Masters Degree in Chemical Engineering

Combination of electrochemical and ion-exchange methods in metal separation

Masters Degree Thesis

Foreign Institution Development Project

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July 2009

Acknowledgement

To all that helped me during the elaboration of this project:

I would like to thank to my family, without them nothing would have been possible,

Mom, thank you for always support me in every sense of the word, thank you for all the love and care that you always knew how to demonstrate.

Dad, thank you for always believe in me, and for encouraging me that every time I thought I could was not capable enough.

I would like to thank the people that worked directly with me in this project,

Eng. Luděk Jelínek, thank you for sharing your vast knowledge in the matters of this work.

Eng. Jana Ďurišová, thank you for your availability and patience, without your help this project could not be concluded.

I would also like to thank my friends for their support,

Thank you Helena, for all the care, all the strength, all the help, for everything, I will never be fare enough putting in words how important you were during this experience.

Thanks to the rest of you, for always being present although the physical distance, for always giving me the strength when I needed it, for always believing in me, with you I could also not do it.

Thank you my Erasmus companions, for all the support and the happy moments that we lived together and for making this experience so unforgettable.

Abstract

Vanadium and Molybdenum can be found together in several industrial effluents and wastewater. It is economically and environmentally important to remove them from aqueous solutions and to separate them for further use.

Due to various mutual chemical properties it is relatively difficult to separate vanadium and molybdenum in aqueous solutions.

The main objective of this project is the selective separation of molybdenum from vanadium using a combination of electrochemical and ion exchange methods.

The electrochemical reduction of these compounds was tried and Mo and V were successfully reduced using a potential of -1.5 V vs. Ag/AgCl reference electrode.

The sorption of Mo aqueous solutions was studied in two different ion exchange resins, a chelating resin, *Purolite D4123,* and a strongly acid cation exchanger, *Lewatit S100,* through dynamic column experiences.

Mo (VI), Mo (V/VI) also referred was blue Mo and Mo (V) sorptions were studied onto *Purolite D4123*.

The sorption of a Mo (V) aqueous solution and two equimolar solutions of Mo and V, one reduced at the potential of -1.5V vs. Ag/AgCl and the other non-reduced was performed onto *Lewatit S100*

Regarding *Purolite D4123* results it was found that Mo (VI) broke through readily from the column, although both reduced forms of Mo were partially taken up by this resin and therefore, *Purolite D4123* is not suitable for the intended separation.

Concerning the sorption experiments with *Lewatit S100*, Mo (V) was not captured by this resin and the separation of Mo and V reduced forms was achieved. Mo (V) broke through immediately from the column while V (IV) was remarkably taken up by this resin.

The breakthrough capacity of *Lewatit S100* for V was 0.454 mol $_{V}$/L $_{resin}$.

Contents

Notation and Glossary

C_i : Initial metal concentration in $^{mg}/_{L}$,

$\overline{EP}$: Average of the equivalence points obtained during the titration experiments in L,

$[Fe]_{AAS}$: Concentration of Fe determined by the AAS in $^{g}/_{L}$,

$[KMnO_4]$: Concentration of $KMnO_4$ in $^{mol}/_{L}$,

M_{Fe} : Molecular weight of Fe in $^{g}/_{mol}$,

$[Mo]_{ICP-OES}$: Mo concentration measured by ICP-OES in $^{mg}/_{L}$,

$[Mo(V)]$: Concentration of Mo (V) in $^{mol}/_{L}$,

$[Mo(V)]_{titration}$: Mo (V) concentration calculated by titration results in $^{mol}/_{L}$,

n : $\frac{Fe\ mol}{KMnO_4\ mol}$ ratio in the first titration reaction ,

V_{resin} : Volume of resin in the column in L,

V_{sol} : Volume of solution used in the titration in L,

$V_{Sol}\,BP$: Volume of solution in the breakthrough point in L,

x : $\frac{Mo\ mol}{KMnO_4\ mol}$ ratio in the second titration reaction,

i: accountant

AAS: Atomic Absorption Spectroscopy

BC: Breakthrough capacity in mol $_{metal}$/L $_{resin,}$

BV: Bed Volume,

D2EHPA: Di(Ethylhexly)Phosphoric Acid,

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy,

NMG: 1-deoxy-1-(methylamino)-D-glucitol,

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1 Introduction

Molybdenum is a transition metal from the Group 6 of the periodic table. Its chemical properties bear a resemblance to tungsten and vanadium, from the Group 5, rather than chromium, from Group 6 [1].

A range of oxidation states are known for molybdenum, from -2 to +6, the last one being the most common and stable oxidation state. Molybdenum forms complexes with several organic and inorganic ligands and the chemical behavior of molybdenum in aqueous solutions is especially complex and it will be approached later [2].

Molybdenum is broadly spread but does not occur uncombined in nature. It can be found in minerals like molybdenite, MoS_2, which is the main source of molybdenum but can also appear as molybdates in wulfenite, $PbMoO_4$ and powellite, $CaMoO_4$ and nowadays Ni-Mo ores are also a primarily source of Mo. It is mined as a primary ore but it is also obtained as a byproduct of copper and tungsten mining.

The most common form of molybdenum is molybdenum trioxide, MoO_3, which is converted to other commonly used molybdenum compounds such as sodium molybdate, $Na_2MoO_4.2H_2O$ and ammonium dimolybdate, $(NH_4)_2Mo_2O_7$ [1].

Vanadium is a soft, ductile, transition metal. It is found in several minerals but the most significant sources of vanadium are patronite, VS_4, and vanadite, $Pb_5(VO_4)_3Cl$, but it is also present in fossil fuels in considerable concentrations.

It is found in the same ores as uranium ores, where molybdenum appears as a contaminant [3], and in phosphorous ores [4].

The chemical behavior of vanadium is interesting given that it presents four stable oxidation states, from +2 to +5. Vanadium is stable in pentavalent state in the solution, forming different isopolyanions. In special conditions of low pH and low redox potential, it is possible to reduce vanadium to quadrivalent, which forms vanadyl cation VO^{2+} [5].
The pentoxide compound V_2O_5 is the commercially most important form of vanadium, but ammonium vanadate, NH_4VO_3 is another common compound of vanadium.

Besides other similarities, vanadium and molybdenum have common applications. Due to their mechanical properties, molybdenum and vanadium are used in ceramic and glass industries but its chief application is as alloying elements to produce special steel alloys to specific applications, such as bridges and high speed tools, since they are corrosion inhibitors and improve toughness and strength of the alloys.

Other important use of these two metals is in chemical industry as catalysts, especially in the petroleum-refining industry, where they are used as catalysts in several processes, for instance, hydrogenation, isomeration and alkylation of fuel [6].

Therefore, vanadium and molybdenum are frequently found together in several wastewaters, due to leaching processes, natural or as consequence of mining activities, and in industrial effluents, owing to their common applications, either in the steel alloy industry or in the petroleum-refining industry as result of the disposal of enormous amounts of deactivated catalysts

Both of these metals are toxic and hazardous to animals and humans, thus there is an increasing environmental concern about the industrial effluents treatment and about decontamination of ground waters. Furthermore, Mo and V are non-renewable resources; hence, it becomes important to utilize these resources as raw materials for their numerous applications [7].

Due to various mutual chemical properties it is relatively difficult to separate vanadium and molybdenum in solutions. For a better understanding of the difficulties related to the separation of these metals, it must be studied the speciation of these compounds in aqueous solutions.

Mo (VI) has a complex speciation in aqueous solution and this speciation depends of the pH conditions and the concentration of metal ions in the solution. Mo (VI) has a noticeable affinity for the oxygen and tends to form various oxo-complexes which represent the majority of Mo (VI) coordination compounds [8].

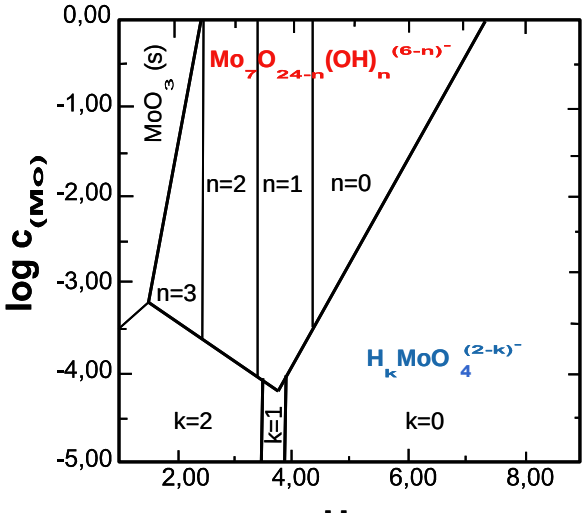

***Figure 1**: Speciation diagram of Mo(VI) in aqueous solutions*

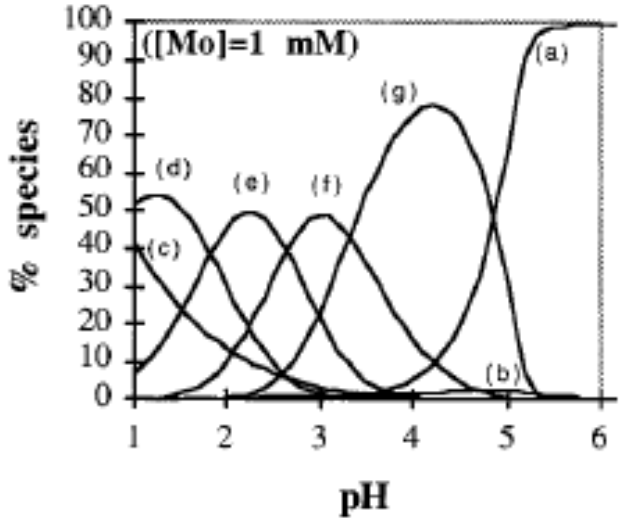

***Figure 2**: Distribution of Mo(VI) species as function of pH at Mo conc. of 1mM. (a) MoO_4^{2-}, (b) $HMoO_4^-$, (c) H_2MoO_4, (d) $Mo_7O_{21}(OH)_3^{3-}$, (e)$Mo_7O_{22}(OH)_2^{4-}$, (f) $Mo_7O_{23}(OH)^{5-}$, (g) $Mo_7O_{24}^{6-}$[10]*

Figures 1 and ***2*** show the species that are present in aqueous solutions at several pH's and concentrations.

At pH < 1, the MoO_2^{2+} is found, at pH >6 or in very dilute solutions (<10^{-4} M), only molybdate anion, MoO_4^{2-} is present in aqueous solution, but in higher concentrations and in lower pH polymeric anions with no less that 7 Mo atoms are formed, which are often called molibdic acids.

Although is not a consensual matter, several authors studied the chemical behavior of Mo(VI) in aqueous solutions and conclude that in concentrations higher than 10^{-4} M and at pH 3 the predominant specie is $Mo_7O_{22}(OH)^{4-}$ even though other species can coexist with this, like $Mo_7O_{24}^{6-}$ and $Mo_7O_{23}(OH)^{5-}$.The important knowledge for this work is that, at the utilized operational conditions which were pH 3 and 0.5-1.0 mM solutions, anionic species are present in aqueous solutions[9-12].

Vanadium (V) speciation must also be discussed. Vanadium (V) species in aqueous solutions also depends on pH conditions and metal ions concentration. There can be 12 different soluble species in solution and they are cationic species like VO_2^+, neutral species HVO_3 and anionic species as decavanadates ($H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$, $V_{10}O_{28}^{6-}$) and other mono or polyvanadates such as VO_3^-, HVO_4^{2-}, $V_2O_7^{3-}$ $V_4O_{12}^{4-}$, etc [13].

The ***Figure 3*** present the speciation diagram at different pH conditions and different V (V) concentrations and the ***Figure 4*** show the fraction of each species in aqueous solutions at pH 3 and at different concentrations.

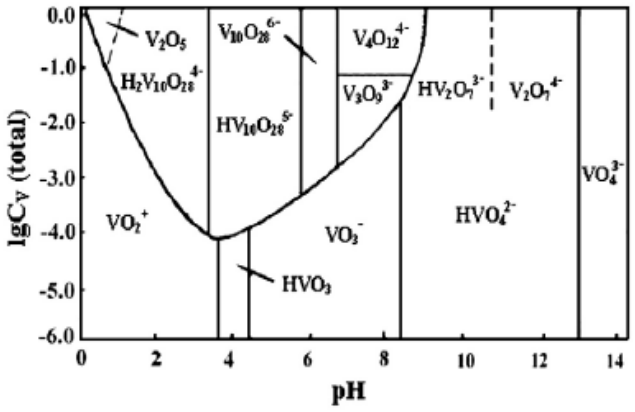

Figure 3: *Vanadium (V) compounds in water solutions [13]*

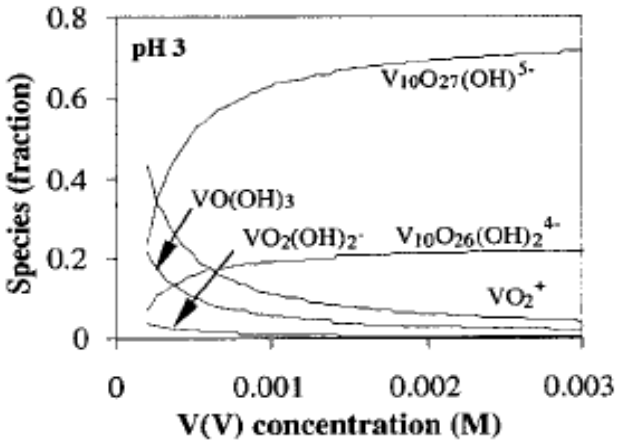

Figure 4: *Fraction of V (V) species as function of V concentration at pH 3 [41]*

As it is possible to observe, at pH 3 and 0.001 M the predominant specie is $V_{10}O_{27}(OH)_8^{5-}$ and the others present in solution are also anions.

