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Estimation of Parameters
for the Bohart-Adams Model

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Abstract

The vision of the Hydrogen Economy is to use renewable energy to power Fuel Cells. Power systems based on this pattern have reduced carbon footprint, minimal production of pollutants and potentially high efficiency. Biomass is of particular interest as large quantities of plant and wood (cellulose) residues are generated annually and are presently considered a waste product.

Anaerobic Digesters are a commercial, well established, technology for converting a wide range of biomass (manure and some plant residues) into a benign solids product and a methane rich gas (biogas).

A number of demonstration projects have shown that Fuel Cells can operate on biogas, a pattern of energy production that is a realization of the Hydrogen Economy.

The biogas contains a number of contaminants, such as hydrogen sulphide, that are detrimental to Fuel Cells. Currently, adsorbent beds are the primary technology for the removal of these containments. These beds must be sized correctly in order to protect the Fuel Cell but not oversized in order to minimize capital and operating costs.

The Bohart-Adams model is widely used to size fixed bed adsorbers. A critical role of the model is to fit it to breakthrough curves from laboratory beds, extract model parameters and use the parameters to design the commercial adsorber. With properly calibrated parameters, the design of the bed can proceed with confidence.

This article investigates the method of fitting the Bohart-Adams model to breakthrough data, using methanol adsorption on activated carbon as a test case, and computes the consequent error in the model parameters.

1 Introduction

A key element in the development of the Hydrogen Economy is the linking of Fuel Cells to a renewable energy resource such wind power, solar or biomass. The overall power system has many benefits. As the raw fuel is renewable, the power system is carbon neutral: there is no net addition of carbon dioxide to the atmosphere. The Fuel Cell ensures reduced or even no emissions of common pollutants such as NO_x, SO_x and particulates. In addition, Fuel Cells are potentially efficiency with efficiencies greater than the prevalent energy conversion technology: the internal combustion engine. If the Fuel Cell operates at high temperature (SOFC or MCFC), there is a further advantage as the high quality heat can be converted to additional power.

There are a number of well noted weaknesses in the vision of the Hydrogen Economy. First, renewable energy from wind or solar has significant variation with the time of day and season. There must significant means to store energy when it is being produced and not needed, so that it is available for use when demanded by the user. The requirement for storage capacity greatly increases the cost of power generation with the consequence that 'green' power is much more expensive then power generated from combustion of fossil fuels.

The weakness with biomass as a renewable energy lies in processing it to a useful form suitable for a fuel cell. Biomass is a complex material that varies with the plant. Some technologies show promise of being able to handle a wide range of plant material such as enzyme technology or gasification. However, these technologies are pre-commercial or still under research.

Anaerobic Digestion (AD) is one well established, commercial, technology able to process a wide range of biomass. AD technology is very attractive for decomposing animal manure (cattle, pig or chicken), sewage at waste water treatment plants, or kitchen waste in urban areas. The AD converts the 'waste' into a methane rich biogas and solids which can be used as a soil amendment. The biogas can be converted to power with a 'genset' which offsets the costs of the AD installation.

Moreover, the hydraulic retention time of an AD can be quite long (many days). The AD can 'store' biomass for significant periods smoothing variation in the feed of raw biomass.

The AD technology provides a critical link between a renewable energy source and Fuel Cells. There are a number of demonstration projects that show this link is technically feasible and that the biogas is suitable fuel for Fuel Cells [1].

A common element in these demonstrations is the cleanup of the biogas. Biogas contains a large number of impurities, such as hydrogen sulphide, that are detrimental to the Fuel Cell. One technology used to remove impurities are adsorbents such as activated carbon [2]. The correct sizing of the beds is important in protecting the Fuel Cell and the overall economics of the process.

The Bohart-Adams model is widely used to size fixed bed adsorbers [3]. A critical role of the model is to fit it to breakthrough curves from laboratory beds, extract model parameters and use the parameters to design the commercial adsorber.

In this article, we compare linear and non-linear methods to fit the Bohart-Adams model to a sample breakthrough curve.

