



**COMPARISON OF DISTRIBUTION COEFFICIENTS OF 14 ELEMENTS ON THREE  
CATION EXCHANGERS**

**by**

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## ABSTRACT

Certain resins used in ion-exchange separation techniques have become very expensive. Although ion-exchange is an economical method to soften water it is important to keep the cost low during the process. Any exorbitant costs will make a process unattractive and eventually obsolete. Bio-Rad AG MP-50 macroporous resin (supplied by Bio-Rad Laboratories, Ltd.) at present costs approximately R20000 (twenty thousand rand) for 500 g compared to Amberlyst 15 R840.00 for 500 mL and Dowex Marathon MSC R312.34 macroporous resin for 500 mL (both supplied by Dow, Rohm and Haas Co).

This motivated the research to determine by a comparative study if there is any difference in the efficiency and effectiveness in the quantitative analysis of trace elements when these resins are used.

The following elements will be used to determine distribution coefficients for the elements on these resins: Mn, Fe(III), Co, Ni, Cu, Zn, Al, Ag, Cd, In, Ga, Tl, Pb and Bi in 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0 M nitric acid solutions. Another question is whether there is a difference or a preference when selecting either a microporous or a macroporous resin for the ion-exchange separation. Determination of distribution coefficients for 46 elements had been done by Strelow (Strelow F. W., 1984) in nitric acid on Bio-Rad AG 50W-X8. The results obtained in this study will be compared with the distribution coefficients obtained by Strelow.

The Bio-Rad, Amberlyst and Dowex resins were stirred for approximately 30 minutes in deionised water and then packed in a column. Impurities in the resin column were eluted with 5 M HCl and the resin was then rinsed with deionised water to remove the acid. Thereafter the resins was rinsed out of the column with deionised water, filtered off and then dried under vacuum in an oven at 60 °C for approximately 24 hours. Stock solutions of the elements were prepared as 0.1 M solutions and then diluted with deionised water to obtain solutions having the respective concentrations of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 4.0 M. Quadruplicate reference standards of each element were prepared. Distribution coefficients of the elements on each resin were determined as described by Strelow (Strelow F. W., Distribution coefficients and ion exchange behaviour of some chloride complex forming elements with Bio Rad AG50W - X8 cation exchange resin in mixed Nitric-Hydrochloric acid solutions, 1989).

From the distribution coefficients, obtained from the ICP-OES data, a selectivity series for the 14 elements, mentioned above, was arranged in the decreasing order for each resin's affinity for the elements.

The distribution coefficients also give an indication whether the elements can be quantitatively separated by the cation exchangers in nitric acid media. Elution curves for some elements were done to establish the experimental conditions for quantitative separations of the elements by column cation exchange chromatography.

## ACKNOWLEDGEMENTS

**I wish to thank:**

- Prof T.N van der Walt, for being instrumental from the beginning to the end of my studies.

## **DEDICATION**

I dedicate my dissertation work to my family and many friends. A special feeling of gratitude to my parents, Thomas J.P(deceased) and Naomi Wells, whose words of encouragement and motivation has been an inspiration to me.

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## GLOSSARY

### Terms/Acronyms/Abbreviations

**Chelation** (Muller, 1994)

### Definition/Explanation

The formation or presence of bonds (or other attractive interactions) between two or more separate binding sites within the same ligand and a single central atom. A molecular entity in which there is chelation (and the corresponding chemical species) is called a 'chelate'. The terms bidentate (or didentate), tridentate, tetradentate, multidentate are used to indicate the number of potential binding sites of the ligand, at least two of which must be used by the ligand in forming a 'chelate'. For example, the bidentate ethylenediamine forms a chelate with CuI in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.) The phrase 'separate binding sites' is intended to exclude cases such as  $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]^-$ , ferrocene and (benzene) tricarbonylchromium in which ethene, the cyclopentadienyl group and benzene, respectively, are considered to present single binding sites to the respective metal atom and which are not normally thought of as chelates.

**Cross-linked** (Jenkins (UK), Kratochvil (Czech Repub), Stepto (UK), & Suter (Switzerland), 1996)

A small region in a macromolecule from which at least four chains emanate, and formed by reactions involving sites or groups on existing macromolecules or by inter-actions between existing macromolecules.

### Notes

1. The small region may be an atom, a group of atoms, or a number of branch points connected by bonds, groups of atoms or oligomeric chains.
2. In the majority of cases, a crosslink is a covalent structure but the term is also used to describe sites of weaker chemical interactions, portions of crystallites and even physical entanglements.

**Elute** (Ettre, 1993)

To remove an element by elution chromatography. This term is preferred to the term 'develop', which has been used in paper chromatography and in thin-layer chromatography. The process of elution

may continue until the components have left the chromatographic bed.

**Fouling** (Koros, Ma, & Shimidzu, 1996)  
(in membrane processes)

Process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores.

**Immiscibility** (Work, 2004)

Inability of a mixture to form a single phase.  
Notes:

- 1) Immiscibility may be limited to certain ranges of temperature, pressure, and composition.
- 2) Immiscibility depends on the chemical structures, molar-mass distributions, and molecular architectures of the components.

**Macroporous polymer** (Horie, Work, Hess, & Stepto, 2004)

Glass or rubbery polymer that includes a large number of macropores (50 nm – 1  $\mu$ m in diameter) that persist when the polymer is immersed in solvents or in the dry state.

Notes:

- 1) Macroporous polymers are often network polymers produced in bead form. However, linear polymers can also be prepared in the form of macroporous polymer beads.
- 2) Macroporous polymers swell only slightly in solvents.
- 3) Macroporous polymers are used, for example, as precursors for ion-exchange polymers, as adsorbents, as supports for catalysts or reagents, and as stationary phases in size-exclusion chromatography columns.
- 4) Porous polymers with pore diameters from ca 2 to 50 nm are called mesoporous polymers.

**Macroreticular** (Amberlite and Amberlyst Resins - Technical Information Bulletin, 2017)

Macroreticular resins comprise a tough, rigid, spongelike material with large, discrete pores, and have a somewhat lower capacity than gel-type resins, but can have longer operating life and effect separations not possible with gel-type resins. High molecular weight ions can be more completely removed from solution and more completely eluted from the resin on regeneration. Moreover, the open structure allows application with tough copolymers which would be too dense for use in a strictly gel-type system.



<b>Matrix (in analysis)</b>	The components of the sample other than the analyte.
<b>Monomer</b> (Guilbault, 1989)	A substance composed of monomer molecules.
<b>Osmotic pressure</b> (Cohen, et al., 2008)	Excess pressure required to maintain osmotic equilibrium between a solution and the pure solvent separated by a membrane permeable only to the solvent:
<b>Porosity</b> (R. L. Burwell, 1976)	A concept related to texture, referring to the pore space in a material.

