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SORPTION PROPERTIES OF LITHIUM IONS ON STRONG ACID CATION EXCHANGES

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Sorption properties of lithium ions on strong acid cation exchanges

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ABSTRACT

Lithium is the lightest solid element. It is a value element because it has presence in huge range of areas, from nuclear industry till medicine. Lithium applications are increasing and, consequently, its demand.

Lithium waste is an important issue. Lithium recovering from exit industrial liquids is very useful in order to reuse this element. One way to remove the valuable lithium ions from the liquid solution is using ion exchangers.

Ion exchange is a reversible process. Lithium ions are fixed in the resin beads and then they are able to be exchanged from the resin beads to other solution.

This project studies this lithium ion exchange on strong acid cation exchangers. Three types of strong acid cation exchangers were used but, finally, only one of them was suitable.

A column was filled with 40 mL of resin. After that, lithium solution went through the column and lithium ions were fixed in the resin beads. Ammonium chloride solutions of different concentration went through the column in order to remove lithium from the resin beads. Finally, lithium concentration was measured from eluate of the column along the time.

After six experiments some conclusions were evidences. The resin used is able to remove high concentration of lithium. The process speed is controlled by mass transfer (ion diffusion). Moreover, some mass transfer problems appear when the concentration is low (below 0.5M).

RESUMEN

El Litio es el elemento sólido más ligero en la Tierra. Es un elemento valioso porque está presente en un amplio abanico de áreas, desde la industria nuclear hasta el campo de la medicina. Además, las aplicaciones de este elemento siguen aumentando y, como consecuencia, también se incrementa su demanda.

Evitar el desaprovechamiento de Litio es posible y por eso se impulsa la recuperación de Litio de las corrientes industriales de desecho. Una forma de hacerlo es realizar un proceso de intercambio iónico.

El intercambio iónico es un proceso reversible que permite que los iones de Litio se fijen en una resina iónica. Posteriormente, estos iones pueden ser transferidos a otra corriente siguiendo el mismo proceso.

Este proyecto estudia el intercambio iónico de Litio en resinas catiónicas de ácido fuerte. Se prepararon tres tipos de estas resinas pero, finalmente, solo una de ellas fue adecuada.

Los experimentos se llevaron a cabo en una columna con 40mL de resina. Una corriente de Litio de concentración conocida pasa a través de la resina permitiendo el intercambio de iones entre la resina y la disolución. Después, los iones de Litio son recuperados mediante una disolución de cloruro de amonio de distintas concentraciones. Finalmente, se mide la concentración de Litio en la corriente de salida de la columna a lo largo del tiempo.

Tras seis experimentos se pueden extraer las siguientes conclusiones. La resina empleada es capaz de eliminar completamente el Litio de la corriente. La cinética del proceso depende de la transferencia de materia. Además, se detectan problemas en la transferencia de materia cuando la concentración es demasiado baja (por debajo de 0.5M).

Ending this project supposes the ending of a beautiful stage of my life. Doing it in a foreign country was a challenge, both academic and personal, and I am proud of doing it successfully.

It could not have been possible without my family. I specially want to thank to my mother who has always been a model for me.

I also want to thank to Ludek Jelinek and Gloria Gea, for helping me along this experience, as well as all people in the laboratory.

Finally, I would like to mention to my friends, especially friends that I met in Prague. This experience would not have been unforgettable without them.

Terminar este proyecto supone el fin de una bonita etapa de mi vida. El hecho de realizarlo en otro país supuso un reto no solo académico sino también personal que me enorgullece haber superado con éxito.

Esto no habría sido posible sin el apoyo de mi familia que, aunque en la distancia, siempre ha estado presente. Especialmente agradecer a mi madre que para mí ella siempre ha sido un ejemplo a seguir.

Agradecer también a Ludek Jelinek y Gloria Gea por acogerme y ayudarme en esta etapa. Así como al resto de integrantes del laboratorio de investigación.

Finalmente, me gustaría mencionar a mis amigos. Especialmente a los conocidos durante esta estancia en Praga. Sin ellos esta experiencia no hubiera sido tan inolvidable.

CONTENTS

1 Introduction and project purpose

Lithium is a really valued metal. Its properties make this element unique and, in several cases, it is not able to be substituted [1].

Lithium compounds have always been used because of its huge application range. In late 1940s, it had a lot of applications. This fact grew up along time and lithium customs increase when further applications, like Li-ion batteries, ceramics or glass production, were developed [2],[3]. Nowadays, industries of chemistry, technology, battery manufacture and pharmacology uses lithium [4]. Even in medicine areas lithium is developed. This element is used in psychiatry, neurology, oncology, immunotherapy and other medicine areas [4]. However, lithium treatments have to be careful because this element is toxic and it can caused kidney problems; moreover it is bad for pregnant, children, etc [4].

Accord to [5], there are four types of lithium products. Technical products (such as lithium carbonate or lithium chloride) require only one or two process steps. Battery products which employs the same products than the first type but they need "*more rigorous feed and quality control*". Organolithium reagent, like butylithium or methylithium. Lithium metal and speciality products, for example lithium salts of high quality or lithium aluminium hydride. [5]

The major number of lithium applications suppose a higher lithium demand. This fact is shown in the higher lithium consumption. In early 1900s, the lithium consumption was less than 25 tonnes per year [3],[5]. This amount increased until being 28000 tonnes per year, in 2012 [5]. By 2014, the lithium consumption is 36000 tonnes per year [5]. Consequently, it is estimated that lithium industry grows 7% per year [5].

As a result, it is too important to get lithium. Apart from lithium mines, this metal has important presence in salt lakes, which have about 33 million tons of lithium, and seawater where lithium concentration is about 17 ppm but the quantity of element lithium is about 260 billion tons [1]. So, there are more and more researches about recovery lithium from seawater and salt lakes [1]. Furthermore, it is really interesting to recover lithium from processes which use this element. Lithium is able to be recovered from a solution through sorption in ion exchangers as it will be shown in this research. Recovery of lithium is an important issue for companies in order to save money and reduce waste. In this research, sorption of lithium ions on strong acid cation

exchangers is the first step in broader research about lithium isotope separation onto ion exchangers.

Future of lithium is still growing up. More applications will be developed, like secondary batteries (in electric cars) and nuclear fusion [3]. Natural lithium contains approximately 7.6% of ^{6}Li which is used to produce tritium fuel for nuclear fusion [6].

To sum up, lithium is a really important element in nature which is involved in huge amount of different areas. It has a high value and good properties so it is important recycling and recovering of this element at the same time that new ways of production are developed because lithium applications are still increasing.

2 Ion Exchangers

Ion exchange materials are insoluble materials (acids or bases), whose salts are also insoluble. They exchange their ions (anions or cations) with other ions in solutions in contact with them, without any physical alteration to the ion exchange material [7],[8]. In this situation, these ions are able to be exchanged for the same amount of other ions of the same sign. It is a stoichiometric process.[8]

This process is represented in the Fig 1 where the stoichiometric exchange of ion is shown. There are ions A inside a solution of ions B in the initial state. Then, some A ions are replaced by the same amount of B ions.

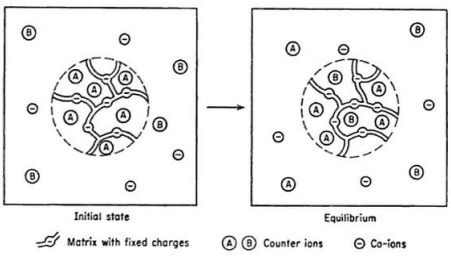

Fig 1. Representation of ion exchange process [8].

Little time after, the equilibrium take place and no more ions are replaced. The concentration ratio of the two different ions, however, is not the same in the equilibrium in both phases.

Ion exchangers are characterized by their capacity. This is the equivalents of ions they are able to exchange per gramme of ion exchanger. Capacity depends on the amount of ionic groups. [9]

According to the type of ions who are exchanged there are two types of ion exchangers, cation or anion exchangers. Both of them are also able to be strong or weak. In addition, there is another type of ion exchange which involves both previous types.

2.1 Cation exchangers

Ion exchangers are able to exchange positively charged ions. The fixed group (see section 3 and 4) has negative sign whereas the exchangeable ion has positive sign. As a result, one cation is replaced for a different cation.

2.1.1 Strong Acid Cation (SAC)

SAC exchanger contains sulfonic acid groups (HSO_3^-) or the corresponding salts. They can neutralize strong bases and convert neutral salts into their corresponding acids. Moreover, SAC exchangers are able to be used in all pH ranges.

2.1.2 Weak Acid Cation (WAC)

WAC contains carboxylic acid groups ($-COO^-$) or the corresponding salts. The ionization appears only at high pH values whereas at low pH values these ionic groups react with H^+ to form -COOH. They have high capacity of regeneration so, the amount of acid required to regenerate the resin is reduced and the acid waste is decreased too. For this reason, they minimize disposal problems.

2.2 Anion exchangers

Ion exchangers are able to exchange negatively charged ions. The fixed group (see section 3 and 4) is charged positively whereas the exchangeable ion is charge negatively. Consequently, an anion is replaced by a different anion in the resin.

2.2.1 Strong Base Anion (SBA)

SBA contains quaternary ammonium groups. There are two types. Type I (Fig 2) resins contain trialkyl ammonium chloride or hydroxide and type II resins (Fig 3) contain dialkyl 2-hidroxyethyl ammonium chloride or hydroxide, one of the methyl groups is replaced by an ethanol group.

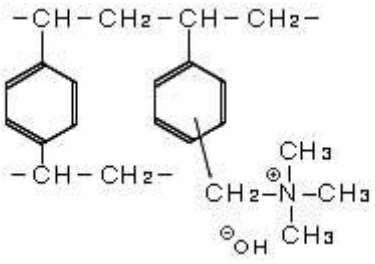

Fig 2. Strong Base Anion exchanger type I [10].

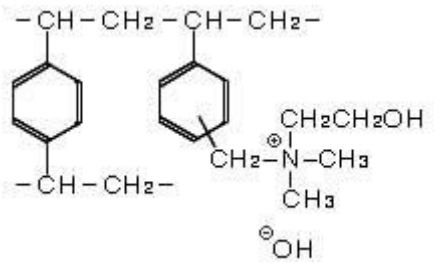

Fig 3. Strong Base Anion exchanger type II [10].

They can neutralize strong acids and convert neutral salts into their corresponding bases. Both of them are able to remain ionized even at high pH values.

Type I resin has more stability and can remove more of the weakly ionized acids whereas type II resin has better regeneration efficiency and greater capacity for the same amount of chemical regenerator used. [11]

2.2.2 Weak Base Anion (WBA)

WBA contains ammonium chloride or ammonium hydroxide. It is able to remove sulphur, nitric and hydrochloric acids. It works at low pH values. When pH is high, weak base groups, as $–NH_3^+$, loose a proton forming $–NH_2$. In consequence, an ion group is lost.

There are other types of resins called mixed bed resins, which have anion and cation exchange resins in a single vessel. This resin, which contains both anion and cation ions and both negatively and positively fixed group, is named as *amphoteric* ion exchanger.

Resins are able to be modified in order to improve their properties. For example, there are some resins which contain chelating agents to become more selective towards metallic ions. [12]

2.3 Types of ion exchangers

According to the material of the exchanger substance, it is possible to distinguish between natural and synthetic substances. Most important natural ion exchangers are ion exchange coals and mineral ion exchangers. However, the most common ion

exchangers are synthetic ones like ion exchange resins or synthetic inorganic ion exchangers.