Time (mins)	Exit Conc. (mg/m^3)
13	0.13
14	0.26
15	0.53
16	1.18
17	2.49
18	5.52
19	10.64
20	19.83
21	37.29
22	61.19
23	96.25
24	150.61

Table 1 Breakthrough data
For AGC exposed to methanol

2 Experimental

A standard breakthrough experiment was performed using a proprietary activated carbon. A canister was loaded with 175 cm^3 of the carbon and dehumidified (RH<15%) by dried air until a constant mass was achieved. The bed was then exposed to dried air at 30 SLPM containing 2007 mg/m3 of methanol (Aldrich). The exhaust from the bed was monitored by an IR detector that was calibrated for methanol concentrations from 0 - 150 mg/m3 (115 ppm). The data from the experiment are presented in Table 1. Methanol was detected in the exit stream after 13 minutes and reached the limits of the detector calibration after 24 minutes. The run was extended beyond 24 minutes but the data is not considered reliable due to a possible saturation of the IR monitor.

3 Bohart-Adams Model

The Bohart-Adams model is well established in the literature [3]. The key assumption of the model is the 'rectangle' or step isotherm: the equilibrium capacity of the adsorbent is fixed at q_s (mg/cm^3) and independent of the concentration of the species in the vapour phase. Application of a molar balance over a differential cylinder of the material gives the following governing equations:

$$\frac{\partial c}{\partial t}+v\frac{\partial c}{\partial z}+\frac{(1-\varepsilon)}{\varepsilon}\frac{\partial \overline{q}}{\partial t}=0 \qquad \text{Equation 1}$$

$$\frac{\partial \overline{q}}{\partial t}=kc\left(q_s-\overline{q}\right) \qquad \text{Equation 2}$$

In equation (1) and (2), c is the interstitial concentration of adsorbate (methanol, mg /cm^3 of void space), v the interstitial velocity (cm/sec), ε the void fraction, $\overline{q}$ the uptake of adsorbate (mg/cm^3 of adsorbent) and q_s the equilibrium uptake. The parameter k, the adsorption coefficient, has units of cm^3 of void space/ (mg-sec).

The bed is assumed to be homogenous and gradients occur only in the axial direction.

At the time t = 0, the bed is free of adsorbate ($\overline{q}=0$) and exposed to an inlet stream of inert gas carrying the adsorbate at a constant concentration of c_0. The solution to equations (1) & (2) is:

$$\frac{c}{c_0}=\frac{e^{\tau}}{e^{\tau}+e^{\xi}-1} \qquad \text{Equation 3}$$

where $\tau=kc_0\left(t-\frac{z}{v}\right)$ and $\xi=\frac{kq_s z}{v}\left(\frac{1-\varepsilon}{\varepsilon}\right)$. The transformed variables τ and ξ are, respectively, a dimensionless time and distance. The exit concentration is obtained by setting $z=L$, where L is the length of the bed.

The use of the Bohart-Adams model to design adsorbent beds requires accurate knowledge of the two parameters k and q_s. These parameters are not easily predicted since they represent the aggregate effects of mass transfer, pore diffusion, kinetics of adsorption and equilibrium.

It is standard practice to measure a breakthrough curve for the contaminated stream and a proposed adsorbent with flows, concentrations and compositions typical of the actual application. Equation (3) is fit to the breakthrough data to determine the two parameters. This calibrates the Bohart-Adams model so that it can be applied with confidence to size the bed.

It is custom to rewrite Equation (3) to facilitate the fit to the breakthrough data. The reciprocal of Equation (3), after some trivial algebra, can be written as:

$$\frac{c_0}{c}-1=e^{\xi-\tau}-e^{-\tau} \qquad \text{Equation 4}$$

The second term on the right side is usually small and can be neglected. We also recognize that for long times, the term z/v in the expression for τ can be ignored. Taking natural logarithms yields the equation:

$$\ln\left(\frac{c_0}{c}-1\right)=\frac{kq_s z}{v}\left(\frac{1-\varepsilon}{\varepsilon}\right)-kc_0 t \qquad \text{Equation 5}$$

A plot of LHS versus time yields a straight line. The tools of linear regression are used to compute the intercept and slope, from which it is simple to find k and q_s.