# CHAPTER 1

## INTRODUCTION

### 1.0 Introduction

This study came about because of a number of researchers at the institution has conducted research in the field of ion exchange chromatography and the resin of preference being Bio Rad MP 50. No major companies funded their research so there was no huge budgets available to conduct research in the field of cation exchange chromatography. All funding thus came from funders to the institution which meant budgets were minimal and the need for cost cutting was real.

The use of resins within industry have grown exponentially to the point where resins are not used only in water technology industries anymore but has made in roads into pharmaceutical industry, medical biological industry, mining industry, food industry and is also used in the treatment of radioactive water.

The potential to influence any one of these industries with significant research data will attract research funding.

### 1.1 The objective of the study

The objective of the study was to determine whether there were cheaper and reliable alternatives for the expensive resins used in research to obtain reliable results when separating 14 elements from each other using Strelow's research as a basis (Strelow F. W.E., 1960). Strelow used BioRad AG 50W-X8 and in this study two Dowex resins will be used, namely Amberlyst 15 and Dowex Marathon MSC.

The trace elements selected by Strelow was used for comparison purposes in this study.

### 1.2 Research approach

In this study three types of ion exchange resins will be used, namely BioRad AG MP50 , Dowex Marathon MSC and Amberlyst 15, to test their effectiveness and efficiency to separate the 14 selected trace elements.

The research overview will include the following:

- i. Preparation of the three resin materials.
- ii. Eluting the 14 trace elements using column chromatographic method.
- iii. Determination of the elements in the reference standards and the eluates using the ICP-OES.
- iv. Comparison of the obtained results with the results of Strelow who had use the BioRad AG 50W –X8 resin (Strelow F. W., 1960).

### **1.3 Problem statement**

As mentioned earlier the ion exchange of preference used by researchers at the institution is BioRad AG MP-50, which is an expensive product manufactured in the USA and furthermore, its purchased price is also dependent on the R/US\$ exchange rate which increased the price even more. At the time of this study the rate of exchange was about R16 per US dollar and with so much political and economical instability currently in South Africa one can expect further decline in the value of the Rand against the US\$.

The much cheaper macroporous resins Dowex Marathon MSC and Amberlyst 15 (both consist of coarse beads) were compared with BioRad AG MP-50 (which consists of fine particles and is also a macroporous resin) to see whether the Dowex and Amberlyst resins can be used instead of the expensive BioRad AG MP-50.

### **1.4 Delimitation of research**

In the current study, the following areas will be investigated and the following delimitations may occur:

- i. Availability of the three named resins.
- ii. Availability of the appropriate salts of the elements to prepare stock solutions of the elements
- iii. Retention of the elements on the resins or the elution of the elements from the resins.
- iv. Availability of the ICP-OES to determine the elements in the reference standards and eluates for each of the trace element in triplicate.
- v. Availability of argon gas for the ICP-OES.
- vi. Setting up distribution coefficient curves for each trace element.

## CHAPTER 2

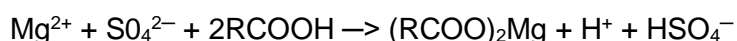
### ION EXCHANGERS

#### 2.0 Literature Review for Ion Exchangers

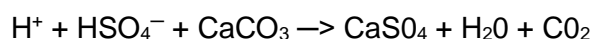
It is very important to discuss the history of resin material, what it is? How does it function? This chapter will give clarity on ion exchange resins and try and explain how ion exchange resins has replaced many systems due to one of its uniqueness that it can be regenerated. The cation exchange resin was first used mainly in the treatment of water but when different synthesis methods for resins became available its applications has impacted many types of industry.

#### 2.1 History of Ion Exchangers

Some interesting history of ion exchangers has been documented. We find the first recording in history that suggests that an ion exchanger was probably used in the Bible. In the book of Exodus, Yahweh points out a dead tree which Moses had to throw in the water. If the tree was dead Rieman and Walton suggests that its cellulose would have oxidised whereby carboxyl groups were formed (Rieman III & Walton, 1970). Therefore it was possible the “brackish” ions of the water was removed by an ion exchange reaction



Neutralisation of the resulting sulphuric acid by deposits of limestone then followed,



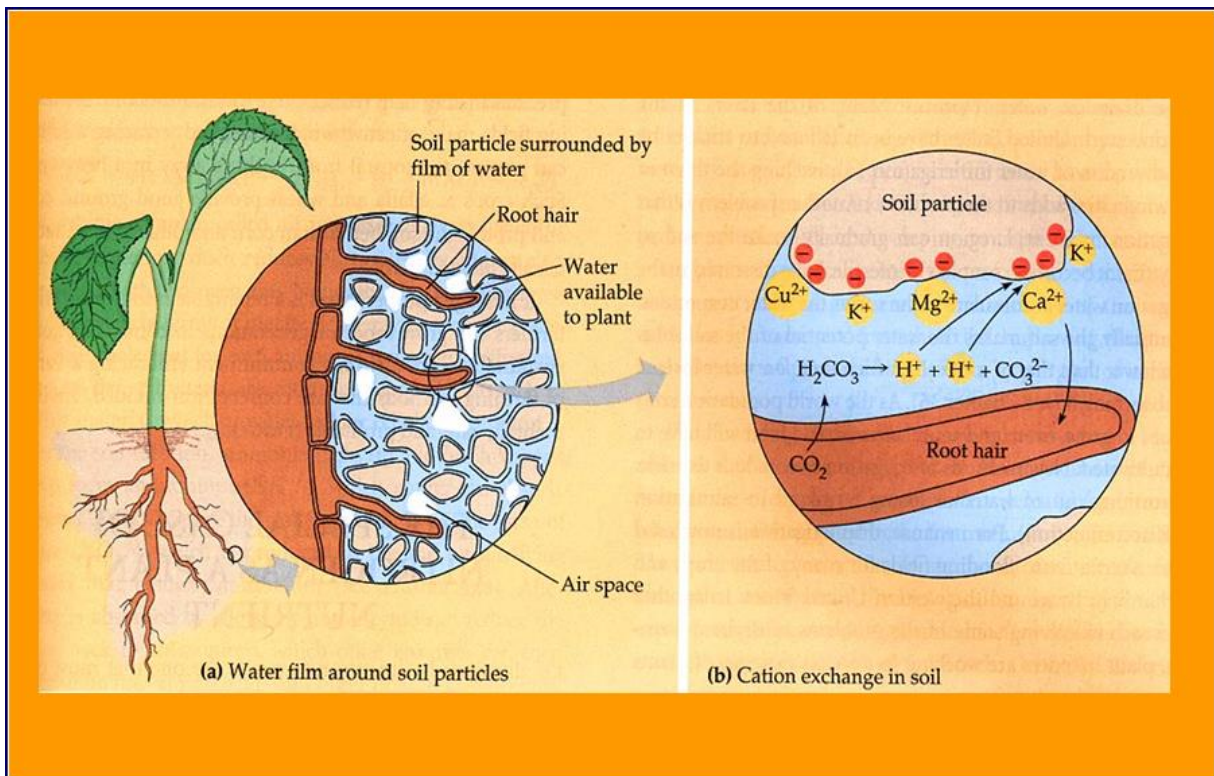
Although Moses did not have the time to conduct any research to confirm this suggestion, at that time Rieman continues by bringing to our attention that the Spanish Bible recorded that Moses threw into the spring an ‘un madero’ (translated a log) and not ‘un árbol’ (translated a tree).