As one of the objectives of this project is the electroreduction of Mo (VI) and V (V), it became important to also study the chemical behavior of the reduced compounds in water.

The reduced vanadium compound is V (IV) and his speciation in water is quite simpler than V (V), even though it also depends on the pH conditions and the concentration. In ***Figure 5*** are represented the V (IV) species in an aqueous solution with a concentration of 50 mg/L of vanadium [14].

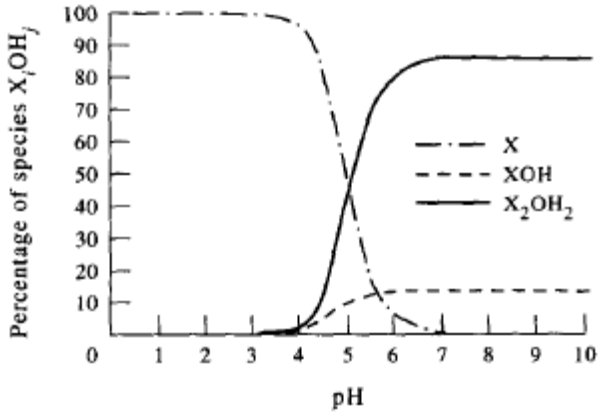

***Figure 5**: Distribution of Vanadium (IV) species in aqueous solutions as function of pH with Conc: 50 mg V/L [14]*

The X corresponds to the vanadyl cation VO^{2+} and the other hydroxylated forms, $VO(OH)^+$ and $(VO)_2(OH)_2^{2+}$. An increase of the concentration resulted in an increase of the $(VO)_2(OH)_2^{2+}$/ $VO(OH)^+$ ratio. In solutions at pH 3 and with 50 mg/L of V the principal specie present is VO^{2+}.

Regarding Mo electroreduction, it seems important to refer that in aqueous acidic media it was reported that the present species is the dimeric cation $Mo_2O_4(H_2O)_6^{2+}$ [15-17].

Intending to recover and selective separate Mo and V from aqueous solutions, ion exchange methods can be applied, given that all ions can be captured from a solution, allowing high recoveries, and separated, if followed by effective regeneration processes. Therefore, the propose of this work was to study the sorption of molybdenum (VI) and the electroreduced compounds onto a chelating resin *Purolite D 4123*®. The electroredution was performed in a laboratory electrolyzer. It was also studied the sorption of Mo(V) onto a strongly acid cationic ion exchange resin, *Lewatit S 100*®, and the possible separation of Mo from vanadium on this resin.

2 State of Art

2.1 Molybdenum and Vanadium Removal from Aqueous Solutions

Molybdenum and vanadium can be found in several water streams, along with several impurities resulting from mining activities, refining processes, and industrial effluents.

In this chapter a literature review of the principal processes to remove and recover Mo and V from aqueous is presented.

2.1.1 Precipitation

Precipitation is a widely used process to recover molybdenum and vanadium from aqueous or multimetal solutions. The reviewed work report procedures to precipitate either Mo or V with several precipitants, as well as combined techniques along with precipitation that permit the removal of these metals from solutions; filtration is a process that is many times useful after precipitation allowing better results.

Among the most common methods is the precipitation of Mo as sulphides or as carbonates. H_2S precipitates Mo as MoS_2 in acidic media; $CaCl_2$ and $CaSO_4$ precipitate Mo as $CaMoO_4$ in alkali media [18]. Potassium thiocarbonate also precipitate Mo, as thiocarbonate in alkaline solutions and as sulphide in acidic solutions [19].

Vanadium can also easily be removed by precipitation. The most common precipitants are Na_2SO_4 which precipitate vanadium as $NaVO_3$ [20] and NH_4Cl which precipitate vanadium as NH_4VO_3 [21].

Precipitation is not a suitable method when dealing with large volumes of solution with low metals ions concentration. One major problem is the formation of a large amount of sediments containing metal ions. Precipitation methods depend on several operational conditions such as suitable pH conditions, temperature, concentration of metal ions and controlled stirring intensity. Frequently after final filtration, concentration of metal ions in the filtrate still remains on the level of a few mg/L.

2.1.2 Solvent extraction

A considerable number of works have been devoted to recovering molybdenum and vanadium from aqueous solutions by solvent extraction using numerous extractants.

Amines are the most common extractants [22]. Alamine 333 (tricaprylamine) [23] and tri-n-octyl amine [24] were reported as very effective extractants but tributyl phosphates shown also very good results [25]. Solutions of kerosene or chloroform with alcohols and acetones as phase modifiers are the most usual diluents in the solvent extraction separations [24].

Although solvent extraction is an effective method to remove V and Mo from aqueous solutions it requires a large amount of solvents, high investments and operational costs and is not suitable for drinking water treatments since it uses organic solvents that some times are toxic and it does not achieve metal concentrations as low as the drinking water treatments must achieve.

2.1.3 Flotation

Flotation is a widely used method to uptake Mo and/or V from aqueous solutions.

Although it has some limitations, it is only applicable in solutions with relatively low concentrations of metals and it is not suitable in drinking water treatments because it cannot achieve appropriately low concentrations, it is a very effective process to remove them from water streams.

Among the most common utilized flotation processes are the ion flotation and adsorbing colloidal flotation.

Regarding the ion flotation, several different surfactants (or collectors) have been reported to recover Mo ions from aqueous solutions and separate it from impurities as arsenic, tungsten, phosphates or silicates. A widely used procedure is utilize ferric hydroxide as a precipitant for molybdenum and primary aliphatic amines as surfactant. Dodecyl [26] and octadecyl amines [27] have been reported as the most efficient collectors and they can accomplish separations of 98% of Mo from impurities. Rosin amine hydrochloride as a collector has also been mentioned in the literature. About the removal and separation of V by ion flotation, HMBPT and HDMBAC have been used as complexing agents and oleic acid as surfactant with good results [28].

Adsorbing colloidal flotation is a promising method to recovery Mo from solutions with other metals as impurities. Studies have been made using ferric hydroxide as co-precipitant and as adsorbent and dodecylamine as surfactant and they claim good results but not so good

comparing with ion flotation because it is only effective in acidic media and the Mo concentration has to be lower than 60 mg/L [26].

2.1.4 Adsorption

Adsorbents like pyrite (FeS_2) [29], γ-Al_2O_3 [30], goethite [31], and some biosorbents as chitosan [10], cellulose [32], brown seaweed [33], coir pith carbon [12], montmorillonite [34], bentonite [35], carbon cloth [36] among others, have been studied to remove either vanadium and/or molybdenum from aqueous solutions.

Adsorption is a very effective process to remove these metals, achieving in most cases, removals higher than 99%.

Some adsorption capacities can be compared. For instance regarding Mo adsorption, pyrite presents an adsorption capacity of 130 µmol/g [29], while γ-Al_2O_3 has 193 µmol/g [30], goethite 162 µmol/g [31] and chitosan 1148 µmol/g [10].

Although adsorption is an effective, simple and rapid method to remove metal ions from water, has some limitations; adsorbents have a short life period, as they get saturated relatively fast. Moreover, they can only perform effective removal in solutions with low concentration of metals and the metals recovery is not always possible due to difficulties in the desorption process which turn the adsorption economically inapplicable in the industry.

2.1.5 Ion exchange

Ion exchange is a relatively inexpensive, non-hazardous, rapid and versatile technique that permits selective recovery of metals from solutions. By ion exchange all ions can be removed from a solution and compounds are separated, the high selectivity allows total removal of metals and the recovery of substances with high purity [37].

Mo and V can be efficiently removed by ion exchange and the best results have been accomplished with chelating resins, which form complexes with the metal ions.

Some chelating resins have been reported with very good results, one of them is resin based on acrylic copolymers aminated with ethylenediamine, which is very effective removing Mo from nitric acid solutions [7]. Other successful case is a magnetic chelating resin functionalized with tetraethylene pentamine that due to his high uptake capacity and the readiness to collect anions using a magnetic field [38]. Chelating resins with methylamino-glucitol groups also presents good results uptaking Mo and V [39].

2.2 Selective Separation of Molybdenum from Vanadium

2.2.1 Precipitation

Precipitation techniques are the most common method to separate metals from solutions.

Regarding the separation of Mo and V, there are two main approaches to precipitation. One is the sulphide precipitation, in which Mo is precipitated as MoS_3 leaving vanadium in the solution and it is usually applied to acidic solutions. The other is ammonium salt precipitation in which vanadium is precipitated as NH_4VO_3 by addition of ammonium sulphate or chloride and is usually followed by precipitating Mo adjusting the solution pH and applied to alkali solutions.

Concerning sulphide precipitation, the usual method is the addition of H_2S in a acidic solution in which Mo precipitate and vanadium remains in the solution in the form of vanadyl cation VO^{2+} that was then precipitated as hydrated oxide V $(OH)_4 \cdot 1.5H_2O$ by neutralization of the solution or as $Na_2H_2V_6O_{17}$ by oxidizing vanadium in the solution with $NaClO_3$ when pH was adjusted with NaOH or Na_2CO_3.

As to the ammonium salt precipitation, vanadium can be precipitated as NH_4VO_3 with $(NH_4)_2SO_4$ at pH 8, the Mo in the remaining solution is recovered by solvent extraction. Other commonly used way is using NH_4Cl at pH 8 is used to precipitate vanadium as NH_4VO_3, and molybdenum is then precipitated as $H_2MoO_4.H_2O$ by adjusting pH with HNO_3.

Although precipitation is simple and the costs associated are low, the complete separation of Mo from V is not possible and it is suitable for highly concentrated solutions [40].

2.2.2 Solvent extraction

A number of articles have been published relating to the solvent extraction of Mo and V using several organic reagents from various aqueous solutions.

In acidic solutions, when the predominant vanadium and molybdenum species are cations, cationic extractants are appropriated; in neutral and alkaline media quaternary long-chain alkyl ammonium salts are suitable to extract anionic species and the use of basic long-chain alkyl amines to extract anionic metal complexes in the acidic range where anionic species is favorable.

The acid-base behavior observed for both metals suggests that two kinds of liquid extractants could be used for the separation of molybdenum and vanadium.

Regarding solvent extraction with extractants involving compounds formation it was reported that kerosene solutions containing 5–20% (v/v) D2EHPA (Di(Ethylhexly)Phosphoric Acid) extracted VO^{2+} with fast kinetics in a pH range of 1.5–2.5 and the extracted VO^{2+} species were readily stripped with dilute H_2SO_4. Also it was reported that D2EHPA can be used to extract the cationic species of molybdenum and vanadium like MoO_2^{2+} and VO^{2+} at pH 1 from their solutions [40].

Others studies proposed selective extraction of V(V) from Mo(VI) by a liquid chelating extractant, LIX 26.The extraction is possible within a restrict pH range between 1-2 and when the aqueous solution is equilibrated with an organic solution containing 2% LIX 26 and 10% n-octanol in hexane [40].

Extractants involving ion association include primary, secondary and tertiary amines and quaternary ammonium salts. The tertiary amine Alamine 336 and the quaternary ammonium salt Aliquat 336 are usually the preferred basic extractants, which are used for extraction of anionic complexes of molybdenum and vanadium from their HCl, H_2SO_4 or HNO_3 solutions.

The separation of V (V) from Mo (VI) by 0.1 mol/L Alamine 336 and Aliquat 336 dissolved in toluene was studied. With Alamine 336/toluene, molybdenum is quantitatively extracted in the region pH<4 and suppressed at pH>7 and vanadium was extracted in the range of 1<pH<8 but quantitative extraction was reached in the region of 3<pH<4.5. For the Aliquat 336/toluene solution, vanadium is quantitatively extracted in the range 3.5<pH<9 while the extraction of molybdenum is quantitatively extracted at pH<5 and is suppressed at pH>8. Thus, it is suggested that the separation of vanadium (V) and molybdenum (VI) can be carried out in two ways. In the most acidic range (pH<1), the Alamine 336/toluene system can be used to extract molybdenum in the presence of vanadium. In the slight basic range (8<pH<9), the Aliquat 336/toluene system can be used to selectively extract vanadium in the presence of molybdenum [40]. (40)

The final analysis of the solvent extraction methods to separate vanadium from molybdenum in all pH ranges is that solvent extraction is a very effective process to separate these two metals, achieving separations of 100%.

2.2.3 Ion Exchange

Ion exchange is a well-know technology for metal separation and purification and works have been reported about the separation of vanadium from Molybdenum by ion exchange.

The use of a chelating resin D418 with a $-NHCH_2PO_3Na_2$ functional group resulted in a 99.8% of vanadium from a molybdenum solution at pH 7.2 when the concentration of Mo and V was 50 g/L and 0,638 g/L respectively. The desorption results were very good with 2M NaOH solution and the resin can be re-used when washed with HCl [40].

Afterwards, the complete removal of vanadium was recently proposed with a solution of 60 g/L of Mo, 0.6 g/L of V and 20 g/L of chloride ions on a strong base anion exchange resin D296. The separation could only be possible in the pH range of 6.5-8.5 and the resin was regenerated with 6 M HCl solution, with 98.5% of the vanadium desorbed [41].

Electrochemical ion exchange technique was proposed to separate both metals. An initial loaded resin with 9.3 kg/m^3 of V and 130 kg/m^3 of Mo was fed to an electrochemical cell. The cell with three compartments had a reticulated vitreous carbon cathode mixed with a resin, Amberlite IRA 94S, and two Ti-Pt anodes separated by a Daramic diaphragm.
In the cell, the pentavalent vanadate anion was reduced to a tetravalent vanadyl cation, which was selectively desorbed.93% of V and 7% of Mo were eluted from the resin and the further elution of Mo was accomplished with an alkaline solution resulting in a molybdate solution with a 1000 Mo/V ratio [42].