The alternative is non-linear regression: fit equation (3) directly to the data and determine the value of k and q_s that minimize the sum of squares.

It is worthwhile noting that equation (5) has the same form as the Wheeler-Jonas equation [4] which has broad use in the literature for calculating breakthrough times. Linear regression is also used to fits the model to data in order to determine the parameters. This investigation offers insight into the quality of the parameters for the Wheeler-Jonas equation.

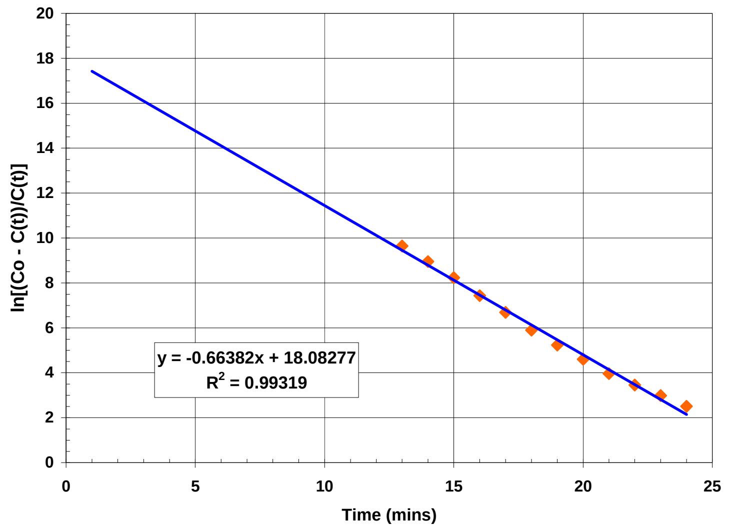

Figure 1 Linear Regression of methanol data according to Equation (5)

3.1 Linear Regression

The results of fitting Equation (5) to the data of Table 1 are presented in Figure 1. The methanol breakthrough data are well represented by Equation (5) as the $R^2 = 0.9934$ – most of the variance in the data is removed by the model. The values for k and q_s are, respectively, 5.5125 cm^3·mg^{-1}·sec^{-1} and 18.7446 mg·cm^{-3}

The interdependence of slope and intercept (and also k and q_s) is evident in the graph. The intercept is obtained by extrapolating the regression backwards to zero time (as suggested by the backwards extrapolation of the trend line). Small changes in the slope lead to significant changes in the intercept. We also note that the transformation (LHS of Equation (5)) is not well defined as time approaches zero. The concentration at the exit of the bed is zero at t=0 leading to an undefined calculation. At times near zero, small measurement errors in the concentration are amplified via the transformation leading to large uncertainties in the intercept.

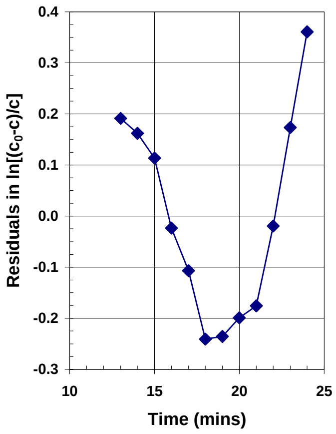

Figure 2 Residuals in linear regression of Figure 1. Residuals are evenly distributed about zero although there is a systematic variation indictaing a second order (parabolic) effect is present

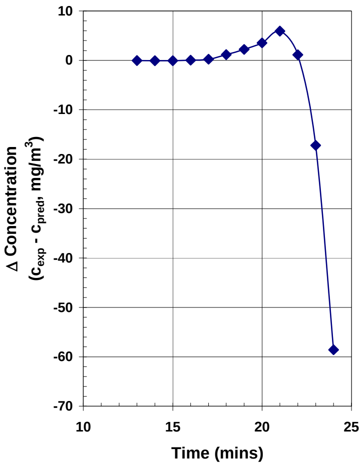

Figure 3 Residuals in concentration derived from linear regression of Figure 1. Residuals are not evenly distributed about zero and there is a systematic variation with time

The residuals of the fit for equation (5) are presented in Figure 2. The residuals show that there is a small systematic trend in the data – a second order term could be included in Equation (5) to improve the fit. However, they are evenly distributed about zero and the high R^2 of 0.9913 indicates that equation (5) is an excellent representation of the transformed data.