Later in history we read about Aristotle who suggested filtering sea water through certain types of soil to make sea water potable. Presuming in the improvement of the taste of water the ion-exchange property of wood cellulose played a role in the first case and that of silicates in the second one (Inczedy, 1966).

The first documented research on this topic occurred just after 1850, but before the 1850 the agricultural scientist regarded soil only as an inert material. The soil was therefore just a non-

reactive material and support for plants. Even the well-known agricultural scientist of that time Justus von Liebig who proposed the Law of the Minimum at that time could not explain the exchange of nutrients from the soil to the plant through its roots. His understanding was that plants need nutrients, and when one adds more of one nutrient to the soil that it would affect the yield of the crop (Essington, 2004).

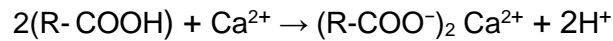
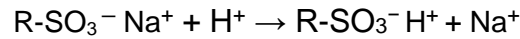
During the years 1850-1854, Thompson and Way (Ayres, 1968) observed that when ammonium salts are added to soils it released the necessary minerals to the fruit trees. Thompson took two types of soils, one being a black soil which was considered fertile and the second which consisted of strong clay and packed them in separate glass columns. He added an Ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) to both glass columns and then leached them with water. The leachate obtained after drying it was found to be gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), which meant that the ammonia ( $\text{NH}_4^-$ ) was retained by the soil as depicted in Fig 2.1 (Fern Group, 2011).



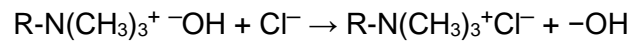
**Figure 2.1 Example of ion exchange within the soil**

They extensively investigated this phenomenon which we understand as ion exchange today using the natural soils and synthesised different ion exchange materials to let the roots of the plant be exposed to all the necessary minerals in the ground. Their ion exchange studies were limited to calcium displacing sodium-, potassium-, ammonium- and magnesium ions, until 1880 when J. M. van Bemmelen expanded on the work of Thompson and Way (Essington, 2004).

Examples of cation exchange and the principle of equivalent displacement:



Example of anion exchange



Inorganic ion exchangers, such as clay zeolites, were produced to treat water. This inorganic ion exchange was limited in their use as they only operated within a narrow pH range. The first synthetic ion exchange resins were developed by Adams and Holmes in 1935, based on a phenol-formaldehyde structure. Table 2.1 is a summary of the history of how ion exchange technology grew to what it is today, these ion exchange resins (organic) and inorganic ion exchangers are now used in every sphere of industry and therefore widely researched from farming, mining, water treatment, food industry, pharmaceutical industry and air quality

After this introduction of the synthetic ion exchange resin by Holmes and Adams (Ayres, 1968) further developments occurred in this field. Commercial ion exchange resins based on a cross-linked polystyrene matrix were manufactured, which occupies 90% of the resin market presently. More recently polyacrylic resins have been introduced which widened the scope and versatility of the synthetic ion exchange resins, which occupies the other 10% of the resin market today.

How does ion exchange work? Ion exchange is a sorption process whereby the cation or anion is attached to an insoluble solid surface. The cations or anions will exchange in equal amounts with its surrounding environment, i.e. displacing the attached ions into the environment and the ions from the environment attaches to the functional group of the solid surface.

**Table 2.1: The table below shows the main development steps of ion exchange** ( de Dardel F., 2011)

<b>~1400 BC</b>	Moses experiments water debittering (Exodus 15, 22 - 25)
<b>~330 BC</b>	Aristotle finds that sea water loses part of its salt contents when percolated through certain sand
<b>1850</b>	Discovery of ion exchange by Thompson & Way (England)
<b>1876</b>	Zeolites recognised as carriers of base exchange in soils (Lemberg)
<b>1901</b>	Artificial zeolites used for removal of potassium from sugar juices
<b>1905</b>	Commercial use of ion exchange with inorganic aluminosilicates (zeolites) developed by Gans (Germany)
<b>1935</b>	Industrial manufacture of sulphonated coals for water softening filters (Liebknecht and Smit)
<b>1935</b>	Synthetic ion exchange resins (phenol-formaldehyde polycondensates) invented by Adams & Holmes
<b>1940</b>	First commercial phenol-formaldehyde ion exchange resins; both strongly acidic and weakly basic exchangers. Examples: Duolite C3 and Duolite A7.
<b>1944</b>	First patent for sulphonated polystyrene resin (D'Alelio, USA)
<b>1946</b>	McBurney invents strongly basic anion exchangers made by chloromethylation and amination of polystyrene
<b>1947</b>	First commercial strongly acidic cation exchangers based upon cross-linked polystyrene
<b>1948</b>	First commercial strongly basic anion exchangers based on McBurney's invention
<b>1948</b>	Rohm and Haas introduces the first weakly acidic cation exchanger (methacrylic Amberlite IRC50)
<b>1949</b>	First commercial use of Mixed-bed resin technology
<b>1950</b>	First use of weakly acid resins for recovery of antibiotics (streptomycin) from fermentation broth
<b>1950</b>	First commercial synthesis of styrene-based weakly basic anion exchanger (Amberlite IRA45)
<b>1950</b>	Development of ion exchange resins in powdered form for sodium reduction therapy
<b>1951</b>	First use of ion exchange resins for treatment of sugar
<b>1952</b>	First commercial use of anion exchange resins for recovery of uranium from leach liquor
<b>1952</b>	Invention and development of chelating polymers (Gregor)
<b>1953</b>	Rohm and Haas develops acrylic based weakly basic anion exchange resin (now Amberlite IRA67)

1957	Rohm and Haas introduces liquid anion exchange materials (Amberlite LA1, LA2)
1959	Discovery of phase extension polymerisation technique for production of macroporous ion exchange resins. Patents in Germany (Bayer), USA (Rohm and Haas) and UK (Permutit). Rohm and Haas used to call the products <i>macroreticular</i> .
1961	Rohm and Haas introduces macroreticular (macroporous) ion exchange resins for use as catalysts
1963	Bayer files a patent for the "floating bed" (Schwebebett) packed bed ion exchange technology
1965	New macroreticular polymeric adsorbents (Amberlite XAD2, XAD4, etc.) introduced
1974	First commercial use of boron-specific resin (Amberlite IRA743, methyl-glucamine)
1988	Dow Chemical introduces uniform particle size Dowex Monosphere resins