All of them are based on electric surplus charge and mobile ions but there are some differences between the different types of ion exchangers.

There are other substances which have ion exchange properties like alumina, alginic acid or keratin. However, their importance as ion exchangers is very little. On the other hand, there are other substances which do not have ion exchange properties but they will be able to be ion exchangers through different chemical treatments. For example, pectin or paper.

2.3.1 Mineral ion exchangers

They are inorganic ion exchangers; they usually are crystalline aluminosilicates with cation exchange properties.

Zeolites are the most important mineral ion exchangers. They are formed by a lattice structure of SiO_4 and AlO_4 tetrahedra. This lattice carries a negative electric charge which attracts alkali cations. These cations do not occupy fixed positions; they are free to move inside the lattice. These cations in movement can be replaced by other cations.

Zeolites are not hard minerals and they have less open and more firm structure than other ion exchangers. Consequently, ions cannot move easily. Large cations are not be able to been exchanged because the pores size of zeolites are small and uniform. [8]

Other type of mineral ion exchangers is aluminosilicates. They have a layer structure where ions are carried between the layers. They can either act as cation exchangers like ferrous alumosilicates and as anion exchangers like apalite.

Inorganic ion exchangers have high thermal stability and resistance to radiation, even more than organic resins.

2.3.2 Synthetic inorganic ion exchangers

First synthetic inorganic ion exchangers pretend to be similar to natural zeolites. They were made through fusion of different components like soda, potash, feldspar... Its structure was more irregular than natural zeolites so it had to improve.

Later, other process was used. It consists in a precipitation with caustic following by drying of the gelatinous precipitate which finally has an irregular gel structure. Nowadays, it is possible to obtain a regular crystal structure using a hydrothermal method. This process is a high temperature crystallization of silica, alumina and alkali solutions. However, these substances are commonly used as sorbents and not usually as ion exchangers. There also are inorganic cation exchangers prepared by combination of group IV oxides with group V and VI oxides. [8]

They are really important because of its high stability at elevated temperatures even if the radiation is strong. [20]

2.3.3 Ion exchange coals

Many coals have weak acid groups like carboxylic. As a result they are natural ion exchangers. One of the inconvenient is their easy decomposition which can be solved stabilizing the coal before its use. Different types of coals are treated with different compounds in order to stabilize them.

Even the coals have carboxylic groups, they can be strong acid cation exchangers by sulfonation with fuming sulfuric acid. There are other activation methods and all of them get a gelation of the coal.

2.3.4 Ion exchange resins

See section 3.

2.3.5 Liquid ion exchangers

Despite most of conventional ion exchangers are insoluble solids, there are some liquids with ion exchange properties. These liquids are compounds with ionogenic groups which are dissolved in organic solvents as trichloroethylene or chloroform. They absorb very little water from aqueous solutions.

Their main applications are ion exchange with aqueous electrolytes and liquid-liquid extraction of electrolytes from aqueous solutions.

3 Ion exchange resins

Ion exchange resins are synthetic ion exchangers which consist in insoluble granular substances whose molecular structure has acid or basic radicals which are able to be exchanged. It consists in a matrix of irregular, macromolecular, three dimensional networks of hydrocarbon chains which has ionic radicals. The positive or negative ions fixed on these radicals are replaced by ions of the same sign located in the solution in contact with them. [13]

The matrix of the resins is hydrophobic and it can contain hydrophilic ionic groups. However, ion exchange resins are insoluble because several hydrocarbon chains are connected. There resin's structure is a flexible random network. The degree of crosslinking determines the thermal and mechanical stability and the ion exchange behaviour. This fact set the mobility of the ions in the resin. Hardly crosslinked resins are harder and has more mechanical resistance but ions has less mobility.

Ion exchange resins are able to suffer deterioration. Main causes are the presence of strong oxidizing or reducing agents and temperatures above 100ºC (except strong base anion exchange resins which start deteriorating over 60ºC).

Organic resins are the most important ion exchangers because they have high chemical and mechanical stability, high ion-exchange capacity and high exchange rates. Furthermore, the degree of crosslinking of the matrix can be selected depending on the applications of this resin.

Ion exchange capacity depends on the number of fixed ionic groups. The more ionic groups have, the higher ion exchange capacity has.

Ion exchange equilibrium depends on the chemical nature of the ionic groups. According to this fact, the classification done in these previous sections 2.1.1, 2.1.2, 2.2.1, 2.2.2 can be done.

Other type of classification is accord to beads resin's size:

- Microporous resins allow solute ions to diffuse through the particle to interact with exchange sites. This kind of resins are less fragile, react faster and possess higher loading capacities than macroporous ones. [12]
- Macroporous resins have high effective surface area so that, the ion exchange process is easier and more effective. Larger ions are able to be fixed easier than in

microporous resins. Furthermore, they are able to be used with almost any solvent and to take up the solvent with little or no change in volume. The beads are easier to be removed from the reaction system because they are more rigid than microporous ones. [12]

This resin feature is really important because the particle size distribution of the resin affect to the kinetics (velocity of reaction). Higher particle size has more superficial area and more ions are able to be exchanged. If the size is small, the superficial area is also smaller and there are less pores and their access is worse.

4 Ion exchange process

Ion exchange is a diffusion process. Usually, this process is selective; it means there are some ions in preference to others.

The process can be explained as follow. Spherical ion exchanger beads containing the ion A are located in a stirred solution of a compound BY which have ions B. The ion exchange happens when ions A diffuse from the beads to the solution and ions B diffuse from the solution to the beads. Both things happen simultaneously and ions B occupy the place left by ions A. So, it is a stoichiometric process as it is shown in section 2.

The equation of this process is shown in Eq. 1 where A and B are the ions with the same sign and Y has the opposite sign and it is located in the solution.

$$A + BY \leftrightarrow B + AY$$

Eq. 1

The BY compound has a matrix formed by a fixed part and a counter ion charged with opposite signs. The counter ion is the interchangeable ion (B in this case) and the fixed part is the functional group which is not exchangeable in the ion process, in this case is represented by Y part. When the counter ion is dissociated from the functional group and then leaves the resin, the functional group is charged with the opposite sign of the counter ion. The system is stabilized when different counter ion (A in this case) with the same charge occupies the place left by the B ion. At this moment, the ion exchange had taken place in the resin.

The most common way to carry out an ion exchange process is having a resin bed inside a column. [8] In this case, resin bed is fixed within the column and the solution with exchangeable ions is going through the resin beads (see Fig 4).

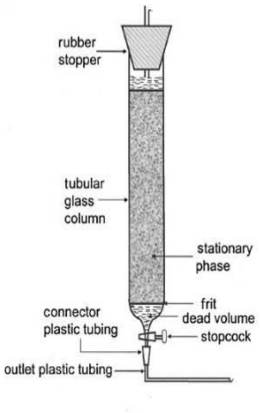

Fig 4. Ion exchange resin column [14].

The length of ion exchanger bed resin requires for the complete replacement of ions depends on the affinity of the ion exchange resin for the ion removed from solution. The higher the affinity is the shorter is the ion exchange resin bed needed for the process. [15]

There are some applications where ion exchange process is used to separate mixtures of substances that react similarly. In this case, the resin selectivity toward the mixture's components determines the separation grade.

This separation grade is measured by the equilibrium separation coefficient (α):

$$\alpha = \frac{y(1-x)}{(1-y)x}$$

Eq. 2

Where, y and x are equivalent fractions of one of the mixture components in the resin and solution phases, respectively [15],

The separation is higher when higher is the equilibrium separation coefficient. The coefficient has to be higher than 1 to be properly separated.

On the other hand, if the ion exchanger capacity is more effective, the investments on resin regeneration and the amount of waste will be reduced.

The ion exchange capacity of ion exchange materials is valued by the number of fixed charges which has to be compensated by counter ions. The more number of fixed

charges has to be compensated, the more capacity of the resin in an ion exchange process. This fact is easy to understand, if more fixed groups have to compensate their charge, more counter ions will be exchanged. Consequently, more ions are removed from the liquid phase and the efficiency of the process is better. This property is one of the most important properties of ion exchangers.[15],[16]

5 Regeneration process

Ion exchange is a reversible and discontinuous process. Consequently, the ions fixed in the functional group are able to be removed and the first counter ions are able to be restored. This is another ion exchange process where the first counter ions are in the solution and are exchangeable and fixed in the functional group of the ion exchanger.

This process is performed when the ion exchanger is exhausted. It means, there are not free functional groups, all of them are joined to ions from the solution. As a result, ions are not able to be exchanged from the solution and the ion exchange process is stopped. By this moment, the ion exchanger has to be regenerated and, after that, the ion exchange process will be able to go on.

There are two main ways to carry the regeneration process: co-flow regeneration and reverse flow regeneration.

5.1 Co-flow regeneration

The ionic solution and the regenerant solution go in the same way, from the top to the bottom of the column (see Fig 5).

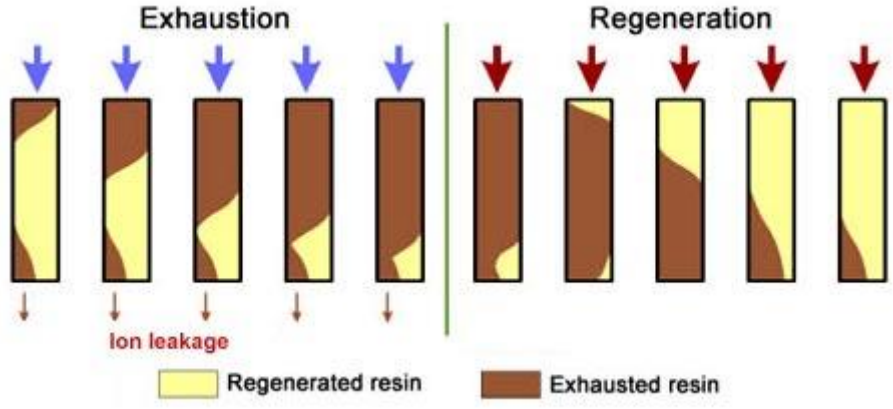

Fig 5. Co- flow regeneration process [17].

The main problem of this type of regeneration is that all ion exchanger is not regenerated, as it shown in Fig 5. In the end of the regeneration process, some ion exchanger particles are still exhausted. The ionic leakage is higher than reverse flow

regeneration. Consequently, in the next experiments there will be less free functional groups which compensate their charge. So, the efficiency of the ion exchanger decreases. The way to solve this problem is using a huge amount of regenerant solution which involves huge waste and it does not worth. [17],[18]

5.2 Reverse flow regeneration

This process is also named counter flow regeneration. In this process, the regenerant solution goes through the ion exchanger in the opposite way than the initial ionic solution.

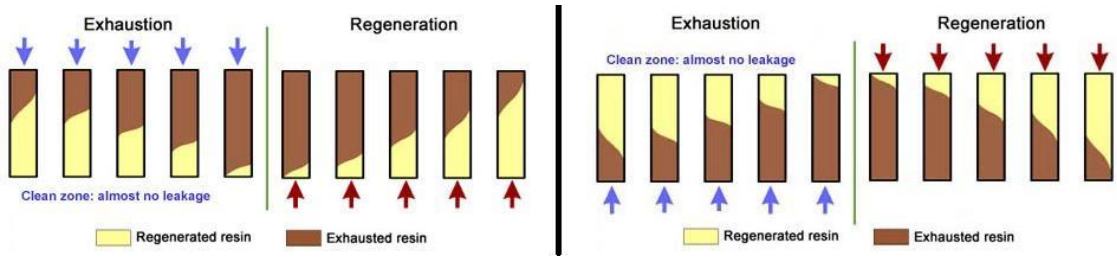

Fig 6. Reverse flow regeneration process [17].

