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Recovery of metal oxoanions from basic solutions using cooperative sorption – Separation of Na_2MoO_4 and NaOH

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HIGHLIGHTS

- Non-ionic microporous adsorbents are used to separate Na_2MoO_4 and NaOH.
- Attractive rather than repulsive interactions gives better separation.
- Non-ionic cellulose adsorbent has better selectivity than charged adsorbents.
- Cooperative sorption model explains well the static and dynamic data.

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ABSTRACT

Chromatographic separation of molybdate oxoanions and NaOH was studied using cooperative sorption as a method to recover both Mo and the base as concentrated solutions. Commercial non-ionic microporous adsorbents composed of hyper-crosslinked polystyrene and cross-linked cellulose were investigated at 22 and 60 °C. For comparison, some separation tests were made also with ion exchange resins. Separation was modeled using rigorous thermodynamic treatment and an explicit sorption model. Good separation in batch column was obtained with the non-ionic cellulose adsorbent, while the polystyrene adsorbent and the ion exchangers give only moderate fractionation. Typical cooperative behavior was found in both cases but the sorption mechanisms are different. In the polystyrene adsorbent, uptake of the electrolytes separately and as binary mixtures can be explained in terms of electrostatic and steric exclusion of the constituent ions and no attractive interactions appear to be present. On the contrary, no steric exclusion operates in the cellulose adsorbent and separation is based on attractive interactions between NaOH and the weakly acidic hydroxyl groups of the polysaccharide chains. At the conditions used in this study, separation was not affected by molybdate polymerization taking place at low NaOH concentrations.

1. Introduction

Hydrometallurgical processing of primary and secondary resources frequently involves steps, where the target metal is dissolved as oxoanions in strongly basic solutions. Typical examples of such anions include $Al(OH)_4^-$, $B(OH)_4^-$, $Ge(OH)_3O^-$, ReO_4^-, MoO_4^{2-} and WO_4^{2-}. In some cases the product can be directly precipitated from the solution but often neutralization is required. Acid precipitation of ammonium molybdates from NH_4OH or NaOH solutions is a typical example. Such solutions are produced in dissolution of roasting residues, in desorption of molybdate from ion exchangers or adsorbents and in the stripping step after solvent extraction [1,2]. Mo exists in basic solutions solely as tetrahedral MoO_4^{2-} anion but under neutral and acidic conditions, transition to octahedral geometry takes place. At the same time, tendency to form polymeric species like $Mo_7O_{24}^{6-}$ and $Mo_8O_{28}^{7-}$ increases [3]. Depending on the precipitation conditions, ammonium molybdates of different stoichiometry are finally obtained [2].

In this paper, we propose a simple method for efficient recovery of the base before precipitation with acid. This procedure allows recycling of the base to the dissolution step and leads to substantial decrease in acid consumption. The base is separated from the molybdate species using the co-operative sorption described in our earlier publication [4]. Steric exclusion of electrolytes in non-ionic microporous adsorbents

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Abbreviations: ARD, average relative deviation; BV, bed volume; CA16G, weak acid cation exchanger; CS24G, strong acid cation exchanger; GH-25, Cellufine GH-25 adsorbent; HCPS, hypercrosslinked polystyrene; MN-270, Hypersol Macronet MN-270 adsorbent

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Nomenclature

a	activity, –
b	interaction parameter in Eq. (9), –
c	molar concentration, mol/L
d_p	average particle diameter, m
D_p	pore diffusion coefficient, m^2/s
k_d	distribution coefficient, –
k_{pol}	rate constant for the MoO_4^{2-} polymerization reaction, mol/Ls
K_a	dissociation constant, –
K_F	Freundlich parameter, –
K_{pol}	equilibrium constant for the MoO_4^{2-} polymerization reaction, mol/L
K_{st}	steric distribution coefficient, –
K_w	ion product of water, –
H_b	bed height, m
L_{ion}	hydrated ion diameter, nm
L_p	average pore diameter, nm
m	molal concentration, mol/kg
n_F	Freundlich exponent, –
N	number of mixing stages, –
q	total uptake, mol/L
Q	adsorbed amount, mol/kg
R	gas constant, 8.314 J/(mol K)
t	time, s
T	temperature, K
u	interstitial velocity, m/s
V_m	partial molar volume, L/mol
x	axial coordinate, m
z	ion charge, –
α	adjustable parameter in Eq. (6), L/mol
ε_b	bed void fraction, –
ε_p	pore void fraction, –
γ	activity coefficient, –
ν	stoichiometric coefficient, –
π	swelling pressure, Pa
ρ_S	polymer content in swollen resin, kg/L

