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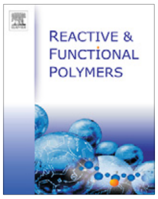

Controlled partial neutralization of amphoteric ion exchange resin for improved metals separation

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ABSTRACT

Controlled partial neutralization of an amphoteric aminomethylphosphonium functional ion exchange resin (Lewatit TP-260) was investigated. The particular goal of controlled neutralization was to replace H^+ in the acidic phosphonium groups with Na^+ ions but leave the basic amino groups protonated. In this manner, metals' sorption is enhanced and undesired pH changes during the metal separation process are avoided. The conjugate bases of organic weak acids (sodium formiate, sodium acetate and sodium citrate), sodium phosphate and NaOH were studied as neutralizing agents. The organic acid salts and sodium phosphate were all found to be suitable. Lengthening the neutralization cycle and using more concentrated neutralization agents were found to yield higher extents of neutralization and more uniform profiles along a resin bed. Concentrated NaOH also neutralized the amine group from the resin. With dilute NaOH, desired extent of neutralization was not achieved within a reasonable time. The effect of partial neutralization on metal sorption was tested with dynamic single column experiments. 5.5 BV of Ag–NaCl solution could be purified from Ca, Mg, Pb and Zn when the resin was partially neutralized with 2.0 M NaAc. With the acid form resin, the impurity metals broke through at 1.0 BV.

1. Introduction

Chelating ion exchangers are known to be effective adsorbents for base metals and heavy metals in the form of divalent cations [1,2]. Consequently, they have potential for purification of hydrometallurgical solutions of many rare and valuable metals, which are often in form of complexes, oxoanions, monovalent cations, etc.

When working with solutions having pH near the neutral range and with ion exchangers that have functional groups with both acid and base properties, it is important to modify the functional groups to the desired form before the actual adsorption stage. This step is required because functional groups may bind or release H^+ ions and cause pH changes in the column. Such changes may lead to decreased metal sorption, if the pH decreases, or precipitation problems, if it increases.

A usual pretreatment or regeneration of amphoteric resins is to totally convert the resin either into acid or base form by using a concentrated acid or base. An iminodiacetate resin, for example, is usually regenerated with concentrated acid to remove bound metals. Maximal dynamic metal binding capacity is obtained by subsequently neutralizing the resin with a strong base. The drawback is that the amine group becomes converted to the free base form and will capture H^+ ions from the solution to be purified, increasing its pH and causing a risk of precipitation. A method is needed to neutralize in a controlled manner only the carboxylic groups while leaving the amine group protonated.

Although weak acids or bases have been used in regeneration instead of strong acids and bases, controlled partial neutralization of ion exchange resins has not been studied systematically in the available literature. For example, CO_2 regeneration has been proposed for weak acid resins by Kiehling and Hoell [3], Kunin and Vasillou [4] and Larsen [5], and the resulting HCO_3^- solutions were used for regenerating weak base resins. Greenleaf and Sengupta [6] have used CO_2 (in rainwater or snowmelt) regeneration for ion exchange fibers with weak acid functionality as a part of a water softening process. Bayard and Bayard [7] describe a procedure for preparing a packed bed of an iminodiacetic acid resin where part of the resin particles are completely in acid form and part in half neutralized form. 20% Of the resin volume is moved into a separate column where it is treated with 2 N HCl followed by water elution to pH 4.5. This fraction is then mixed with particles that have previously been converted to monosodium iminodiacetate form (most probably by titration). Such a complicated procedure is hardly suitable for high throughput industrial processes.

A different approach to eliminate pH variations was employed by Trochimczuk and Streat [8,9], who used an acetate buffer in the feed when studying adsorption of metals into chelating resins that were used in H^+ form. This method introduces an additional chemical to the target metal solution, which may be undesirable.

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Moreover, sorption of metals by the resin is greatly reduced if they form complexes with the organic acids in the solution phase.

Citrate, tartrate and complexing agents in general (e.g. EDTA) have been used to improve stripping of metals from ion exchange resins. They also have a strong tendency to capture species that they have affinity to associate with, such as H^+ ions, from resins [10].

If partial neutralization is needed in a dynamic column operation, it is important to have as even a neutralization profile along the column as possible to ensure good performance. For example, if a stoichiometric amount of a strong acid or a strong base is used for partial neutralization of a bed, the extent of neutralization averaged over the column length may be appropriate, but there may be a steep gradient in the concentration of protonated functional groups near the column inlet.

The purpose of this work was to find suitable chemicals and conditions for controlled partial neutralization of an amphoteric aminomethylphosphonium resin in order to prevent precipitations while maintaining good removal capacity for impurity metals in dynamic column operation. The conjugate bases of organic weak acids (sodium formiate NaFo, sodium acetate NaAc, and sodium citrate Na_3Ci), sodium phosphate (Na_2HPO_3) and NaOH were studied as neutralizing agents. The influence of partial neutralization on metals' sorption was tested in a single column for purification of Ag(I) from divalent impurity metals in concentrated chloride medium. Process performance was evaluated based on the volume of purified AgCl solution obtained before the breakthrough of the impurity metals. Only a single flow rate was used and the influence of extent of neutralization on mass transfer rates was thus not investigated in detail.