## 2.2 Principle of Ion Exchange

An efficient and effective ion exchanger has the ability to remove an ion from an aqueous solution and this ion is replaced by a monomer. The monomer is attached to a functional group and the functional group is attached to the solid synthetic ion exchange resin material. Only the monomer unit will participate in an exchange reaction with the mobile ions of similar charge moving in the solution. In principle the ion exchange resin material consists of small porous beads (three dimensional structure with a cross-linked matrix of hydrocarbon chains, e.g. styrene) which are insoluble in water and most organic solvents. Divinylbenzene (DVB) is a crosslinking agent that gives the beads their physical strength, and without which the styrene would be water-soluble) (Agency, 2002)

The functional group of a strong cation exchanger in an acidic medium is a negative sulphonic group and attached to it is a hydrogen ion ( $H^+$ ) which replaces then the cation from the aqueous solution. This cation can be replaced again, through elution, by another cation in a solution. For ion exchange to be successful an electronically neutral media in two phases must be present. One media being the mobile phase which carries the ion that will replace the ion from the stationary ion exchange resin (see Figure 2.2).



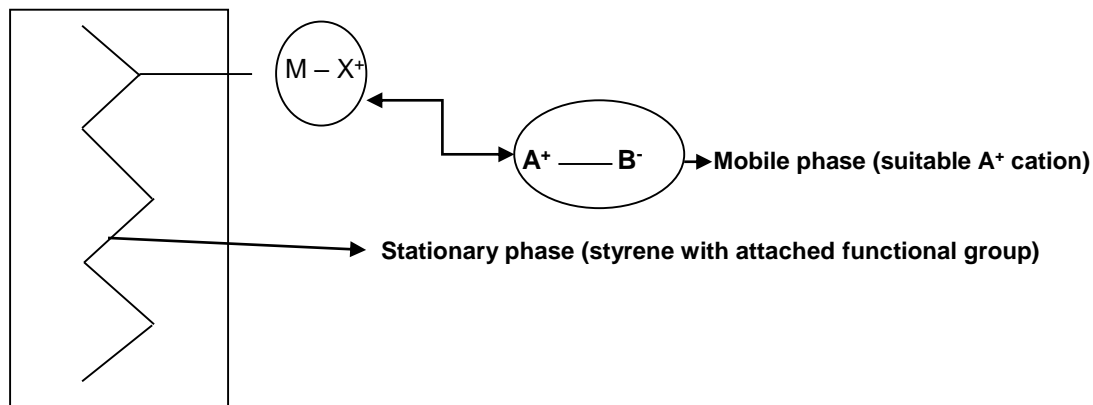


Figure 2.2 Basic principle of cation exchanger resin material

## 2.3 Synthesis of Ion Exchange Resins

Golden (Berg, 1963) described the synthesis of the modern day ion exchange process as a two-step process which will be discussed below, i.e.:

1. Polymerisation process
2. Activation process.

### 2.3.1 Polymerisation process

#### 2.3.1.1 Gel type resin

A spherical bead is produced by polymerisation of styrene (or an acrylic monomer, usually methyl acrylate) and a crosslinking agent (usually divinylbenzene, DVB) in an aqueous suspension (Inczedy, 1966)

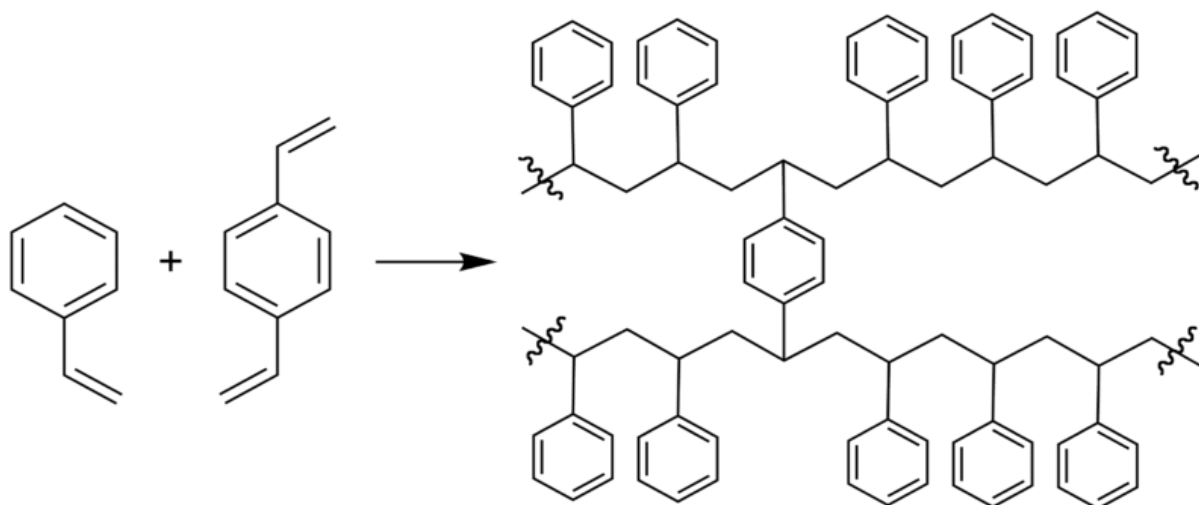
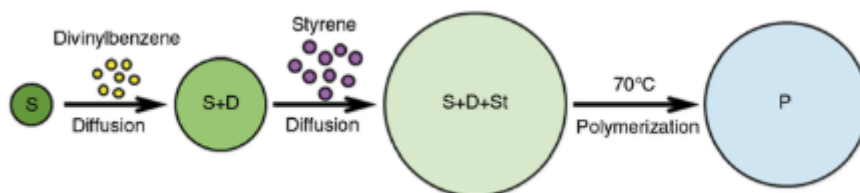


Figure 2.3 Chemical structure of Polystyrene Divinylbenzene (DVB) (Macks, 2011)

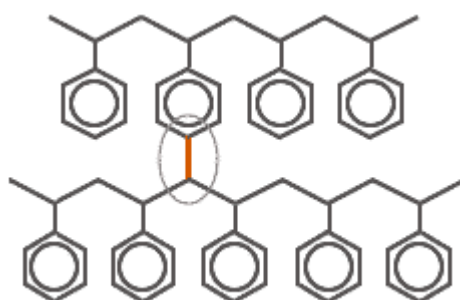
This technique of suspension polymerisation (Fig 2.4) is used extensively in the production of pearl (or bead) polymers, not specifically to make ion exchange resins, and is dependent on the fact that the monomer is essentially insoluble in water. The monomer will disperse into spherical droplets once stirred with water. Small quantities of various stabilising ingredients are added to the water to make this dispersion more permanent.