Regarding the combination of electrochemical reduction and ion exchange techniques to separate molybdenum from vanadium, no paper has been reported yet which makes this a pioneer investigation.

3 Experimental

3.1 Samples

The molybdenum solutions were prepared from dehydrate of sodium molybdate, $Na_2MoO_4 \cdot 2H_2O$ (Lachema Brno, Czech Rep.) and the vanadium solutions were prepared from ammonium metavanadate, NH_4VO_3 (PENTA, Czech Rep.).The SO_4^{2-} anions were introduced in the solutions by adding Na_2SO_4 (PENTA, Czech Rep.). All reagents used were of analytical purity.

The pH was adjusted by H_2SO_4 and NaOH solutions.

3.2 Ion Exchange Resins

Two ion exchange resins were used. One was the chelating resin, *Purolite D 4123*® (Purolite Int., UK), with a 1-deoxy-1-(methylamino)-D-glucitol functional group (NMG) in a polystyrene/DVB copolymer macroporous matrix. The particle size was 18–50 mesh.

The sorbent was used in free-base and in protonated form.

All the volumes are expressed in terms of bed volumes (BV).One bed volume corresponds to the volume of wet settled resin in the column.

As in free-base form, the sorbent was soaked with distilled water, with 20 BV for 1 hour. To turn it into protonated form, the sorbent was washed with 1 M HCl with 10 BV for 1 hour and then washed with water as above mentioned. The loaded resin was stripped with 1M HCl, 1M NaOH or both at 3 BV/h for 5 hours followed by a final wash with distilled water at 20 BV for 1 hour.

The other sorbent used was a strongly acid cationic ion exchange resin *Lewatit S 100*® (LANXESS, Germany) with a sulfonic acid functional group in styrene-divinylbenzene matrix and the beads diameter was 0.58±0.05.The resin was used in the protonated form and therefore it was first washed with 10 BV of 1M HCl for 1 hour followed by rinsing with distilled water at 20 BV/h for 1 hour

3.3 Electrochemical Reduction

To reduce both Mo and V a laboratory flow-by (current lines perpendicular to the electrolyte flow direction) electrolyzer was used. The image of the electrolyzer can be seen in ***Figure 6***.

A 3D carbon felt with a depth of 10 mm was utilized as cathode and placed in the cathode compartment with a volume of 10 mL. A Pt wire was used as anode. Between the cathode and anode compartments was a Nafion membrane. Between the cathode and the Nafion membrane was positioned an Ag/AgCl reference electrode. A perforated Pt plate was used as current feeder for cathode. The schematic representation of the electrolyzer is illustrated in ***Figure 7***.

As a catholyte, solutions of Mo or Mo and V mixture at pH 3 were used. The volume of catholyte was 1 L, and it was continuously circulated through the cathode compartment with a flow rate of 100 mL/min.

The reduction semi-equations (1) and (2) performed in the cathode were:

$$2H_2MoO_4 + 4H^+ + 2e^- \rightarrow Mo_2O_4^{2+} + 4H_2O \qquad E^0 = -0.50\,V \tag{1}$$

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \qquad E^0 = +1.00V \tag{2}$$

for either Mo or Mo and V reduction.

As an anolyte, 200 mL of 0.1 M H_2SO_4 was used also with a flow rate of 100 mL/min. In both cases, the oxidation semi-equation was equation (3):

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad E^0 = -1.23\,V \tag{3}$$

To proceeding the reduction, potentials at working electrode of -250 mV and -1500 mV vs. Ag/AgCl reference electrode were used and the electrolyzer was connected to a Solartron-Schlumberger 1186 electrochemical interface (Schlumberger Technologies, UK) which controlled the potential.

The degree of reduction was monitored visually, according to the color change.

V (V) solutions are light yellow and they turn greenish blue when reduced to V (IV). Mo (VI) solutions are colorless, but they turn blue when there is a mixture of Mo (VI) and reduced Mo (V) while Mo (V) solutions are amber.

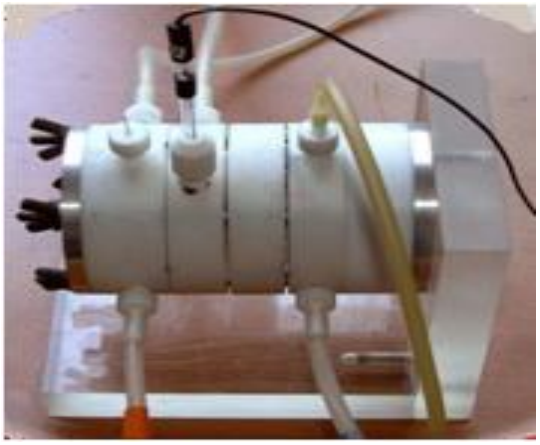

Figure 6: *Image of the laboratory electrolyzer*

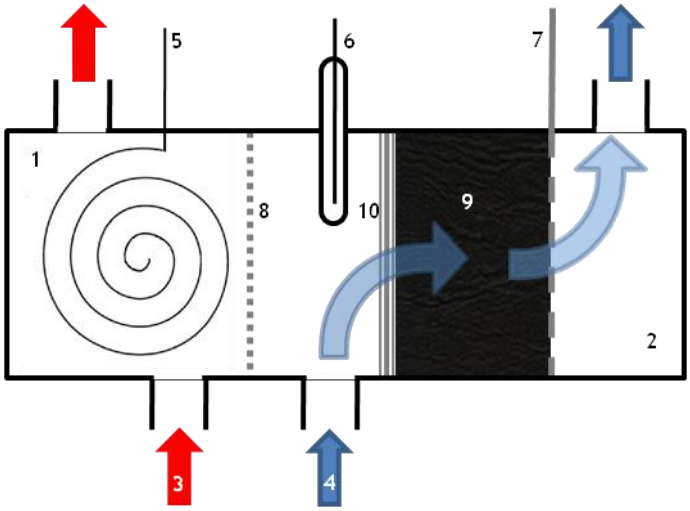

Figure 7: Schematic representation of the electrolyzer: (1) anodic compartment, (2) cathodic compartment, (3) anolyte flux, (4) catholyte flux, (5) auxiliary electrode (Pt wire), (6) reference electrode (Ag/AgCl), (7) working electrode (Pt),(8) Nafion membrane, (9) carbon felt, (10) support reticle

3.4 Batch Experiments

The batch experiments were carried out by mixing 50 mL of the initial Mo (V) solution with a concentration of 1 mmol Mo/L with 0.5 mL of *Purolite D 4123*®. The solutions pHs were adjusted with 1 M HCl or 1 M NaOH before adding the sorbent. The solutions along with the sorbent were shaken at 250 rpm by a Unimax 1010 shaker (Heidolph Instruments, Germany) for 22 hours.

3.5 Column Experiments

Glass columns with an inner diameter of 10 mm were used. 10 mL of sorbent were packed into the columns. The inlet solutions were 1 mmol Mo/L with 10 mmol SO_4^{2-}/L at pH 3 or an equimolar solution of 0.5 mmol/L of Mo and V also with 10 mmol SO_4^{2-}/L at pH 3.

The sorption proceeded continuously at the specific flow rate 6 BV/h and the desorption at 3 BV/h, using a peristaltic pump *PCD 31.2* (Kouřil, Czech Rep.). The outlet flow from both

sorption and desorption were continuously taken by a fraction collector *FCC 61* (Laboratorní Přistroje, Prague).

The color changes of the sorbent during the sorption and desorption were monitored.

The *Purolite D 4123*® initially beige, changed color during the sorption to the color of inlet solutions, blue from blue Mo and amber from Mo (V) solution. The color changes can be seen in ***Figures 8*** and ***9***.

The *Lewatit S 100*® which was translucent brown, turn into greenish blue, the color of reduced V (IV) that was uptake as the sorption progressed, as it can be seen in ***Figure 10***.

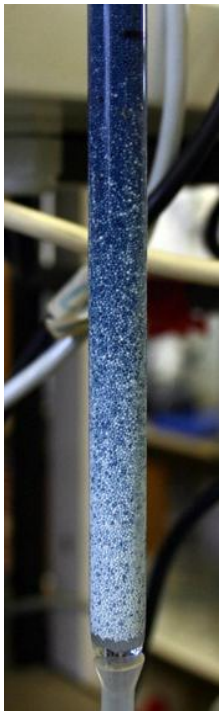

Figure 8: Image of the adsorption of blue Mo onto *Purolite D 4123*®

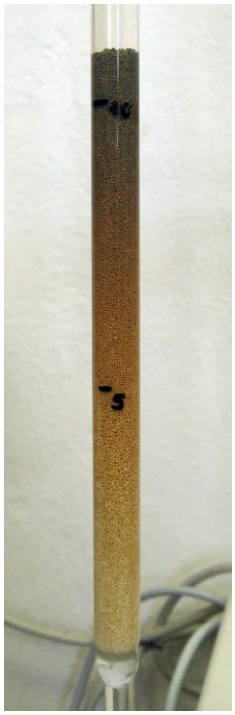

Figure 10: Image of the adsorption of Mo (V) onto *Purolite D 4123*®

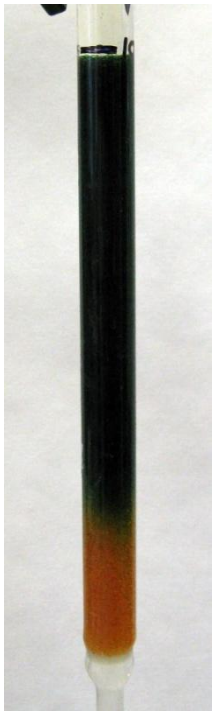

Figure 9*: Image of the adsorption of V(IV) onto Lewatit S100*®

3.6 Chemical Analysis

3.6.1 Mo and V measurements

Molybdenum and vanadium concentration in the solutions was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) *Optima 2000 DV* (Perkin-Elmer Instruments, USA).The chosen sample were diluted to be within the maximum concentration limit of this device which is 10 mg metal/L.

3.6.2 Titrations

Two types of measurements were made by titration and they were performed using a potenciometric titrator *716 DMS Titrino* connected to a *728* stirrer and a *716 DMS titrino* keyboard (all from Metrohm, Switzerland) identical to the ***Figure 11***.The potenciometric titration was connected to a computer with the software *Datalog*, which treated the experimental data. The volume of solutions to titrate necessary to perform the titrations was 25 mL.

Figure 11: *Image of the laboratory titrator*

The titrator solution was a 0.005 M $KMnO_4$.To know the exact concentration of this solution a previous titration was made, a 0.001M $Fe(NH_4)_2(SO_4)_2$ solution was used as a standard. Before the titration, the Fe concentration was measured by Atomic Absorption Spectroscopy (AAS) (*SpectrAA*, Varian Inc., USA).

Afterwards, the same $KMnO_4$ solution was used to titrate Mo and estimate the reduction degree to Mo (V) achieved with the electrolyzer procedure.

The titration allows estimating the amount of Mo (V) in the outgoing solution of the electrolyzer and therefore, identifying the degree of reduction of Mo (VI).

3.6.3 Other Analytical Measurements

All pH were adjusted with sulfuric acid solution and sodium hydroxide and were measured by pH meter InoLab Level 1 (WTW, Germany).

4 Results and Discussion

4.1 Sorption of Molybdenum

Before starting with the concrete study of the sorption experiments, a previous study regarding the reduction behaviour of Mo was made and it can be consulted in the ***Annex A***.

Although it is possible to separate Mo from V using the chelating resin *Purolite D4123* in free base form in which vanadium is sorbed and Mo is not, this work is focused on utilization of electrochemical reduction for separation. This approach is based on the fact that a change of oxidation state is accompanied with a change of sorption properties.

4.1.1 Non-reduced Mo (VI)

A solution with 1 mmol/L of Mo (VI) with 10 mmol/L of Na_2SO_4 and pH 3 was used in all the experiments with *Purolite D 4123*.The functional group of this resin in the protonated form, as it was used for the following experiments, is represented in the ***Figure 14***:

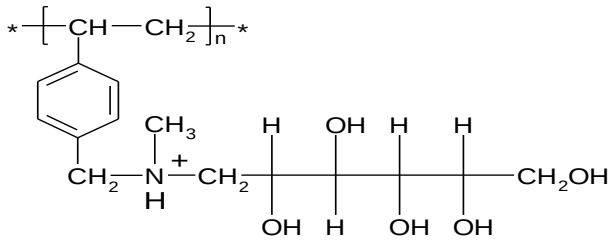

Figure 12*: Representation of the NMG functional group in the protonated form*

The metal oxoanions form the coordination complexes with organic molecules containing OH-groups, in suitable steric configuration which is at least two OH-groups in the neighborhood of C atoms. The optimal pH range for the diol-complex formation of Mo (VI) is 1-6 [39]. Therefore, it is expected that Mo form diol-complexes with the NMG functional group of this resin. A representation of the complex formed between the resin functional groups and Mo can be seen in the ***Figure 15:***

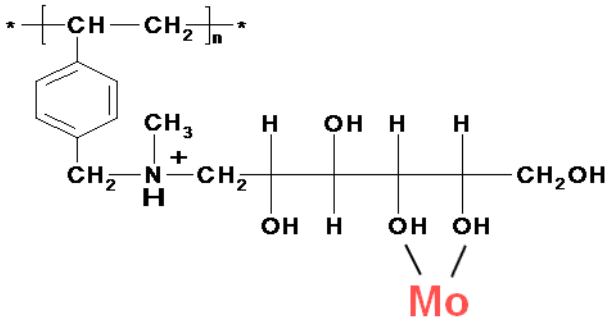

***Figure 13**: Representation of the complex formed between Mo and the resin functional group*

The graphic representation of the obtained results is presented in the ***Figure 16***.

