asymmetric breakthrough curve. The inflection point locations for the three predicted breakthrough curves depicted in Figs. 5–7 can be calculated from Eq. 23. In Fig. 8, the inflection point locations calculated from Eq. 23 using the relevant parameter estimates listed in Table 1 are shown. To fit the mildly asymmetric copper data, the modified model placed the inflection point slightly below the midpoint \( (c/c_0 = 0.46) \). To handle the
moderately asymmetric reactive red 141 data, the modified model moved the inflection point further away from the midpoint \((c/c_0 = 0.39)\). To track the strongly asymmetric fluoride data, the modified model placed the inflection point close to the (0,0) origin \((c/c_0 = 0.17)\). The flexibility of inflection point placement allows the modified Belter model to fit a diverse array of asymmetric breakthrough curves. In contrast, the location of the inflection point for a breakthrough curve predicted by the original Belter model is always fixed at \(c/c_0 = 0.5\). Consequently, the original Belter model is confined to fitting highly symmetric breakthrough curves, which are rarely observed in fixed bed adsorption experiments.

**Fig. 8** Inflection point locations for breakthrough curves predicted by the modified Belter model

### 4 Conclusions

The results presented here have shown that the scale and shape parameters of the Belter model, \(\tau\) and \(\sigma\) (or \(\sigma\tau\)), are analogous to the equilibrium capacity and rate parameters of the widely used Bohart–Adams and Thomas models. The parameter \(\tau\) controls the position of a Belter
breakthrough curve on the time coordinate whereas the parameter $\sigma$ (or $\sigma_\tau$) dictates the spread of the curve. Through a detailed mathematical analysis, this work has shown that a Belter breakthrough curve is characterized by an invariant inflection point, which is always located at the midpoint of the curve ($c/c_0 = 0.5$). This property restricts the Belter model to correlating perfectly symmetric breakthrough curves. Consequently, the Belter model can only track highly symmetric breakthrough data, as demonstrated by the correlation of the copper breakthrough curve. Another goal of the present study has been to develop a new version of the Belter model capable of handling breakthrough curve asymmetry. The new Belter model with a floating inflection point has been shown to correlate the asymmetric breakthrough curves of reactive red 141 and fluoride to a significant degree of precision.

References
Apiratikul, R., & Chu, K. H. (2021). Improved fixed bed models for correlating asymmetric adsorption breakthrough curves. *Journal of Water Process Engineering, 40*, 101810.
Belter, P. A., Cussler, E. L., & Hu, W.-S. (1988). *Bioseparations: Downstream processing for biotechnology*, John Wiley & Sons, New York.
Bohart, G. S., & Adams, E. Q. (1920). Some aspects of the behavior of charcoal with respect to chlorine. *Journal of the American Chemical Society, 42*, 523–529.
Brady, J. M., Tobin, J. M., & Roux, J.-C. (1999). Continuous fixed bed biosorption of Cu$^{2+}$ ions: Application of a simple two parameter mathematical model. *Journal of Chemical Technology and Biotechnology, 74*, 71–77.
Chatterjee, A., & Schiewer, S. (2011). Biosorption of cadmium(II) ions by citrus peels in a packed bed column: Effect of process parameters and comparison of different breakthrough curve models. *Clean-Soil Air Water, 39*, 874–881.
Chu, K. H. (2020). Breakthrough curve analysis by simplistic models of fixed bed adsorption: In defense of the century-old Bohart-Adams model. *Chemical Engineering Journal, 380*, 122513.
Da Costa Rocha, A. C., Scaratti, G., Moura-Nickel, C. D., da Silva, T. L., Gurgel Adeodato Vieira, M., Peralta, R. M., Peralta, R. A., de Noni Jr, A., & Peralta Muniz Moreira, R. d. F. (2020). Economical and technological aspects of copper removal from water using a geopolymer and natural zeolite. *Water, Air, & Soil Pollution, 231*, 361.
Faisal, A. A. H., Ali, I. M., Naji, L. A., Madhloom, H. M., & Al-Ansari, N. (2020). Using different materials as a permeable reactive barrier for remediation of groundwater contaminated with landfill’s leachate. *Desalination and Water Treatment, 175*, 152–163.

Faisal, A. A. H., Jasim, H. K., Naji, L. A., Naushad, Mu., & Ahamad, T. (2021). Cement kiln dust-sand permeable reactive barrier for remediation of groundwater contaminated with dissolved benzene. *Separation Science and Technology, 56*, 870–883.

Fernandez, M. E., Nunell, G. V., Bonelli, P. R., & Cukierman, A. L. (2014). Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes. *Industrial Crops and Products, 62*, 437–445.

Ghasemi, M., Keshtkar, A. R., Dabbagh, R., & Safdari, S. J. (2011). Biosorption of uranium(VI) from aqueous solutions by Ca-pretreated *Cystoseira indica* alga: Breakthrough curves studies and modeling. *Journal of Hazardous Materials, 189*, 141–149.

Khoo, E.-C., Ong, S.-T., & Ha, S.-T. (2012). Removal of basic dyes from aqueous environment in single and binary systems by sugarcane bagasse in a fixed-bed column. *Desalination and Water Treatment, 37*, 215–222.