Both ways of solution transport (shown in Fig 6) are possible.

The regenerant solution, in this case, is in touch firstly with the ion exchanger less exhausted. In this way, the less exhausted layers are regenerated first and the most exhausted layers are the last ones. Thus, the “contaminating” ions will be completely removed in the less exhausted layers and it is probably that the most exhausted layers will still have some “contaminating” ions after the regeneration process. The leakage is very low. When the ionic solution (exhaustion) goes through the ion exchanger after the regeneration process, the first layers will be completely cleaned so the efficiency of the process will be better. Furthermore, less regenerant solution is needed. [17],[18]

6 Equilibrium in ion exchange process

Ion exchange is a reversible process. Consequently, equilibrium conditions take place in this process.

Equilibrium is the determining factor in ion exchange process when the preference of the ion in the solution by the ion exchanger is not big. If the ion exchanger has a strong preference for the ion in the solution, the ion exchange process will be controlled both by the equilibrium and the kinetics. [16]

Crosslinkage has very influence in ion equilibrium. If the ion exchanger is strongly crosslinked, the diffusion of ion from the ion exchanger to the solution will be more difficult and the time to reach the equilibrium state will be longer. [19]

Equilibrium is affected by some physical conditions. As a result, there are some conditions which are preferable in order to get a higher efficiency of the ion exchange process. These preferable conditions are expressed by selectivity. Selectivity factor is an important aspect in ion exchange process. The ion exchanger selects one counter ion in preference to other one for physical causes, mainly. In many cases, the selectivity (in the sense of preference for one ion more than other one) is affected by changes in equilibrium. These causes are explained in the following sections.

6.1 Electroselectivity

Selectivity is affected by the effect of counter ions valences because it affects the equilibrium.

This is caused by the electric potential which appears in a system when the system is not in equilibrium (Donnan potential). This potential attracts counter ions into the ion exchanger and the tendency of these counter ions to diffuse out into the solution decreases.

The force which potential attracts a counter ion depends on the ionic charge. The more charge of the counter ion, the more strongly attracted it is. As a result, the ion exchanger prefers the counter ion of higher valence. Furthermore, the preference also increases if the solution increases its dilution grade and if the molality of the fixed ionic groups increases; because of the potential increases in these cases. So,

the preference of the ion exchanger for one ion will increase if the electrical potential increases.

6.2 Size of counter ions

Equilibrium depends on the size of the (solvated) counter ions. Large solvated counter ions caused higher swelling pressure than small ones. The ion exchanger prefers the counter ion with the smaller solvated equivalent volume because with higher swelling pressures the matrix swells more and the matrix became stretched. So, large counter ion can be replaced by small counter ion. Consequently, the smaller counter ion is preferred by the ion exchanger. [8],[20]

6.3 Matrix composition

Ion exchanger prefers counter ions with organic groups similar to the components of the matrix.

6.4 Complex formation in the external solution

Counter ions in ion exchanger are able to interact and form complex with other components of the external solution. If the tendency of forming complex with substances of the external solution is high, the counter ion will be less attracted by the ion exchanger. So, ion exchanger prefers counter ions with less easiness to form complex in the external solution.

Moreover, some counter ions inside the solution can be removed by precipitation. Consequently, the efficiency of the ion exchange decreases because there are fewer ions which can be associated (the ion concentration in the solution is reduced) with the fixed groups in the ion exchanger.

6.5 Temperature

Temperature appears not having high influence on equilibrium. “Rothmund and Kornfeld and Patton and Ferguson say that temperature has no effect on equilibria between ions of the same valence [20]”.

The temperature coefficient of ion exchange equilibrium is small. As a result, the heat of reaction is also small. This is probably caused because ion exchange is not a chemical reaction so, there are no covalent bonds formed or broken. Thus, the only effect on temperature is due to activity coefficients, and this effect is small. [8],[20]

7 Applications

Io exchange process has a lot of application in many sectors. Main sectors which used this method are described in this section.

- Isotope separation in nuclear industry. Valuable elements are able to be recovered from exit nuclear waste by ion exchange process.

- Water treatment technologies. Ion exchange is one of the basic methods for water treatment if ionic impurities are involved. Water has a lot of ion restriction in order to be suitable for human consumption. Keeping ion concentration within the suitable average is possible, in some cases, because of ion exchange. For example, some ions of Calcium and Magnesium are able to be removed by this method in order to get less hard water. Other important application is the desalinization process, where salt is removed from sea water, or demineralization [20][21].

- Pharmaceutics and food industry. One of the examples of ion exchange in this area is in sugar refining where this process is used in order to remove colour and ashes from sugar [21].

- Hydrometallurgy (extraction of Uranium or noble metals, for example). This process is very value in order to recovery some metals which can be used in other processes. Waste water from metallurgic industries has metallic elements which are very useful in the process. So that, it is really important to recover this elements from the fluent and ion exchange is the best process to recover them. Some examples of metallic elements recovered by this process are: copper, silver, precious metals or chromium.

- Biochemistry and biotechnology applications. This sector employs ion exchange to separate amino acids, mainly. This is one the most important ion exchange process in this area.

- Medicine applications. Medicine area is increasing their researchers about application of ion exchange [22]. One of the most important applications of this method in this sector is in controlled drug release. Ion exchange allows drug to be discharged into a body in a controlled way.

8 Kinetics

The rate-determining step is the interdiffusion of ions as first recognized by G Schulze in 1915.

The diffusion process of ion exchange takes places in two steps.

- Interdiffusion of ions within the ion exchanger bead.
- Interdiffusion of ions through a liquid layer adhered to the bead surface, called “film”.

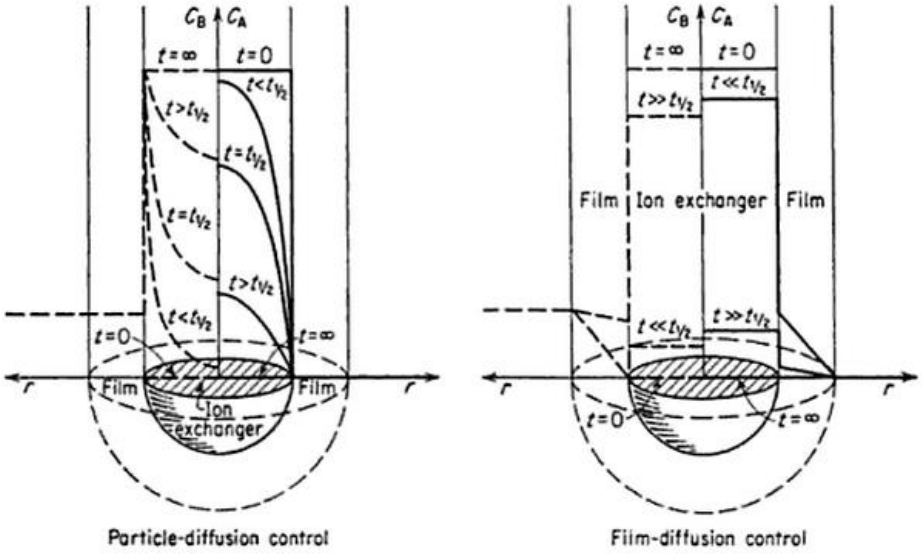

Fig 7. Radial concentration profiles for ideal particle diffusion process and ideal film diffusion control. [8]

The right side of the diagram shows the profile of ions A (initially in the ion exchanger) and the left sides those of ions B (initially in the solution).

The two limiting cases are an ideal particle diffusion control and an ideal film diffusion control.

8.1 Particle diffusion control

Concentration differences in the film are instantaneously levelled out so, concentration gradients exist only in the beads (shown in Fig 7 - left). Consequently, film diffusion is so much faster than particle diffusion.

8.2 Film diffusion control

In that case, particle diffusion is much faster than film diffusion and the concentration gradients exist only in the film. It is shown in the right side of Fig 7. The flux is proportional to the solution concentration and to the interdiffusion coefficient in the film, inversely proportional to the film thickness and independent of the fixed-charged concentration, interdiffusion concentrate in the bead and bead radius.

The rate determining-step is the slower of the two processes. It depends on the value of the factor which affects positively or negatively to both options. Therefore, systems with ion exchangers of high concentration of fixed ionic groups, low degree of crosslinking and small particle size, have film diffusion control [8]. The stage of diffusion control can be predicted by the following equation:

$$\frac{X\bar{D}\delta}{CDr_0}\left(5+2\alpha_B^A\right) \ll 1 \qquad particle\ diffusion\ control$$

Eq. 3

$$\frac{X\bar{D}\delta}{CDr_0}\left(5+2\alpha_B^A\right) \gg 1 \qquad film\ diffusion\ control$$

Eq. 4

Where, X is the concentration of fixed ionic groups; C is the concentration of solution (in equivalents); $\bar{D}$ is the interdiffusion coefficient in the ion exchanger; D is the interdiffusion coefficient in the film; r_0 is the bead radius; δ is the film thickness; $\alpha_B^A = \overline{C_A}C_B \big/ \overline{C_B}C_A$ is the separation factor; the concentration are on molarity scale.

When $\frac{X\bar{D}\delta}{CDr_0}\left(5+2\alpha_B^A\right) \approx 1$, diffusion is about equally fast in both phases, the beads and the film. In this case, the diffusion rate is affect by both mechanisms.

In these equations (Eq. 3 , Eq. 4) , the effect of selectivity is included.

8.3 Isotopic exchange

There are some limiting cases in which this equation cannot be used. One of these cases is a system with isotopic exchange it means, a system which is in equilibrium except for isotopic distribution. In this case, isotopic exchange will be tested first and then the results will be generalized for actual exchange of ions of different properties. See APPENDIX I.

9 Ion exchange resins used

9.1 AMBERLITE CG50 (Type 1)

Amberlite CG50 is a weak acid exchange resin. It has carboxylic groups with 4% of crosslinking. [23] Its capacity is 10.0 mmol of active groups per gram of dry resin. [24]

This resin is able to be used in chromatography separation in columns because of their mesh size which is nominally from 75 to 150 µm. [25], [26].

See APPENDIX II, section II. 1.

9.2 DOWEX 50W X2 100-200 mesh

It is a strong acid cation resin which has very light orange colour. Their ionic groups are sulfonic acid functional groups which are in a gel matrix of styrene-divinylbenzene with 2% of crosslinkage. [27] This type of Dowex 50W has 2% of divinylbenzene in their matrix. [28]

Its small mesh size, from 100 to 200, makes it suitable for ion exchange chromatography.

Some of its advantages are:

- High physical stability
- Good elution characteristics
- High resolution.

Dowex 50XW2 is used in fine chemical purification and bioprocessing. [29]

Its total exchange capacity is 0.6 meq/mL as it is shown in 00.

Table 1 Properties of DOWEX 50W.