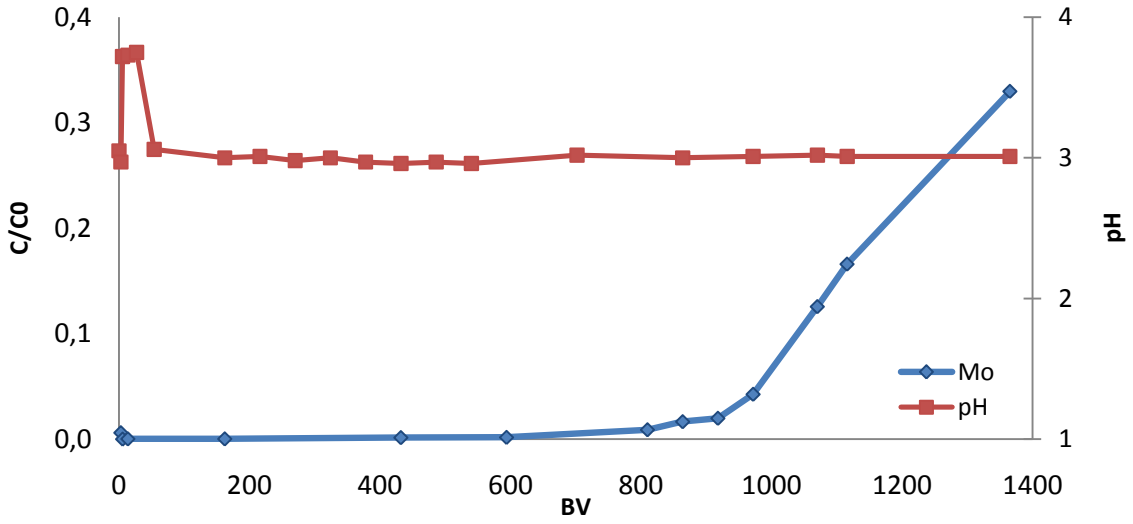

Figure *14: Graphic representation of the experimental data regarding the Mo(VI) adsorption onto Purolite D 4123*

Mo (VI) solution was readily captured in the *Purolite D 4123* until reaching the breakthrough curve. The breakthrough capacity (BC) is calculated by the equation (11) [43]:

$$BC\left(\frac{mg_{metal}}{L_{resin}}\right) = \frac{V_{Sol}\,BP(L) \times C_i(\frac{mg}{L})}{V_{resin}\,(L)} \qquad (11)$$

In which $V_{Sol}\,BP$ is the Volume of solution in the breakthrough point, C_i is the initial metal concentration and V_{resin} is the volume of resin in the column. Thus, the breakthrough capacity of the resin is 80000 $\frac{mg\ metal}{L_{resin}}$ which correspond to 0.834 $\frac{mol\ Mo}{L_{resin}}$.

Afterwards, the column was stripped with a solution of 1M NaOH and the results can be seen in the ***Figure 17***:

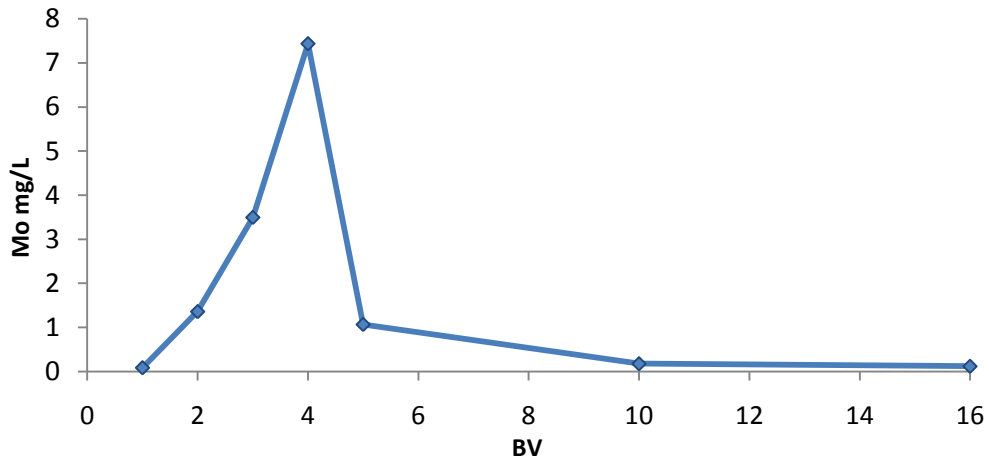

***Figure 15**: Graphic representation of the experimental data regarding the Mo(VI) desorption onto Purolite D 4123*

With the increasing of pH the stability of the diol-complexs formed decreased, and for this reason the Mo were easily and totally rinsed of the column in the first 10 BV with NaOH.

The efficiency of regeneration was calculated by the equation (12):

$$\eta_{regenation} = [(total\ amount\ of\ Mo\ desorbed\ (mg))/(total\ amount\ of\ Mo\ sorbed(mg))] \times 100 \quad (12)$$

The total amount of Mo sorbed is calculated as being the sum of the differences between the amount of Mo in the inlet solution and in each BV of outlet solution by the equation (13):

$$total\ amount\ of\ Mo\ sorbed(mg) = \sum_{i=1} \left[(BV_i(L) - BV_{i-1}(L)) \times \left(C_0(\tfrac{mg}{L}) - C_i\left(\tfrac{mg}{L}\right) \right) \right] \quad (13)$$

In which BV_i is the volume of each sample of outlet solution taken, C_0 is the inlet solution concentration and C_i is the concentration of metal in each sample taken.

The total amount of Mo desorbed is calculated as being the sum of the Mo amount in each BV of outlet solution by the equation (14):

$$total\ amount\ of\ Mo\ desorbed(mg) = \sum_{i=1} \left(Volume\ of\ oulet\ solution_i(L) \times C_i\left(\tfrac{mg}{L}\right) \right) \quad (14)$$

Hence the regeneration efficiency of this experiment was higher than 100% possibly due to some experimental errors related with the sample dilutions that were made so that the concentration of Mo in each one stayed below the maximum concentration limit measured by ICP-OES.

4.1.2 Partially reduced Molybdenum (V/VI)

One liter of the initial solution was continuously fed to the electrolyzer at a flow rate of 100 mL/min during 24 hours. The potential used to reduce Mo was -0.25 V vs. Ag/AgCl. The obtained solution was blue. Blue Molybdenum is reported in the literature as a mixture of Mo (VI) and Mo (V) [44].

This solution was then fed to a column with 10 mL of Purolite D4123 and in the ***Figure 18*** are represented the experience regarding the blue Mo adsorption onto the chelating resin in the protonated form:

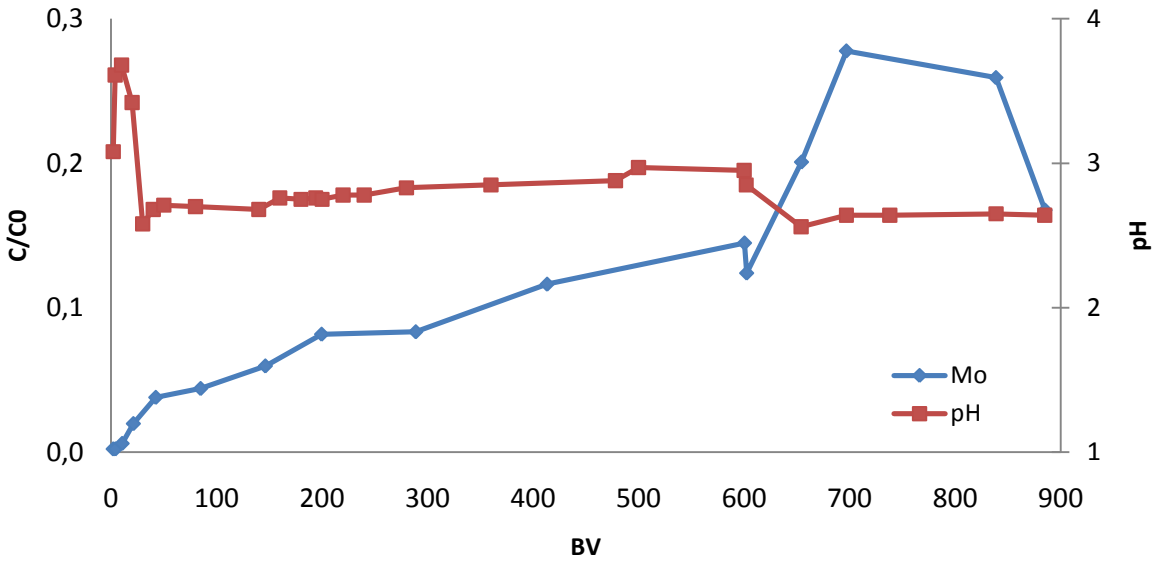

Figure 16 *: Graphic representation of the blue Mo adsorption onto Purolite D 4123 in the protonated form.*

Although blue Mo readily breakthrough the column, it was greatly adsorbed in the resin. Until 800 BV, only 10-20% of Mo was not uptake in the column and a possible reason for that is that 10-20 % of the Mo in the solution is present as a cation. As it was mentioned, only anions are able to form diol-complexs with the resin functional group and consequently being adsorbed. Mo breakthrough curve showed a slowly increase during the experiment.

The regeneration of the column was made by using 1 M NaOH solution at a flow rate of 10 BV/h during 1.5 hours, washed with distilled water at a flow rate of 20 BV/h for 1 hour and

then with 1M HCl solution at flow rate of 10 BV/h during 1 hour. The ***Figure 19*** presents the results:

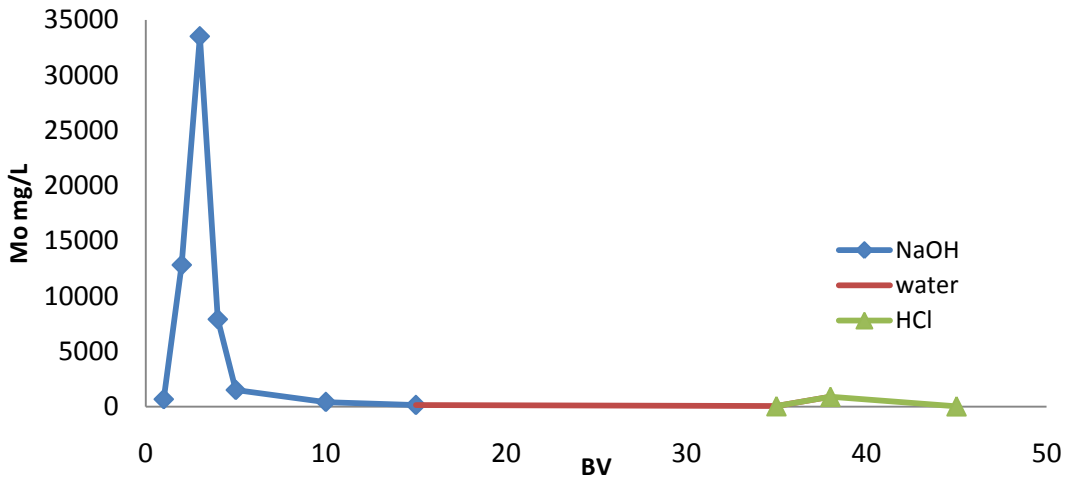

***Figure 17**: Graphic representation of the blue Mo desorption onto Purolite D 4123 in the protonated form*

The first 35 BV almost all Mo was stripped of the column, but a residual amount, from 35 to 45 BV was stripped with HCl. The regeneration efficiency obtained was once again higher than 100% and it may be due to experimental errors.

An experiment was made with *Purolite D 4123* in the free-base form.

In the free-base form, the column was only washed with distilled water, and the sorption behavior of blue Mo and the pH throughout the sorption are represented in ***Figure 20***:

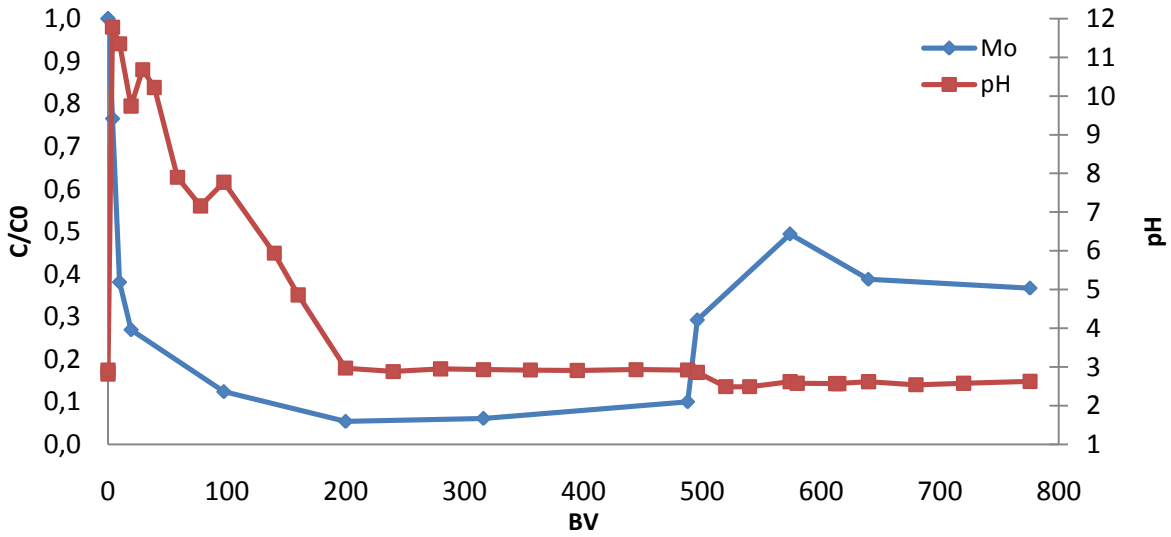

Figure 18: Graphic representation of the blue Mo adsorption onto Purolite D 4123 in the free-base form

The blue Mo sorption in the resin in the free-base form was identical to the sorption in protonated form. Once more, around 10% of Mo was not taken up in the column and the breakthrough curve showed a slowly increase.