2. Experimental

2.1. Materials

All the chemicals used were of analytical grade, except NaCl, which was of technical grade. The chemicals were supplied by VWR Prolabo (NaCl, AgCl, citric acid H_3Ci), Alfa Aesar ($PbCl_2$), Merck ($ZnCl_2$, acetic acid HAc, HCl, formic acid HFo, NaOH), Riedel de Haën ($MgCl_2{\cdot}6H_2O$, Na_2HPO_4) and J.T. Baker ($CaCl_2{\cdot}2H_20$).

Lewatit TP-260 (supplied by Lanxess) is a macroporous aminomethylphosphonic acid functional resin that has a crosslinked polystyrene divinylbenzene matrix (Fig. 1) [11]. Physical properties given by manufacturer [11] of the resin are following: total capacity 2.3 eq/L, particle size 0.4–1.25 mm (>90%), water retention 58–62%, volume change from Na^+ to H^+ form max 25%. The density of the resin was determined as 1.19 g/mL in 4.8 M NaCl in this work. Before the experiments the resin was subjected to two four-stage pretreatment cycles where 10–20 bed volumes of 1 M NaOH, water, 1 M HCl, and water were passed through a resin bed.

2.2. Titration of resin

Titrations of the Lewatit TP-260 resin with and without NaCl background were done batchwise in test tubes. Wet free base form resin, 0.5 M NaOH, 1 M HCl and purified water were weighed into the test tube. The total liquid volume was 10 mL. Test tubes were shaken for 2 days at 50 °C and solution pH was measured after separation of the phases. Calibration curves were constructed to both acidic and base side to convert the pH readings to H^+ and OH^- concentrations.

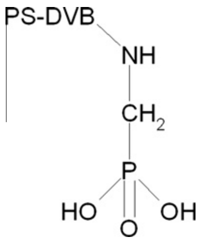

Fig. 1. Chemical structure of the aminomethylphosphonic acid functional group of Lewatit TP-260.

Table 1
Experimental procedure for studying the neutralization profiles in the resin bed after controlled partial neutralization.

Step description	Feed solution	Duration (min)	Flow rate (mL/min)
Conversion to acid form	2.0 M HCl + 2.0 M NaCl	30	6
Washing	4.8 M NaCl, pH 6.5	5	10
Partial neutralization			
Run 1	4.8 M NaCl, pH 6.5	10	5
Run 2	0.001 M NaOH + 4.8 M NaCl, pH 9.2	10	5
Run 3	1.5 M NaOH + 3.0 M NaCl	10	5
Run 4	0.2 M NaAc + 4.5 M NaCl, pH 7.1	10	10
Run 5	0.2 M NaFo + 4.5 M NaCl, pH 8.8	10	10
Run 6	0.2 M Na_2HPO_4 + 4.5 M NaCl, pH 7.9	10	10
Run 7	0.5 M NaAc + 4.5 M NaCl, pH 6.1	10	10
Run 8	0.5 M NaFo + 4.5 M NaCl, pH 9.0	10	10
Run 9	0.5 M Na_3Ci + 4.5 M NaCl, pH 8.7	10	10
Run 10	2.0 M NaAc + 2.8 M NaCl, pH 9.0	10	10
Run 11	0.2 M NaAc + 4.5 M NaCl, pH 8.9	20	10
Run 12	0.2 M NaFo + 4.5 M NaCl, pH 8.6	20	10
Run 13	2.0 M NaAc + 4.5 M NaCl, pH 9.0	20	10
Washing	4.8 M NaCl	5	10
Rinse	Deionized water	15	4

2.3. Neutralization and separation experiments

Neutralization of the resin and removal of divalent impurity metals from an Ag(I) solution were investigated in laboratory scale columns. The experiments were done at 50 °C in 15 mm diameter columns (Kronlab ECO15/120M3K-K) with a 24.0–27.6 mL resin bed. All feed solutions were placed on scales to monitor flow rates. Air was removed from the solutions with a vacuum pump before experiments and the solutions were passed through a degassing unit (Phenomenex Degassex DG-4400) before the column to remove traces of dissolved gases.

Partial neutralization of the resin was carried out in five consecutive steps as described in Table 1. The procedure was otherwise identical in all runs but the neutralization solution in step 3 was varied. A high salt concentration was used in all steps to maintain the ionic strength, and thus the extent of resin swelling, at approximately the same level as in the Ag solution to be purified. After the final rinse with H_2O, the resin bed was divided into five or six sections of approximately equal height that were removed from the column and titrated with NaOH to determine the H^+ content. The H^+ content was then compared to the H^+ content of completely protonated resin to calculate the extent of neutralization.

The influence of partial neutralization on the purification of divalent impurity metals from an AgCl solution was investigated by determining breakthrough curves. Details of the procedure are given in Table 2. Metal analyses of aqueous samples from the