Cation resins	Mesh size	Ionic form	Water retention capacity (%)	Total exchange capacity (meq/mL)	lbs/ft³	lbs/5 ft³ drum
DOWEX 50WX2	50 - 100	H^+	74 - 82	0.6	46	230
DOWEX 50WX2	100 - 200	H^+	74 - 82	0.6	46	230
DOWEX 50WX2	200 - 400	H^+	74 - 82	0.6	46	230
DOWEX 50WX4	50 - 100	H^+	64 - 72	1.1	48	240
DOWEX 50WX4	100 - 200	H^+	64 - 72	1.1	48	240
DOWEX 50WX4	200 - 400	H^+	64 - 72	1.1	48	240
DOWEX 50WX8	50 - 100	H^+	50 - 56	1.7	50	250
DOWEX 50WX8	100 - 200	H^+	50 - 58	1.7	50	250
DOWEX 50WX8	200 - 400	H^+	50 - 58	1.7	50	250

9.3 SEPHADEX C-50

Sephadex is a dextran gel which has crosslinked dextran matrix. It is a weak cation exchanger with carboxymethyl main functional group.

The properties of this type of resins are:

- Low nonspecific adsorption
- Quantitative desorption
- High flow rate
- God reproducibility
- Easy column packing

They are suitable for chromatography. Sephadex C-50 is suitable for range pH 6-10. [30]

See APPENDIX II, section II. 2.

10 Experimental

10.1Instrumental

10.1.1 Peristaltic pump

Peristaltic pump is a positive displacement pump. It consists in a rotor and rollers, mainly. There is a flexible pipe filled of liquid in it. The liquid is carried along the pipe by rollers. Rollers, linked to the rotor, compress the pipe. While rotor moves in circle, liquid in compressed part of the pipe has to move along the pipe. This is the process that peristaltic pump follows in order to carry the liquid.

Fig 8. Peristaltic pump process [31].

10.1.2 Fraction collector

Fraction collector is a device to collect the eluate from a column [32]. It has a microprocessor which allows taking regular samples from the column and putting them in different tubes. This device has a moving part which receives a signal from the microprocessor and then it changes their place in order to collect the eluate in other tube. This process is repeated until the experiment ends and the moving part change its place at determined time fixed on dependence on the requirements. [33]

Fig 9. Fraction collector [34].

10.1.3 Varian SpectrAA 200 atomic absorption spectometer

Staff used in order to measure the lithium concentration of the solutions is an atomic emission spectrometry (AES) using Varian SpectrAA 200 atomic absorption spectrometer.

Fig 10. Varian SpectrAA 200 atomic absorption spectrometer. [35]

Atomic absorption spectroscopy (AAS) is a procedure of analytical chemistry in order to obtain the concentration of a particular element, called analyte, in a sample. This concentration is able to be measured because free atoms in the gaseous state absorb optical radiation. Electrons can absorb energy to be

promoted to an excited level. The amount of energy that the electron absorbs is specific for each electron in each element. Consequently, this amount of energy can be measured. This value of absorption is compared with optical absorption of standard solutions (solutions with known analyte content). [36], [37].

The atoms are irradiated by optical radiation in order to get enough energy. In this research project, flame atomizer is used. Acetylene and oxygen are mixed to get the flame.

The program is able to measure 70 different elements. So, first of all the analyte has to be determined. After that, the flame has to be turn on. Standard solution are measured and then the solution which are wanted to be measured. Standard solutions used have the following concentration: 0 mg/l, 1 mg/L, 5 mg/L and 10 mg/L. The machine absorbs a little amount of each solution which is atomized in the flame. The absorption energy is measured and compared with the values of the standard solutions. The relation between the values of absorption is not linear.

10.2 Characterization of the resins

Resins are cleaned with water. Thus, they are cleaning of impurities. However, the most important objective of this process is characterizing the behaviour of the resins inside the water. This is too important because resins are going to stay in a column where different solutions are through along. So that, resins need to have good behaviour inside liquid solutions like water.

It is needed a resin which allow to pass liquid through it but it is not allowed to be completely dissolved in this liquid, because it is needed to have a column with constant length of resin and this resin cannot be missed mixed with the liquid exiting from the column.

All resins are put into a glass with water and their behaviour is observed along the time. Firstly, 50 mL of each resin are mixed with 55 mL of water. If the behaviour in the water is satisfactory, the resin will be regenerated with sodium hydroxide (NaOH) and acid chloride (HCl) in order to remove all impurities.

10.2.1 AMBERLITE CG50 (Type 1)

Amberlite CG50 has powdered texture and light cream colour. Resin is dissolved in water firstly. However, after 5 hours resin has compacted in the bottom of the glass

and the water is above it without being mixed. 24 hours later resin is completely rigid and totally separated from the water.

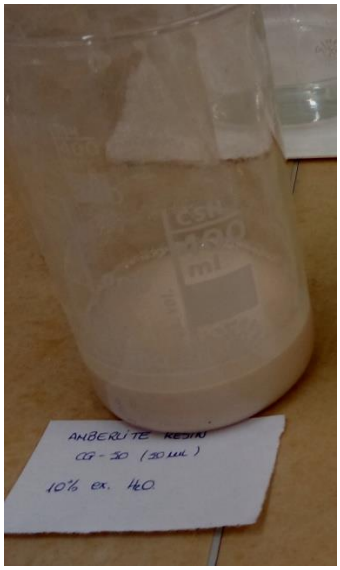

Fig 11. AMBERLITE CG50 resin cleaned by water.

Resin is tried to be shake. Little amount of resin was diluted and a huge amount of water was needed. After that, resin is cleaned by NaOH in a beaker. The resin behaviour is, now, completely different. Resin is diluted in this base even few hours later. Therefore, high amount of resin particles are removed from the solution when liquid is gone out. Then resin is cleaned by water. The same behaviour is shown. Resin are not completely separated from NaOH so, resin is cleaned by water 5 times. Thus, most of resin is precipitated in the bottom of the vessel. However, the amount of resin is not the same than firstly because some of this was removed when the base liquid gone out. HCl cleaning has the same behaviour than NaOH cleaning.

Resin is too much diluted when basic or acidic solution goes through it.

This behaviour is not good enough. If this resin is put inside a column, after water cleaning, none solution are able to be through it because of its rigid behaviour. Even basic or acidic solutions. This is because only particles in the top of the column will be mixed with the liquid. If an acidic or basic solution through the column whose particles are diluted, most of resin particles will be gone from the

column when liquid will go out from it. As a result, this resin is insoluble in water and it is not suitable for being inside a column.

Consequently, Amberlite CG50 ion exchange resin is not suitable and it is discarded.

10.2.2 DOWEX 50W X2 100-200 mesh

Dowex 50W X2 are soft yellow-orange beads of resin. When this resin is in contact with water, very small spherical particles appear and the resin does not have soft texture any more. Moreover, their colour change and now they have orange colour.

The resin is diluted in water, firstly. Few hours later, this resin has precipitated in the bottom of the glass. However, the resin is not completely separated from the water because the water above the resin has really light orange colour. This is caused by resin particles which are diluted in the water. Furthermore, the resins in the bottom of are not totally compacted. They still have orange colour since they are mixed with very little amount of water.

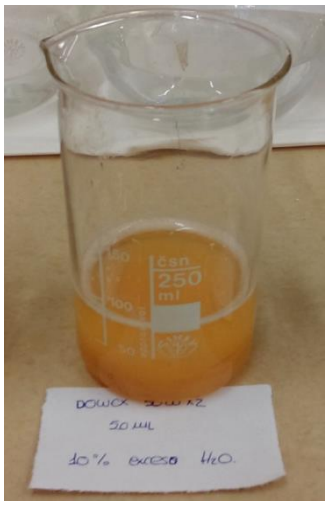

Fig 12. DOWEX 50W X2 (100-200 mesh) resin cleaned by water.

24 hours later the resin looks like equal than before. Then, the sample is removed. It is observed that the resin is easily mixed with the water and, in few seconds, its appearance is the same than first moment they were mixed. This resin is not totally compacted like Amberlite one.

As a result, this resin is slightly soluble in liquids like water and it is suitable for this experiments.

The second cleaning of this resin is with NaOH and HCl. For this process, Dowex resin is located in a column. There is a lot of resin so; there are two columns to clean it.

This is a regeneration process, explain in section 5, in order to remove all the impurities and be sure that the resin has all its ion exchangers free and no other ions occupy these places. New anions and cations are supplied to resin.

The concentration of NaOH is 1 M and the concentration of HCl is 2 M.

This process take place as follow: resin is firstly cleaned by NaOH. The amount of NaOH used is 1.3 the amount of resin. After all NaOH has gone through the resin and has gone out the column, water is used. Water goes through the resin and goes out the column in the same way than NaOH. Following, HCl is used to clean. This procedure is the same than before, with NaOH and water. Finally, water is used again like before.

This whole process will be repeated three times.

Fig 13. Dowex resin cleaned by HCl.

Dowex resin colour changes along the process. First of all, the resin is diluted in water and its colour is light orange. When the resin is cleaned with NaOH, its colour

is dark orange. If resin is cleaned by water again, resin will be light orange. Then, resin is cleaned by HCl and resin colour is now light yellow.

Fig 14. Dowex resin cleaned by NaOH.

This resin is suitable for being inside a column. This is because it is able to be slightly diluted in acidic, neutral and basic solution. The dilution grade is big enough to permit liquid goes through resin particles and it is small enough to not permit diluted resin exit.

10.2.3 SEPHADEX C-50

Sephadex C-50 resin is compound by really tiny white particles.

When water gets in touch this resin, resin particles on the top of the vessel change their texture. Since first time that water touch resin, resin particles get bigger and bigger, they increase their volume and soft texture appears in them. Their colour also changes. Now, resin particles are almost transparent as it is shown in Fig 15. But this does not happen in all resin particles. This fact only happens in resin particles which are located on the top of the vessel. Water cannot percolate to the bottom of the beaker.

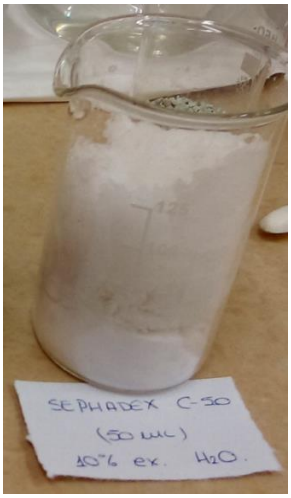

Fig 15. SEPHADEX C-50 resin cleaned by water.

In this picture, Fig 15, it is possible to distinguee resin particles without mix with water in the bottom of the beaker, and resin particles which were mixed with water in the top of the beaker. Texture change is appreciated in that image (Fig 15).

Second cleaning is done because all resin is not cleaned. Put less amount of resin and water in few steps is carried out. First a layer of resin is put in the bottom of the glass. Above it, water is thrown. This resin layer changes its texture and increase volume. This process is repeated three times. Result is shown in Fig 16.

Fig 16. Sephadex resin cleaned by water in three steps.

In the case shown in Fig 16, 30 mL of resin had been cleaned by 85 mL of water. Instead of this fact, several resin particles had not been mixed with water.

More water is put above resin particles which were mixed with water before, in order to see the behaviour of the new texture particles. When water gets in touch these particles, they star increasing their volume again. Water never goes through the particles until arrive the bottom of the vessel.

This behaviour shows that Sephadex resin is not suitable to remove lithium from a solution because this dilution will never be able to reach the bottom of the column. Consequently, this resin is removed from the research.

Finally, only Dowex resin is going to be used in experiments in order to fill the column because this is the only one which allows water to go through resin particles from the top to the bottom of the column.

10.3Column preparation

Experiment is carry out in the column shown in Fig 17. 40 cm of Dowex resin is located inside the column. Top of the column has a little pipe which transports dissolution from the beaker to the column. This pipe has a peristaltic pump to pump out liquid to the top of the column. Bottom of the column has a little pipe which carries final solution from the column to the collector. Both pipes are tiny diameter plastic pipes. Final installation is shown in Fig 17.