Figure 3 presents the residuals in the concentration. This is the difference between the data and the concentration computed using Equation (3) with the values for k and q_s computed from the linear regression. It is quite clear that there is a bias. The residuals increase significantly with time rather being evenly distributed about zero as in Figure 2. The predicted values for the concentration are presented in Table 2.

An exposition of the theory and calculation of the joint confidence region for the parameters in a linear model is given in [5]. The general linear model is written as:

$$Y = X\beta + Z \qquad \text{Equation 6}$$

where Y is the response (concentration), X the regressor variable (time) and Z, a random variable representing error in the model. The variable β are the parameters, the slope and intercept of equation (5).The fit of the model to data is obtained by minimizing the sum of squares:

$$S(\beta) = \left\| y - Y \right\|^2 \qquad \text{Equation 7}$$

Carrying out the least squares fitting procedure yields the best estimates of the parameters, called $\hat{\beta}$. The estimates can be calculated by the expression:

$$\hat{\beta} = \left(X^T X\right)^{-1} X^T Y \qquad \text{Equation 8}$$

The joint confidence region for the parameters β at the α confidence level is the ellipsoid:

$$\left(\beta - \hat{\beta}\right)^T X^T X \left(\beta - \hat{\beta}\right) \leq P \cdot s^2 \cdot F(P, N-P; 1-\alpha) \qquad \text{Equation 9}$$

where P is the number of parameters in the model, N is the number of data points and F(P,N-P;1-α) is Fishers F distribution with P and N-P degrees of freedom. The residual mean square, s^2, is calculated from the expression:

$$s^2 = \frac{S\left(\hat{\beta}\right)}{N-P} \qquad \text{Equation 10}$$

For the data in Table 1, X^T=[1 13; 1 14; 1 15; …,1 23; 1 24] and

$$X^T X = \begin{bmatrix} 12 & 222 \\ 222 & 4250 \end{bmatrix} \qquad \text{Equation 11}$$

Other values entering into equation (9) are: P = 2; N-P = 10; F(2,10;0.05) = 4.10 and s^2 = 0.04323 ($S\left(\hat{\beta}\right)$ = 0.4328). The RHS of equation (9) is 0.3545.

Equation (9) develops into a quadratic that can be solved for combinations of slope and intercept of Equation (3) that defines the boundary of the 95% confidence region centred on $\hat{\beta}$. From the slope and intercept, the 95% confidence region for k and q_s can be developed.

The results of the calculations are presented in Figure 4. The confidence region is a symmetric ellipsoid while the range of k and q_s is surprisingly large. The adsorption coefficient varies from about 5.1 to 5.9 around the optimum value is 5.5. This corresponds to a relative variation of about 7% (0.4/5.5*100). The capacity varies from 18.3 to 19.3 around the optimal value of 18.7 or a relative variation of about 3% (0.6/18.7*100).

3.2 Non-Linear Regression

The non-linear regression involves minimizing the sum of squares (equation (7)) where the model predictions (Y) are provided by equation (3). The initial guess for the parameters k and q_s was the results of the linear regression. Indeed, the numerical routine (SOLVER function in Excel) had great difficulty locating the minimum sum of squares without a good initial estimate. The minimum was checked by preparing a two dimensional matrix of values k and q_s, computing the sum of