Although, the pH of the solution immediately increased after pass through to the columns and no Mo was uptake. The pH increased due to the protonization of the column, initially the amino group in the resin captured the H^+ groups in the inlet acid solution until a total protonization of the column. Mo back oxidation might have happened because reduced forms of Mo are only stable in acidic solutions.

The pH decreased until 200 BV and inhibited the Mo sorption and after establish on pH 3.The sorption of Mo increased while the pH decreased and establish simultaneously with pH stabilization.

The regeneration of the column was performed only with NaOH and then washed with water and in ***Figure 21*** is possible to see the amount of Mo stripped off the column.

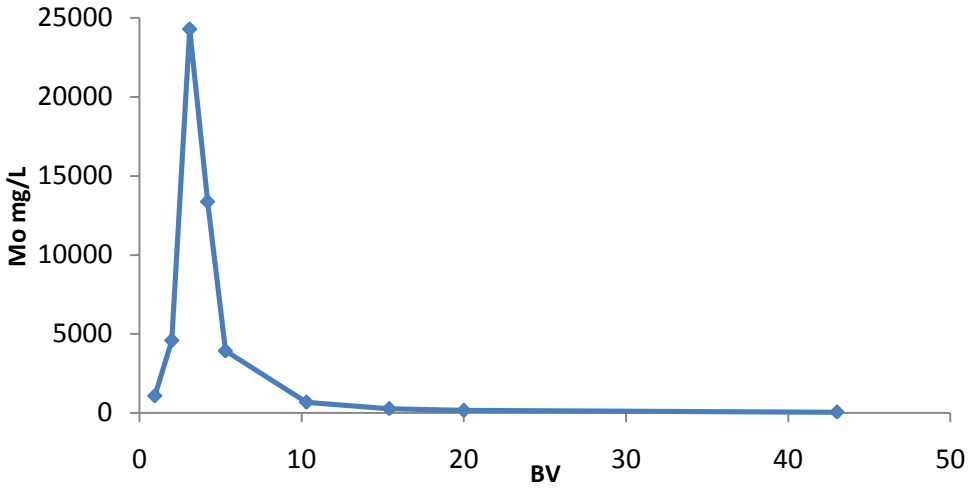

Figure 19: *Graphic representation of the blue Mo desorption onto Purolite D 4123 in the free-base form*

The entire Mo captured in the column was stripped off the column in the first 10 BV using a solution of 1M NaOH. The regeneration efficiency of this experiment was much higher than 100% .This value so high due to the fact that four different inlet solutions were used and only two were measured. Every inlet solution had a different concentration due to the adsorption of Mo in the carbon felt cathode, thus is important to measure them all and see the actual concentration of Mo in the inlet solutions. Furthermore, the two inlet solutions measured presented a significantly lower concentration than the inlet solutions of the experiment with blue Mo onto the resin in the protonated form; hence some experimental error may have also occurred.

Even thought in both cases around 10% of Mo was not capture in the column, the protonated form of the resin show better results and therefore, this form was used to perform the other experiments with this resin.

4.1.3 Reduced Mo (V)

The batch experiments were performed by mixing 250 mL of an initial Mo (V) solution with a concentration of 1 mmol Mo/L reduced using 1.5 V vs. Ag/AgCl with 0.5 mL of *Purolite D 4123*®.

The objective of these experiments was to find the optimal pH range for the formation of complexes between Mo (V) and the resin functional group because unlike ion exchangers which capture ions in a whole pH range, the sorption ability of selective sorbents is based on complex formation with metals and his efficiency depends on pH.

The experimental results are represented in the ***Figure 22***:

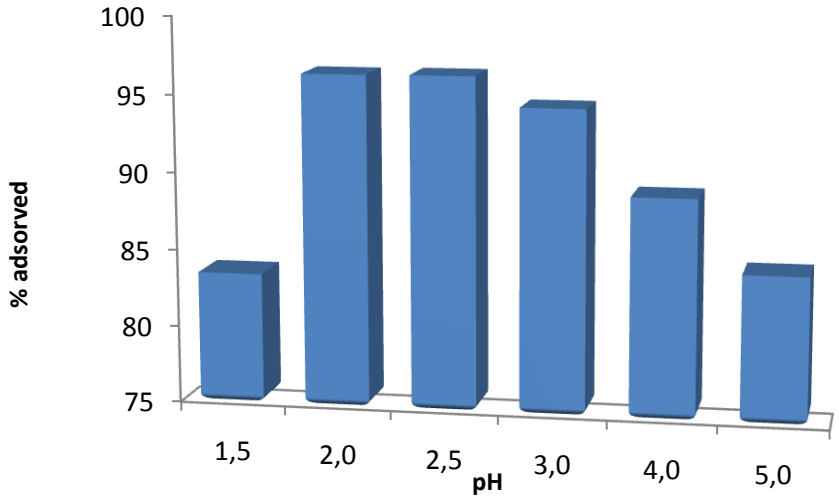

Figure 20: *Graphic representation of Mo adsorption as a function of pH*

Although in the pH range 1.5-5.0 the Mo (V) is strongly adsorbed, the best results are obtained in the region 2.0-3.0 where the maximum amount of adsorbed Mo was 96.6%.

Therefore this will be the range of pH used in the following experiments.

Moreover, it is also the same pH range that was reported to be optimal to adsorb Mo (VI) onto *Purolite D 4123* [39].

The column experiments using the electroreduced solution were performed onto *Purolite D 4123* and the sorption behavior is described in the ***Figure 23:***

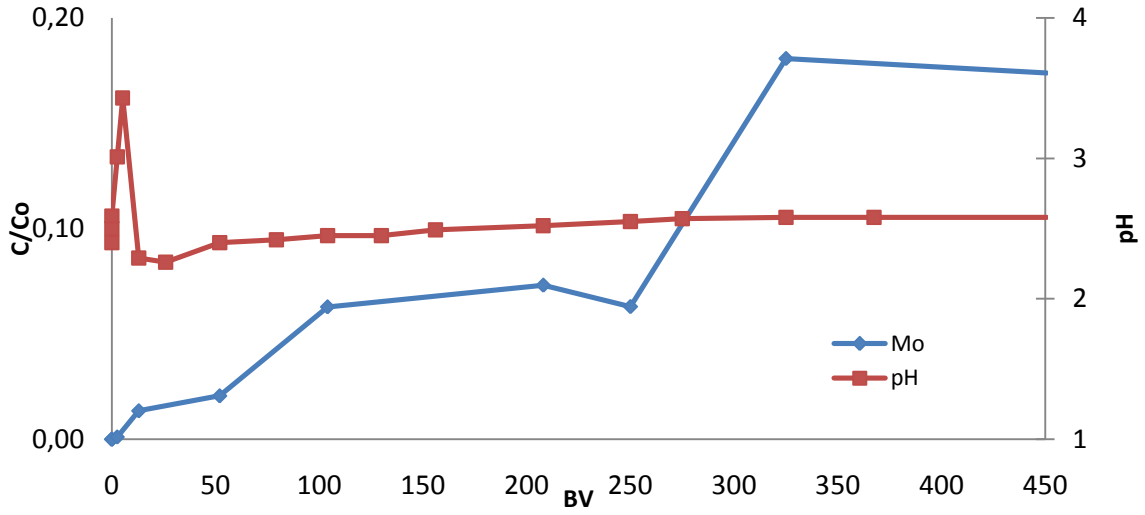

***Figure 21**: Graphic representation of the Mo (V) sorption onto Purolite D 4123 in the protonated form*

The Mo (V) immediately breakthrough the column, though very slowly and it was captured by the chelating resin.

These results were not expected because as it was above mentioned in the introduction chapter, at pH 3 and 1 mmol/L, Mo (V) is reported to form dimeric cations in aqueous solutions which are not able to form diol-complexes with the resin functional group and therefore was not expected that Mo (V) would be taken up by the resin.

The regeneration of this column was carried out with 1 M NaOH followed by a wash with distilled water and then 1 M HCl also followed by a wash with water. The results are represented in the ***Figure 24:***

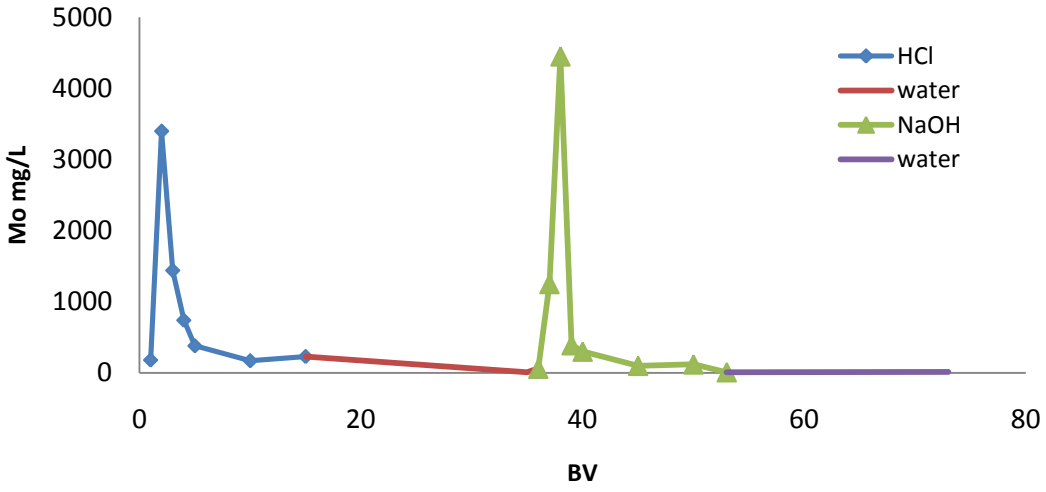

***Figure 22**: Graphic representation of the Mo(V) desorption onto Purolite D 4123 in the protonated form*

Mo was stripped out the column by either NaOH in the first 10 BV and HCl from 35 to 50 BV but the regeneration efficiency was only 51% within both solutions.

Analyzing the previous results is possible to realize that *Purolite D 4123* is not suitable to use in the separation of Mo from V, since both Mo (V) and Mo (V/VI) are adsorbed. The last results also suggest that Mo (V) is not present in aqueous solutions as cationic species.

Therefore, to study this matter a strongly acid cationic exchanger, *Lewatit S 100*, was used to perform dynamic column experiments with Mo (V).

Lewatit S 100 is a strongly acid cationic ion exchange resin with a sulfonic acid functional group, which is represented in the ***Figure 25***:

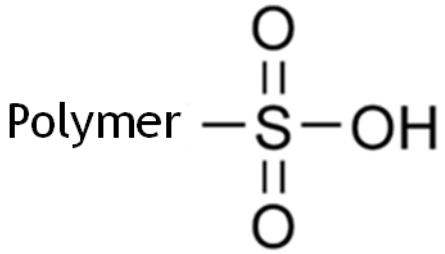

Figure 23*: Schematic representation of the sulfonic acid functional group*

This resin was used in protonated form and thus it was rinsed with a 1 M HCl solution at a flow rate of 10 BV/h for one hour followed by a wash with distilled water at a flow rate of 20 BV/h for one hour.

One liter of a solution with 1 mmol/L of Mo and 10 mmol/L of Na_2SO_4 at pH 3 was continuously fed to the electrolyzer during 24 hours at a potential of -1.50 V vs. Ag/AgCl reference electrode. The Mo (VI) in the solution was reduced to Mo (V) and this was the inlet solution for the sorption experiment performed onto *Lewatit S 100*. The results of this experiment are represented in the ***Figure 26***:

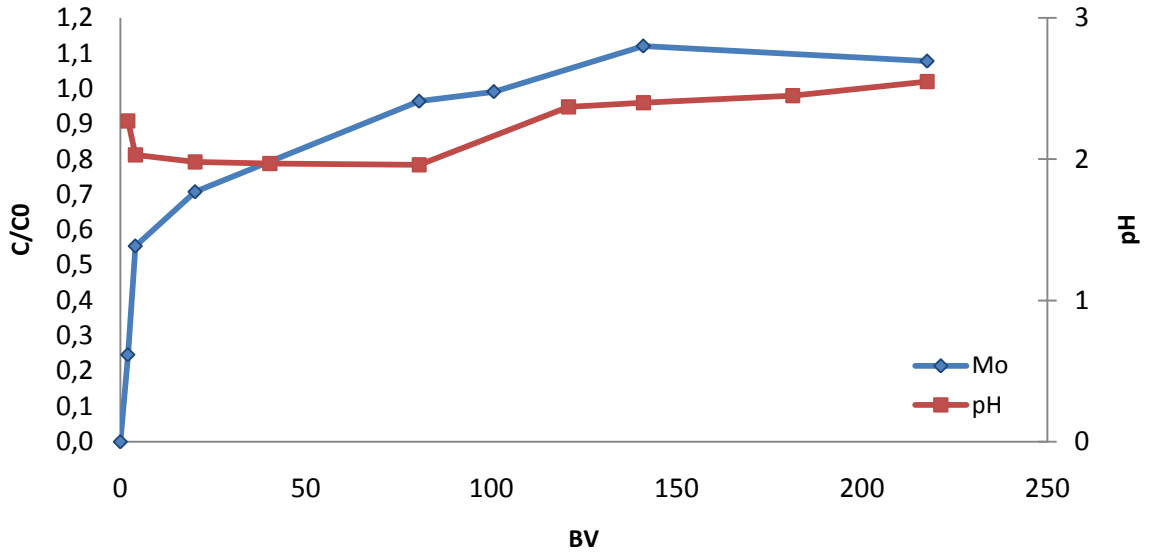

***Figure 24**: Graphic representation of the sorption of Mo(V) onto Lewatit S 100*

Examining the ***Figure 26*** is possible to notice that Mo (V) immediately breakthrough the column not being retained by the cation exchanger, confirming the previous results that suggested that Mo (V) does not occur as cationic specie.