Fig 17. Experimental installation.

The previous picture (Fig 17) illustrates all parts of the installation. The column with resin inside is circled in black. Colour resin predicts that resin has been cleaned by water. Peristaltic pump, where pipe is located, is circled in red. Fraction collector is circled in blue. All components of this machine, which were explained in section 10.1.2, are able to be distinguished in that picture. Both arrows indicate the pipes. Red one points at entrance pipe, which exit from the pump, and purple one indicates exit pipe.

10.4Problems and solutions

The main problem in this research was in the installation stage. Resin occupies almost the entire column. Dissolution takes long time to go through the column so, maximum pump velocity is required. However, pressure drop in the column increase a lot and resin length decrease when liquid is going through it. Even more when higher velocity the pump has. This fact causes that cap, where entrance pipe is located, runs away from the column and liquid does not enter in it.

Solution of this problem is reducing velocity at top value in which cap will not leave the column. An engagement, between the higher velocity and the maintenance of the cap in the column, has to be got. As a result, pump velocity in the first experiments is the highest one. That problem was appeared and the following experiments were performed with half of the first pump velocity.

10.5Experiments

10.5.1 Fundaments

Lithium is an alkali element which is the lightest metallic one. Its valence is +1 and its ionic form is Li^+.

$LiNO_3$ in water is dissociated in their ionic form: Li^+ and NO_3^-. These ions go through the column and they are attracted by carboxylic groups and they are fixed on them. So, lithium ions are removed from the fluent liquid by ion exchange process (see section 4).

Then, the amount of lithium ions which was fixed in resin beads has to be measured. For this reason, NH_4Cl dissolution is required to go along the column. This compound in water is dissociated as NH_4^+ and Cl^-. NH_4^+ ions are exchanged

by Li^+ ions. Consequently, Li^+ ions are in the dissolution which exits from the column. This dilution is collected in different tubes along time in order to measure the lithium distribution inside the column. These measures are really useful to study the lithium ion exchange in Dowex 50W X2 resin.

20 mL of lithium are going to be used in each experiment. Lithium will go through the column first. Then NH_4Cl solution will pass along the column in order to remove lithium ions fixed in ion exchange resin. Liquid which exit from the column is collected in different tubes in the fraction collector. They will be measured when experiments end in order to know the lithium concentration along time. Each experiment uses different NH_4Cl concentration.

The amount of NH_4Cl dissolution has to be big enough to remove all lithium ions from the resin. This amount is set changing the time than the fractor collector collects liquid in each tube. Because, the fractor collector only has 61 tubes.

Atomic absorption spectrometer has the top standard lithium solution of 10 mg/L. Consequently, solutions of lithium with higher concentration than 10 mg/L cannot be measured. In that case, liquid from the tubes has to be diluted until fit in range from 0 mg/L to 10 mg/L. Most of collected solutions have to be diluted 100, 1000 or 10000 times and after that they will be able to be measures in the atomic absorption spectrometer.

10.5.2 Preparation

Dowex 50W X2 is the only resin tested in these experiments like it was explained in sections 10.2.1 and 10.2.3.

40 mL of this resin is inside the column (Fig 18, a). Fill the column takes long time because the clean resin used is mixed with water, so resin occupies more volume. Compacted bed of resin beads is required. Consequently, it is needed to wait for water to disappear from the column. It takes long time because water has to percolate through resin beads and go out for the bottom of the column. More beads the system has, more time water spends going through beads.

a) b)

Fig 18. Resin column used in experiments. Picture a) shows 40 mL of resin in the column and picture b) is the same column with less length of resin beads.

1 litter of 2M lithium dissolution is prepared. It is done dissolving $LiNO_3$ of 68.95g/mol in water. So, 137.9 g of LiNO3 (Eq. 5) has to be dissolved in 1 litter of water in order to obtain 1 litter of lithium dilution.

$$\frac{2\ mol\ Li}{1\ L} \times \frac{1\ mol\ LiNO_3}{1\ mol\ Li} \times \frac{68.95\ g\ LiNO_3}{1\ mol\ LiNO_3} = 137.9\ g\ LiNO_3/1L$$

Eq. 5

Different NH4Cl dilutions of different concentrations are prepared. 26.745 g (Eq. 6), 13.373 g (Eq. 7), 10.698 g (Eq. 8) and 5.349 g (Eq. 9) of NH4Cl are dissolved in water to obtain NH4Cl solutions of concentration 0.5M, 0.25M, 0.2M and 0.1M, respectively.

$$\frac{0.5\ mol\ NH_4Cl}{1\ L} \times \frac{53.49\ g\ NH_4Cl}{1\ mol\ NH_4Cl} = 26.745\ g\ NH_4Cl/1L$$

Eq. 6

$$\frac{0.25\ mol\ NH_4Cl}{1\ L} \times \frac{53.49\ g\ NH_4Cl}{1\ mol\ NH_4Cl} = 13.373\ g\ NH_4Cl/1L$$

Eq. 7

$$\frac{0.2\ mol\ NH_4Cl}{1\ L} \times \frac{53.49\ g\ NH_4Cl}{1\ mol\ NH_4Cl} = 10.698\ gNH_4Cl/1L$$

Eq. 8

$$\frac{0.1\ mol\ NH_4Cl}{1\ L} \times \frac{53.49\ g\ NH_4Cl}{1\ mol\ NH_4Cl} = 5.349\ g\ NH_4Cl/1L$$

Eq. 9

10.5.3 Experiment I

Experiment I uses NH_4CL of 0,5 M concentration. About 350 mL of 0,5M NH4CL are used. 5 mL of exit liquid has been collected in each tube for 2 minutes. Whole experiment takes 2 hours.

Along the experiment takes place, length of resin decrease because of the pressure drop. At the beginning of the experiment the length was 40 ml and at the end it was about 36 mL, as is shown in Fig 18.

Resin colour changes when lithium starts going through the column. This fact assumes that ion exchange is taking place.

10.5.4 Experiment II

New cleaned resin is introduced in the column until reaching 43 mL. This length is more than 40 mL required because when pump starts working, resin length in the column decreases because of the high pressure drop.

Experiment II is the same than experiment I, the difference is that experiment II has 40 mL resin length in the column and experiment I has about 36 mL.

The amount of resin was so high that several minutes after experiment starts, the tap which has the entrance pipe gone out (see section 10.4).

As a result, experiment II is not valid and only few results are convincing. Consequently, this experiment is not going to be carefully examined.

10.5.5 Experiment III

Experiment III uses 0,25 M concentration of NH_4Cl. In addition, pump velocity is half than in the experiment I.

Now, each tube has filled for 9 minutes and whole experiment takes about 9 hours.

10.5.6 Experiment IV

Experiment IV is performed by 0,1 M concentration of NH_4CL and its pump speed is the same than in experiment III (10.5.5), V and VI. 9 hours were spent.

10.5.7 Experiment V

Experiment V has the same NH_4CL concentration than experiment IV and the same pump velocity. However, time of liquid collection in each tube increases. Liquid has collected in each tube for 18 minutes. Consequently, experiment takes about 18 hours.

10.5.8 Experiment VI

Experiment VI uses 0,2 M concentration of NH_4Cl in the same conditions than experiment IV (see 10.5.6).

11 Analysis of the results

Graphics of all experiments are put together in Fig 19 in order to compare all cases and get conclusions. It is useful to remember the Table 2 .

Table 2 Brief summary of experiments.

EXPERIMENT	[NH4Cl] mol/L	time/tube (min)	Column length (mL)
I	0,50	2	36
II	0,50	2	40
III	0,25	9	40
IV	0,10	9	40
V	0,10	18	40
VI	0,20	9	40

Equilibrium in this process is easily reached so; the ion exchange is controlled by mass transfer. Velocity of mass transfer depends primarily on the concentration gradient between the solution and the resin beads (see section 8). Consequently, it is expected to have the higher mass transfer at the end of the process and the lowest mass transfer at the end because the lithium concentration decreases along the experiment.

However, experiments have two different conducts.

On the one hand, the experiment I has the expected behaviour. All lithium ions are exchanged from the solution because the first minutes, when lithium is going through the column, none lithium exits from the column. Lithium solution is going into the column for 8 minutes (20 mL) and first amount of lithium in the eluent appears after 18 minutes (see APPENDIX III, section III. 1). Ammonium chloride spends 10 minutes going from the top to the bottom of the column while it is exchanging ions with the resin beads. In this case, higher velocity of mass transfer appears at the beginning because the concentration gradient is higher. It can be appreciated in the high peak in Fig 19. The peak corresponds to the saturation concentration. When lithium ions are in the exit solution its concentration is the highest one and after that, the lithium concentration decrease because the concentration gradient is lower, less lithium ions are in the resin

beads and less lithium ions are exchanged. This is the reason for having less amount of lithium in the solutions after reaching the highest lithium concentration.

As a result, highest peak of lithium concentration is shown at the beginning and after that the lithium concentration is decreasing. The maximum amount of lithium only appears once because the amount of lithium is not too high. At the beginning, maximum amount of ions are exchanged reaching the saturation concentration but then, the saturation concentration is not sustained because there are not enough lithium ions to get this concentration again.

Experiment I uses the highest ammonium chloride concentration. This is the reason to get the lowest time to remove all the lithium from the resin. Ion exchange is a stoichiometric process, so more ions are able to be exchanged. Consequently, time to remove all lithium ions is lower than in other experiments.

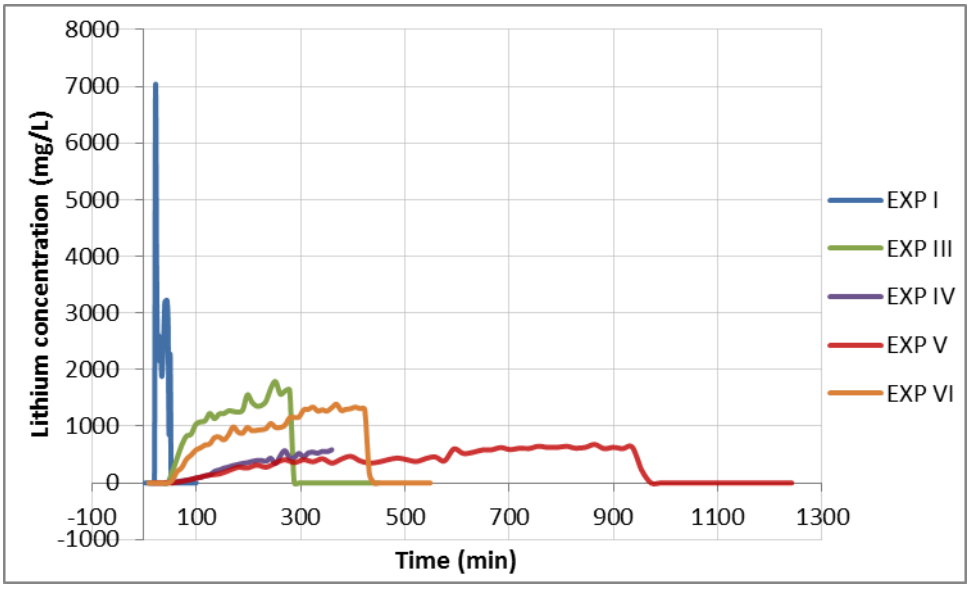

Fig 19. Comparison of all experiments.