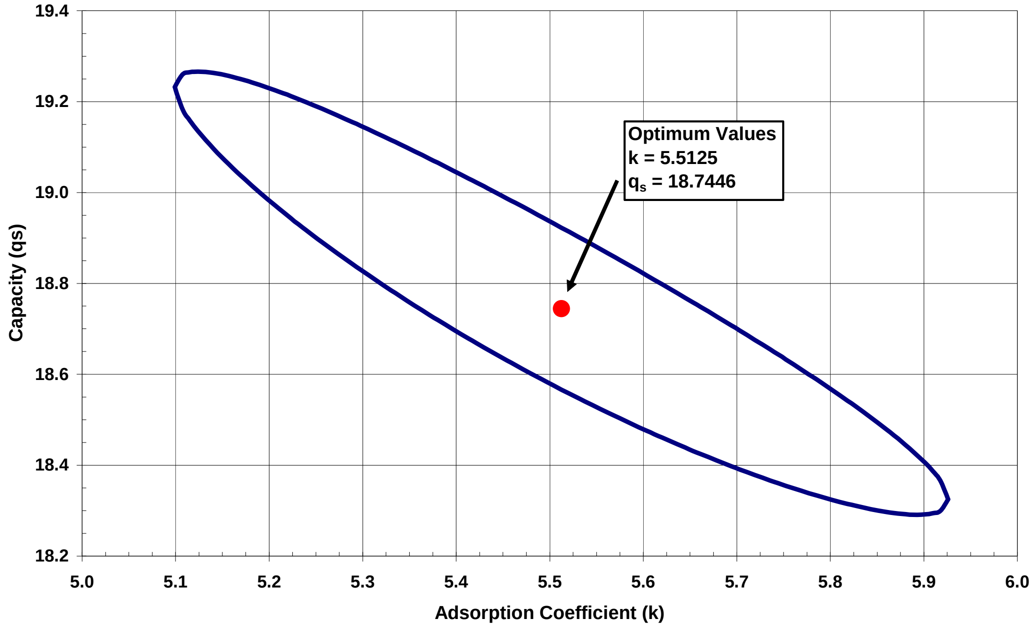

Figure 4 The joint confidence region (95% confidence level) for k and q_s based upon linear regression. The blue line is the boundary of the confidence region and the red dot is the value of k and q_s that minimize the sum of squares (Optimum Values).

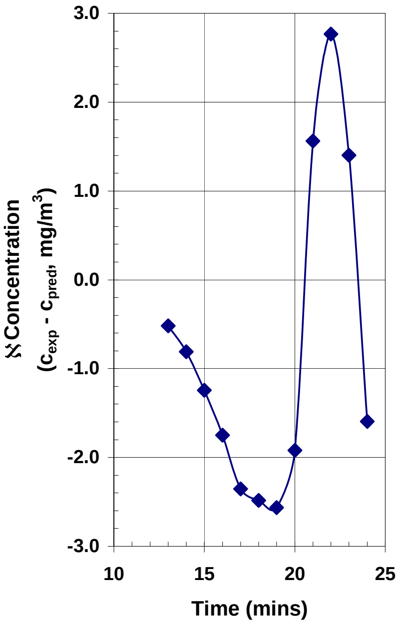

Figure 5 Residuals in concentration derived from the non-linear regression. Residuals are evenly distributed about zero but show a sinusoidal (systematic) variation with time

squares for each combination and manually checking for the minimum sum of squares. These efforts lead to values for k and q_s of, respectively, 4.1804 cm^3·mg^{-1}·sec^{-1} and 19.9305 mg·cm^{-3}.

The residuals in the concentration of the fit of equation (3) are presented in Figure 5. The residuals are evenly distributed about zero but show a sinusoidal variation that suggests a small systematic trend. This is consistent with the similar observation for the linear regression.

The predicted values for the concentration for the linear and non-linear fit are presented in Table 2. The non-linear fit gives much better representation of the data at larger times, especially for times 21 – 24 minutes. The relative error at small times (13 – 15 minutes) is much larger than the error in the linear fit but is still close to the data.

