Rebuttal to Comment on “Breakthrough curve analysis by simplistic models of fixed bed adsorption: in defense of the century-old Bohart-Adams model”

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Abstract
In a comment on my article [1] published in the Chemical Engineering Journal, Hu and Zhang [2] assert that I have misinterpreted the Bohart-Adams equation derived by Amundson and that the Bohart-Adams equation lacks the bed voidage parameter. I argue that Hu and Zhang are wrong on both counts. I further contend that their version of the Bohart-Adams equation derived by Amundson contains a glaring error of a rudimentary nature.

Keywords: adsorption, Amundson, Bohart-Adams, breakthrough curve, fixed bed.

Introduction
Hu and Zhang [2] assert that my article [1] offers an incorrect form of the Bohart-Adams equation derived by Amundson and that the Bohart-Adams equation cannot be used to study the effect of bed voidage. Here, I briefly discuss the assertions and demonstrate that they are wrong and ill-considered. No corrections to my article are necessary.

Amundson solution
Exactly one hundred years ago, in 1920, Bohart and Adams [3] published what is now known as the Bohart-Adams model of fixed bed adsorption. Using the kinetics rate expression of Bohart and Adams, Amundson [4] derived a more rigorous version of the original Bohart-Adams solution. The model equations formulated by Amundson are

\[
\frac{v}{\varepsilon} \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1}{\varepsilon} \frac{\partial n}{\partial t} = 0 \\
\frac{1}{\varepsilon} \frac{\partial n}{\partial t} = kC(N_0 - n)
\]

Eq. (1) is a differential mass balance for a point in a fixed bed adsorption column without an axial dispersion term while Eq. (2) is a slightly modified form of the quasi-chemical kinetics rate expression of Bohart and Adams, which at equilibrium reduces to an irreversible or rectangular isotherm. Across the landscape of present-day adsorption modeling it is common to express the solid phase concentration in terms of \( q \) rather than \( n \) (see Nomenclature list for definition of symbols). Then Eqs. (1) and (2) can be rewritten in the form

\[
The second equation can be written as

\[
\frac{1}{\varepsilon} \frac{\partial q}{\partial t} = kC(N_0 - q) \\
\frac{1}{\varepsilon} \frac{\partial n}{\partial t} = kC(N_0 - n)
\]

Then Eqs. (1) and (2) can be rewritten in the form

\[
\frac{v}{\varepsilon} \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1}{\varepsilon} \frac{\partial n}{\partial t} = 0 \\
\frac{1}{\varepsilon} \frac{\partial q}{\partial t} = kC(N_0 - q)
\]

Eq. (3) is a differential mass balance for a point in a fixed bed adsorption column without an axial dispersion term while Eq. (4) is a slightly modified form of the quasi-chemical kinetics rate expression of Bohart and Adams, which at equilibrium reduces to an irreversible or rectangular isotherm. Across the landscape of present-day adsorption modeling it is common to express the solid phase concentration in terms of \( q \) rather than \( n \) (see Nomenclature list for definition of symbols). Then Eqs. (3) and (4) can be rewritten in the form

\[
\frac{v}{\varepsilon} \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1}{\varepsilon} \frac{\partial n}{\partial t} = 0 \\
\frac{1}{\varepsilon} \frac{\partial q}{\partial t} = kC(N_0 - q)
\]
\[
\frac{\partial C}{\partial z} + \frac{1}{\varepsilon} \frac{\partial C}{\partial t} + \frac{(1-\varepsilon)\rho_p}{\varepsilon} \frac{\partial q}{\partial t} = 0 \tag{3}
\]

\[
\frac{1}{\varepsilon} \frac{\partial q}{\partial t} = kC(q_o - q) \tag{4}
\]

For an initially clean bed subjected at time zero to a constant step change in adsorbate concentration at the bed inlet, Amundson’s solution to Eqs. (3) and (4) is

\[
\frac{C}{C_o} = \frac{\exp\left[keC_o \left(t - \frac{L}{v}\right)\right]}{\exp\left[k(1-\varepsilon)\rho_p q_o L_v\right] + \exp\left[keC_o \left(t - \frac{L}{v}\right)\right] - 1} \tag{5}
\]

One may use the following relation to express the preceding equation in terms of the adsorption capacity parameter \(N_o\) adopted by Amundson.

\[
N_o = (1-\varepsilon)\rho_p q_o \tag{6}
\]

