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Mutual Separation of (W, As, Mo, V, Ge, B) Oxoanions from Bi-metallic Solution by Resin having Methyl-Amino-Glucitol Moiety

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Abstract: The mutual separation of (W, As, Mo, V, Ge, B)-oxoanions using resin having methyl-amino-glucitol polymeric moiety from bimetallic solution was investigated by means of dynamic column experiments. The effect of solution pH on the separation efficiency and on the co-removal level of metallic impurities was followed in this study. The conditions for efficient desorption of metals were determined in order to get the highly concentrated, impurities free solution suitable for recovery and reuse of separated metal. Effective separation of molybdenum and vanadium from boron or germanium and tungsten from arsenic was achieved.

Keywords: Separation, molybdenum, boron, vanadium, germanium, tungsten, arsenic

INTRODUCTION

Oxoanions of metals from the group (W, As, V, Mo, Ge, and B) can be frequently found as contaminant species in various water streams having high excess of accompanying anions (mainly chlorides and sulfates).

The mutual separation of metals is becoming very attractive, because it enables the recovery of pure metals from contaminated water and their

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[†] This study was originated by late Prof. Zdeněk Matějka who passed away in the midst of the work on October 2nd 2006.

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reuse. It is important to know that the co-removal of unwanted metals will be very low in order to get the very high purity of separated metals which will make their efficient reuse easier.

The mutual separation of some metal-oxoanions from other metals in liquid waste streams was already studied previously applying such processes as precipitation, solvent extraction (1), ion flotation (2) and standard ion exchange. However, no reliable results have appeared in the literature yet, suggesting, that none of these techniques exhibited selectivity high enough to achieve the efficient mutual separation of metals from the group W, As, Mo, V, Ge, and B.

Especially, the separation of W from As–impurity was investigated thoroughly by Matis using ion flotation (2). The As co-removal level by this technique was found in the range of 10–20%. Separation of tungstate from arsenate (or arsenite) is very important from the industrial point of view because of wide applications of W in the manufacture of steel alloys, catalysts, pigments, dyestuffs, and electronic parts (3) where the presence of As compounds deteriorates the quality of products. The goal of separation in this case is to recover the valuable tungstate anions in a pure As-free form.

Selective separation, i.e. separation efficiency and co-removal level, of molybdate from arsenate was also studied (4) and was found similar to the case of W-As separation.

The high co-removal of metal-impurities—in the level of 15–20%—was always found, resulting in poor selectivity and economic impracticability of these above-mentioned processes.

In this paper, the mutual separation of metal-oxoanions has been investigated using a commercially available polymeric resin having methyl-amino-glucitol moiety. This resin has been developed (5) for selective and efficient sorption of borate anions from solutions rich in chloride and sulfate. It is known (6–9), that metal-oxoanions form the coordination complexes with organic molecules containing OH-groups (mainly variable saccharides). The complex formation ability and reaction kinetics depend on the suitable steric configuration of OH-groups within the saccharide molecule. Usually it is required, that at least two OH-groups will be located at neighboring C-atoms. However, complexation of boron with 1,3-dioles was also described (10, 11). The stability of these complexes, which is responsible also for mutual separation efficiency, depends also strongly on pH values. The optimum pH ranges for the complex formation of various metals with methyl-amino-glucitol resin are available in literature (6–9, 12, 13) (Table 1).

This methyl-amino-glucitol resin was also tested for the sorption of other metal-oxoanions than borate (12–17), but mainly from alkaline solutions and without any emphasis to achieve the quantitative removal of one metal from bi-metallic solution, which is of vital importance for mutual separation of metals.

In our previous laboratory experiments it was pointed out (11) that the kinetics of complex formation of metal-oxoanions with methyl-amino-glucitol resin is fast enough to achieve the quantitative sorption of metals from solution at proper pH by dynamic column experiment. Leakage of metals

Table 1. Optimum pH-range for diol-complexes of oxoanions

Metal	pH-range
V	2–7
W	1–6
Mo	1–6
Ge	6–12
B	7–11
As (V)	1–6
As (III)	9–12

during the sorption run is constantly below 0.1 $\mathrm{mg \cdot L^{-1}}$. The only exception is arsenic, where coordination complex with methyl-amino-glucitol moiety and other saccharides, as well, is very weak, the kinetics of complex formation is very slow and, consequently, the breakthrough capacity is very small and the leakage of As is very high at any pH values.

