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Equilibrium and column studies of iron exchange with strong acid cation resin

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ABSTRACT

The exchange of iron species from iron(III) chloride solutions with a strong acid cation resin has been investigated in relation to a variety of water and wastewater applications. A detailed equilibrium isotherm analysis was conducted wherein models such as Langmuir–Vageler, Competitive Langmuir, Freundlich, Temkin, Dubinin–Astakhov, Sips and Brouers–Sotolongo were applied to the experimental data. An important conclusion was that both the bottle-point method chosen and solution normality used to generate the ion exchange equilibrium isotherm influenced which sorption model fitted the isotherm profiles optimally. Invariably, the calculated value for the maximum loading of iron on strong acid cation resin was substantially higher than the value of 47.1 g/kg of resin which would occur if one Fe^{3+} ion exchanged for three "H^+" sites on the resin surface. Consequently, it was suggested that above pH 1, various iron complexes sorbed to the resin in a manner which required less than 3 sites per iron moiety. Column trials suggested that the iron loading was 86.6 g/kg of resin when 1342 mg/L Fe(III) ions in water were flowed at 31.7 BV/h. Regeneration with 5–10% HCl solutions reclaimed approximately 90% of exchange sites.

Introduction

Metal pollution of our water resources remains a major concern [1–3]. Several methods have been employed to remediate contaminated solutions including precipitation [4], coagulation–flocculation [5], adsorption [6–8], ion exchange [9,10], membrane filtration [11], flotation [12,13] and electrochemical means [14]. Physico-chemical techniques are attractive due to a variety of reasons such as process economics, reliability and ease of use [15]. Ion exchange is of particular interest as not only can the metals potentially be recovered but also the technology is well developed, simple and effective [16].

Iron is a common contaminant in natural waters [17], mining effluents [18], hydrometallurgical solutions [19] and a range of other industrial wastes [20]. Demineralization of water and wastewater solutions is widely practiced in industry, usually with a combination of cation and anion resins to remove the dissolved ions [21]. Kaya et al. [22] have shown that the presence of iron even at low concentration can significantly reduce the operating capacity of synthetic strong acid cation resins. Victor-Ortega

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Abbreviations: A, Temkin isotherm parameter (L/mmol or L/mg); a_s, Sips equilibrium isotherm coefficient; α, exponent which represents the inherent energy heterogeneity of the sorbent surface; AIC, Akaike information criterion; ARE, average relative error; b_T, Temkin constant related to the heat of adsorption (J/mol); BV, bed volumes; C_e, equilibrium concentration of iron ions in solution (mg/L); C_o, initial concentration of iron ions in solution (mg/L); ε, adsorption potential (J/mol); E, energy of adsorption (J/mol); eq, equivalents; EABS, sum of the absolute errors; HYBRID, hybrid fractional error function; K_{CL}, Competitive Langmuir equilibrium coefficient (L/mg); K_F, Freundlich equilibrium coefficient ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$ or $mmol^{1-1/n}\,L^{1/n}\,mol^{-1}$); K_{LV}, rate coefficient termed the "half value"; K_w, K_F/q_{max} where K_F is the Freundlich constant for low values of C_e ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$); m, mass of resin (g); MPSD, Marquardt's percent standard deviation; n_D, heterogeneity factor (dimensionless); n_F, Freundlich exponent (dimensionless); n_s, Sips isotherm exponent (dimensionless); N, total number of data points; N_p, number of variable parameters in the isotherm expression; q_e, equilibrium loading of ions on the resin (g/kg); $q_{e,calc}$, calculated equilibrium loading of ions on the resin (g/kg); $q_{e,meas}$, measured equilibrium loading of ions on the resin (g/kg); q_{max}, maximum (monolayer) loading of ions on the resin (g/kg); q_t, total loading capacity of ions on the resin (g/kg); R, universal gas constant (8.314 J/mol/K); T, temperature (K); V, volume of solution (L); SAC, strong acid cation; SNE, sum of normalized errors; SSE, sum of the squares of the errors.

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et al. [23] employed strong acid cation resin as a means to inhibit membrane fouling by dissolved species such as iron, with reported success. Lasanta et al. [24] investigated the ability of chelating ion exchange resins to remove Fe^{3+} species from wine, in order to improve the oxidative stability. Likewise, Benítez et al. [25] studied the exchange of iron and other dissolved metal ions from white wine using both chelating and acidic cation resins. In both the latter outlined cases, resins were demonstrated to be highly effective at removing the iron contaminant. Woodberry et al. [26] also confirmed the applicability of chelating resins to remove iron and other metal ions from meltwater emanating from an abandoned waste site in Antarctica. Riveros [27] compared the performance of a range of weak acid cation resins to remove Fe^{3+} ions from acidic sulphate solutions commonly encountered in the mining industry. A key finding was that macroporous resins were more effective than gel type materials due to increased rates of diffusion of the iron species. Solution pH was also reported to be important, since adjusting the solution pH to a constant value of 2.2 by addition of sodium bicarbonate produced a favourable equilibrium isotherm. In contrast, the unmodified experiment wherein the pH was lowered due to release of protons from the resin, resulted in an unfavourable exchange isotherm. In the column studies conducted by Rao et al. [28] solution pH was also discovered to be an influential factor controlling the removal of iron from solution with a chelating ion exchange resin. Approximately 30% less iron was loaded on the resin at pH 3 compared to pH 2. Flow rate has also been shown to impact the ability of strong acid cation resins to exchange dissolved iron species from solution. Marañón et al. [29] completed ion exchange column trials of simulated rinse water from a galvanizing process and concluded that increasing feed flow rate generally reduced the exchange capacity of the resin for iron and other metal ions such as Zn^{2+}.

