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Binding of transition metals by soluble and silica-bound branched poly(ethyleneimine) Part II: Binding kinetics in silica-bound BPEI

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Abstract

Metal-binding rates of a commercial adsorbent containing silica-supported branched poly(ethyleneimine) (BPEI) have been studied. Binding kinetics of H_2SO_4 and Cu, Ni and Zn sulfates have been measured by batch experiments at 25 °C and at high ionic strength. Competitive binding of a binary Cu–Ni system was also studied. The data were correlated with the non-ideal adsorption model (NICA) and a diffusion model of porous particles.

The adsorption kinetics of sulfuric acid in the adsorbent is controlled by pore and surface diffusion as well as by film mass transfer. The uptake rate of the metal ions depend both on the pore diffusion of the metal salt and the desorption rate of the displaced acid. The uptake curves measured with and without pH control can be well correlated with the diffusion model and with constant diffusion coefficients.

Keywords: Silica-supported branched poly(ethyleneimine); Sulfuric acid; Transition metals; Binding kinetics

1. Introduction

The equilibrium binding of sulfuric acid and transition metal sulfates in soluble and silica-supported branched poly(ethyleneimine) (BPEI) was investigated in Part I of this study [1]. BPEI is a basic polymer, which binds effectively strong acids and forms stable metal complexes via Lewis acid/base interactions. The BPEI–silica composite WP-1 was shown to retain the favorable binding properties of the soluble polymer and good selectivity could be attained in separation of binary metal mixtures. However, the technical potential of the material depends also on the binding rate and therefore the results of the kinetic measurements are reported in this part of the study. Beatty and co-workers [2,3] have compared the metal-binding rates of WP-1 and of a conventional chelating polymer resin. They have reported a relatively fast uptake of copper, but no detailed analysis of the data was given.

Binding kinetics of acids and transition metal cations in other complex-forming solid materials has been studied and modeled to some extent. Bhandari et al. [4,5] have investigated sorption of strong acids in conventional weak anion exchangers. In particular, they have measured the uptake rates of sulfuric acid and the results have been correlated with a model based on the Nernst–Planck formalism [5], which was originally applied to ion exchangers by Helfferich (Ref. [6] and the references therein). The same approach has been applied by Agrawal et al. [7] to heavy metal uptake in a chelating resin containing imido-diacetic acid (IDA) functionality. Mijangos et al. [8] have determined ion exchange rates and intraparticle concentration profiles of copper and cobalt in a macroporous IDA resin. The system was modeled by solving the differential mass balances of a porous particle. Under certain conditions the binding of acids or metal ions can be considered irreversible and the uptake kinetics can be approximated using the shrinking-core model [5,9]. Furthermore, simplified treatments based on the apparent rate laws have been adopted for chelating ion exchangers or adsorbents [10,11].

The objective of this part of the study was to investigate in detail the binding rates of sulfuric acid as well as copper, nickel

Abbreviations: BPEI, branched poly(ethyleneimine); NICA, non-ideal competitive adsorption model; WP-1, silica-supported BPEI adsorbent

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Nomenclature

c	concentration (mol/L)
D_p	pore diffusion coefficient (m^2/s)
D_s	surface diffusion coefficient (m^2/s)
F_a	fractional uptake (Eq. (4))
F_d	fractional desorption (Eq. (4))
h_i	empirical parameter (Eq. (5))
I_s	ionic strength of the supporting electrolyte (mol/L)
k_f	film mass transfer coefficient (m/s)
K	affinity constant (L/mol)
K_{assoc}	association constant (L/mol)
p	heterogeneity parameter (Eq. (5))
Q	bound amount per unit weight of BPEI contained in the adsorbent (mmol/g_{BPEI})
$\hat{Q}^*$	amount of amine groups in base-form WP-1 (mmol/g)
r	radial coordinate (m)
R	radius (m)
t	time (s)
T	temperature (°C)
V	volume (L)
w_{BPEI}	weight fraction of BPEI in the base-form adsorbent
x	dimensionless pore liquid concentration
y	dimensionless adsorbed amount
z	modified dimensionless concentration variable (Eq. (9))

Greek letters

ε_p	porosity
ϕ	dimensionless solution concentration
Γ	dimensionless parameter
Λ	dimensionless parameter
θ	coverage
ρ_s	density of the solid (kg/L)
τ	dimensionless time
ω_k	fraction of amine groups in population k
ζ	dimensionless radial coordinate

Subscripts and superscripts

a	stoichiometric acid concentration
ads	adsorbent phase
b	bulk solution
H	proton
i, j	component
init	initial value
k	population
liq	external liquid phase
Me	metal
s	salt or solid phase
tot	total amount
0	total concentration

and zinc sulfates in WP-1. For this purpose, batch experiments with and without pH control were carried out and the results were correlated by means of a diffusion model for porous particles. Because of the high ionic strength used in this study, the system was considered as neutral and a simplified treatment without coupling of the ionic fluxes was adopted. The equilibrium conditions were written by means of the non-ideal competitive adsorption (NICA) model reported by Kinniburgh et al. [12] and the pertinent parameters were taken from Part I [1].

2. Experimental

2.1. Reagents and materials

Silica-supported branched poly(ethyleneimine) (WP-1) was obtained from Purity Systems Inc. This composite adsorbent consists of a porous silica support and of a covalently bound BPEI layer. Due to the amine functionality, WP-1 is a weak anion exchanger but because binding of acids and metal cations proceeds via the lone electron pairs of the nitrogen atoms, it is considered here as an adsorbent. Electroneutrality thus requires that equivalent amount of cations and anions are adsorbed. The properties and pre-treatment of WP-1 are described in Part I of this paper [1]. The weight fraction of the polymer, w_{BPEI}, and the amount of the amine groups, $\hat{Q}^*$, in base-form WP-1 are 0.163 and 3.78 mmol/g. The intra-particle porosity, ε_p, is 0.46. The average particle diameter of the spherical particles is 224 μm with a standard deviation of 23 μm.

The solutions were prepared from reagent-grade metal salts ($CuSO_4{\cdot}5H_2O$, $NiSO_4{\cdot}6H_2O$, $ZnSO_4{\cdot}7H_2O$), sodium hydroxide, sulfuric acid and ammonium hydroxide. The supporting ionic strength, I_s, was 2 mol/L in all experiments and it was adjusted with reagent grade $Na_2SO_4{\cdot}10H_2O$. Deionized water was used to prepare all solutions.

2.2. Methods

All experiments were made in sulfate solutions and the ionic strength of Na_2SO_4 was kept at 2 mol/L. Therefore, dissociation of sulfuric acid in sodium sulfate solutions has to be taken account. As discussed in Part I [1] of this paper, a relationship between the proton concentration, c_H, and the stoichiometric acid concentration, c_a^0, can be established on the basis of literature data. At the conditions of the present experiments, this relationship reduces to the simple form of Eq. (1).

$$c_H = 0.44 c_a^0 \tag{1}$$

The proton concentration at a given pH was calculated from Eq. (2), which was obtained from the pH calibration data and from Eq. (1).

$$-\log(c_H) = \frac{\mathrm{pH} - 0.0777}{1.0433} \tag{2}$$

The incomplete dissociation of the metal sulfates was taken into account by means of Eq. (3). Here c_{Me} represents the concentration of the free metal cations and c_{Me}^0 and c_s^0 are the