Supporting Information for

Mathematical Modeling of Fixed-Bed Columns Adsorption: Hexavalent Chromium onto Chitosan Flakes

Jimena B Dima [124*]***, Mariano Ferrari,*** [23]***& Noemi Zaritzky,*** [4]

(1) Instituto de Biología de Organismos Marinos (CCT CONICET- CENPAT). Bv. Almirante Brown 2915(U9120), Chubut, Argentina.

(2)Facultad de Ingeniería, Universidad Nacional de la Patagonia San Juan Bosco. Bv. Almirante Brown 3051(U9120), Chubut, Argentina.

(3) Centro Para el Estudio de Sistemas Marinos (CCT CONICET- CENPAT). Bv. Almirante Brown 2915, (U9120), Chubut, Argentina.

(4) Facultad de Ingeniería. Universidad Nacional de La Plata. Calle 1 y 47 - La Plata (B1900TAG), Argentina.

E-mail address: jimenabdima@gmail.com (J.B.Dima); mferrari7@gmail.com (M.A.Ferrari); and zaritzkynoemi@gmail.com (N.E.Zaritzky)

Corresponding author: J.B.Dima

E-mail: jimenabdima@gmail.com

Instituto de Biología de Organismos Marinos (IBIOMAR CCT CONICET- CENPAT), Blvd. Brown Nº 2915, U9120ACD Puerto Madryn, Chubut, Argentina.

Tel: +54-280-488-3184

Fax: +54-280-488-3543

Mathematical Deduction of Model Proposed

Let us assume that we have a column of height h and a solute is starting to flow at time $t = 0$, with a linear flow v. To model the adsorption process in the column, the adsorbate molecule is considered to be adsorbed by the adsorbent at height x at time t, with a cumulative probability distribution $F_a(x,t)$ and density $f_a(x, t)$. The distribution $f_a(x, t)$ is modeled as a combination of two processes: the displacement of the adsorption zone and the trajectory of the solute through the unsaturated zone. The displacement of the front of the adsorption zone is modeled through a probability density $f_d(x, t)$ that represents the probability that the adsorption front is at the height x at time t. The solute path is modeled through a density $f_r(x)$ that represents the probability that the solute travels a distance x, from an available adsorption zone until it is adsorbed. Taking into account these processes $f_a(x, t)$ can be calculated as a convolution:

$$f_a(x,t) = \int_0^x f_d\left(x - y, t - \frac{y}{v}\right) f_r(y)dy \qquad \text{(a1)}$$

representing the multiplication of the two probabilities. The probability that the adsorbate exceeds the adsorption front at the height $x - y$, at time $t - (y / v)$, by the probability that then, moving at speed v, it travels a height y until it is absorbed at the height x at time t.

For a given time t, the complement of the cumulative probability $1 - F_a(x,t)$ represents the concentration profile in the fluid, that is the relative concentration Ct/C_0 at a height x, when x varies between 0 and h. Then $C(t) = 1 - F_a(h,t)$ is the function that represents the breakthrough curve, and the breakthrough time of the model is $t = tb$ such that $C(tb) = 0.1$.

Normal Model

As a first simplification we will assume that the column extends between $-\infty$ and $+\infty$ beyond the region occupied by adsorbent between 0 and h. The probability distributions are modeled with normal densities $f_N(x|\mu, \sigma)$ having mean μ and standard deviation σ that depend on certain parameters to be estimated. Specifically, for the displacement of the adsorption zone it will be considered a normal density with mean $v_d t$ and standard deviation σ_d, $f_d(x, t) = f_N(x|v_d t, \sigma_d)$, where v_d corresponds to the linear velocity of the adsorption zone displacement and $v_d t$ is the average height of the adsorption front. For the distance of the adsorbate displacement, until it is absorbed, a normal density with mean μ_r and standard deviation σ_r, $fr(x) = f_N(x|\mu_r, \sigma_r)$ can be considered.

We remark that by assuming normal distributions we allows negative values with no null probability density, this implies the possibility of negative distances and that the adsorbate could travel backwards in the column rather than forwards. This has no physical meaning and is only a theoretical simplification that allows us to deduce simple approximate formulas.

