ANALYSIS OF BOHART-ADAMS MODEL EQUATIONS FOR DESCRIPTION OF ADSORPTION IN FIXED BED-COLUMN

Nediljka Vukojević Medvidović, Sandra Svilović
Faculty of Chemistry and Technology, University of Split, Ruđera Boškovića 35, 21000 Split, Croatia
E-mail: nvukojev@ktf-split.hr

ABSTRACT

Bohart and Adams developed mathematical model for description of adsorption in fixed bed column. However, some researchers used the original model, some used a simplified version of the model, while others used the same equation expressed in different forms. This paper is analyzing all Bohart-Adams model equations in order to clarify their differences and similarities.

Keywords: Bohart-Adams model, adsorption, fixed-bed column, breakthrough curve, nonlinear least square methods.

INTRODUCTION

Bohart and Adam (1920) developed a model based on assumption that the adsorption rate is proportional to the residual capacity of the adsorbent and the concentration of adsorbate [1]. The original form of the Bohart-Adams (BA) model is given by Equation (1). However, in literature, one can find also Equation (2) which was obtained when the second term in the denominator (=1) was entirely negligible, except for very small values of both $k_{BA} \cdot q_{BA} \cdot H / v$ and $k_{BA} \cdot c_0 \cdot t$. Several researchers used simplified Equation (3), especially in publications related to environmental protection [2]. The nonlinear and linear forms of the BA model are compared in Table 1.

Table 1. Nonlinear and linear form of Bohart-Adams model equations.

Nonlinear form	Linear form	Eq. no.	Ref.
$\frac{c}{c_o} = \frac{\exp(k_{BA} \cdot c_o \cdot t)}{\exp(k_{BA} \cdot q_{BA} \cdot H / v) - 1 + \exp(k_{BA} \cdot c_o \cdot t)}$	$\ln(\frac{c_0}{c} - 1) = \ln\left[\exp(k_{BA} \cdot q_{BA} \cdot H / v) - 1\right] - k_{BA} \cdot c_0 \cdot t$	(1)	[1]
$\frac{c}{c_o} = \frac{1}{1 + \exp\left[\frac{k_{BA} \cdot q_{BA} \cdot H}{v} - k_{BA} \cdot c_0 \cdot t\right]}$	$\ln(\frac{c_0}{c} - 1) = k_{BA} \cdot q_{BA} \cdot H / v - k_{BA} \cdot c_0 \cdot t$	(2)	[2]
$\frac{c}{c_o} = \exp\left[k_{BA} \cdot c_0 \cdot t - \frac{k_{BA} \cdot q_{BA} \cdot H}{v}\right]$	$\ln(\frac{c_0}{c}) = k_{BA} \cdot q_{BA} \cdot H / v - k_{BA} \cdot c_0 \cdot t$	(3)	[2]

Note: c - the effluent adsorbent concentration (mmol/L), c_0 – the influent adsorbent concentration (mmol/L), t – the time (h), v – the linear flow velocity (m/h), H - the fixed bed depth (m), k_{BA} - the rate constant of the Bohart-Adams model (L /(mmol h)), q_{BA}- the adsorption capacity of Bohart-Adams model (mmol/L)

In this paper, nonlinear forms of Bohart-Adams model equations are tested on experimental breakthrough curve of zinc removal onto Na-zeolite in order to clarify their differences and similarities.

EXPERIMENTAL

The nonlinear least square method was used for testing of the model equations in the Mathcad program. The testing was performed on experimental breakthrough curve of zinc removal onto Na-zeolite, performed at three different bed depths (H = 120, 80 and 40 mm - at initial zinc concentration of 1.083 mmol/L and flowrate of 1 mL/min) [3]. The natural zeolite clinoptilolite used in this study was originated from Zlatokop deposit, Vranjska Banja, Serbia, with granulation of 0.6-0.8 mm and pre-treated into Na-form. The characterization of zeolites was previously published [4]. The parameters were calculated from the Equations (1), (2), and (3) using Solve block and Minerr as output function. Constrains for the used models could be presented as:

$$\frac{\mathrm{d}}{\mathrm{d}X}\sum_{i=1}^{z}\left[(c/c_0)_{\mathrm{exp}}-(c/c_0)_{\mathrm{m}}\right]^2=0 \qquad (4)$$

where $(c/c_0)_{\mathrm{exp}}$ is experimental c/c_0 data, $(c/c_0)_{\mathrm{m}}$ represents the right side of nonlinear form in models given by equations (1), (2) and (3), X is a parameter (k_{BA} and q_{BA}). The number of constraints is equal to the number of the parameters.

The correlation coefficient (r^2) and the root mean square error (RMSE) were used as indicators of fitting of the experimental results with the results obtained by the model.

$$\mathrm{RMSE}=\sqrt{\frac{1}{z}\sum_{i=1}^{z}\left[(c/c_0)_{\mathrm{m}}-(c/c_0)_{\mathrm{exp}}\right]^2} \qquad (5)$$

The saturation capacity of the Bohart-Adams model, q can be evaluated as follows [5]:

$$q=q_{\mathrm{BA}}\cdot BV_{\mathrm{S}}/m=q_{\mathrm{BA}}/\rho \qquad (6)$$

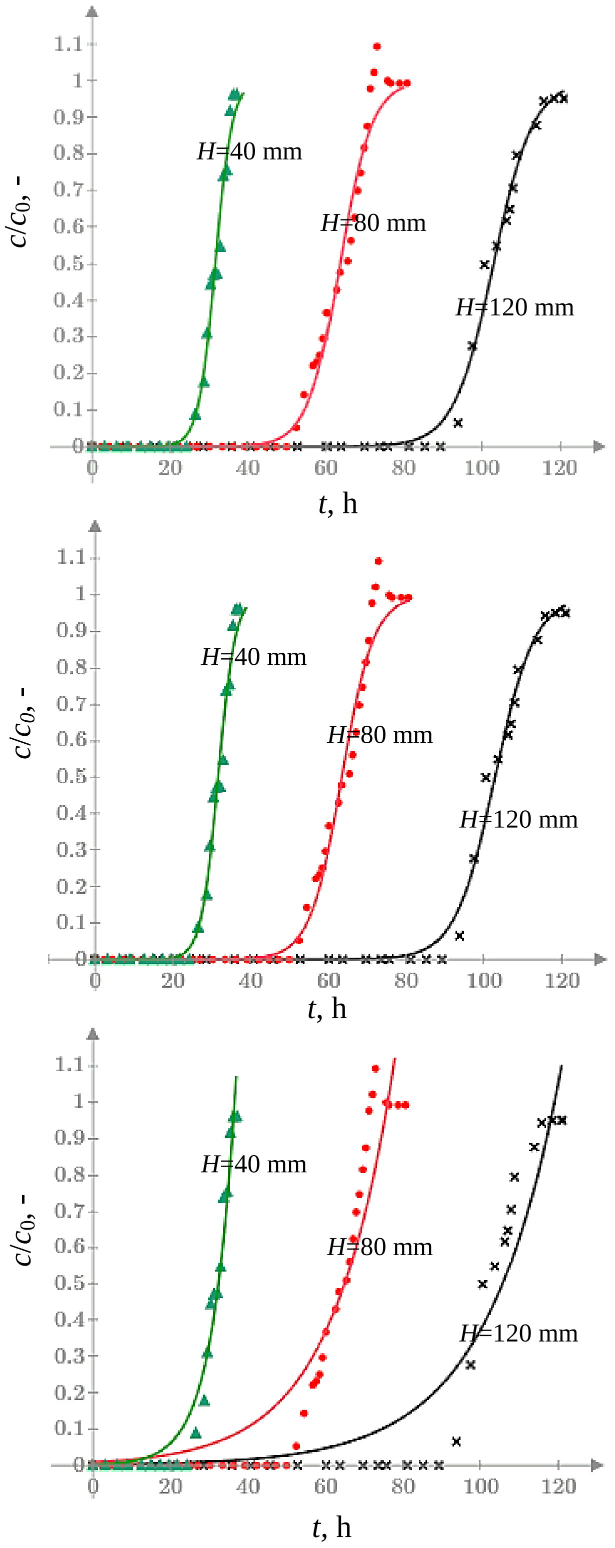
where q is the saturation capacity of the Bohart-Adams model (mmol/g), BVs is the fixed bed volume (L), m - the mass of the adsorbent bed in column (g), ρ is the apparent density of the adsorbent in the packed bed.