On the other hand, the other experiments have different behaviour. In these cases, the mass transfer speed is not so high and the maximum lithium concentration does not appear at the beginning. This is cause because of the mass transfer resistance. It is probably to have mass transfer resistance in the liquid phase which can be reduced starting turbulent flux. This fact does not appear in the first experiment because the concentration gradient is so high that the resistance to mass transfer is insignificant. Furthermore, it has to be remembered that this is not an ideal situation. Therefore,

mass transfer resistance usually appears. Mass transfer resistance caused the slower inclination of the graphic and the lithium concentration in the exit solution increases slowly until reaching the highest concentration or removing all lithium ions.

Experiment I uses the double ammonium concentration than experiment III. This fact assumes that experiment I has the double ammonium ions to be exchange in resin beads. Consequently, in ideal situation, experiment III takes the double time than experiment I to remove all lithium ions. As it is shown in Fig 19, experiment III takes more than double time removing all lithium from resin beads. Mass transfer resistance causes ions need more time to diffuse. The same behaviour appears in the following experiments.

As the ammonium chloride concentration is lower, the time taken to remove all lithium ions increases. This increase is due to the lower amount of exchangeable ions presents in the solution and the mass transfer resistance mentioned in the previous paragraph.

The highest lithium concentration decreases with decreasing the ammonium concentration in the solution. It is caused because less exchangeable ions are presented in the solution; therefore less lithium ions are able to be removed from the resin beads, the saturation concentration in the solution is lower. It is shown in the peak of each experiment in Fig 19, lower ammonium solution suppose smaller amount of lithium in the highest peak.

Experiments III, IV, V and VI revealed a fast change between the highest concentration and the lowest concentration of lithium in the exit solution. It is caused because no more lithium ions are in the resin beads to approach the saturation concentration. The highest concentration is not sustained because there are not enough lithium ions. Consequently, ion concentration goes from the highest level to the lower level in just a moment.

If less ammonium concentration is used, more amount of ammonium solution will be needed.

The ion exchange process starts in the top of the column. So, first ions are exchanged in the top of the column. The colour change in the column supports it. While lithium ions go from the resin beads to the solution, colour resin changes from yellow to orange, as it is shown in Fig 20.

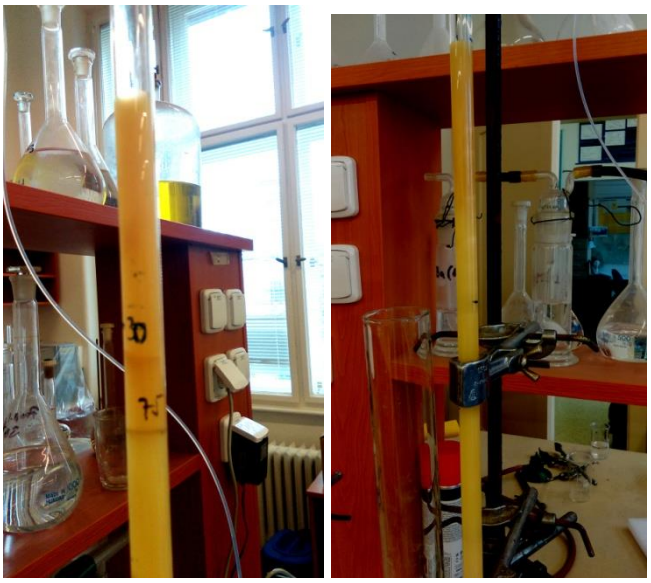

Fig 20. Colour change in the resin column.

Lithium is completely fixed by the resin. As a result the breakthrough curve is not able to be measured. Same problem appears if exchange capacity is wanted to be calculated. More experiments are needed to measure the characteristics of the resin because it is need to use more lithium ions than resin can remove.

12 Conclusion

Lithium ions are able to be fixed on strong acid cation exchangers like Dowex resin. The lithium removal is easy and all lithium ions are completely removed from the solution. Furthermore, lithium ions are able to be almost totally recovered from the ion exchanger.

This process is controlled by diffusion (mass transfer) and equilibrium does not affect because it is easily reached.

Lithium sorption is really fast when lithium concentration is high. In this case, the concentration gradient between the liquid phase and the resin beads is high and the diffusion speed is also high. Consequently, lithium ions are quickly exchanged. The top of the resin column has a lot of lithium ions whereas the bottom of the column does not have.

If high sorption speed is wanted, higher concentration of lithium solution will have to be used. However, if the removal speed has to be slow, lower lithium concentration will be used.

There are mass transfer problems when the solution concentration is not high enough. Nevertheless, these problems disappear if high concentration in the dissolution is used because of the high concentration gradient which works against the diffusion problems in the liquid film.

To sum up, strong acid cation exchanger is able to fix lithium. Its capacity is high enough. However, time will be longer if the lithium concentration is low because of mass transfer problems.

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SORPTION PROPERTIES OF LITHIUM IONS ON STRONG ACID CATION EXCHANGES

APPENDIX

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APPENDIX I. **Isotopic ion exchange**

In this case, the diffusion coefficient is constant. The system consists in isotope A ions which are initially in the ion exchanger and isotopic B ions. Both limiting cases are going to be treated separately.

Particle diffusion control

$$J_A = -\bar{D}\nabla\bar{C}_A$$

Eq. I.1

Where, J_A is the flux of isotope A[1] in the ion exchanger given by Fick's first law, D is the self-diffusion coefficient of the isotopes and $\nabla\bar{C}_A$ is the gradient of the concentration of isotopic A ions inside the particle. This concentration is given by material balance as it is shown in Eq. I.2 .

$$\frac{\partial\bar{C}_A}{\partial t} + \nabla J_A = 0$$

Eq. I.2

Where t is time and ∇J_A is the divergent of the flux of the isotope A in the ion exchanger.

To solve the system two conditions have to be applied to Eq. I.1 and Eq. I.2 :

$$r > r_0, \quad t = 0 \quad \rightarrow \quad \bar{C}_A(r) = 0$$

Eq. I.3

$$0 \leq r \leq r_0, \ t = 0 \quad \rightarrow \quad \bar{C}_A(r) = \bar{C}_A^0 = const$$

Eq. I.4

Where r is the distance from bead centre, r_0 is the bead radius and $\bar{C}_A^0$ is the initial concentration of A isotope.

[1] It is only considered the flux of one isotope because the system is in equilibrium except for isotopic redistribution. Consequently, the flux of the other isotope is the same magnitude and opposite sign.

There are two boundary conditions which are applied in order to solve the system. They are called “infinite solution volume” and “finite solution volume” condition. The first one is applied when the concentration of A in the solution remains insignificant during the process It means:

$$When \quad r = r_0 \quad and \quad t > 0 \quad \rightarrow \quad \bar{C}_A(t) = 0$$

Eq. I.5

Mixing the Eq. I.1 , Eq. I.2 , Eq. I.3 , Eq. I.4 and Eq. I.5 , the fractional attainment of equilibrium is got.

$$U(t) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(-\frac{\bar{D}t\pi^2n^2}{r_0^2}\right)$$

Eq. I.6

Where U(t) is:

$$U(t) = \frac{\bar{Q}_A^0 - \bar{Q}_A(t)}{\bar{Q}_A^0 - \bar{Q}_A^\infty}$$

Eq. I.7

Where $\bar{Q}_A^0$ is the amount of A in the ion exchanger at time t; $\bar{Q}_A^0$ is the initial amount of A in the ion exchanger and $\bar{Q}_A^\infty$ is the amount of A left in the ion exchanger when equilibrium is reached.

The following figure shows the dependant of the attainment of equilibrium on the time parameter.

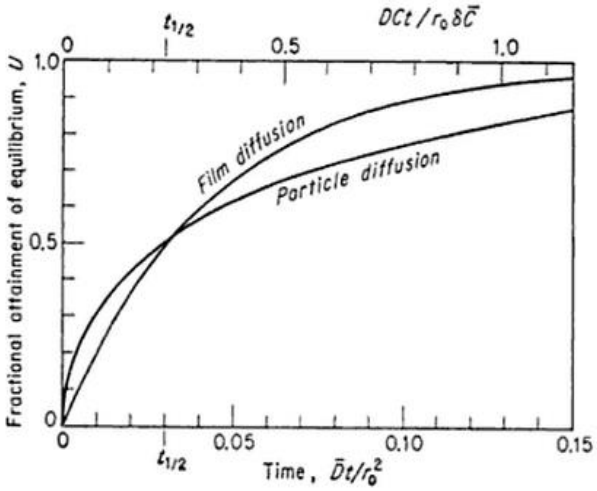

Fig I.1. Fractional attainment of equilibrium as a function of time for particle and film diffusion controlled isotopic exchange.

The finite solution volume is applied when the infinite volume condition cannot be applied. This condition is got from the material balance $-d\bar{Q}_A = dQ_A$. This condition assume he equilibrium at the interface and it is shown in:

$$r = r_0, \qquad t > 0 \quad \rightarrow \quad \bar{C}_A(t) = \frac{3\bar{V}\bar{C}}{r_0 VC}\int_0^t J_A(t)dt$$

Eq. I.8

APPENDIX II. Ion Exchange resins used

II. 1 AMBERLITE CG50

ROHM HAAS

AMBERLITE™ CG50 (Type 1)
Weak Acid Cation Exchange Resin Powder

Description

AMBERLITE CG50 (Type 1) is a crosslinked methacrylic type of weakly acidic cation exchange resin powder. The resin has a high concentration of carboxylic groups which serve as the ion exchange site of the resin.

The principal application of AMBERLITE CG50 (Type 1) is the recovery, separation and purification of a wide range of pharmaceutically active compounds such as aminoglycosides, antibiotics, vitamins, etc.

Typical Properties

These properties are typical but do not constitute specifications.

Matrix	Macroporous crosslinked methacrylate
Functional groups	$-COO^-$
Physical form	Dry fine powder
Ionic form as supplied	H^+
Total exchange capacity	10 meq/g min
Moisture content	10% max
Particle size	Nominally 100 to 200 mesh (US Std) 75 to 150 µm

Food Processing

Rohm and Haas manufactures special resins for food processing and potable water applications. As governmental regulations vary from country to country, it is recommended that potential users seek advice from their Amberlite representative in order to determine the best resin choice and optimum operating conditions and a correctly classified bed.

All our products are produced in ISO 9002 certified manufacturing facilities.

II. 2 SHEPADEX

[42]

PHARMACIA
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Sephadex® A NEW CONCEPT IN ION EXCHANGERS

New Cation Exchangers Specifically for Chromatography of Labile Compounds

SEPHADEX cation exchangers, the high-capacity exchangers derived from SEPHADEX, are now commercially available. These new ion exchangers were developed by Pharmacia of Uppsala, Sweden. Under extensive testing, SEPHADEX ion exchangers exhibited the following properties: High capacity for large molecules ■ Low nonspecific adsorption ■ Quantitative desorption ■ High flow rate ■ Good reproducibility ■ Easy column packing

These new products include both weak and strong cation exchangers. CM-SEPHADEX is the carboxymethylether of SEPHADEX. SE-SEPHADEX is a sulfoethylether derivative.