Subscripts and Superscripts

0	initial, pure component or infinite dilution value
feed	feed value
i, j, k	component
p	pore, pore solution
R	fixed charges
w	water

was originally proposed by Davankov and co-workers [5–7]. Conventionally, steric exclusion is applied only on substances that have large difference in their molar masses. With microporous adsorbents, however, separation of even simple electrolytes like HCl and NaCl becomes feasible. Separation stems from the tendency of the common anion to distribute evenly between the bulk liquid and the pore-filling liquid. Equivalent amount of cation is required and the smaller H^+ is preferred in the pore liquid, while Na^+ concentrates in the bulk solution [5,6]. This method was also applied to Na_2SO_4/NaOH separation that is similar to the case of this study and reasonably good separation was found using a microporous polystyrene resin [5]. In this paper, we show that qualitatively similar results are obtained in systems, where the cooperativity stems from attractive interactions rather than from exclusion. This finding opens up new possibilities for utilization of cooperativity as a separation method. It has been shown that cooperative sorption can be applied to very high solution concentration and/or adsorbent loadings [7] and no chemicals other than water are needed to run the process [8]. Moreover, dilution effects are small and in some cases, the components can be recovered at concentrations exceeding the feed values. These features are quite opposite to the practice of ion exchange that is conventionally used in electrolyte separations. Cooperative sorption is not feasible in treatment of dilute solutions and conventional adsorption or ion exchange are more amenable for removal of trace amounts of oxoanions [9,10].

In this study, separation of Na_2MoO_4/NaOH mixtures is studied experimentally and by model calculations using two different microporous non-ionic adsorbents. We have previously used hyper-cross-linked polystyrene and densely crosslinked dextran gel in separation of strong and weak electrolyte pairs [4]. Good results were obtained with the polysaccharide resin and, therefore, a novel cellulose-based material (GH-25) was selected for this study because of its superior stability under basic conditions. The experimental data measured at 22 and 60 °C are correlated using the generalized Donnan model described previously [4]. For GH-25, dissociation of very weakly acidic hydroxyl groups in polysaccharide chains is included in the model to explain the high NaOH affinity. Dissociation of cellulose is well-known and it is used in synthesis of cellulose derivatives [11] but to the best of our knowledge, this property has not been utilized in separation technology. Some separation tests are also made using conventional cation exchangers as the adsorbent. Moreover, influence of molybdate polymerization on the separation efficiency is investigated, because formation of larger species is advantageous in separation based on molecular size.

2. Experimental

2.1. Materials

Macronet MN-270 is a microporous adsorbent composed of hyper-crosslinked polystyrene and it was obtained from Purolite Inc. Porous Cellufine GH-25 resin composed of densely crosslinked cellulose was supplied by JNC Corp. Both resins are considered as rigid materials containing permanent micropores and the properties are listed in Table 1. Some separation tests were also made using weak and strong cation exchange resins CA16G and CS24G obtained from Finex Oy. CA16G is an acrylic resin containing carboxylic groups and CS24G is sulfonated polystyrene resin. Both are densely crosslinked gel-type resins with no permanent porosity and they were used in Na form.

Standard reagent grade chemicals (Na_2MoO_4, NaOH, NaCl, HCl) were used and the electrolyte solutions were prepared in purified water (> 0.1 μS/cm).

2.2. Methods

Water content was measured by drying the adsorbent samples after equilibrating with water and centrifugating for 15 min at 3000 min^{-1}.

Table 1
Properties of the water-swollen adsorbents. n.a. = not available.

	MN-270	GH-25
Average particle size d_p, mm	0.7	0.1
Pore size L_p, nm	2–3	n.a.
Particle porosity ε_p, –	0.59[a]	0.61[a]
Density ρ_S, kg/L[b]	0.47	0.52
Water content, kg/kg	0.46	0.56

[a] Calculated from the D_2O or methanol retention data.
[b] Polymer content in the swollen resin. Estimated from the water sorption data.