



Chelating adsorption with variable stoichiometry: Separation of nickel and zinc in concentrated sulfate solution



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HIGHLIGHTS

- A step-wise chelation model is proposed for metal uptake in chelating adsorbents.
- The model is tested for nickel adsorption from concentrated zinc sulfate solutions.
- The proposed model explains well the experimental batch and break-through data.
- Strong competition by zinc is explained by the variable nickel/ligand ratio.

ARTICLE INFO

Article history:

Received 22 September 2015
Received in revised form 4 November 2015
Accepted 5 November 2015
Available online 1 December 2015

Keywords:

Chelating adsorption
Step-wise complexation model
Nickel/zinc separation
Fixed-bed separation

ABSTRACT

A new approach is proposed for modeling of metal uptake data in chelating ion exchangers and adsorbents. In contrast to conventional equilibrium models assuming a constant stoichiometry for the surface complex, a step-wise reaction scheme is used in analogy with complex formation in bulk solution. The model is tested against equilibrium and dynamic uptake data, and the results are compared with those obtained using a conventional isotherm model. Nickel removal from $ZnSO_4$ solutions using a commercial chelating adsorbent is used as test case. According to the results, the observed decrease in nickel uptake with increasing zinc concentration can be explained much better using the proposed model than with conventional isotherm models. Model parameters estimated from single-metal equilibrium data predict the behavior of batch and fixed-bed systems up to zinc concentrations of 2.2 mol/L with Zn/Ni mole ratio of about 10^4 .

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1. Introduction

Solid materials containing chelate-forming functional groups are important in solid phase extraction (SPE) [1–3] as well as in industrial-scale separation of metals from aqueous process solutions [4–7]. Depending on the type of the functional group, metal uptake can be described as competitive ion exchange of the metal cations or adsorption of the metal salts. Irrespective of the mechanism, equilibrium uptake is treated in vast majority of studies with simple models like Langmuir and Freundlich isotherms. Moreover, only single-metal parameters are in many cases determined without adequate testing in multi-component systems. Although these isotherms can be extended also to multi-component and competitive systems, more advanced models are needed in cases involving strongly competing metal species. Non-ideal competitive adsorption (NICA) model [8] has been developed for geochemical

purposes but it has been also applied to metal sorption from concentrated metal processing streams [9,10]. Another approach widely used in geoscience is based on the concept of surface complexation (SC) [11]. Large number of different SC models exists and a variant for engineering purposes was developed by Höll and co-workers [12].

Understanding of the phenomena involved in industrially relevant metals separation processes is important for modeling and development of tools for process design. A major challenge in modeling of real process solutions is that the concentrations of the competing species usually vary in wide limits [13–15]. In our previous studies we have investigated removal of copper and nickel from concentrated $ZnSO_4$ solutions using a commercial chelating adsorbent functionalized with 2-(aminomethyl)pyridine (amp) [10,16–17]. In that system, feed concentrations of nickel and zinc are $2.2 \cdot 10^{-4}$ and 2.2 mol/L, which means that the Zn^{2+}/Ni^{2+} ratio is as high as 10^4 . We noticed that copper uptake from the $ZnSO_4$ matrix can be correlated well using conventional isotherm models but nickel behaved differently. Nickel uptake from the $ZnSO_4$

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