Knapik, E., Chruszcz-Lipska, K., Stopa, J., Marszalek, M., & Makara, A. (2020). Separation of BTX fraction from reservoir brines by sorption onto hydrophobized biomass in a fixed-bed-column system. *Energies, 13*, 1064.

Lee, C. K., Ong, S. T., & Zainal, Z. (2008). Ethylenediamine modified rice hull as a sorbent for the removal of Basic Blue 3 and Reactive Orange 16. *International Journal of Environmental Pollution, 34*, 246–260.

Lee, C.-G., Kim, J.-H., Kang, J.-K., Kim, S.-B., Park, S.-J., Lee, S.-H., & Choi, J.-W. (2015). Comparative analysis of fixed-bed sorption models using phosphate breakthrough curves in slag filter media. *Desalination and Water Treatment, 55*, 1795–1805.

Lodeiro, P., Herrero, R., & de Vicente, M. E. S. (2006). The use of protonated *Sargassum muticum* as biosorbent for cadmium removal in a fixed-bed column. *Journal of Hazardous Materials, B137*, 244–253.

Mouldar, J., Hatimi, B., Hafdi, H., Joudi, M., Belghiti, M. E. A., Nasrellah, H., El Mhammedi, M. A., El Gaini, L., & Bakasse, M. (2020). Pyrrhotite ash waste for capacitive adsorption and fixed-bed column studies: Application for reactive red 141 dye. *Water, Air, & Soil Pollution, 231*, 205.

Naji, L. A., Faisal, A. A. H., Rashid, H. M., Naushad, Mu., & Ahamad, T. (2020). Environmental remediation of synthetic leachate produced from sanitary landfills using low-cost composite sorbent. *Environmental Technology & Innovation, 18*, 100680.
Ramirez, C.M., da Silva, M. P., Ferreira, L. S. G., & Vasco, E. O. (2007). Mathematical models applied to the Cr(III) and Cr(VI) breakthrough curves. *Journal of Hazardous Materials, 146*, 86–90.

Riazi, M., Keshtkar, A. R., & Moosavian, M. A. (2016). Biosorption of Th(IV) in a fixed-bed column by Ca-pretreated *Cystoseira indica*. *Journal of Environmental Chemical Engineering, 4*, 1890–1898.

Ruthven, D. M. (1984). *Principles of adsorption and adsorption processes*. John Wiley & Sons, New York.

Saldaña-Robles, A., Damian-Ascencio, C. E., Guerra-Sanchez, R. J., Saldaña-Robles, A. L., Saldaña-Robles, N., Gallegos-Muñoz, A., & Cano-Andrade, S. (2018). Effects of the presence of organic matter on the removal of arsenic from groundwater. *Journal of Cleaner Production, 183*, 720–728.

Sigrist, M. E., Beldomenico, H. R., Tarifa, E. E., Pieck, C. L., & Vera, C. R. (2011). Modelling diffusion and adsorption of As species in Fe/GAC adsorbent beds. *Journal of Chemical Technology and Biotechnology, 86*, 1256–1264.

Srinivasan, A., & Viraraghavan, T. (2014). Oil removal in a biosorption column using immobilized *M. rouxii* biomass. *Desalination and Water Treatment, 52*, 3085–3095.

Stanley, L. C., & Ogden, K. L. (2003). Biosorption of copper (II) from chemical mechanical planarization wastewaters. *Journal of Environmental Management, 69*, 289–297.

Sulaymon, A. H., Ebrahim, S. E., Abdullah, S. M., & Al-Musawi, T. J. (2010). Removal of lead, cadmium, and mercury ions using biosorption. *Desalination and Water Treatment, 24*, 344–352.

Sulaymon, A. H., Faisal, A. A. H., & Khaliefa, Q. M. (2015). Cement kiln dust (CKD)-filter sand permeable reactive barrier for the removal of Cu(II) and Zn(II) from simulated acidic groundwater. *Journal of Hazardous Materials, 297*, 160–172.

Teng, M.-Y., & Lin, S.-H. (2006). Removal of basic dye from water onto pristine and HCl-activated montmorillonite in fixed beds. *Desalination, 194*, 156–165.

Thomas, H. C. (1944). Heterogeneous ion exchange in a flowing system. *Journal of the American Chemical Society, 66*, 1664–1666.

Tovar-Gómez, R., Moreno-Virgen, M. R., Dena-Aguilar, J. A., Hernández-Montoya, V., Bonilla-Petriciolet, A., & Montes-Morán, M. A. (2013). Modeling of fixed-bed adsorption of fluoride on bone char using a hybrid neural network approach. *Chemical Engineering Journal, 228*, 1098–1109.
Wong, K. K., Lee, C. K., Low, K. S., & Haron, M. J. (2003). Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. *Process Biochemistry, 39*, 437–445.

Xiu, G.-H., Nitta, T., Li, P., & Jin, G. (1997). Breakthrough curves for fixed-bed adsorbers: Quasi-lognormal distribution approximation. *American Institute of Chemical Engineers Journal, 43*, 979–985.

Yoon, Y. H., & Nelson, J. A. (1984). Application of gas adsorption kinetics. I. A theoretical model for respirator cartridge service life. *American Industrial Hygiene Association Journal, 45*, 509–516.