**Figure 2.4 Preparation of highly monodisperse PS-DVB particles by using Ugelstad method, S: seed; D: divinylbenzene; St: styrene; P: particle** (J. Y. He, Z. L. Zhang, Kristiansen, & Redf, 2012)

Free radicals are produced once an initiator is added and heat is then applied to the monomer mixture. This starts a chain reaction with the monomer units which are progressively added to the growing polymer chains. Styrene consists only of one double bond which is capable of reacting into the polymer chain. The polymer that is produced here from styrene is a hydrophobic polymer yet soluble in organic solvents, e.g. Aromatic hydrocarbons.

Cross-linking agents (Fig 2.5), e.g. divinylbenzene (DVB), have two or more reactive double bonds, each of these double bonds will react with a separate polymer chain leading eventually to an 'infinite' single polymer chain network. The polymer chain swells while it sorbs more of the solvents and finally the solvents are unable to dissolve the polymer chain. The size or the extent of the swelling depends on the proportion of the Divinylbenzene, DVB in the monomer – the rule being the more DVB, the less the polymer will swell.



**Figure 2.5 Cross-linked polystyrene** (de Dardel F. , 2015)

### ***2.3.1.2 Macroporous type resin***

For the resin matrix to contain pores that will not end in dead ends within the resin matrix it is necessary that the monomers undergo a chemical reaction within an inert solvent to produce pore structures within the resin that, which is miscible with the monomers but essentially immiscible with the growing polymer chain. Golden (Berg, 1963) describes that to manufacture during polymerisation of the resin matrix progresses, the mixture separates into two phases, i.e. first phase being the growing polymer and the other being the diluent plus a continuously decreasing amount of monomer. At the end of the polymerisation process of the resin matrix the remaining solvent is then removed from the polymerised structure through distillation or washing to leave the interconnecting network of pores.

### ***2.3.2 Addition of the functional groups to the resin material***

Once the polymer chain or network is formed the next step is to add the functional group to the polymer. This polymer will contain the labile ion which is capable to exchange with the other ions in solutions. The functional group makes the polymer structure hydrophilic. Water will swell the resin material, but cannot dissolve it due to the polymer chain structure. The extent of this swelling is an important characteristic of an ion exchange resin, and controls its behaviour in many applications.

#### ***2.3.2.1 Addition of the sulphonic acid functional group***

Sulphuric acid is added to the resin material to react with the polystyrene polymer at temperatures between 90<sup>0</sup> and 140<sup>0</sup> C to obtain the functional sulphonic acid group.

#### ***2.3.2.2 Addition of the amino functional group***

The amino group of the strong and weak base resins is added in two stages. Chloromethylation is the first phase – a chloromethyl group is added to the polystyrene chain and followed by the addition of an amine to give the final quaternary or tertiary amino functionality. The choice of amine affects the resin properties.

#### ***2.3.2.3 Addition of carboxylic functional groups to polyacrylic resins***

Polyacrylic resin material are produced as either weak acid cation resins with carboxylic acid functional group or as a strong or weak base anion resin whose properties are similar, however not the same, as those produced with polystyrene.

## 2.4 Types of Ion Exchangers

Since the development in synthetic ion exchangers the material used are almost exclusively under the name of the resins. There are two types of resins made, i.e. **gel** type and the **macroporous** cross-linked type. Their basic structure is the same where the polymeric structure is obtained for both by co-polymerisation. The difference of the two resin types are noted by their porosity.

**Gel** type resins (introduced into the market since 1945) have a natural porosity limited to intermolecular distances and a micro porous type structure. The exchange takes place by diffusion of the ions through the resin structure to and from the ion exchange sites.

**Macroporous** type of resins (introduced into the market since 1956) has additional artificial porosity which is obtained by adding a substance designed for this purpose. The resins comprise a continuous polymer matrix interspersed with a continuous pore matrix. (Lenntech).

Although the gel type resin matrix was used extensively at first, but had its weaknesses. The gel resin matrix bead is spherical in shape and the pores are continuous which reflects light through, making the bead have a transparent appearance. This transparent appearance comes about due to the light that enters into the bead will flow through the polymer structure without being diffracted, and therefore being visible from the other side of the bead.

Within the macroporous bead, there are different phase boundaries between the pores and the resin matrix, which meant at each point where the light enters the bead will it refract the light, where little or no light exits the bead, and therefore the appearance of the macroporous bead looks opaque.

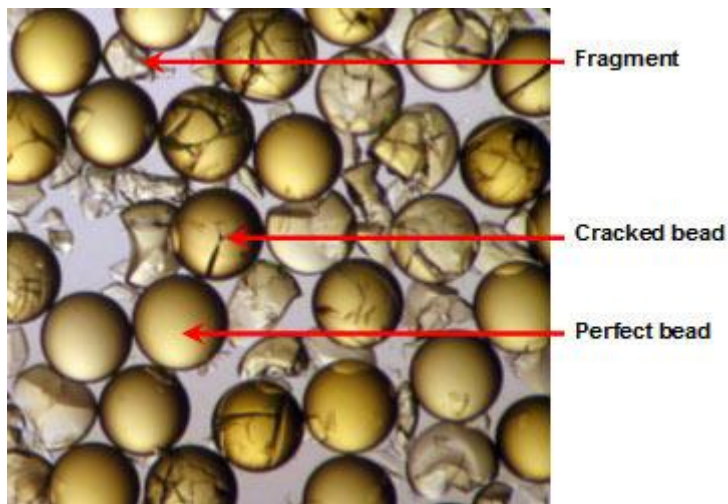
Two advantages were found using macroporous beads over the gel type. Macroporous beads were found to be less susceptible to osmotic shock and less liable to organic fouling (i.e. organic substances displace the mobile phase and hence the resin matrix becomes ineffective).

Gel type beads mostly collapse under osmotic pressure due to the contracting and swelling of the bead when in use. The bead will contract in the presence of strong electrolyte solutions which encountered during regeneration, and will rapidly swell again when the regenerating solution is washed out of the resin. These volume changes exert osmotic stress and resulting that the gel bead collapses and crack or even smash the bead. The bead will still be usable however will delay or prevent the flow of the exchange materials through the pores.

The differences between a gel ion exchange resin and macroporous ion exchange resin is further summarised in Table 2.2.