On the other hand, in a previous work of this laboratory it was found that electroreduced V which is present in aqueous solutions as vanadyl cations was well captured onto *Lewatit S 100* on the protonated form. The results of this work are illustrated in the ***Figure 27:***

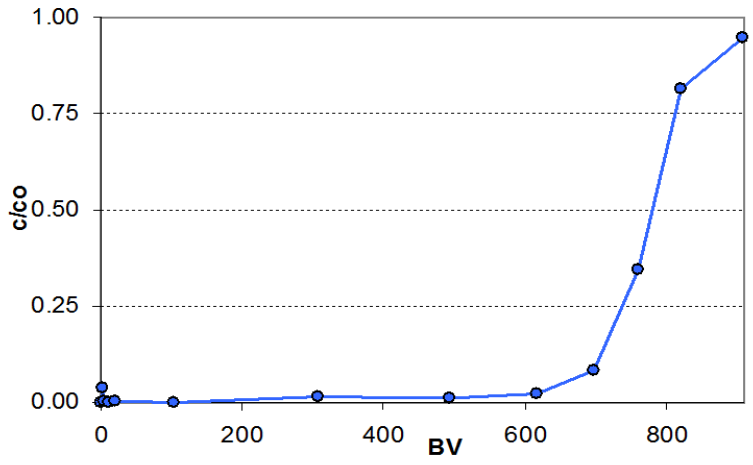

***Figure 25** : Graphic representation of the V(IV) sorption onto Lewatit S100*

These results lead to the next experiments which consisted in try the separation of Mo from V using this cation exchanger resin.

4.2 Separation of Vanadium/Molybdenum

4.2.1 Molybdenum and Vanadium non-reduced

An equimolar solution of 0.5 mmol/L of Mo, 0.5 mmol/L of V and 10 mmol/L of Na_2SO_4 at pH 3 was prepared. This solution was fed to the column and the sorption history is presented in the ***Figure 28***:

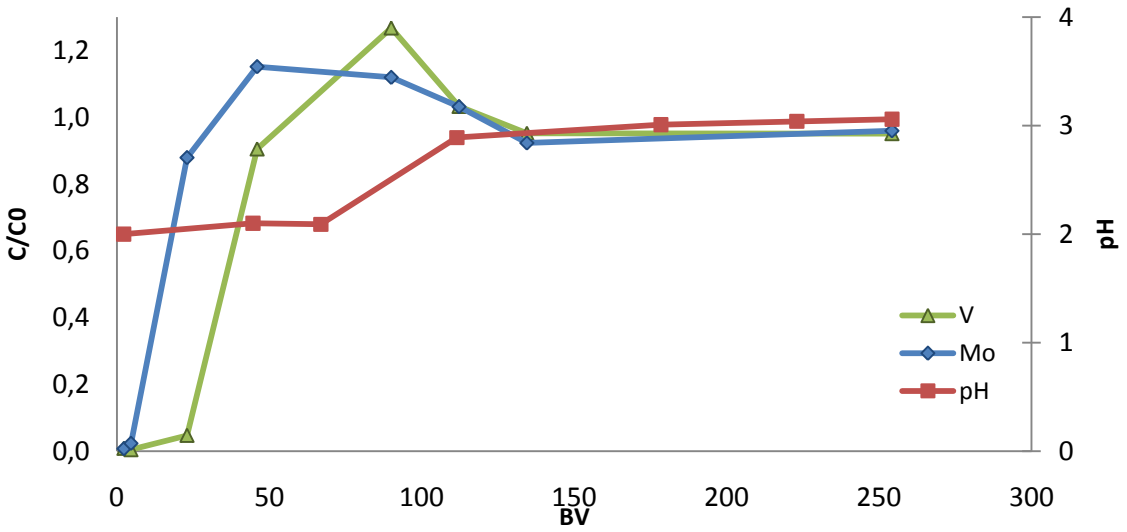

Figure 26: *Graphic representation of the sorption of Mo (VI) + V (V) onto Lewatit S 100*

Mo and V had a rapid breakthrough from the column, although some small amount of both was retained.

From the results it can be notice that a competitive sorption took place which is perceptible by the C/Co values that are higher than 1, suggesting that both Mo and V were sorbed and then eluted from the resin by other cationic species, making their outlet concentration higher than the inlet one.

Regarding the ion exchange mechanism, as Na^+ is present in the solution his sorption on the resin took place:

$$-SO_3^-H^+ + Na^+ \rightarrow -SO_3^-Na^+ + H^+ \quad (15)$$

With the decrease of pH in the solution, Mo (VI) and V (V) cations, such as MoO_2^{2+} and VO_2^+, can exist in small amounts in equilibrium with anions as it is illustrated in ***Figures 2*** and ***3*** in the speciation diagrams. At low pH this species exit in aqueous solutions. And as the cationic species are presents their sorption started. The amount of Mo and V cations in solution

is probably correspondent to the amount of Mo and V that was captured in the resin, explaining the small amount of these compounds that was retained.

Since MoO_2^{2+} is highly charged than VO_2^+, Mo cations should elute V cations from the resin and be preferentially sorbed. According to this mechanism, the first compound to breakthrough the column should have been V and the last one should be Mo.

In the obtained results, that did not happen. Mo was the first compound to be eluted, followed by V and even though the Na concentrations were not measured, it seems that Na was the last compound to breakthrough the column because both Mo and V reached C/C0 values higher than 1 and that is only possible if the compounds were sorbed and then eluted by other species. The Na concentration in the effluent solution should have been measured for a better comprehension of this specific sorption behavior.

A possible justification for these results is that V cations, which are easier formed than Mo cations, are in higher concentration in solution and that is way they breakthrough from the column later than Mo cations.

Another possible explanation is that Mo is not present in the aqueous solution as a double-charged but a single-charged cation, since V eluted Mo and is not possible that a 1+ cation substitutes a 2+ cation in ion exchanger.

However, the results cannot be completely understood and further experiments must be performed for a clearer knowledge of Mo (VI) and V (V) speciation in aqueous solutions and their sorption behaviour.

The regeneration of the column was made using 1 M HCl in a total of 10 BV, was washed with water with 20 BV followed by a final wash with 1 M NaOH at 10 BV/h for one hour.

The results of the regeneration are illustrated in the ***Figure 29:***

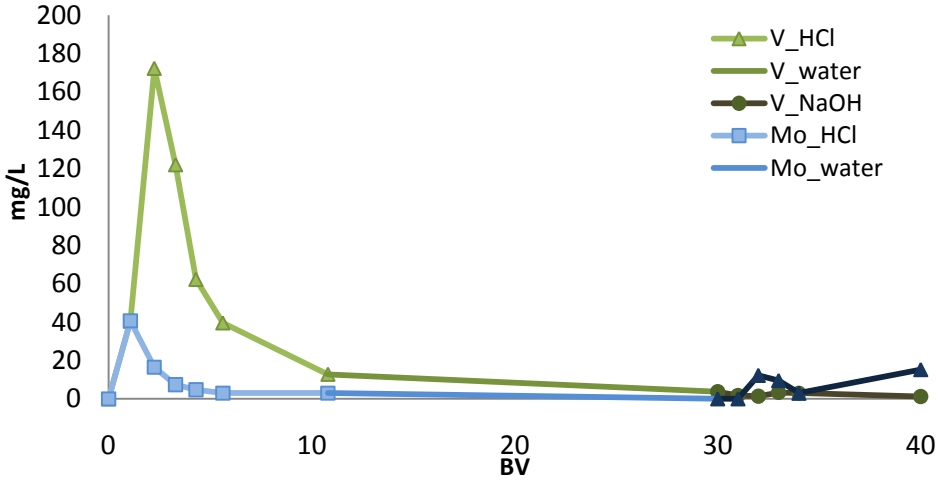

Figure 27: *Graphic representation of the desorption of Mo(VI) + V(V) onto Lewatit S 100*

Almost all V was stripped from the column using HCl, just a residual amount was washed with NaOH. The regeneration efficiency was 127.08%

Regarding Mo desorption, more than 40% of Mo was stripped out the column with HCl and the resting Mo was washed with NaOH. Mo was completely removed from the resin.

The regeneration efficiency was 124.83%.

The efficiencies are higher than 100% because the amount of Mo and V that was sorbed cannot be correctly calculated. Given that the outlet solutions had higher concentrations than the inlet solution, the amount of metal sorbed in some samples was negative and thus the amount of metal sorbed in lower than the one that was desorbed which bring us to these efficiency results.

4.2.2 Molybdenum and Vanadium reduced

The same equimolar solution of Mo and V used in the previous experiment was fed to the electrolyzer at a flow rate of 100mL/min during 24 hours at a potential of -1.50 V vs. Ag/AgCl reference electrode. The solution turned out green due to the amber color of reduced Mo (V) and the greenish blue color of reduced V (IV). This solution was afterward fed to the column with *Lewatit S 100* and the experimental results regarding Mo and V retention are demonstrated on the ***Figure 30***:

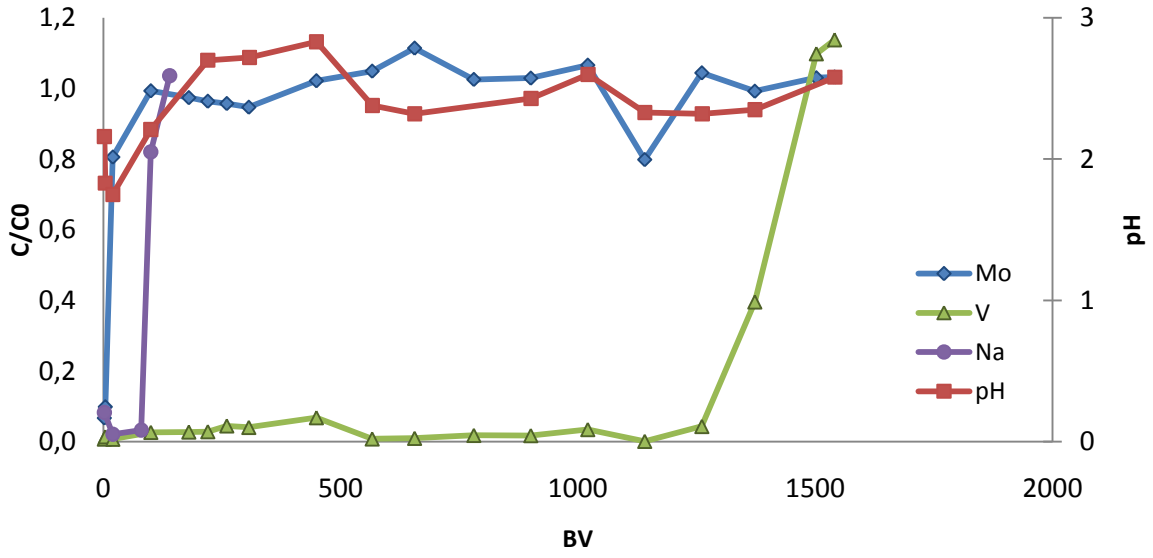

Figure 28: *Graphic representation of the sorption of Mo(V) + V(IV) onto Lewatit S 100*

Observing the ***Figure 30*** is possible to see that Mo (V) breakthrough instantly from the column while V (IV) was completely retained in the column until 1200 BV.V (IV) specie is VO^{2+}; hence it is captured by the cationic exchanger resin, according to the following mechanism:

$$(-SO_3^-H^+)_2 + VO^{2+} \rightarrow (-SO_3^-)_2VO^{2+} + 2H^+ \quad (16)$$

These results represent a remarkable separation of Mo from V and therefore the principal aim of this work was fulfilled.

