Boron removal from aqueous solutions by a polyethylenimine––epichlorohydrin resin

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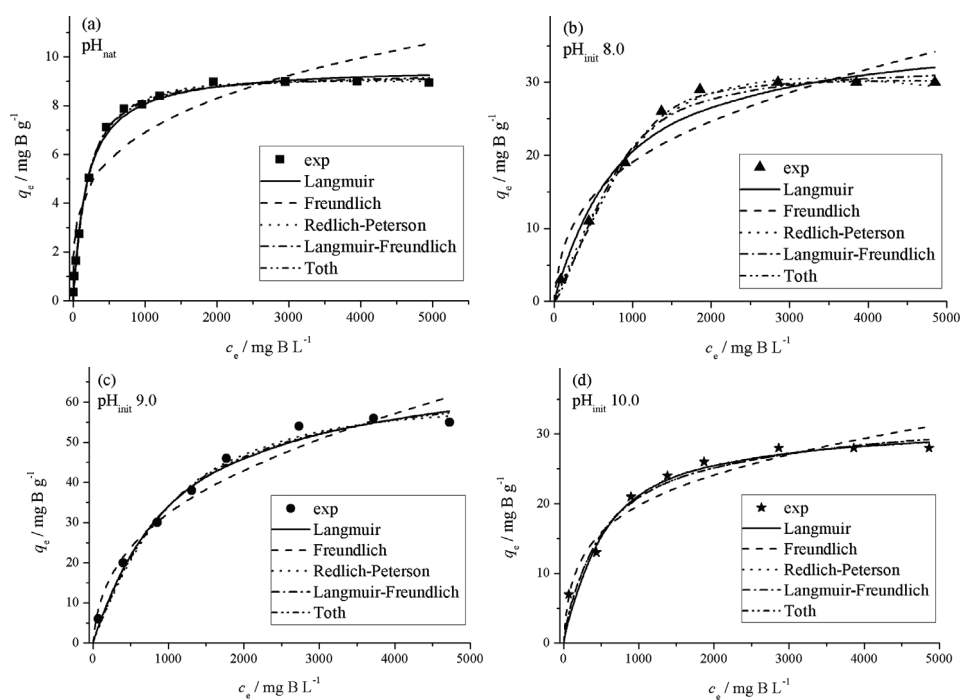
Fig. S-1. Experimental (symbols) and calculated (lines) isotherms for the boron sorption from solutions of pH_{nat} (a), pH 8.0 (b), pH 9.0 (c), pH 10.0 (d) by the resin under investigation.

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TABLE S-I. Isotherm constants of the equilibrium models for the boron sorption from solutions of pH_{nat} and pre-adj. pH 8.0, 9.0 and 10.0 (σ: standard deviation, *F:* the Fisher test and *ME* the percent mean error)