Consideration of the published literature confirms the interest in the application of synthetic resins to remove dissolved iron from solution. However, as indicated by Agrawal et al. [20] there exists a relative lack of papers concerning the fundamental ion exchange process involved in the treatment of dilute iron solutions. Greater insight into the equilibrium and column behaviour of the latter ion exchange process would provide a better understanding of the practical application. Of particular relevance is the need to: identify the importance of the bottle-point method used; elucidate the influence of solution pH upon iron loading; relate equilibrium information to column breakthrough behaviour; and, determine the impact of regeneration conditions upon iron recovery percentages. This paper therefore examines the equilibrium and column performance of iron(III) species with a strong acid cation resin.

Material and methods

Resins

A strong acid cation resin was supplied in the proton exchanged form by Lanxess and termed S108H. A summary of the intrinsic physical properties of the resin is shown in Table 1. The resin was used as received in all experiments.

Table 1
Characteristics of ion exchange resin Lanxess S108H.

Item	Value	Units
Structural type	Gel	
Matrix	Styrene–divinylbenzene	
Functional group	Sulphonic acid	
Ionic form as shipped	H^+	
Stated minimum exchange capacity	2.0	eq/L
Moisture content	47–53	%
Shipping density	790	g/L
Mean bead size	0.65	mm
Operating pH	0–14	
Degree of reversible swelling	−10 (H^+ to Na^+)	vol%

Chemicals

Triply distilled water was used in all instances to prepare solutions for equilibrium and column testing. Iron(III) chloride hexahydrate was supplied by Sigma–Aldrich.

ICP-OES analysis

Solutions were analysed using a PerkinElmer Optima 8300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for integration times of 0.15 s with 10 replications. Samples were diluted to a concentration between 1 and 100 mg/L using a Hamilton auto-dilutor with 10 and 1 mL syringes. A certified standard from Australian Chemical Reagents (ACR) was diluted to form multi-level calibration curves. An external reference was used to monitor instrument drift and accuracy of the results.

Equilibrium studies

Inspection of the sorption literature revealed that three common bottle-point methods for creating equilibrium isotherms have been adopted. In the first variant, the solution concentration is kept at a constant value and the resin mass varied [30–32]. The second version employs a constant resin mass and a range of solutions of varying metal ion concentration [33,34]. Finally, the third version uses a solution comprised of a constant normality mixture of the two cations (or anions as the case may be) involved in the exchange process and a constant resin mass in each instance [35]. The methods used for each bottle-point experiment are outlined below.

Constant concentration bottle-point method

A set of 12 sealed Nalgene bottles were used to create a batch equilibrium study. Inside each canister was placed a varied mass of the S108H Lanxess strong acid cation resin. 200 mL of an aqueous solution comprising of 84 mg/L of iron was added to each of the 12 canisters and the values for initial pH and conductivity of the solution were recorded. Equilibration time was based upon previous kinetic studies and set to 2 h using a temperature controlled incubator (Innova 42R, New Brunswick Scientific). The solution temperature was maintained at 30 °C and the samples were shaken at 200 rpm to promote the ion exchange process. Following, equilibration again the values of pH and conductivity were recorded. From each 200 mL container a 50 mL liquid only sample was removed and stored in a smaller canister and kept for further analysis. This latter liquid sample was diluted with a 2.5–5% nitric acid solution for analysis using ICP-OES. Based upon the ICP-OES results the concentrations of the iron in solution were calculated. Each set of experiments was conducted twice for accuracy. Concentrations of iron ions remaining after the equilibration period C_e (mg/L) were measured and the equilibrium concentration in the resin phase q_e (mg/g) deduced from Eq. (1):

$$q_e = \frac{V}{m}(C_o - C_e) \quad (1)$$

Constant resin mass bottle-point method

A constant mass of resin, typically 0.1 or 0.2 g, was placed in each of the 12 Nalgene bottles and then solutions of varying concentration of iron(III) chloride were added. The equilibrium isotherm data were then generated using the approach described above for the constant concentration bottle-point method.