The regeneration proceeded with a 1 M HCl solution fed with a flow rate of 10 BV/h during 1.5 hours. The history of the column regeneration is described in the ***Figure 31:***

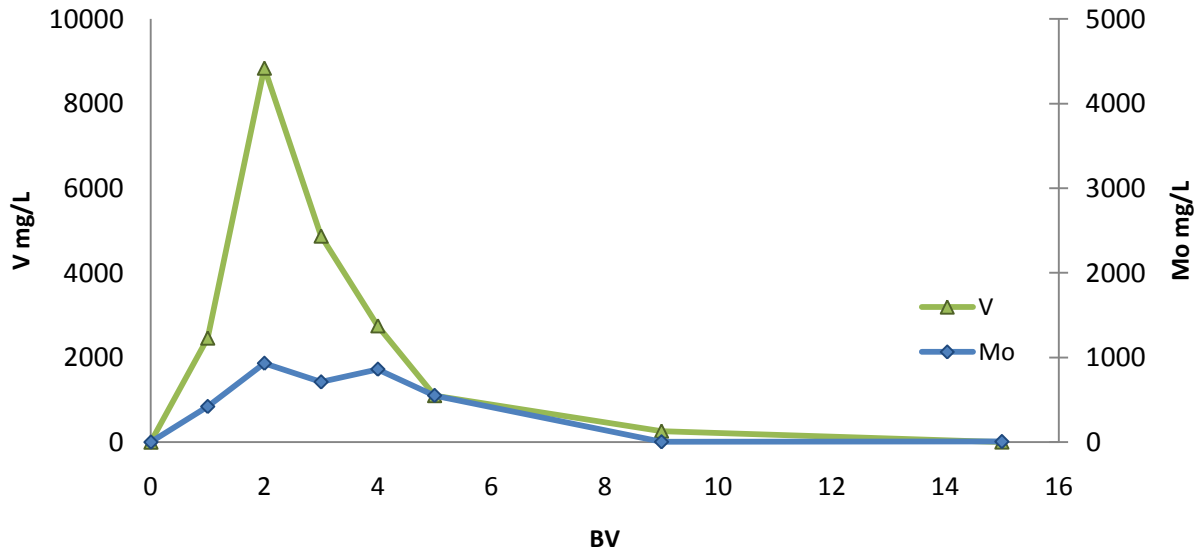

Figure 29: *Graphic representation of the desorption of Mo (V) + V(IV) onto Lewatit S 100*

Mo and V are desorpted with HCl and the regeneration efficiency was 81.60 % for V. The breakthrough capacity of this resin is 23.161 $g_V/L_{sorbent}$ which corresponds to 0.454 $mol_V/L_{sorbent}$

5 Conclusions

About the reduction of Mo (V) , which can be seen in ***Annex A***, is possible to say that Mo (V) can be successfully and totally reduced to Mo (V) using a potential of -1.5 V vs. Ag/AgCl reference electrode. V (V), which was a yellow solution, also successfully reduced to V (IV), which was a greenish blue solution.

Mo (VI) was also completely reduced to Mo (V/VI) blue, using a potential of -0.25 V vs. Ag/AgCl.

During the reduction, Mo concentration decreased nearly 50% due to Mo sorption in the carbon felt cathode of the electrolyzer.

In reduced Mo sorption a chelating resin, *Purolite D 4123*, was used since good results regarding the sorption of metal oxoanions and their selective separation from bimetallic solutions were reported.

Wanting to find the optimal pH for the complex formation between Mo (V) and the resin functional group batch experiments were made, since selective sorbents have sorption efficiency dependent of pH. The ph range 2.0-3.0 was found to be optimal.

Regarding sorption results, Mo (V) was partially retained onto *Purolite D 4123* in the protonated form.

Mo (V/VI) was partially captured by the resin in both protonated and free-base form and it was found that the inlet solution, which was at pH 3, protonized the resin in free-base form in the first BV.

After these results it is possible to conclude that *Purolite D 4123* is not suitable for the separation of Mo from V using electrochemical reduction, since all the reduced form of Mo were only partially taken up by the resin.

A strongly acid cationic exchanger, *Lewatit S100*, was used to perform Mo (V) sorption.

Although Mo (V) is referred in the literature as a cation in aqueous solutions at pH 3 and 1 mM concentrations, it was not taken up by the cation exchanger, breaking through from the column immediately.

These last results, in which Mo(V) was not sorbed and the fact that is known from a previous work that V(V) was well taken up by this cation exchanger lead to the next experiment, to try Mo and V equimolar solutions sorption in the cation exchanger.

Mo (VI) and V (V) non-reduced equimolar solution was fed to a column with *Lewatit S100* and both compounds breakthrough rapidly from the column. Nevertheless, a small amount of both metals was taken up by the resin in the first BV's.

A possible explanation is that even though Mo (V) and V (IV) predominant species are anions, some cationic species can be found in small amounts in equilibrium with anionic species, and therefore this cationic species were the ones that were captures in the resin.

The results also suggested that a competitive sorption took place, because the C/C0 values were higher than 1, meaning that the outlet concentrations of the metals were higher than the inlet concentration, which happen when the species are retained in the resin and then are eluted by other species. It could be possible that Mo cations which are reported to be MoO_2^{2+} could elute V cations, VO_2^+, and so V would be the first one to breakthrough the column followed by Mo. That did not happened, Mo was the first one to breakthought the column followed by V and it is not possible that a 1+ cation can be able to elute a 2+ cation. These results suggest that Mo (V) cations in solutions are not double-charged but single-charged.

A reduced equimolar solution of Mo (V) and V (IV) using a potential of -1.5 V vs. Ag/AgCl was used to perform a sorption onto *Lewatit S100* and V was completely retained onto the resin and Mo broke through the column immediately, not being retained. Therefore the complete separation of Mo and V reduced forms was obtained and the BC for V was 0.454 mol $_V/L_{resin}$

6 Work Assessments

6.1 Aims accomplished

The objective of this project was to use electrochemical reduction and ion exchange methods to separate Mo from V in aqueous solution.

The objectives were fulfilled, it was found that electrochemical reduction of these metals was possible and their sorption properties changed along with the oxidation state changes.

It was also found that a strongly acid cation exchanger resin, *Lewatit S100*, was suitable for the separation of the electrochemically reduced Mo and V and their separation was successful and complete.

6.2 Limitations and further work

One of the major problems that I found was the lack of initial accompaniment by the supervisors of this project. The information needed to realize this project was not clearly given and the initial rhythm of the work was slow. Only after a few months since the beginning of this project the work ran faster and some results' discussion took place.

Other problem that occurred during the realization of this project was that it was never done before, so what was planned to do in the beginning changed several times during the 5 months that I spent in the laboratory.

As a suggestion about further development in this work, I believe that it should focus on study the speciation of Mo in aqueous solutions. It is reported in the literature that Mo(V), in the operational conditions of this work, is a cationic specie and the results of this work suggest that it is an anion, so it would be interesting to have more accurate information in this matter.

6.3 Final appreciation

Several contingencies regarding the development of this project were particular.

The fact that it was performed on a foreign country and the difficulties that I overturned demanded more determination and obstinacy, but I believe it was beneficial for me, both personally and academically. I believe it became a good project and that I put all my effort to finish it in the best way.

References

1. http://www.imoa.com. *International Molybdenum Association.*Aceded in April 2009

2. **Cotton, F. A. and Wilkinson, G.** *Advanced inorganic chemistry.* Wiley-Interscience, USA , 1988.

3. **Morrison, S.J. and Spangler, R.R**. *Extraction of Uranium and Molybdenum from Aqueous Solutions: A Survey of Industrial Materials for Use in Chemical Barriers for Uranium Mill Tailings Remediation.*, Environmental Science and Technology , Vol. 26, pp. 1922-1931, 1992

4. **Naeem, A., Westerhoff, P. and Mustafa, S.** *Vanadium removal by metal (hydr)oxide adsorbents,* Water Research , Vol. 41, pp. 1596 – 1602, 2007

5. **Ďurišová, J. and Jelínek, L.** *Separation of V and W from Aqueous Solutions by Combination of Electrolysis and Ion Exchange*.Topical Issues of Rational Use of Natural Resources , St.Petersburg , 2009.

6. **Jezowska-Trzebiatowska, Boguslawa**. *The rare Elements ocurrence and technology.* Polish Scientific Publishers, Wroclaw,Poland, 1990.

7. **Kononova, O.N., Kholmogorov, A.G and Kachin, S.V.***Ion exchange recovery of molybdenum from nitric acidic solutions using macroporous anion exchangers with long-chained cross-linking agents.* Hydrometallurgy, Vol. 68, pp. 83–87, 2003 .

8. **Tkac, P. and Paulenova, A.** *Speciation of Molybdenum (VI) In Aqueous and Organic Phases of Selected Extraction Systems.* Separation Science and Technology, Vol. 43, pp. 2641–2657, 2008.

9. **Baes, C. F. and Mesmer, R.E.** *The Hydrolysis of Cations.* Wiley, New York, 1976.

10. **Guibal, E., Milot, C. and Tobin, J.M.** *Metal-Anion Sorption by Chitosan Beads: Equilibrium and Kinetic studies.* Ind. Eng. Chem. Res., pp. 1454-1463, 1998.

11. **Navarro, R., et al.** *Recovery of Metal Ions by Chitosan: Sorption Mechanisms and Influence of Metal Speciation*Macromolecular Bioscience, Vol. 3, pp. 552–561,2003.

12. **Namasivayam, C. and Sangeetha, D.** *Removal of molybdate from water by adsorption onto $ZnCl_2$ activated coir pith carbon*Bioresource Technology , pp. 1194–1200, 2006.

13. **Guzmán, J., et al.** *Vanadium Interactions with Chitosan: Influence of Polymer Protonation and Metal Speciation.* Langmuir, Vol. 18, pp. 1567-1573 , 2002.

14. **Jansson-Charrier, M., et al.** *Vanadium (IV) Sorption by Chitosan: Kinetics and Equilibrium.* Water Resources , Vol. 30, pp. 465-475, 1996.

15. **Ghosh, M. C. and Gould, E. S.** *Electron Transfer. 101. Reaction of Carboxylato-Bound Chromium(V) with Dimeric Molybdenum(V).* American Chemical Society, Vol. 30, pp. 483-487, 1991.

16. **Helm, L.; Pitte, P-A.; Merbach;A. E.** *Structural Elucidation of Oligomeric Aqua-molybdenum Cations in Solution by 0 NMR.* Inorganica Chimica Acta,, Vol. 132, pp. 85-89, 1987.

17. **Charney, L.M. and Schultz, F.A.** *Electrochemistry of Aqueous Molybdenum(VI), -(V), and -(III) Catechol Complexes.Dimerization of Molybdenum(V) in Weakly Acidic Solution.* Inorganic Chemistry, Vol. 19, pp. 1527-1532, 1980.

18. **Marafi, M. and Stanislaus, A.** *Spent hydroprocessing catalyst management: A review Part II. Advances in metal recovery and safe disposal methods.* Resources, Conservation and Recycling , Vol. 53, pp. 1–26,2008.

19. **Yusuf, M., et al.** *Separation and Determination of Selenium(IV) and Molybdenum(VI) in Mixtures by Selective Precipitation with Potassium Thiocarbonate.* Talanta, Vol. 35, pp. 496-498,1988.

20. . **Parks, J.L. and Edwards, M.** *Precipitative removal of As, Ba, B, Cr, Sr, and V using sodium carbonate* . Journal of Environmental Engineering, Vol. 132, pp. 489-496, 2006.

21. **Lortie, R. and Klvana, D.** *Selective Recovery of Vanadium from Effluent of a Plant Producing Titanium Dioxide.* Canadian Journal of Chemical Engineering, Vol. 61, pp. 833-841, 1983 .

22. **Chen, Y., et al.** *Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst.* International Journal of Mineral Processing , Vol. 79 , pp. 42– 48, . 2006.

23. **Morís, M.A., Díez, F.V. and Coca, J.** *Solvent extraction of molybdenum and tungsten by Alamine 336 and DEHPA in a rotating disc contactor.* Separation and Purification Technology , Vol. 17, pp. 173–179, 1999.

24. **Gerhardt, N.I., et al.** *Solvent extraction of molybdenum (VI), tungsten (VI) and rhenium(VII by diisododecylamine from leach liquors.* Hydrometallurgy , Vol. 60, pp. 1–5, 2001.

25. **Komasawa, I., Hosoba, H. and Otake, T.** *Solvent Extraction Process for Separation and Purification of Molybdenum and Vanadium by Tri-n-Butyl Phosphatein Xylene.* Journal of Chemical Engineering of Japan, 1987.

26. **Zhao, Y.-C., Zouboulis, A.I. and Marls, K.A.** *Flotation of molybdate oxyanions from dilute solutions Part II. Selective separation from phosphates, arsenates and silicates.* Hydrometallurgy , Vol. 43 , pp. 155-167, 1996.

27. **Skyrlev, L.D., Pavlenko, S.N. and Sazonova, V.F.** *Separation of Molybdenum and Tungsten by Ionic Flotation.* Izvestiya Vysshikh Uchebnykh Zavedenij, Vol. 1, pp. 28-32, 1986.

28. **Akl, M.A., El-Asmy, A.A. and Yossef, W.M.***Separation via Flotation Spectrophotometric speciation, and Determination of Vanadium in Wastes of Power Stations.* The Japan Society of Analytical Chemistry, Vol. 21, pp. 1325-1336, 2005.

29. **Bostick, B.C., Fendorf, S. and Helz, G.R.** *Differencial adsorption of molybdate and tetrathiomolybdateon pyrite (feS2).* Environmental Science and technology, pp. 285-291, 2003.

30. **Wu, H.-C, Lo, L.-S and Lin, F.-C.** *Competitive adsorption of molybdadte, chromat, sulfate, selenate and selenite on* Al_2O_3. Colloids and Surfaces A: Physicochemical and Engineering Aspects, pp. 251-259, 2000.

31. **Xu, N., Christodoulatos, C. and Braida, W.** *Modeling the competitive effect of phosphate, sulfate, silicate,and tungstate anions on the adsorption of molybdate onto goethite.* Chemosphere, pp. 1325–1333, 2006.

32. **Mištová, E., Parschová, H. and Matjka, Z.** *Selective Sorption of Metal Oxoanions from Dilute Solution by Bead Cellulose Sorbent.* Separation Science and Technology, pp. 1231–1243, 2007.

33. **Mištová, E., et al.** *Selective Sorption of Metal Oxoanions from Dilute Solution by Chemicaly Modified Brown Seaweed Ascophyllum Nodosum.* Separation Science and Technology, pp. 3168–3182, 2008.

34. **Peinemann, N. and Helmy, A.K.** *Molybdate sorption by hydroxy-aluminium treated montmorillonite.* Applied Clay Science, pp. 389-396, 1994.