The preceding equation is given in an earlier paper of mine where various aspects of the Bohart-Adams equation were investigated [5]. It is also available in Cooney’s book [6, p. 169]. Substitution of Eq. (6) in Eq. (5) gives

\[
\frac{C}{C_o} = \frac{\exp\left[keC_o \left(t - \frac{L}{v}\right)\right]}{\exp\left[kN_o L_v\right] + \exp\left[keC_o \left(t - \frac{L}{v}\right)\right] - 1} \tag{7}
\]

The preceding equation is a special case of a more general solution derived by Amundson [4] in 1948. For the present discussion, Eq. (7) is referred to as the Amundson solution. As one looks carefully at the Bohart-Adams rate expression devised by Amundson (Eq. (2) or (4)), one sees that it is somewhat unconventional in that the \((1/\varepsilon)\) term appears on the left-hand side of the equation. Although Amundson’s rate formulation is perfectly satisfactory, it is anachronistic and rarely used by modern practitioners who favor the following form:

\[
\frac{\partial q}{\partial t} = k_{BA} C(q_o - q) \tag{8}
\]

Note that the left-hand side of the preceding equation does not contain the \((1/\varepsilon)\) term. By comparing Eqs. (4) and (8) the following expression can be readily derived:

\[
k\varepsilon = k_{BA} \tag{9}
\]

The preceding equation allows us to express the Amundson solution in terms of \(k_{BA}\).

\[
\frac{C}{C_o} = \frac{\exp\left[k_{BA} C_o \left(t - \frac{L}{v}\right)\right]}{\exp\left[k_{BA} N_o L_v\right] + \exp\left[k_{BA} C_o \left(t - \frac{L}{v}\right)\right] - 1} \tag{10}
\]
The following well-known expression linking the superficial and interstitial velocity frames may be used to further modify Eq. (10).

\[ u = \epsilon V \]  

(11)

Applying the preceding equation to Eq. (10) we obtain

\[
\frac{C}{C_o} = \frac{\exp \left[ k_{BA} C_o \left( t - \frac{\epsilon L}{u} \right) \right]}{\exp \left( \frac{k_{BA} N_o \epsilon L}{u} \right) + \exp \left[ k_{BA} C_o \left( t - \frac{\epsilon L}{u} \right) \right] - 1}
\]

(12)

I have put forward in my article [1] the preceding equation as the Bohart-Adams equation derived by Amundson, which, according to Hu and Zhang, is erroneous and should be called into question. What Hu and Zhang fail to realize is that Eq. (12) is an updated version of the Amundson solution given by Eq. (7). The derivation laid out above unequivocally demonstrates how one can update the Amundson solution by making use of Eq. (9). The updated Amundson solution, Eq. (12), can also be found in the work of Borba et al. [7], which seems to have escaped the attention of Hu and Zhang. Furthermore, several books on adsorption present Eq. (12) as the Bohart-Adams equation (Cooney [6, p. 130]; Ruthven [8, p. 251]; Tien [9, p. 168]). These books, like my paper and the Borba et al. article, all have updated the Amundson solution to the modern version given by Eq. (12). There is no issue here. Nowhere in my article did I claim to have presented the Amundson solution. Can Hu and Zhang not read? The inescapable conclusion is that their assertion is patently false. The unfounded claim of Hu and Zhang arises from their ignorance of the archaic rate expression underlying the Amundson modeling approach. In their letter, Hu and Zhang invoke Eq. (9) to convert \( k \) to \( k_{BA} \) without knowing how the expression \( k\epsilon = k_{BA} \) came about. Now, they know for sure.

As mentioned above, Eq. (12) is consistent with the kinetics rate expression given by Eq. (8). It is of note that Eq. (8) has been widely adopted in this field of research, and has long been in authoritative books on adsorption, such as the ones by Cooney [6, p. 130] and Ruthven [8, p. 251]. By contrast, Amundson’s rate expression has gained little traction with the modern adsorption community. Given the prevalent misuse of mathematical models in environmental adsorption research, one should avoid introducing antiquated models to the modern reader because they have the potential to create confusion and misunderstanding. That is particularly the case with the Amundson solution, which has certainly confused Hu and Zhang. I am of the firm belief that—and I cannot stress this enough—all contemporary versions of the Bohart-Adams equation should be based on the kinetics rate expression defined by Eq. (8). In this way, we can ensure that there is never any ambiguity in the interpretation of \( k_{BA} \). The rate expression defined by Eq. (2) or (4) is noted to be only of historical interest. Even Amundson himself discarded the \((1/\epsilon)\) term when he devised a different kinetics rate expression in a related paper [10] published four years after the 1948 paper [4].