The mutual separation of metal-oxoanions using methyl-amino-glucitol resin is based on very high pH-sensitivity to form stable coordination complexes of particular metal-oxoanions with OH-groups of saccharide molecules. From the data in Table 1 it follows, that for instance Mo will not form the coordination complex in alkaline solution, while Ge is able to form a complex in this alkaline environment. It means, that Mo will not be taken up from the alkaline solution by methyl-amino-glucitol resin, while Ge will be removed from this solution.

In order to achieve the efficient mutual separation of metals it is required to apply a suitable pH value where one metal only will be removed from solution quantitatively, while the other one will pass into the effluent. The quantitative sorption of metals calls for application of dynamic column sorption.

The goal of this study is to investigate the effect of pH on metal removal efficiency and, hence, the mutual separation of metals from bi-metallic solution by methyl-amino-glucitol resin.

EXPERIMENTAL

This work was concerned with separation of oxoanions by methyl-amino-glucitol resin Purolite D 4123 (Purolite Int., UK) having total N-capacity 1.2 $\mathrm{mol \cdot L^{-1}}$ (Fig. 1).

All presented results were obtained by dynamic column experiments that were carried out using synthetic metal solution containing 5 $\mathrm{mg \cdot L^{-1}}$ of metal ions and 500 $\mathrm{mg \cdot L^{-1}}$ of accompanying anions (chlorides and sulfates). The specific flow rate of solution was $s = 6\ \mathrm{BV \cdot h^{-1}}$. Column inner diameter was 12 mm, bed volume was 30 mL and bed height was 26.5 mm.

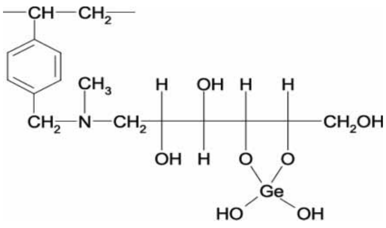

Figure 1. Structure of Ge-complex with methyl-amino-glucitol resin (Purolite D 4123).

Concentrations of metals were analyzed by ICP-OES technique (Perkin Elmer Optima 2000).

RESULTS AND DISCUSSION

Metal Separation in Acidic Solution using Resin in the Protonated Form

The Separation of W from As

W-As separation using resin having methyl-amino-glucitol moiety in the protonated form (Purolite D 4123) is demonstrated on Fig. 2. The pH value of loading solution is 7.0. As the solution passes through the bed of protonated sorbent, the pH value drops to the level of 4.5 as a consequence of hydrolysis of functional moiety in the protonated form. This pH is suitable for rather fast W-complex formation (6, 10) with

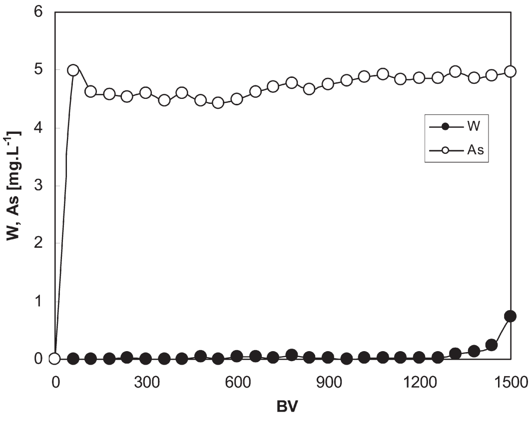

Figure 2. W-As separation by protonated form of Purolite D 4123 (solution pH 7).

glucitol moiety and, hence, for the quantitative removal of W from solution. Leakage of W is constantly less than 0.1 mg · L^{-1}. Arsenate does not form under this condition a stable complex with functional moiety of the resin (7) and therefore it is not sorbed from solution at all. The concentration of As in the effluent is almost equal to that of the load solution during the whole sorption run. The sorption run was terminated at 1300 BV of treated solution, when breakthrough of W into the effluent has appeared.

Desorption of tungstate was carried out using 10 BV of 1 M-NaOH solution. The concentration of W and As in the spent regenerant solution was 2600 mg · L^{-1} and 7.3 mg · L^{-1}, respectively. The concentration ratio of As/W in the spent regenerant solution is only 0.28%, while the same ratio in the loading waste water was 25% (W−20 mg · L^{-1}; As −4.9 mg · L^{-1}).