**Table 2.2: Comparisons of Gel and Macroporous Ion - Exchange Resins** (Miller, 1981)

	Gel	Macroporous
Uses	Standard resin for most water applications	Widely used for special applications
Appearance	Transparent	Opaque
Porosity	Function of degree of crosslinking	Function of cross-linking and number of discrete pores
Crosslinking Levels	Low	High
Volume Change	Considerable with high porosity (low cross-linked) resins	Less volume change than gel resins
Resistance	Susceptible to oxidizing agents and organic foulants	Good chemical resistance
Capacity and Kinetics	High capacity and fast elution kinetics	Reduced capacity and kinetics



**Figure 2.6 Examples of cracked, fragmented and perfect beads** (De Dardel, 2016)

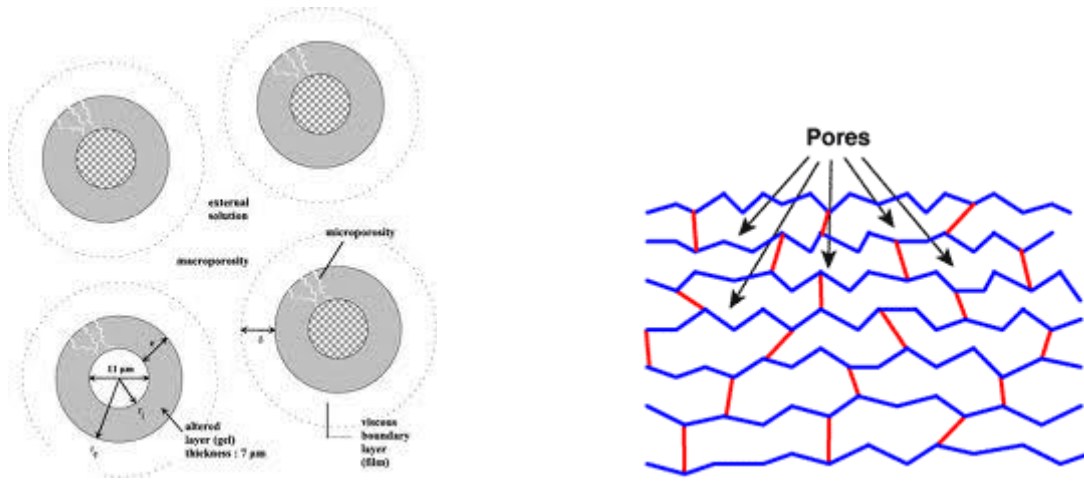


Figure 2.7(a) Example of a gel type microporous resin (de Dardel F. , 2015)

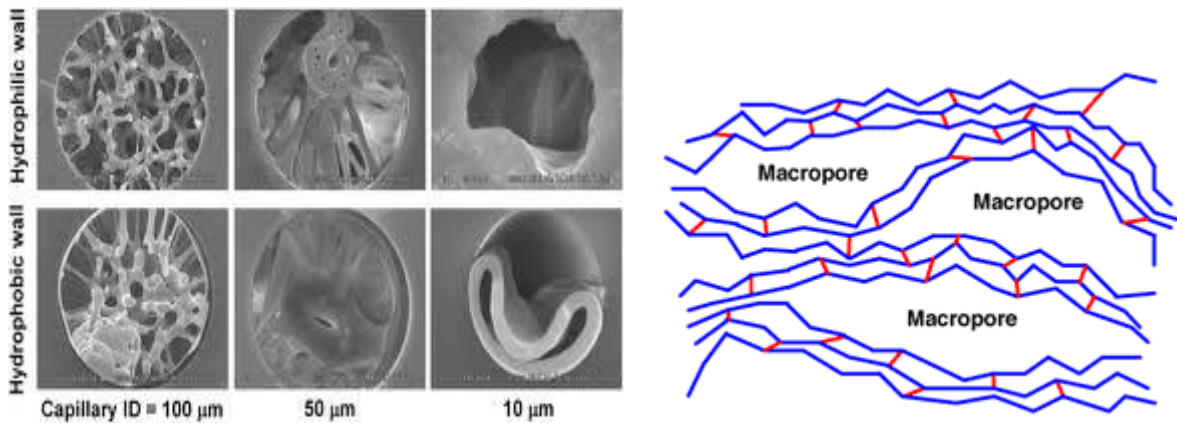


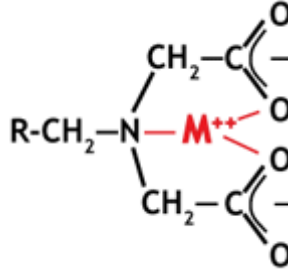
Figure 2.7(b) Example of a macroporous resin (de Dardel F. , 2015)

#### 2.4.1 Classification of ion exchangers

The gel and macroporous type of synthetic ion exchange resin material are classified according to the chemical properties of their functional group. Ion exchangers are classified under these three groups: Cation Exchangers, Anion Exchangers and Chelating Ion Exchangers. The number of functional groups that may be attached to the polymeric matrix is numerous, however commercially these are the common ones:

**Table 2.2 – Functional Groups on typical Synthetic resins** (de Dardel F. )

TYPE OF RESIN	FUNCTION	FUNCTIONAL GROUP	EXAMPLES
Strongly Acidic Cation <b>(SAC)</b> Exchange	In sodium form, they remove hardness (essentially Ca and Mg) water and other solutions. In hydrogen form, they remove all cations. They are also used as catalysts.	$-\text{SO}_3^-\text{H}^+$ <b>(Sulphonic acid)</b>	Amberjet™ 1000 Na Dowex™ Marathon C Lewatit™ Monoplus S100
Weakly Acidic Cation <b>(WAC)</b> Exchange	In hydrogen form, they remove preferentially divalent ions (e.g. Ca and Mg) from solutions containing alkalinity.	$-\text{COOH}$ <b>(Carboxylic group)</b>	Amberlite™ IRC86 Dowex™ MAC3 Lewatit™ CNP80
Strongly Basic Anion <b>(SBA)</b> Exchange	In hydroxyl form, they remove all anions. In chloride form, they remove nitrate, sulphite and several other ions.	$-\text{N}(\text{CH}_3)_3^+\text{OH}^-$ <b>(Quarternary ammonium)</b>	Amberjet™ 4200Cl Dowex™ Marathon A Lewatit™ Monoplus M500
Weakly Basic Anion <b>(WBA)</b> Exchange	After cation exchange, they remove chloride, sulphate, nitrate, and other anions of strong acids, but they do not remove weak acids ( $\text{SiO}_2$ , and $\text{CO}_2$ )	$-\text{N}(\text{CH}_3)_2$ <b>(Amines)</b>	Amberlite™ IRA96 Dowex™ Marathon MWA Lewatit™ Monoplus MP64

Selective <b>Chelating</b> resins	They remove metals, boric acid, perchlorate or other ions selectively.	Many different types 	Amberlite PWA5 Ambersep GT74 Amberlite IRC747 Chelex 100
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Some resin matrix materials are able to form complexes with metals, therefore forming special resins which are of the chelating type. The term chelating is derived from the Greek word  $\chi\eta\lambda\acute{\eta}$  which means “claw”, because of the metallic ions being captured like a claw. Chelating resins makes complexes only with multivalent metals and resulting in stable complexes; however these resins remove the metals from solution selectively due to their selectivity nature.