**Bed voidage parameter**

After mistakenly claiming that I have misinterpreted the Amundson solution, Hu and Zhang go on to state: “Compared with the Amundson model, the Bohart-Adams model does not consider the void fraction of the bed.” They are wholly mistaken here, as I shall show. First, let us simplify Eq. (12) to a popular form of the Bohart-Adams equation:

\[
\frac{C}{C_o} = \frac{1}{1 + \exp(a - bt)}
\]

(13)

where
in my view, solution. simply construct and Zhang solution equation following inserted appear will observe that there is a glaring difference between the two eq. It is not necessary to use the Amundson solution to simulate such effects (see Fig. 1 of Hu and Zhang [2]). Their Fig. 1 plot can be generated using the simplified Bohart-Adams equation defined by Eq. (13) and the $N_o$ expression given by Eq. (6). Hence, the second claim of Hu and Zhang is again blatantly false. They are unaware of the fact that the $\epsilon$ parameter is embedded within the $N_o$ parameter. This ignorance demonstrates that they have little more than a minimal grasp of the Bohart-Adams equation.

**Erroneous Amundson solution**

There is a basic error in the Amundson solution presented in Hu and Zhang’s letter that I wish to point out to prevent its further propagation in the adsorption literature. The Amundson solution put forward by Hu and Zhang is

$$\frac{C}{C_o} = \frac{\exp\left[k\epsilon C_o \left(\frac{t-L}{u}\right)\right]}{\exp\left(kN_o L/u\right) + \exp\left[k\epsilon C_o \left(\frac{t-L}{u}\right)\right] - 1}$$

Note that the adsorption capacity parameter $N_o$ has been replaced by a new parameter ($N_A$). Hu and Zhang simplify Eq. (16) to the following form:

$$\frac{C}{C_o} = \frac{\exp(k\epsilon C_o t)}{\exp\left(kN_A L/u\right) + \exp\left(k\epsilon C_o t\right) - 1}$$

Comparing the Amundson solution and Hu and Zhang’s version given by Eq. (16), the reader will observe that there is a glaring difference between the two equations: $v$, the interstitial velocity, appears in the Amundson solution while $u$, the superficial velocity, appears in Hu and Zhang’s version. Because of this error, the $\epsilon$ parameter will appear in the $\exp(kN_A L/u)$ term when Eq. (9) is inserted into Eq. (17) to convert $k$ to $k_{BA}$. To resolve this problem, Hu and Zhang put forward the following arbitrary expression linking $N_A$ to $N_o$:

$$N_A = N_o \epsilon$$

The correct form of the Bohart-Adams equation can now be obtained by applying the preceding equation to Eq. (17). If one replaces $u$ in Eq. (17) with $v$, one can easily convert the Amundson solution to the Bohart-Adams equation without recourse to the nonsensical Eq. (18) “invented” by Hu and Zhang. In other words, unlike Eq. (9), Eq. (18) is devoid of logical reasoning. It is an artificial construct put forward by Hu and Zhang for the sole purpose of equation manipulation. They have simply confused the $u$ and $v$ parameters and as a result presented a muddled form of the Amundson solution. I don’t mean to sound harsh, and I certainly intend no embarrassment to Hu and Zhang, but in my view, most modelers worth their salt should know the difference between the interstitial and
superficial velocity frames (see Eq. (11)). Their confusion over \( u \) and \( v \) betrays a serious lack of understanding of the Amundson modeling approach. By misinterpreting the Amundson solution, Hu and Zhang have succeeded in tying themselves in knots over the handling of the velocity and bed voidage parameters.

**Trivial issues**

Hu and Zhang put forward a rambling account of equation simplification and curve characteristics, complete with fancy plots that are completely irrelevant to my article. This all adds up to an extremely tedious read. In what follows, I shall ignore most of this material including their Figs. 2-5. Unraveling their convoluted meanderings yields two trivial issues that merit a passing mention.