The arsenic co-removal level (in%) is defined as the total amount of As in the whole spent regenerant solution (7.3 mg · L^{-1} × 10 BV = 73 mg As) divided by total amount of As passed through the resin bed during the sorption run (4.9 mg · L^{-1} × 1300 BV = 6370 mg As), which equals to 1.15%. Both these values show, that W of high purity is recovered and that mutual separation of W from As by selective methyl-amino-glucitol resin in the protonated form is more efficient than the above-mentioned methods (As co-removal level by two-stage ion flotation (2) is, for instance, around 17%).

The W-As separation efficiency of standard weak base anion exchanger (Lewatit MP 62) is also very poor (Fig. 3). W was removed quantitatively, but about 20−25% of As was constantly co-removed from solution, which means that a high level of impurity would be found in the recovered W.

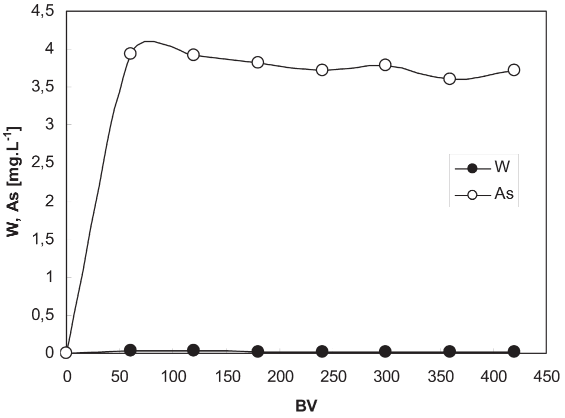

Figure 3. W-As separation by protonated weak base dimethyl-amine anion exchanger Lewatit MP-62.

The reason for the low separation efficiency of this resin is the fact, that complexes with oxoanions, responsible for separation, are not formed at all on this kind of anion exchanger.

Based on the results, received with selective methyl-amino-glucitol polymeric resin in the protonated form, it can be concluded, that also the separation of molybdates from arsenates, described in the literature as rather complicated (4), can be carried out efficiently by methyl-amino-glucitol polymeric sorbent in the protonated form.

Metal Separation in Alkaline Solution using Resin in the Free Base Form

Mutual Separation V-Mo or W-Mo

Mutual separation can be achieved in neutral or slightly alkaline solution (pH 7.0–8.0) using methyl-amino-glucitol resin in the free base form only. Under these conditions, V and/or W are removed from solution while Mo was not sorbed (Fig. 4). Desorption of vanadate or tungstate is carried out by 1 M HCl solution. The spent regenerant solution is Mo-free and contains high concentration of V or W.

In the medium acidic bimetallic solution (pH < 4.5) all these metals (V, W, Mo) are quantitatively removed from the solution with leakage level $<0.01\ \mathrm{mg \cdot L^{-1}}$ by a protonated form of methyl-amino-glucitol resin (Fig. 5). Under these conditions, the simultaneous sorption of both metals from bi-metallic solution is achieved, i.e. Mo and V or W, but no separation is taking place. Desorption of sorbed metals can be carried out by 1 M-NaOH solution.

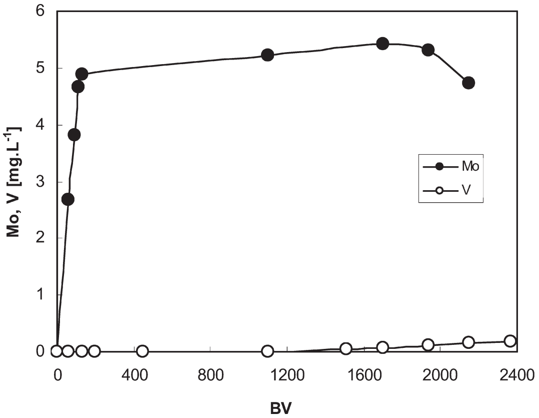

Figure 4. V-Mo separation by free-base form Purolite D 4123 (solution pH 7).