#### 2.4.2 Types of ion exchange materials

This is an attempt to describe the full spectrum of the various types of ion exchange materials available in the market. Cation- and anion exchange material can be either inorganic compounds or organic resins. In organic types of resin we find natural resins and synthetic made resins.

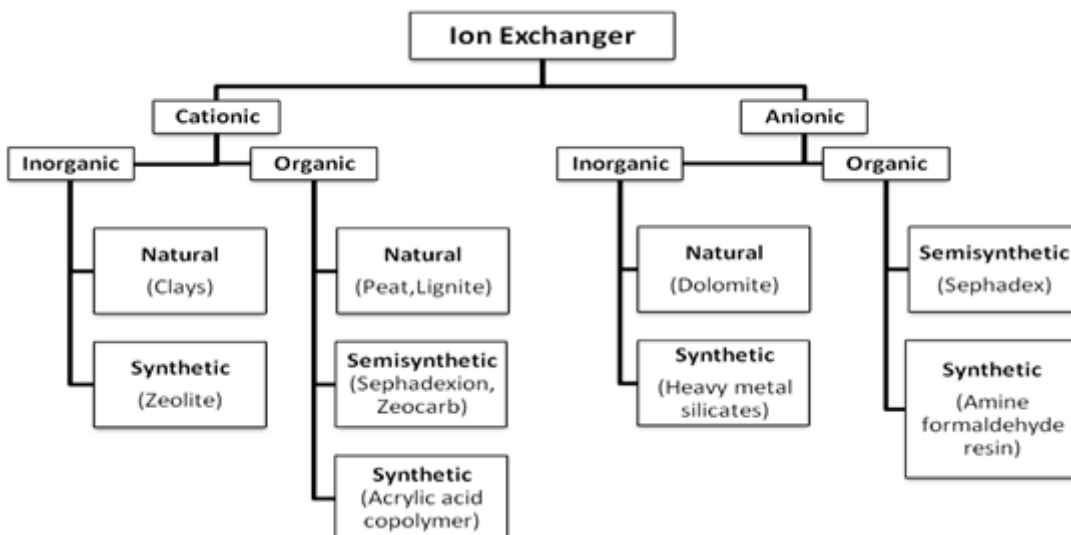


Figure 2.8 The spectrum of ion exchangers available (Pharmatutor.org, 2017)

These types of resins operate in various strengths of solutions - i.e. strong acidic (SAC), strong basic (SBA), weak acidic (WAC) and weak basic (WBA). The strong functional group with its



ionised character within solutions of ions will easily exchange its mobile ion with another ion in the solution.

Resin material with strong functional groups will exchange ions of dissolved salts with ease whereas the weak functional groups are deionised and will therefore have very little ability to exchange with ions of the salts. Weakly functional anions will remove readily anions from an acidic medium. Calcium and magnesium will be readily removed from solutions of bicarbonates and carbonates will be removed by weakly acidic resins.

An aminophosphonic chelating group had also been bound to the polystyrene resin and this resin (in the sodium form) is used to remove calcium and other divalent ions from brine before the caustic soda is produced by the membrane cell process. Purolite S940 and Purolite S950 are examples of this type of chelating resin.

## **2.5 Character and Structure of an Ion Exchanger**

### *2.5.1 Fundamentals in Ion Exchange Resin*

It does not matter what type of ion exchange resin material is in use, certain fundamental characteristics will be found in each one (styrene or acrylic form) of them and will eventually determine how the resin material will perform in its applications.

### *2.5.2 Moisture Retention*

Although the resin material is a solid and insoluble in water due to the DVB crosslinking material used, is it still important that the resin material sorb a certain amount of water. The functional groups attached to the solid styrene structure on the surface and within the pores in the resin. These are therefore active sites throughout the polymer where a labile ion is attached to and any ion that will replace the labile ion has to be dissolved in water and replace the labile ion at the site within or on the surface of the resin.

The amount of swelling or water that a resin will sorb is dependent on the labile ion attached for example a hydrogen ion attached to a sulphonic functional group requires much more water than a sodium ion attached to the same functional group (Golden,2000)

The amount of water that the resin material sorbs – and not dissolves – is one factor within a resin that will determine the performance in specific applications. The amount of water is

dependent on the percentage crosslinking (the more DBV crosslinking the less water can be sorbed). Easily

The water sorbed by the resin can easily be removed by hot air drying, but will be resorbed once the resin is place back into the water. The value of the water content can be determined by weighing the swollen resin and then the dried resin, the difference being the sorbed water.

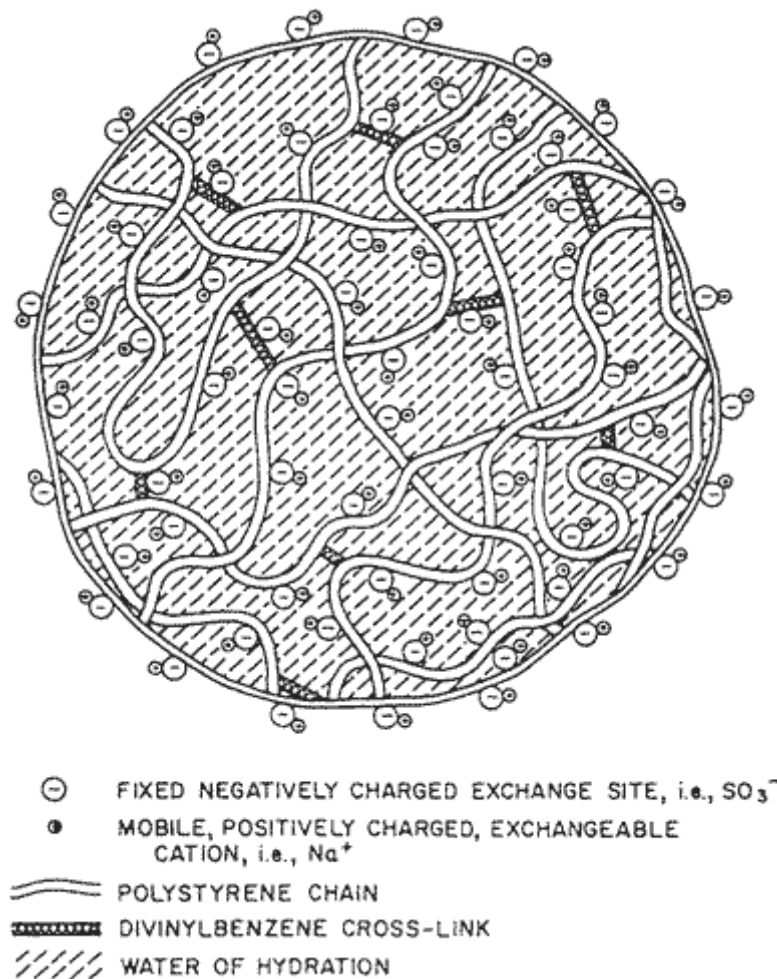


Figure 2.9: Active sites on a resin (XIII-Water-D-Ion Exchange Resins, 2016)

### 2.5.3 Capacity

It is possible for the ion exchange material only to exchange labile ions if there is place available at the active sites. The amount of active sites present on a resin material is a factor that will determine how the resin will perform in specific applications. These active groups are placed during the activation process of the resin material and are known as the capacity of the resin which can be determined by the following:

2.5.2.1 Dry weight capacity

2.5.2.2 Volume capacity

2.5.2.3 Operating capacity.

### **2.5.3.1 Dry weight capacity**

The proportion of active sites in the dry resin material is expressed as equivalents per kilogram (or milli-equivalent per gram, preferred terminology in the industry). This method of using resin material is rarely used in a dry state and is used only in specialised applications.