With these considerations, and integrating Eq. (a1) from $-\infty$ to x, $f_a(x, t)$ has a normal distribution: $f_a(x, t) = f_N(x|\mu_a, \sigma_a)$, with a mean:

$$\mu_a(t) = v_d t + \mu_r \left(1 - \frac{v_d}{v}\right) \tag{a2}$$

and standard deviation

$$\sigma_a = \sqrt{\sigma_d^2 + \sigma_r^2 \left(1 - \frac{v_d}{v}\right)^2} \tag{a3}$$

Since σ_a^2 is a linear combination of σ_d^2 and σ_r^2 these two variances cannot be estimated independently (that is, deviations for each particular process cannot be obtained from experimental data). A single parameter σ_a is then considered to describe the standard deviation associated with both processes. Therefore, the breakthrough curve projected

by this model is given by the function

$$C(t|v_d, \mu_r, \sigma_a) = 1 - f_N(x|\mu_a(t), \sigma_a)$$

$$= \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{\mu_a(t)-h}{\sqrt{2}\sigma_a}\right)$$

$$= \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{v_d t + \mu_r\left(1-{}^{v_d}/_{v}\right)-h}{\sqrt{2}\sigma_a}\right) \quad \text{(a4)}$$

where erf is the error function.

Considering $s > 0$ and a change of variables in Eq. (a4), given by

$$\tilde{v}_d = s v_d$$

$$\tilde{\mu}_r = \frac{s\left(\mu_r\left(1-{}^{v_d}/_{v}\right)-h\right)}{\left(1-s\frac{v_d}{v}\right)-h} \quad \text{(a5)}$$

$$\tilde{\sigma}_a = s\sigma_a$$

it follows that $C(t|v_d, \mu_r, \sigma_a) = C(t|\tilde{v}_d, \tilde{\mu}_r, \tilde{\sigma}_a)$.

Therefore there are infinite combinations of the parameters that produce the same function $C(t)$, and as a consequence v_d, μ_r, and σ_a cannot be simultaneously estimated from the data of the experimental breakthrough curve. Then assuming $\mu_r = 0$ (since it is considered that the adsorption kinetics of the solute is instantaneous when it meets the available adsorbent), a model with two independent parameters is obtained. The breakthrough curve corresponding to the proposed normal model is then:

$$\frac{Ct}{C_0} = C(t|v_d, \sigma_a) = 1 - F_N(h|v_d.t, \sigma_a) = \frac{1}{2} + \frac{1}{2}\,\mathrm{erf}\left(\frac{v_d t - h}{\sqrt{2}\sigma_a}\right) \quad \text{(a6)}$$

The parameters of the model are: v_d the speed of movement of the adsorption zone and σ_a the standard deviation of the position of the adsorption zone front.

Likewise, the breakthrough point of this model can be calculated by solving $C(tb|v_d, \sigma_a) = 1 - F_N(h|v_d.tb, \sigma_a) = 0.1$, that is, $F_N(h|v_d.tb, \sigma_a) = 0.9$, resulting:

$$tb = \frac{1}{v_d}\left(h - \sigma_a \Phi^{-1}(0.9)\right) \quad \text{(a7)}$$

where Φ^{-1} is the Probit function.

We remark that the normal model proposed assumes that the adsorption kinetics of the adsorbate is instantaneous when it meets the available adsorbent (μ_r = 0). This assumption is consistent with the observed results for chromium – chitosan system in batch studies (Dima et al., 2015). On the other hand, if a positive value of μ_r is considered this would correspond to a displacement of the breakthrough curve (Eq. a4), and will only produce a proportional increase in v_d and σ_a parameters (Eq. a5) (without changes in the general parameters performance).

Reference

Dima, J. B.; Sequeiros, C.; Zaritzky, N. E. Hexavalent chromium removal in contaminated water using reticulated chitosan micro/nanoparticles from seafood processing wastes. Chemosphere 2015, 141, 100−111.