They are produced in two types, C-25 and C-50, thus providing selectivity in the degree of porosity; i.e., cross-linkages. These forms of SEPHADEX are available as a powder in three particle sizes—coarse, medium and fine. Due to their porous structure and high degree of substitution, CM-SEPHADEX and SE-SEPHADEX have a high capacity for large molecules. They show a low nonspecific adsorption, therefore are ideal for chromatography of labile substances such as enzymes and hormones. Relative capacities of these two SEPHADEX cation exchangers are as follows:

ADSORPTION CAPACITY FOR HEMOGLOBIN[1]

SEPHADEX ion exchanger	Type	Hemoglobin capacity
CM-SEPHADEX	C-25	0.7 g./g.
CM-SEPHADEX	C-50	4.7 g./g.
SE-SEPHADEX	C-25	0.7 g./g.
SE-SEPHADEX	C-50	2.4 g./g.

[1] The solution was equilibrated at pH 6.5 in a sodium phosphate buffer (ionic strength 0.05)

PHYSICAL AND CHEMICAL CHARACTERISTICS

The matrix in SEPHADEX ion exchangers consists of cross-linked dextran chains, where the functional groups are attached at random by ether linkages to the glucose residues in the polysaccharide chains.

The characteristics of these cation exchangers include:

- Insolubility in water, yet with pronounced hydrophilic properties that produce rapid swelling
- Varying degree of swelling depending on differences in degree of cross-linkages
- Uniform functional group distribution, both on the inside and outside of gel particles

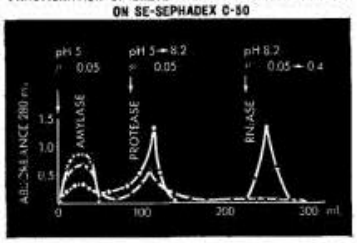
By variation in degree of cross-linkages, different porosities of the network are obtained.

All ionic groups of C-25 and C-50 are available as adsorbing sites. In the C-25 types, molecules less than 10,000 in molecular weight are accessible to all adsorbing sites, although the larger molecules adsorb only on the surface.

SE-SEPHADEX functional groups are strongly acidic and completely dissociated at pH 3. This cation exchanger has a full capacity even at very low pH values, and its exchange capacity is 2-2.5 meq/g.

The fractionation shown below exemplifies many of the purifications possible by an SE-SEPHADEX system:

FRACTIONATION OF ENZYMES IN A PANCREAS EXTRACT ON SE-SEPHADEX C-50



Sample: Extract of pancreas powder with phosphate buffer pH 5.0, $\mu = 0.05$, containing 0.002 M $CaCl_2$.

Elution: Sodium phosphate buffer pH 5.0, $\mu = 0.05$. Then with the same buffer but gradually increasing pH from 5.0 to 8.2, and finally with an ionic strength gradient up to $\mu = 0.4$ at constant pH 8.2. All buffers contain 0.002 M $CaCl_2$.

CM-SEPHADEX is most effective at pH values above 4-5, and the very high exchange capacity of 4-5 meq/g identifies this cation exchanger as exceptionally suitable for protein chromatography.

SEPHADEX cation exchangers do not cause denaturation or irreversible adsorption, and the desorption of both can be performed under mild conditions.

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APPENDIX III. Experiment results

III. 1 Experiment I

Table III. 1 Lithium concentration measures of experiment I.

t (min)	Measure	dilution grade	Li conc. (mg/L)
2	-0,004	-	**-0,004**
4	-0,005	-	**-0,005**
6	-0,005	-	**-0,005**
8	-0,005	-	**-0,005**
10	-0,004	-	**-0,004**
12	-0,004	-	**-0,004**
14	-0,003	-	**-0,003**
16	-0,002	-	**-0,002**
18	4,658	-	**4,658**
20	0,522	100	**52,2**
22	6,955	1000	**6955**
24	3,838	1000	**3838**
26	2,214	1000	**2214**
28	2,602	1000	**2602**
30	2,154	1000	**2154**
32	2,285	1000	**2285**
34	1,88	1000	**1880**
36	2,201	1000	**2201**
38	2,657	1000	**2657**
40	3,194	1000	**3194**
42	3,219	1000	**3219**
44	3,225	1000	**3225**
46	2,876	1000	**2876**
48	0,852	1000	**852**
50	2,269	1000	**2269**
52	0,421	100	**42,1**
54	2,133	-	**2,133**
56	0,9	-	**0,9**
58	0,614	-	**0,614**
60	0,447	-	**0,447**
62	0,341	-	**0,341**
64	0,29	-	**0,29**
66	0,273	-	**0,273**
68	0,253	-	**0,253**
70	0,243	-	**0,243**
72	0,234	-	**0,234**
74	0,234	-	**0,234**
76	0,223	-	**0,223**
78	0,197	-	**0,197**
80	0,184	-	**0,184**
82	0,168	-	**0,168**
84	0,176	-	**0,176**
86	0,168	-	**0,168**
88	0,153	-	**0,153**
90	0,147	-	**0,147**
92	0,132	-	**0,132**
94	0,134	-	**0,134**
96	0,13	-	**0,13**
98	0,125	-	**0,125**
100	0,125	-	**0,125**

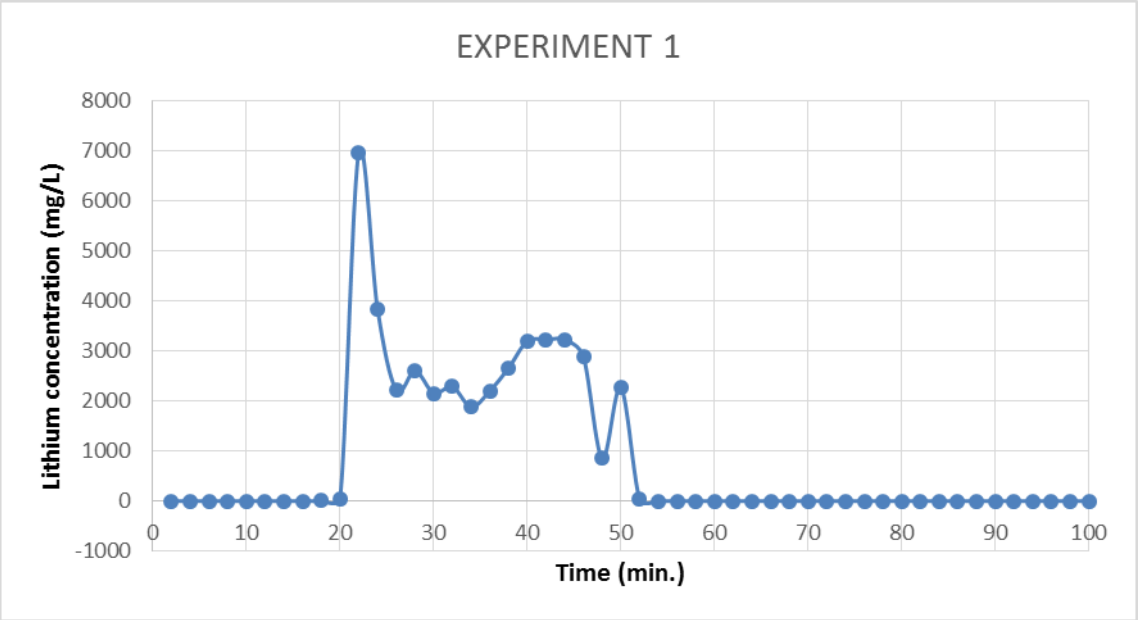

Fig III. 1. Distribution of lithium along time in experiment I.

III. 2 Experiment III

Table III. 2 Lithium concentration measures of experiment III.

t (min)	measure	dilution grade	Li conc. (mg/L)
9	0,025	-	**0,025**
18	0,003	-	**0,003**
27	0,001	-	**0,001**
36	0,003	-	**0,003**
45	0,006	-	**0,006**
54	0,196	1000	**196**
63	0,43	1000	**430**
72	0,662	1000	**662**
81	0,824	1000	**824**
90	0,86	1000	**860**
99	1,033	1000	**1033**
108	1,077	1000	**1077**
117	1,098	1000	**1098**
126	1,228	1000	**1228**
135	1,135	1000	**1135**
144	1,219	1000	**1219**
153	1,225	1000	**1225**
162	1,274	1000	**1274**
171	1,263	1000	**1263**
180	1,251	1000	**1251**
189	1,285	1000	**1285**
198	1,555	1000	**1555**
207	1,423	1000	**1423**
216	1,356	1000	**1356**
225	1,368	1000	**1368**
234	1,446	1000	**1446**
243	0,167	10000	**1670**
252	0,179	10000	**1790**
261	0,157	10000	**1570**
270	0,162	10000	**1620**
279	0,164	10000	**1640**
288	0,753	-	**0,753**
297	0,543	-	**0,543**
306	0,395	-	**0,395**
315	0,301	-	**0,301**
324	0,24	-	**0,24**
333	0,178	-	**0,178**
342	0,124	-	**0,124**
351	0,095	-	**0,095**
360	0,079	-	**0,079**
369	0,072	-	**0,072**
378	0,07	-	**0,07**
387	0,07	-	**0,07**
396	0,071	-	**0,071**
405	0,071	-	**0,071**
414	0,071	-	**0,071**
423	0,072	-	**0,072**
432	0,073	-	**0,073**
441	0,071	-	**0,071**
450	0,068	-	**0,068**

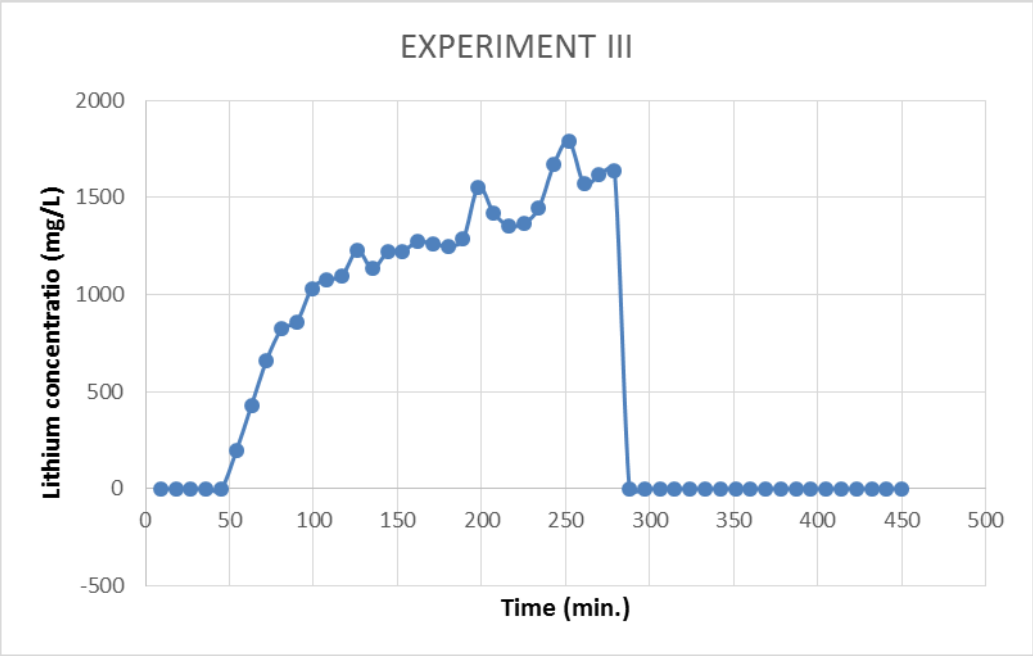

Fig III. 2. Distribution of lithium along time in experiment I.