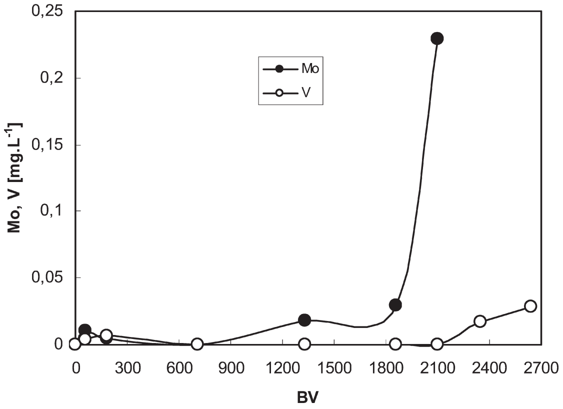

Figure 5. Simultaneous sorption of (Mo, V) from bimetallic solution by protonated form of Purolite D 4123 (solution pH < 4.5).

It was found, however, that at still lower solution pH 2.0 some kind of metal separation was observed (15): Mo is taken up by this resin in the protonated form while V fully remains in the solution. The reason for this change in V sorption behavior is the conversion of vanadate anion V(V) to the cationic form of VO^{2+} at very low pH (18). This VO^{2+} species is no more able to form complex with OH-groups in functional moiety of resin.

Tungstate and vanadate oxoanions exhibited almost identical ability to form complexes with saccharides and therefore their efficient separation using methyl-amino-glucitol resin was not achieved.

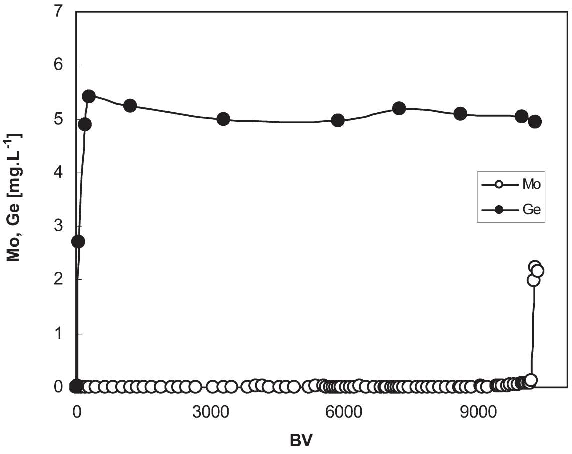

Figure 6. Mo-Ge separation by protonated form of Purolite D 4123 (solution pH 3.5).

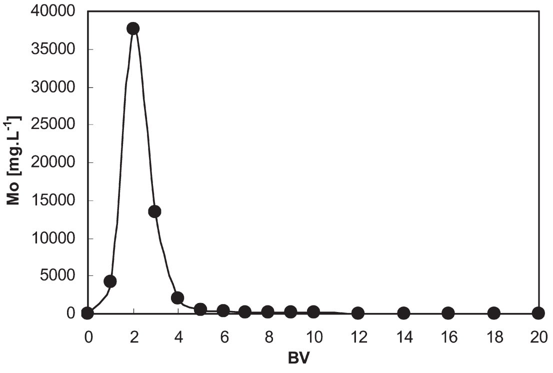

Figure 7. Mo-desorption from Purolite D 4123 by 1 M NaOH solution.

The Separation of Metals (Mo, V, W) from Ge and B in the Bi-Metallic Solution

For the separation of metals in this system the methyl-amino-glucitol resin in the protonated form, and in the free base form, as well, is efficient.

All metals from this group are able to form the coordination complexes with methyl-amino-glucitol moiety of resin, but the stability of particular complexes is highly pH sensitive. Consequently, the proper solution pH is required to achieve the quantitative sorption of one metal only (while the other one has to pass into the effluent), which will guarantee the efficient mutual separation of metals in the bi-metallic solution.

It is known (10), that Mo, V, and W prefer acidic pH for complex formation, while Ge and B require the alkaline pH:

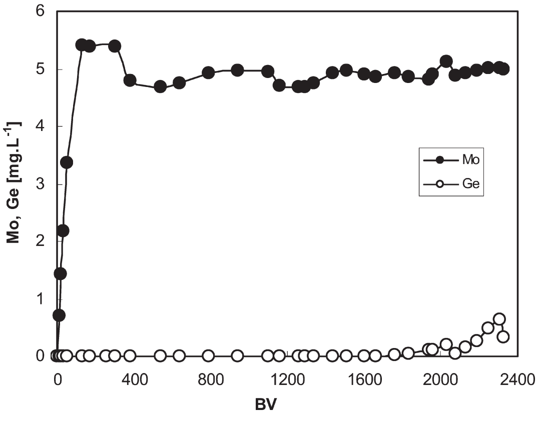

Figure 8. Ge-Mo separation by free-base form of Purolite D 4123 (solution pH 8).