The calculation of the confidence region for the non-linear estimates of the parameters is given by the equation [5]

$$S(\beta) \le S(\hat{\beta})\left(1+\frac{P}{N-P}\cdot F(P,N-P;1-\alpha)\right) \quad \text{Equation 12}$$

Values entering into equation (12) are: P = 2; N-P = 10; F(2,10;0.05) = 4.10, $S(\hat{\beta})$ = 42.0925. Carrying out the calculations gives $S(\beta) \le 76.8213$.

A trial and error method was used to determine values of β that satisfied equation (12) exactly (i.e. $S(\beta) = 76.8213$). This procedure was greatly assisted by the matrix of values, mentioned above, to confirm the location of the minimum sum of squares.

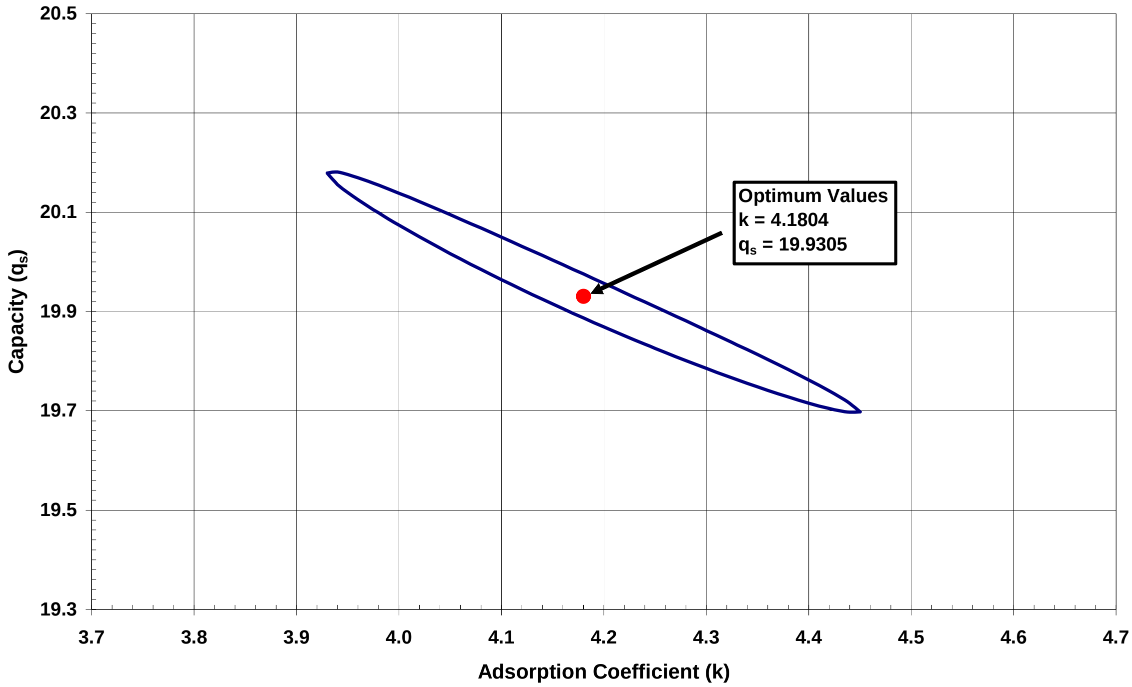

Figure 6 The joint confidence region (95% confidence level) for k and q_s based upon non-linear regression. The blue line is the boundary of the confidence region and the red dot is the value of k and q_s that minimize the sum of squares (Optimum Values). The scales of the graph are the same as Figure 4 to facilitate comparison.

Time	Exit Concentration (mg/m^3)		
(mins)	Measured	Linear Fit	Non-linear Fit
13	0.13	0.16	0.65
14	0.26	0.31	1.07
15	0.53	0.59	1.77
16	1.18	1.15	2.93
17	2.49	2.24	4.84
18	5.52	4.34	8.00
19	10.64	8.41	13.20
20	19.83	16.28	21.75
21	37.29	31.38	35.73
22	61.19	60.06	58.43
23	96.25	113.44	94.85
24	150.61	209.19	152.20

Table 2 Exit concentrations, computed from the linear and non-linear model fits, compared to the experimental data. The linear fit is superior for low concentrations while the non-linear fit is superior for the high concentrations.