RESULTS AND DISCUSSION

Comparison of experimental and model breakthrough curves of zinc uptake onto Na-zeolite bed depth of 120, 80 and 40 mm, obtained by different Bohart-Adams model equations are compared in Fig. 1. The parameters of the Bohart-Adams model equations have been evaluated and summarized in Table 2.

Table 2. The parameters of the Bohart-Adams model equations.

Bohart-Adams eq. no.	Bed depth, mm	k_{BA} L/(mmol h)	q_{BA} mmol/L	r^2	RMSE
(1)	120	0.184	485.818	0.993	0.033
	80	0.225	456.792	0.984	0.054
	40	0.428	456.135	0.986	0.044
(2)	120	0.184	485.818	0.993	0.033
	80	0.225	456.792	0.984	0.054
	40	0.428	456.135	0.986	0.044
(3)	120	0.049	562.092	0.924	0.083
	80	0.058	546.973	0.912	0.124
	40	0.157	525.835	0.966	0.071



a) Eq. (1)

b) Eq. (2)

c) Eq. (3)

Figure 1. Comparison of experimental and model breakthrough curves of zinc uptake onto zeolite bed depth of 120, 80 and 40 mm, obtained by different BA model equations: a) Equation (1); b) Equation (2), c) Equation (3).

From the results in Fig 1, it is evident that experimental and model breakthrough curves obtained from Equations (1) and (2) are almost overlapping, indicating good agreement of the model equations with experimental data of zinc removal on Na-zeolite. However, model breakthrough curves obtained from Equation (3) show good agreement only in the initial part of breakthrough curve. According to Lee at al. (2015) this can be attributed to fact that

Equations (1) and (2) are convergent-type models, while Equation (3) is divergent model type [2]. Thus, Equation (3) is not suitable for the simulation of entire breakthrough curve, but only its initial part. Also, the model parameters k_{BA} and q_{BA} calculated from Equation (3) are different from those calculated from Equations (1) and (2) (see Table 2). The r^2 and RMSE values confirm better agreement of Equations (1) and (2) with experimental data.

Based on evaluated parameter q_{BA}, the saturation capacity of the Bohart-Adams model, q can be evaluated according to Equation (6). Values are compared with experimental values of breakthrough (q_B) and exhaustion capacity (q_E) in Table 3.

Table 3. Comparison of saturation capacity of the Bohart-Adams model, q with breakthrough capacity (q_B) and exhaustion capacity (q_E) experimentally obtained.

Bed depth, mm	Eq (1)	Eq (2)	Eq (3)	Experimental values [3]	
	q mmol/g	q mmol/g	q mmol/g	q_B mmol/g	q_E mmol/g
120	0.732	0.732	0.847	0.604	0.692
8	0.700	0.700	0.838	0.578	0.786
4	0.711	0.711	0.820	0.593	0.703

Better agreement of q is obtained with the experimental values of exhaustion capacity q_E. However, the values of q obtained from BA model Equation (3) are slightly overestimated, which is attributed to divergence-type model as well as exponential function type. This is in agreement with findings by Chu (2020) and Hu and Zhang (2020) [6,7].

CONCLUSION

The three different equations of Bohart-Adams model have been used in modeling of adsorption in a fixed-bed column. This paper confirms that the original form given by Equation (1) and its simplified form given by Equation (2) are totally different from Equation (3). This should be considered when choosing appropriate equation in modeling of adsorption systems.

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