Hu and Zhang draw attention to the exponential Bohart-Adams equation, highlighting their research group’s contribution [11] as well as the work of Sahel and Ferrandon-Dusart [12]. I assume they specifically question the exclusion of the Sahel-Ferrandon-Dusart paper when I discussed in my article the origin of the exponential Bohart-Adams equation and its proliferation in the literature of environmental adsorption. The Sahel-Ferrandon-Dusart paper, available in French only, has been cited 13 times since its publication in 1990, according to Google Scholar. It should be obvious that it has attracted very little attention. The exponential Bohart-Adams equation first emerged in some articles published in the chemistry/chemical engineering literature in the 1940s. Those publications along with the Sahel-Ferrandon-Dusart paper were not discussed in my article for the simple reason that early researchers who promoted the use of the exponential Bohart-Adams equation in environmental adsorption research did not cite them. Incidentally, the exponential and logistic versions of the Bohart-Adams equation have been previously discussed in an article by Lee et al. published in 2015 [13]. This paper of Lee et al. was not cited by Hu et al. [11].

Hu and Zhang lay claim—by way of aside (tenuous claim?)—to new insights regarding the mathematical equivalence of the Bohart-Adams, Thomas, and Yoon-Nelson equations [11]. Unfortunately, however, several previous investigators have already made notable contributions to this area. This fact was pointed out in my article [1]. The similarity between the Bohart-Adams equation and the Yoon-Nelson equation has been discussed by Busmundrud [14] nearly 30 years ago. Since then, the mathematical equivalence of the Bohart-Adams equation and the Thomas equation has been demonstrated by Yan et al. [15] and Chu [5] while the equivalence of the three models has been discussed by Lee et al. [13], Chatterjee and Schiewer [16], and Yan et al. [17]. Curiously, none of these highly relevant prior studies were cited or discussed in the Hu et al. paper [11].

Hu and Zhang end their letter by promoting their modified Bohart-Adams equation for fitting asymmetrical breakthrough curves, a topic not investigated in my article. As such, it is not germane to the present discussion, and ought never be mentioned at all. As stated in my article, the Bohart-Adams equation is analogous to the logistic equation. Both produce an S-shaped curve that is symmetrical around its midpoint. The symmetrical nature of the Bohart-Adams equation is well-known in the environmental engineering literature—first pointed out by Oulman 40 years ago [18]. Should Hu and Zhang wish to engage in dialogue around the topic of breakthrough curve asymmetry, they are welcome to critique a paper of mine that has been published recently, and which deals with this particular subject matter [19].

**Conclusions**

To sum up, I can reassure readers of the Chemical Engineering Journal that the Bohart-Adams equation—Eq. (12)—presented in my article [1] is correct, consistent with the modern formulation of the Bohart-Adams rate expression, and analogous to the Bohart-Adams model of authoritative books. Also, it is possible to use the Bohart-Adams equation to examine the effect of bed voidage. It is clear that the two core criticisms made by Hu and Zhang have been reached by misunderstanding the Amundson solution and the Bohart-Adams equation, and are, therefore, simply off the mark. Worse still, their version of the Amundson solution is marred by the presence of a glaring error. The
environmental adsorption literature is already replete with defective adsorption models of one form or another. By misinterpreting the Amundson solution, Hu and Zhang’s comment may well have the effect of further muddying the already murky waters surrounding the modeling of fixed bed adsorption.

Padding their letter with a mass of superfluous material, along with a healthy dose of extraneous supplementary data thrown in for good measure, suggests that Hu and Zhang’s commentary has very little of substance to say about my article and much to say about their own work. I have presented enough details to proclaim that Hu and Zhang’s letter is riddled with misunderstandings, mistakes, baseless claims, and all manner of irrelevancies. As such, their commentary should be discounted entirely since it adds little, if anything, to a deeper understanding of the Bohart-Adams equation.

Nomenclature

- $a$: Parameter defined by Eq. (14)
- $b$: Parameter defined by Eq. (15)
- $C$: Adsorbate concentration in fluid phase
- $C_o$: Adsorbate concentration at column inlet
- $k$: Rate coefficient based on Eq. (2)
- $k_{BA}$: Rate coefficient based on Eq. (8)
- $L$: Bed depth
- $n$: Mass of adsorbate per unit volume of bed
- $N_A$: Adsorption capacity per unit volume of bed
- $N_o$: Adsorption capacity per unit volume of bed
- $q$: Mass of adsorbate per unit mass of adsorbent
- $q_o$: Adsorption capacity per unit mass of adsorbent
- $t$: Time
- $u$: Superficial velocity
- $v$: Interstitial velocity
- $z$: Column axial coordinate
- $\varepsilon$: Bed voidage
- $\rho_p$: Adsorbent density

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