The results of the calculations are presented in Figure 6. The confidence region is an apparently symmetric ellipsoid. Increasing the confidence level shows that the joint confidence region is asymmetric and is banana shaped. The adsorption coefficient varies from about 3.93 to 4.45 around the centre value of 4.18. This corresponds to a relative variation of about 6% (0.26/4.18*100). The capacity varies from 19.7 to 20.2 around the optimal value of 19.93 or a relative variation of about 1.3% (0.25/19.93*100).

The two regression techniques produce best estimates that are significantly different at the 95% confidence level. That is, the two confidence regions do not intersect and there is no combination of k and q_s that will generate an error that meets the criteria of both equation (9) and (12) simultaneously.

Inspection of the two figures clearly shows that the area of the non-linear confidence region (Figure 6) is smaller than the area of the linear confidence region (Figure 4). The area of the confidence region is estimated by using the trapezoidal rule. Figure 4 has an area of 0.2315 while the area in

Figure 6 is 0.01767, a factor of 10 smaller. The area reflects the random error of the underlying measurements. The fact that Figure 4 has greater area than Figure 6 indicates that fitting procedure (linear regression) is inflating the error. For this data, non-linear regression generates tighter bounds on the parameter estimates

Another metric of the joint confidence region is its ‘thickness’. Consider Figure 4 and a fixed value for the adsorption coefficient. The values of the capacity that lie on the vertical line and within the joint confidence region provide satisfactory fits to the data at the 95% confidence level. Clearly, the wider the region at the given value of the adsorption coefficient, the larger is the uncertainty in the true value of the capacity. The same analysis can be carried out for a horizontal line in this case the thickness is a measure of the uncertainty in the adsorption coefficient for the given capacity.

In view of this, Figure 6 is preferred over Figure 4 since it is slender ellipsoid and its width in both vertical and horizontal directions is smaller.

Now, it is desired that the ellipsoid collapse to a vertical or horizontal line segment. In either case, the estimates of the parameters are independent of each other. For a horizontal line – the uncertainty in the adsorption coefficient has no effect on the capacity; for a vertical line segment the uncertainty in the capacity has no effect on the adsorption coefficient.

In view of this, a final metric of the confidence region is its ‘tilt’. This refers to the angle the region makes with respect to the vertical and is a gross measure of the degree of dependence of the two parameters. The dependence is reflected that if one parameter undergoes a change, a proportionate change in the other parameter is required in order to maintain the same sum of squares or goodness of fit. For a vertical or horizontal line segment, the dependence is zero or absent, and it is possible to estimate the parameters independently.

The extremities of the confidence region are used to define a straight line that lies close to the optimum values and approximately bisects the region in two. For Figure 4, the slope of the line is -1.0972 or an angle of 42º from the horizontal. For Figure 6, the slope of the line is -0.9094 or an angle 48º from the horizontal. Both regions indicate a similar dependence between the parameters.

4 Summary

The Bohart-Adams can be fit to measured breakthrough data in two different ways. The conventional method involves linearization of the model (see equation (5)). The fitting can be conveniently done in a commercial software (excel) with automatic generation of relevant statistical metrics and tests. The non-linear fitting is more involved and finding the parameters that correspond to the true minimum in the sum of squares is difficult. Moreover, the construction of the joint confidence region, the key entity in assessing the quality of the fit and the error in the parameters, is non-trivial.

The two methods generate statistically different parameter estimates but these estimates differ by much less than a factor of 2. For the data presented in this article, the difference in the estimates is on the order of 30% for the adsorption coefficient and 6% for the capacity.

The advantage of the non-linear fit procedure is that the joint confidence region seems to be significantly smaller than the corresponding region generated by linear regression. This leads to better estimates of the parameters (smaller error). However the degree of correlation between the parameters is quite similar for the two fitting methods.

These conclusions are strictly limited to the experimental data presented in this article. However, these findings motivate carrying out a similar investigation on a broader collection of data to confirm advantages of non-linear over linear regression.

5 Acknowledgements

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