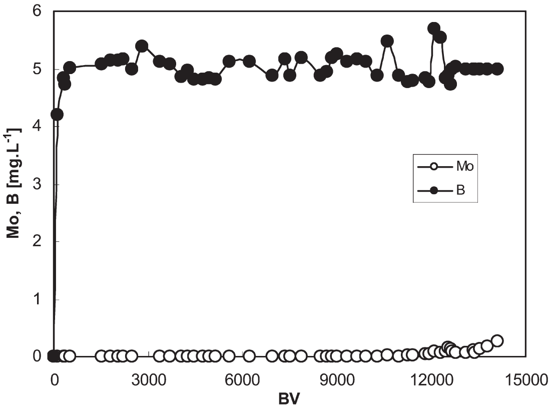

Figure 9. Mo-B separation by protonated form of Purolite D 4123 (solution pH 3.5).

a. at low pH 3.5 Mo, V and W are removed from solution quantitatively and with a high breakthrough capacity by resin in the protonated form while Ge fully passes into the effluent with Ge co-removal level of 0% (Fig. 6). Desorption of Mo and V from the resin by 1 M-NaOH solution is very efficient (Fig. 7) producing concentrated Mo-solution which is free of Ge.
b. at alkaline pH 8.0 (and higher) Ge only is removed from solution by resin in the free base form and Mo co-removal level is close to 0% (Fig. 8). Desorption of Ge from the resin is carried out by 1 M-HCl solution.

In the case of Mo-B separation, Mo is removed from solution by the protonated form of resin at pH 3.5 and B fully passes into the effluent (Fig. 9). Resin in the free base form at pH 9 is effective for B removal while Mo fully passes into the effluent (Fig. 10).

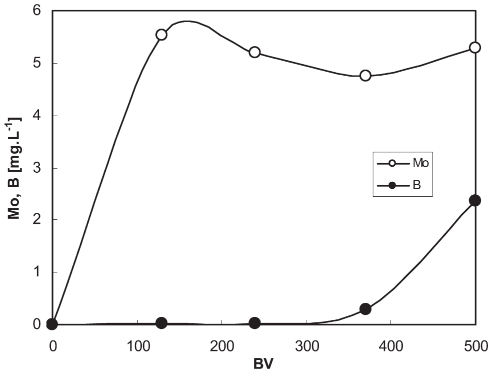

Figure 10. B-Mo separation by free base form of Purolite D 4123 (solution pH 9).

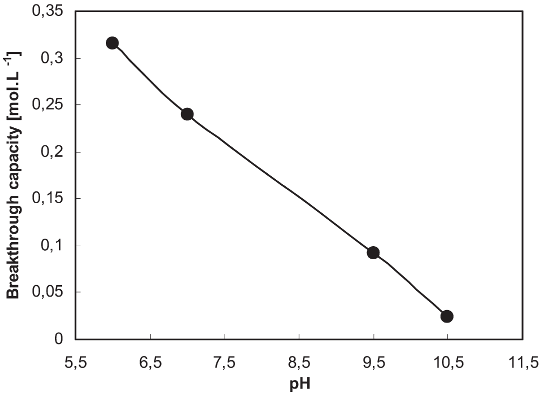

Figure 11. Effect of pH on V-breakthrough capacity (limit concentration 0.1 mg · L^{-1}).

It is true, that V and W−oxoanions are also taken up by the free base form of methyl-amino-glucitol resin, but only from neutral or slightly alkaline solution (pH 7–8). Therefore, the efficient separation of vanadate and tungstate from germanate in this pH range can not be achieved (contrary to the efficient separation of Mo-Ge).

The stability of V (and W) complexes with methyl-amino-glucitol moiety, and, hence, also the breakthrough sorption capacity, decreases with increasing pH (Fig. 11). Consequently, the efficient separation of vanadate-germanate requires the high pH of 10.5 where V is already not taken up and Ge is still exhibiting a fairly high sorption efficiency with acceptable breakthrough capacity (Fig. 12). Ge is displaced from saturated resin by HCl-solution (Fig. 13).