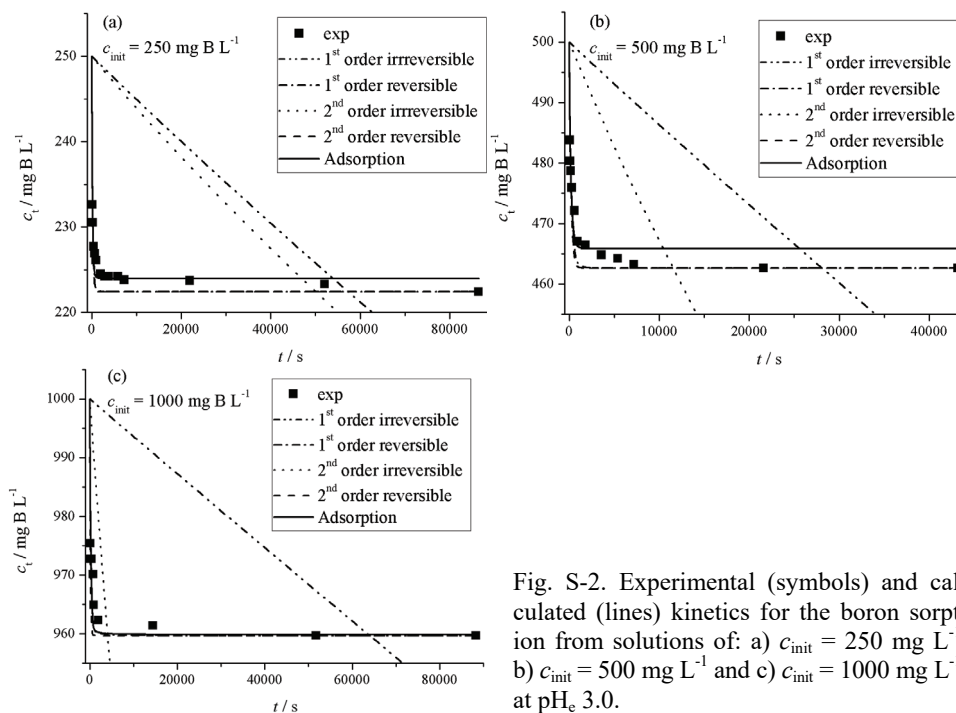| Model	q_m / mg g^{-1}	K	n	σ	F	ME / %
$q_{m,exp}$ = 8.9 mg g^{-1}, pH_{nat}						
L	9.59	0.0053	-	0.21	265.1	5.00
F	-	1.1100	3.78	1.34	6.7	64.98
RP	11.06	0.0004	1.06	0.13	710.9	3.18
LF	9.35	0.0056	1.12	0.17	378.2	5.08
T	9.23	0.0004	1.26	0.15	512.2	3.91
$q_{m,exp}$ = 30 mg g^{-1}, pH 8.0						
L	37.22	0.0013	-	2.55	15.5	11.93
F	-	1.5610	2.75	6.69	2.3	37.68
RP	58.96	0.0005	1.54	2.85	12.4	5.53
LF	31.82	0.0016	1.74	1.37	53.4	10.65
T	30.25	0.0008	3.94	0.64	243.7	4.78
$q_{m,exp}$ = 55 mg g^{-1}, pH 9.0						
L	70.36	0.0010	-	2.01	84.0	5.76
F	-	1.9680	2.46	4.65	15.6	18.23
RP	89.11	0.0006	1.19	1.83	100.9	7.61
LF	69.60	0.0010	1.02	2.18	70.9	6.02
T	64.97	0.0009	1.25	2.06	79.9	7.22
$q_{m,exp}$ = 28 mg g^{-1}, pH 10.0						
L	31.59	0.0021	-	1.65	22.8	9.05
F	-	2.8530	3.55	2.52	9.8	12.44
RP	32.64	0.0020	1.01	1.81	19.0	9.03
LF	34.55	0.0018	0.79	1.65	22.8	7.56
T	35.40	0.0035	0.69	1.73	20.7	8.07

Fig. S-2. Experimental (symbols) and calculated (lines) kinetics for the boron sorption from solutions of: a) c_{init} = 250 mg L^{-1}, b) c_{init} = 500 mg L^{-1} and c) c_{init} = 1000 mg L^{-1}, at pH$_e$ 3.0.

The expression of the boron removal rate (c_t) from the liquid phase can be described by:

the irreversible first-order reaction model:[1,2]

$$-\frac{dc_t}{dt} = kc_t \qquad \text{(S-1)}$$

or the irreversible second-order reaction model:

$$-\frac{dc_t}{dt} = kc_t^2 \qquad \text{(S-2)}$$

where c_t is the boron concentration in liquid phase, present at time t and k is the overall reaction rate constant. If the interaction between boron and sorbent surface is reversible, the rate equation for the reversible first-order reaction model is a combination of the reaction rate equation:[3]

$$-\frac{dc_t}{dt} = k_1 c_t - k_2(c_{init} - c_t) \qquad \text{(S-3)}$$

and the equilibrium constant:

$$K = \frac{k_1}{k_2} = \frac{c_{init} - c_e}{c_e} \qquad \text{(S-4)}$$

where k_1 and k_2 are the forward and backward reaction rate constants, respectively. Accordingly, the reversible second-order reaction model is a combination of the reaction rate equation:

$$-\frac{dc_t}{dt} = k_1 c_t^2 - k_2 (c_{init} - c_t)^2 \qquad (S-5)$$

and the equilibrium constant:

$$K = \frac{k_1}{k_2} = \frac{(c_{init} - c_e)^2}{c_e^2} \qquad (S-6)$$

Alternatively, the rate of boron uptake by the resin in an irreversible interaction can be described by:[4,5]

$$\frac{dq_t}{dt} = k_a c_t (q_m - q_t) - k_d q_t \qquad (S-7)$$

where q_t is the boron concentration in the solid phase at time t and k_a, k_d are the adsorption and desorption reaction rate constants, respectively. When the equilibrium relationship of the adsorption system is of the Langmuir form:

$$K_L = \frac{k_a}{k_d} = \frac{q_e}{c_e (q_m - q_e)} \qquad (S-8)$$

the boron concentration at the adsorbent surface (q_t), for a batch system can be calculated from Eq. (1). The adsorption kinetic model:

$$-\frac{dc_t}{dt} = k_a \left[c_t^2 + \left(-c_{init} + \frac{M}{V} q_m + \frac{1}{K_L}\right)c_t - \frac{c_{init}}{K_L} \right] \qquad (S-9)$$

can be obtained combining Eqs. (1), (S-7) and (S-8). It should be noted that K_L in this case is no longer defined by Eq. (S-6) and it is treated as an empirical parameter that correlates the Langmuir equilibrium constant. The analytic solutions of Eqs. (S-1)–(S-3), (S-5) and (S-9), can be found by integration with the appropriate initial conditions $c_t \in (c_{init}, c_t)$ and $t \in (0, t)$. After rearrangement, the obtained non-linear forms of the rate expressions are presented in Table S-II.

TABLE S-II. The utilized kinetic models; c_{1L} and c_{2L} are the roots of the quadratic Eq. (10). The calculated values were found to be as follows: for c_{init} = 250 mg B L^{-1}, c_{1L} = -210.73, c_{2L} = 223.96; for c_{init} = 500 mg B L^{-1}, c_{1L} = -202.62, c_{2L} = 465.85; for c_{init} = 1000 mg B L^{-1}, c_{1L} = −196.67, c_{2L} = 959.90

Kinetic model	Equation
1st order irreversible	$c_t = c_{init}e^{-kt}$
1st order reversible	$c_t = c_e + \left(c_{init} - c_e\right)e^{-k_1 c_{init} t(c_{init} - c_e)}$
2nd order irreversible	$c_t = \dfrac{c_{init}}{1 + kc_{init}t}$
2nd order reversible	$c_t = \dfrac{c_{init}c_e\left(1 + e^{zk_1 t}\right)}{c_{init}e^{zk_1 t} + 2c_e - c_{init}}$, $\quad z = 2\dfrac{c_{init}c_e}{c_{init} - c_e}$
Adsorption	$c_t = \dfrac{c_{2L}\left(c_{1L} - c_{init}\right) - c_{1L}\left(c_{2L} - c_{init}\right)e^{k_a(c_{1L} - c_{2L})t}}{\left(c_{init} - c_{2L}\right)e^{k_a(c_{1L} - c_{2L})t} - \left(c_{init} - c_{1L}\right)}$

The values of the kinetic rate constants (k, k_1 and k_a) were estimated by a non-linear least-squares regression analysis fitting kinetic equations to the measured concentration decay profiles. It should also be noted that each model contains only one adjustable parameter (k or k_1 or k_a). The other parameters associated with Eq. (10) are either known (c_{init}, M, and V) or have previously been determined from the Langmuir equilibrium model (q_m and K_L, Table S-I).

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