III. 3 Experiment IV

Table III. 3 Lithium concentration measures of experiment IV.

t (min)	measure	dilution grade	Li conc. (mg/L)
9	0,146	-	**0,146**
18	0,137	-	**0,137**
27	0,038	-	**0,038**
36	0,007	-	**0,007**
54	0,009	1000	**9**
63	0,028	1000	**28**
72	0,023	1000	**23**
81	0,035	1000	**35**
90	0,05	1000	**50**
99	0,062	1000	**62**
108	0,088	1000	**88**
117	0,097	1000	**97**
126	0,127	1000	**127**
135	0,143	1000	**143**
144	0,202	1000	**202**
153	0,23	1000	**230**
162	0,262	1000	**262**
171	0,28	1000	**280**
180	0,309	1000	**309**
189	0,326	1000	**326**
198	0,346	1000	**346**
207	0,358	1000	**358**
216	0,381	1000	**381**
225	0,396	1000	**396**
234	0,399	1000	**399**
243	3,834	100	**383,4**
270	0,436	1000	**436**
297	0,341	1000	**341**
315	0,474	1000	**474**
342	0,571	1000	**571**
360	0,442	1000	**442**
387	0,452	1000	**452**
405	0,521	1000	**521**
432	0,462	1000	**462**
450	0,531	1000	**531**
477	0,542	1000	**542**
495	0,526	1000	**526**
522	0,56	1000	**560**
540	0,552	1000	**552**
549	0,585	1000	**585**

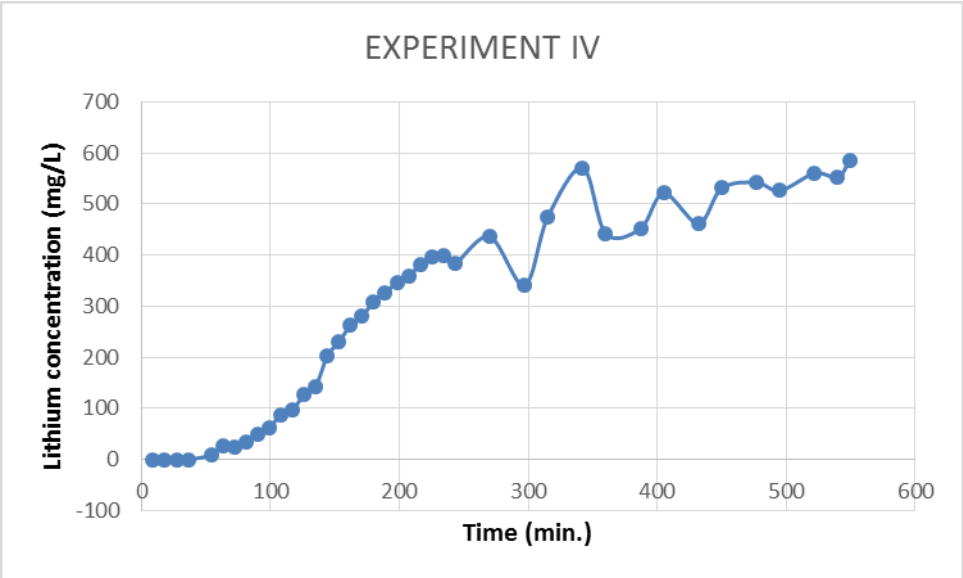

Fig III. 3. Distribution of lithium along time in experiment IV.

III. 4 Experiment V

Table III. 4 Lithium concentration measures of experiment V.

t (min)	measure	dilution grade	Li conc. (mg/L)
18	0,008	-	**0,008**
36	0,004	-	**0,004**
54	0,014	-	**0,014**
72	0,025	1000	**25**
90	0,062	1000	**62**
108	0,103	1000	**103**
126	0,140	1000	**140**
144	0,159	1000	**159**
162	0,215	1000	**215**
180	0,275	1000	**275**
198	0,264	1000	**264**
216	0,316	1000	**316**
234	0,278	1000	**278**
252	0,352	1000	**352**
270	0,410	1000	**410**
288	0,360	1000	**360**
306	0,411	1000	**411**
324	0,375	1000	**375**
342	0,428	1000	**428**
360	0,035	10000	**350**
378	0,042	10000	**420**
396	0,047	10000	**470**
414	0,039	10000	**390**
432	0,035	10000	**350**
450	0,037	10000	**370**
468	0,041	10000	**410**
486	0,044	10000	**440**
504	0,041	10000	**410**
522	0,038	10000	**380**
540	0,043	10000	**430**
558	0,046	10000	**460**
576	0,039	10000	**390**
594	0,060	10000	**600**
612	0,052	10000	**520**
630	0,054	10000	**540**
648	0,580	1000	**580**
666	0,585	1000	**585**
684	0,625	1000	**625**
702	0,589	1000	**589**
720	0,614	1000	**614**
738	0,607	1000	**607**
756	0,648	1000	**648**
774	0,626	1000	**626**
792	0,627	1000	**627**
810	0,648	1000	**648**
828	0,613	1000	**613**
846	0,628	1000	**628**
864	0,680	1000	**680**
882	0,606	1000	**606**
900	0,628	1000	**628**
918	0,606	1000	**606**
936	0,632	1000	**632**
954	0,228	1000	**228**
972	0,156	-	**0,156**
990	0,097	-	**0,097**
1008	0,064	-	**0,064**
1026	0,053	-	**0,053**
1044	0,053	-	**0,053**
1062	0,046	-	**0,046**
1080	0,045	-	**0,045**
1098	0,079	-	**0,079**
1116	0,039	-	**0,039**
1134	0,028	-	**0,028**
1152	0,029	-	**0,029**
1170	0,028	-	**0,028**
1188	0,029	-	**0,029**
1206	0,033	-	**0,033**
1224	0,031	-	**0,031**
1242	0,030	-	**0,030**

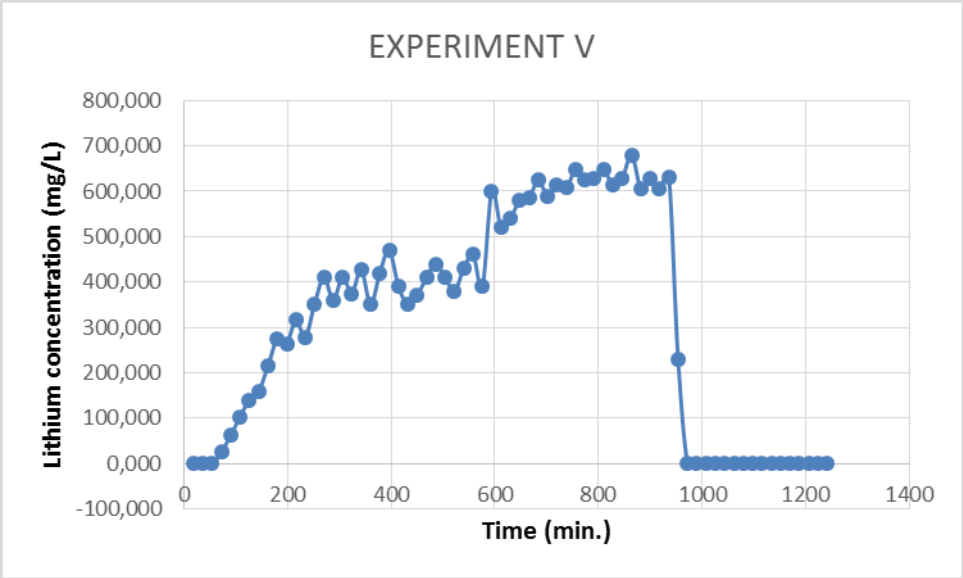

Fig III. 4. Distribution of lithium along time in experiment V.

III. 5 Experiment VI

Table III. 5 Lithium concentration measures of experiment VI.

t (min)	measure	dilution grade	Li conc. (mg/L)
9	0,053		**0,053**
18	0,152		**0,152**
27	0,141		**0,141**
36	0,179		**0,179**
45	0,414		**0,414**
54	0,047	1000	**47**
63	0,197	1000	**197**
72	0,268	1000	**268**
81	0,415	1000	**415**
90	0,049	10000	**490**
99	0,058	10000	**580**
108	0,062	10000	**620**
117	0,067	10000	**670**
126	0,069	10000	**690**
135	0,08	10000	**800**
144	0,081	10000	**810**
153	0,076	10000	**760**
162	0,085	10000	**850**
171	0,099	10000	**990**
180	0,09	10000	**900**
189	0,088	10000	**880**
198	0,098	10000	**980**
207	0,092	10000	**920**
216	0,093	10000	**930**
225	0,094	10000	**940**
234	0,096	10000	**960**
243	0,105	10000	**1050**
252	0,098	10000	**980**
261	0,098	10000	**980**
270	0,102	10000	**1020**
279	1,15	1000	**1150**
288	1,156	1000	**1156**
297	1,165	1000	**1165**
306	0,129	10000	**1290**
315	0,13	10000	**1300**
324	0,134	10000	**1340**
333	0,127	10000	**1270**
342	0,129	10000	**1290**
351	0,127	10000	**1270**
360	0,133	10000	**1330**
369	0,139	10000	**1390**
378	0,128	10000	**1280**
387	0,13	10000	**1300**
396	0,131	10000	**1310**
405	0,134	10000	**1340**
414	0,131	10000	**1310**
423	0,13	10000	**1300**
432	0,016	10000	**160**
441	1,142		**1,142**
450	0,793		**0,793**
459	0,08		**0,08**
468	-0,128		**-0,128**
477	-0,308		**-0,308**
486	-0,408		**-0,408**
495	-0,505		**-0,505**
504	-0,53		**-0,53**
513	-0,557		**-0,557**
522	-0,572		**-0,572**
531	-0,593		**-0,593**
540	-0,606		**-0,606**
549	-0,621		**-0,621**

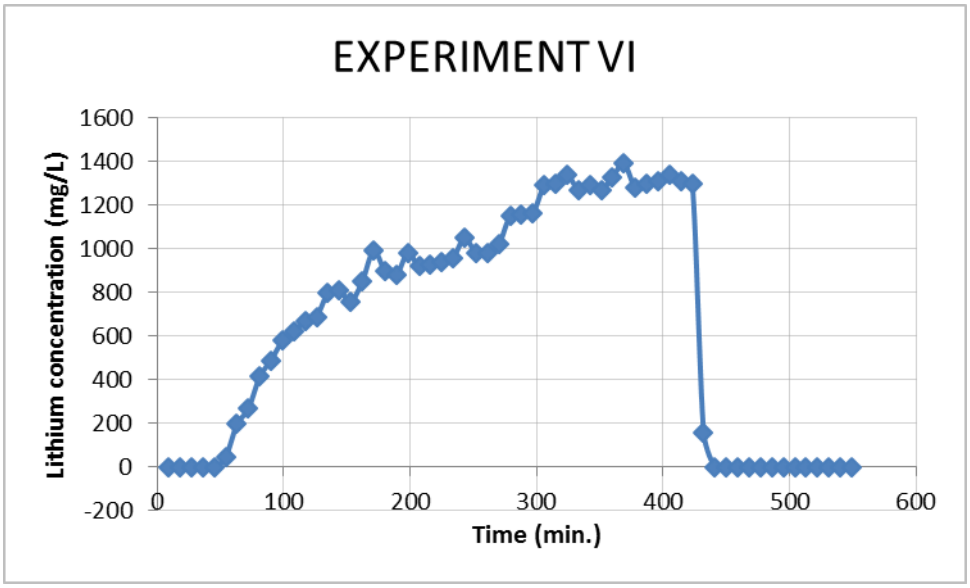

Fig III. 5. Distribution of Lithium along time in experiment VI.