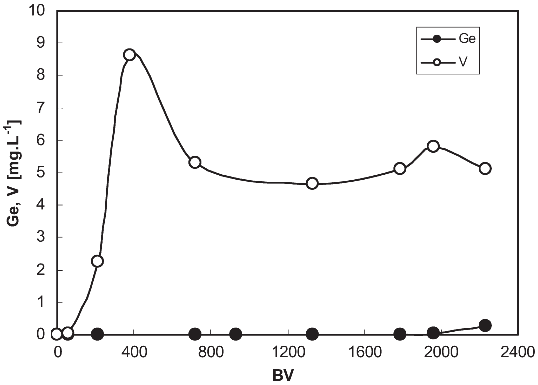

Figure 12. Ge-V separation by free-base form of Purolite D 4123 (solution pH 10.5).

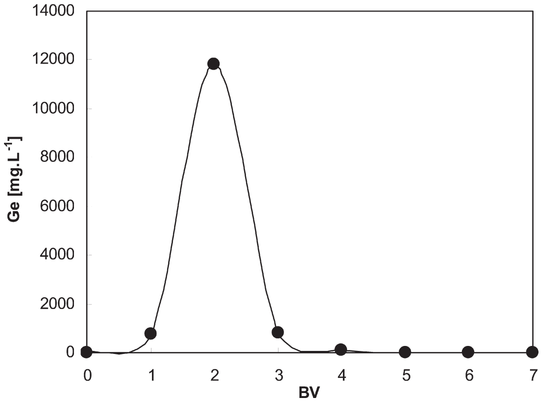

Figure 13. Ge-desorption from Purolite D 4123 by 1 M HCl solution.

CONCLUSIONS

Mutual separation of metal-oxoanions is becoming more attractive, because it is a method enabling recovery of pure valuable metals from multi-metallic waste water for reuse.

The mutual separation of (W, As, Mo, V, Ge, and B)-oxoanions using resin having methyl-amino-glucitol moiety is based on very high pH sensitivity of complex formation between OH groups of glucitol moiety of resin and particular metal-oxoanion. Bi-metallic solutions were used and a proper pH of loading solution enabled that one metal passed fully through the column into effluent while the other metal was quantitatively taken up by selective resin and subsequently was desorbed (by NaOH or HCl solution), concentrated into the spent regenerant solution and thus recovered in a very pure state. Very efficient separation of both metals was thus achieved.

Three groups of experiments were carried out and the following results were found:

a. metal separation using protonated form of resin and solution pH 4.5–7.0. It was found that this experimental condition is suitable for mutual separation of W from As. Tungsten only was removed from solution and recovered in concentrated, As-free spent regenerant solution. Arsenic was not taken up and passed into the effluent. No separation of tungstate from arsenic was achieved using free base form of this selective resin.
b. metal separation using free base form of resin with solution pH 7–8 (but not higher !) is suitable for separation in the system (V, W)–Mo. Molybdate requires the acidic pH for complex formation and therefore remains completely in the solution. Vanadate and tungstate were sorbed

by methyl-amino-glucitol moiety of resin, efficiently separated from molybdate and concentrated in a regenerant effluent solution. During the operation of this sorbent in protonated form, i.e. at pH approx. 4.5 means, all metals from the system (V, W)-Mo were removed from solution, so that simultaneous sorption but not mutual separation is achieved.

c. for the separation of Ge and B from (Mo, V, W) oxoanions both forms of methyl-amino-glucitol moiety of resin can be successfully applied.

Protonated form will keep the solution pH around the value of 4.0 which is suitable for sorption of (Mo, V, W)-oxoanions, while Ge and B passes into effluent and is thus separated.

Free base form at solution pH around 10.5 (but not less !), will take up Ge-oxoanion only (pH 9 is suitable to take up B), and all three other metals (Mo, V, W) will remain in solution and are separated, because their complexes with saccharides can not be formed in a such highly alkaline environment.

Desorption of Metals

It was found, that all metal-oxoanions, investigated in this study, can be efficiently displaced from methyl-amino-glucitol moiety of resin by NaOH or HCl solution, concentrated in regenerant effluent and recovered as very pure metals for reuse.

ACKNOWLEDGMENTS

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