35. **Manohar, D. M., Noeline, B. F. and Anirudhanand, T. S.** *Removal of Vanadium (IV) from Aqueous Solutions by Adsorption Process with Aluminum-Pillared Bentonite.* Ind. Eng. Chem. Res., pp. 6676-6684, 2005.

36. **Afkhami, A., Madrakian, T. and Azadeh ,A. A.** *Mo(VI) and W(VI) removal from water samples by acid-treated high area carbon cloth.* Desalination, pp.258–264, 2009.

37. **Daborowski, A., et al.** *Selective Removal of the heavy metals ions from watres and industrial waste waters by ion-exchange methods.*Chemosphere, pp. 91–106, 2004.

38. **Atia, A.A.;Donia, A.M.;Haytham A.and Awed, H.A.** *Synthesis of magnetic chelating resins functionalized with tetraethylenepentamine for adsorption of molybdate anions from aqueous solutions.* Journal of Hazardous Materials , Vol. 155 , pp. 100–108, 2008 .

39. **Parschová, H., Matějka, Z. and Mištova, E.** *Mutual Separation of (W,As,Mo,V,Ge;B) Oxoanions from Bi-metallic Solution by Resin having Methyl-Amino-Glucitol.* Separation Science and Technology, Vol. 43, pp. 1208-1220, 2008.

40. **Zeng, L. and Cheng, C.Y.** *A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts Part II: Separation and purification and references within.* Hydrometallurgy, 2009.

41. **Hu, J., et al.** *Removal of Vanadium from Molybdate Solution by Iion Exchange.* Hydrometallurgy , Vol. 95, pp. 203–206, 2009.

42. **Henry, P. and Van Lierde, A.** *Selective Separation of Vanadium from Molybdenum by electrochemical Ion exchange.* Hidrometallurgy, Vol. 48, pp. 73-81, 1998.

43. **Schilde, U., Kraudelt, H. and Uhlemann, E.** *Separation of the oxoanions of germanium, tin, arsenic,antimony, tellurium, molybdenum and tungsten with a special chelating resin containing methylaminoglucitol groups.* Reactive Polymers, Vol. 22, pp. 101-106, 1994.

44. **Treadwell, W.D. and Schaeppi,Y.** *Helvetica Chimica Acta,* Vol. 29(IV), pp. 771, 1946.

7 Annex A :Reduction of Molybdenum

One liter of the initial solution containing 1 mmol/L of Mo, 10 mmol/L of Na_2SO_4 at pH 3 was continuously fed to the electrolyzer at a flow rate of 100 mL/min during 24 hours. The potential used to reduce Mo was -1.5 V vs. Ag/AgCl. The obtained solution was yellow. To study if the reduced solution corresponded to Mo (V) titrations experiments were made.

A solution of 0.005 M $KMnO_4$ was used to titrate Mo, but first it became necessary to find the exact concentration of $KMnO_4$. For that, a solution of $Fe(NH_4)_2(SO_4)_2$ was titrated with $KMnO_4$ and the Fe concentration was measured in the AAS. The results obtained by AAS are demonstrated in the ***Table 1***:

Table 1*:Fe concentrations by AAS*

Sample	Fe (mg/L)
1	47.579
2	47.109
3	47.773
Average	47.487

The reaction that occurs in the titration of $KMnO_4$ and $Fe(NH_4)_2(SO_4)_2$ is the following:

$$KMnO_4 + 8\,H^+ + 5\,Fe(NH_4)_2(SO_4)_2 \rightarrow K^+ + Mn^{2+} + 5Fe^{3+} + 10SO_4 + 10NH_4^+ + 4H_2O \qquad (4)$$

Therefore, it is possible to know the exact concentration of $KMnO_4$ after knowing the exact concentration of Fe by the equation (5):

$$[KMnO_4]\left(\frac{mol}{L}\right) = \frac{[Fe]_{AAS}\left(\frac{g}{L}\right)}{M_{Fe}\left(\frac{g}{mol}\right)} \times \frac{V_{sol}\,(L)}{n \times \overline{EP}\,(L)} \qquad (5)$$

In which $[KMnO_4]$ is the concentration of $KMnO_4$, $[Fe]_{AAS}$ is the concentration of Fe determined by the AAS, M_{Fe} is the molecular weight of Fe which is 55.845 $\frac{g}{mol}$, V_{sol} is the

volume of the Fe solution used in the titration, n is the $\frac{Fe\ mol}{KMnO_4\ mol}$ ratio in the reaction which is 5 and $\overline{EP}$ is the average of the equivalence points obtained during the titration experiments.

Before performing the titration with Fe, a blank test with distilled water was executed and the results from this experiment are presented in ***Table 2***:

***Table 2**: Volume of $KMnO_4$ spent to reach equivalence point with distilled water*

Experiment	EP (mL)
1	0.011
2	0.008
3	0.010
Average	0.010

The average volume of 0.010 mL will be subtracted to every equivalence points to correct them.

The titration with Fe was then performed and the results are illustrated in ***Table 3:***

***Table 3:** Volume of $KMnO_4$ spent to reach equivalence point with $Fe(NH_4)_2(SO_4)_2$ solution*

Experiment	EP (mL) corrected
1	0.973
2	0.971
3	0.974
Average	0.973

With the corrected average volume of $KMnO_4$ needed to reach the equilibrium point with Fe and using the equation (6) the exact concentration of $KMnO_4$ was calculated:

$$[KMnO_4]\left(\frac{mol}{L}\right) = \frac{0.0475\left(\frac{g}{L}\right)}{55.845\left(\frac{g}{mol}\right)} \times \frac{0.025(L)}{5 \times 9.73 \times 10^{-4}\ (L)} = 0.00437 \quad (6)$$

Afterwards, the titration with the reduced solutions of Mo used in the column experiences was performed and the following reaction took place:

(7)

$$MnO_4^- + 5Mo(V)^+ \rightarrow Mn^{2+} + 5Mo(VI)$$

The Mo concentration in the solutions was measured by ICP-OES to compare with the titration results and see which percentage of Mo was in the pentavalent form. The titration results are presented in the ***Table 4*:**

Table 4: Volume of $KMnO_4$ spent to reach equivalence point with Mo solution

EP (mL) corrected
0.438

With the present results is possible to exact concentration of Mo(V) in the solution by the equation (8):

$$[Mo(V)]\left(\frac{mol}{L}\right) = \frac{x \times \overline{EP}\ (L)}{V_{sol}\,(L)} \times [KMnO_4]\left(\frac{mol}{L}\right) \quad (8)$$

In which $[Mo(V)]$ is the concentration of Mo (V), $[KMnO_4]$ is the concentration of $KMnO_4$, V_{sol} is the volume of the Mo solution used in the titration, x is the $\frac{Mo\ mol}{KMnO_4\ mol}$ ratio in the reaction which is 5 and $\overline{EP}$ is the average of the equivalence points obtained during the titration experiments.

Knowing the volume of $KMnO_4$ necessary to reach the equilibrium point with Mo and using the equation (8) the exact concentration of Mo (V) in each solution was calculated:

$$[Mo(V)]\left(\frac{mol}{L}\right) = \frac{5 \times 4.38 \times 10^{-4}(L)}{0.025(L)} \times 0.00437\left(\frac{mol}{L}\right) = 3.846 \times 10^{-4} \quad (9)$$

The comparison between the concentrations of Mo measured by ICP-OES and the concentrations of Mo (V) measured by titration are in ***Table 5:***

Table 5*: Comparison between Mo concentrations given by ICP-OES and calculated by titration results*

$[Mo]_{ICP\text{-}OES}$ (mol/L)	$[Mo(V)]_{titration}$ (mol/L)	% Mo(V) in solution
3.54×10^{-4}	3.846×10^{-4}	92.2

After these results it was assumed that all Mo in a solution reduced at -1.50 V vs. Ag/AgCl in the laboratory electrolyzer was pentavalent Mo.

Another titration experiment was made to study the progress of the electroredution. The same inlet solution was fed to the electrolyzer at 100mL/min and samples were taken at different times. These samples were both titrated with $KMnO_4$ and measured in the ICP-OES and the amount of Mo (V) in each one was calculated and compared as in the previous experiment.

The results are presented in the ***Table 6***:

***Table 6**: Time in which samples were taken, equivalence points, Mo concentrations given by ICP-OES, percentage of Mo(V) in solutions and their colors.*

Time	hours	EP (ml)	[$Mo_{ICP-OES}$](mmol/L)	% Mo(V)	color
0 min	0	0.007	0.988	0	colourless
10 min	0.167	0.020	0.966	1.18	Light blue
30 min	0.5	0.157	0.856	15.38	cyan blue
1 hr	1	0.322	0.724	38.18	blue-green
1 hr 40 min	1.67	0.484	0.619	67.64	green
2 hrs 30 min	2.5	0.559	0.514	94.32	yellow-green
5 hrs 20 min	5.33	0.520	0.452	99.57	amber yellow

The samples were taken after the electroredution start at the times mentioned in the first column, they were titrated and the volume of $KMnO_4$ spent to reach the equilibrium point are presented in the third column, the ICP-OES concentration measurements are demonstrated in the fourth column, the amount of Mo (V) in the solutions is represented in the fifth column and the color history of the solution is illustrated in the last column.

The graphic representation of the reduction history can be analyzed in the ***Figure 12:***

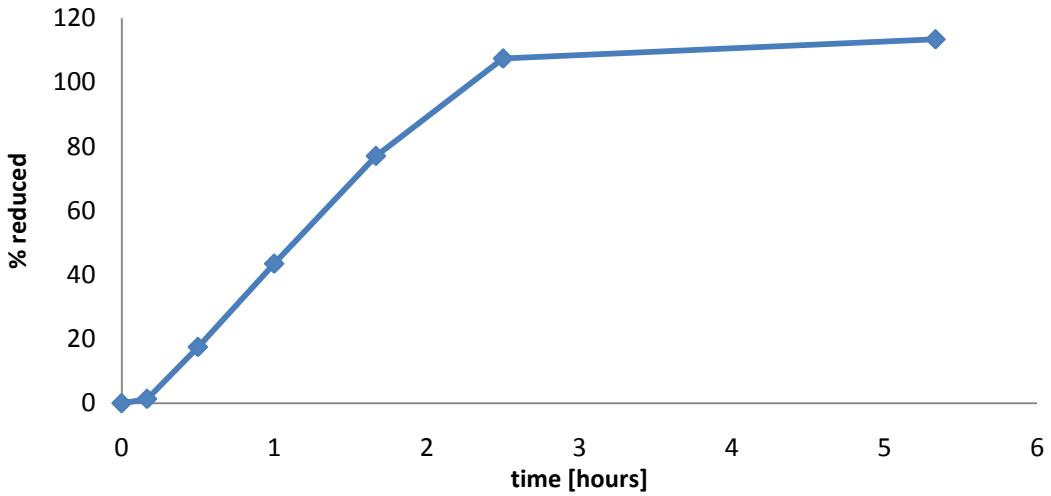

***Figure 30**: Percentage of reduced Mo as a function of time*

After 5 hours in the electrolyzer, the entire Mo in the solution was present as pentavalent Mo, confirming the previous results obtained in the titration of the same initial solution after 24 hours in the electrolyzer. Using the potencial of -1.5 V vs. Ag/AgCl reference electrode Mo(VI) is reduced gradually to blue Mo, refered as a mixture of Mo(V) and Mo(VI) and then to Mo(V).Using a lower potencial of -0.25 V vs. Ag/AgCl the redution stops when blue Mo (V/VI) is reached.

The Mo concentrations in the solution as a function of time are demonstrated in the ***Figure 13:***

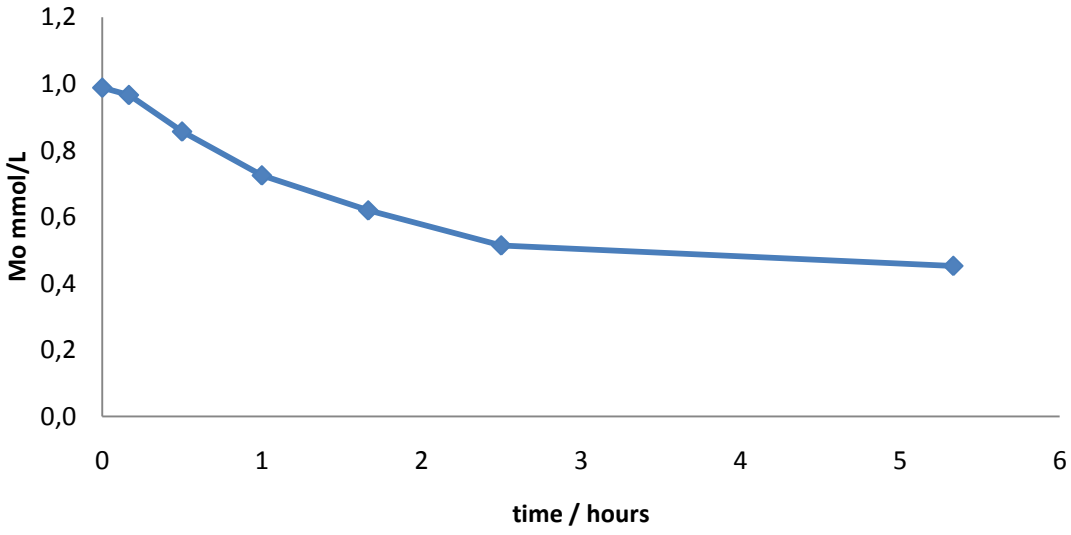

***Figure 31**: Concentration of Mo as a function of time*

After 5 hours the total concentration of Mo decreased 50%.It is owed to Mo adsorption occurring in the carbon felt cathode of the electrolyzer.