### **2.5.3.2 Total Volume Capacity**

Resin material in industry and research environments are supplied and used in its wet form (or fully swollen in solution / water). This measure of capacity is therefore much more useful than to determine the resin material capacity accurately for the dry resin.

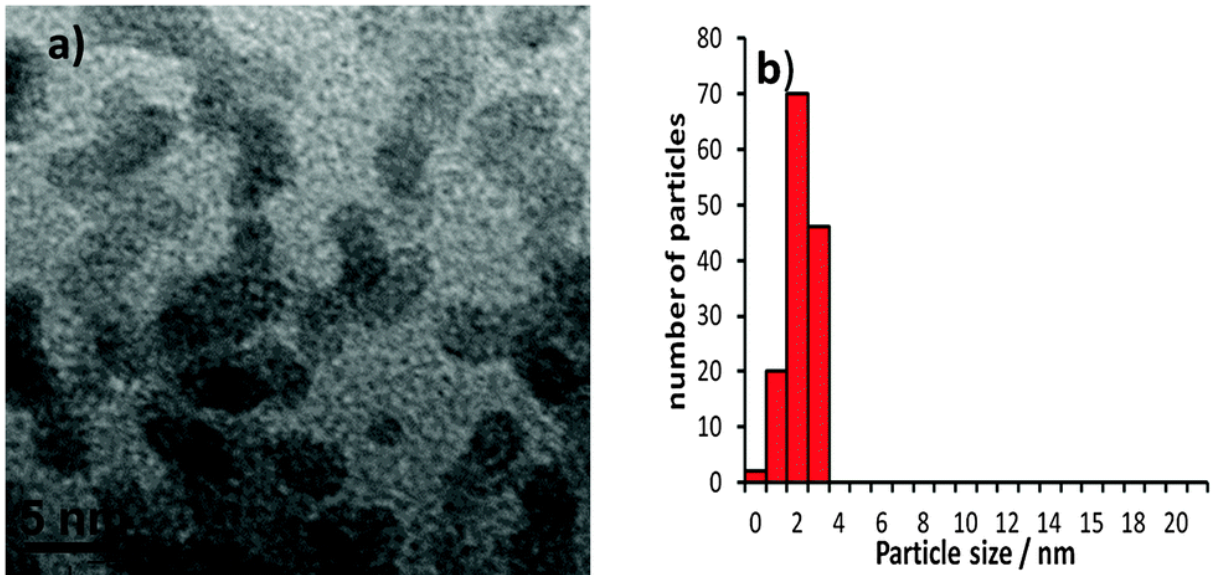
### **2.5.3.3 Operating capacity**

Operating capacity of resin material depends on the operating conditions it has to perform under, e.g. resin dimension, the flow rate and quality of the solution to be treated, the strength of the eluent to treat the resin, the quantity of the regenerating solution and operating temperature. The capacity therefore can only be determined in a laboratory in simulated operating conditions.

Suppliers usually supply this information with their product and these calculations can be made easily by use of computer programs.

### **2.5.4 Particle size distribution**

The ion exchange resin material is in the form of spherical beads. The manufacturing method, i.e. suspension polymerisation technique, does not produce beads of a uniform particle size but the resin size is usually in the range 0.3 – 1.2 mm. As this range was found to be most efficient range most resin materials are of this size, however, resin material can also differ from this range and is dependent on the type of application, as an example functional groups and type of labile ion will be a factor that must be considered, Fig 2.10.



**Figure 2.10: (a) TEM images of as-synthesized Pt nanoparticles prepared with NP9 (Pt + NP9) along with (b) their particle size distributions (Newton, Preece, Rees, & Preece)**

The resin is usually packed in a column to allow the solution to pass through the resin. The solution passes through the resin bed and exits through a polyethylene sinter at the bottom of the column to keep the resin in the column. Therefore, it is important that the resin bead size should never be smaller than the size of the sinter.

Although quite a few resin applications require two resins to operate together it is also necessary to remember that each resin can only be efficiently regenerated separately. This occurs in resin beds where both anion and cation exchange resins are used to sorb their respective ions from the solution. During the backwashing process the anion exchange resin which is the finer structure will lay on top of the coarser cation exchange material.

Ion exchange materials are considered efficient when the path lengths of the ions travelling through the bead are not that long. The uniform size distribution of a normal bead is between 0.4 – 0.8 mm, whereby the coarsest beads are eliminated from this range.

The measurement of a particle size is therefore important and manufacturers use standard sieves as a measurement tool. Light extinction principle are also used as a measuring tool, which is an instrumental technique, examples used are OMEGA (Fortress Dynamics, UK) and HIAC (HIAC-Rogco, USA).

### *2.5.5 Other Resin Characteristics*

Other factors to consider are the pH range and the operating temperatures of the resin material. The recommendations supplied by the supplier should be followed as all the resins of a given type have the same limitations on the parameters specified.

## **2.6 Resin Kinetics**

The rate of reaction and the contact time of the solution with the resin material determine the kinetics of the resin unit. Ion exchange mechanism involves diffusion through a liquid film around the resin particle and diffusion in the particle. The diffusion through the liquid film is considered the rate controlling mechanism for the low concentration and the diffusion within the particle is the rate controlling mechanism for the high concentrations. The size of the resin material is in both cases the determining factor.

In other words ion exchange kinetics means that ions are exchanged optimally between the two phases.

## **2.7 Applications of Ion exchange resins**

Ion exchange resin material is used in many technologies and industries. It is mostly concentrating on the purification and the removal of trace metals, toxic- or any other pollutants at a nano scale. Here below is a short summary extracted from Schubart (Nachod & Schubart, 1956)

1. Removal of objectionable cations and anions from drinking and boiler feed water.
2. Production of de-ionized water.
3. Treatment of trade effluents, both for the purification of such liquors and for the economic recovery of small amounts of inorganic and organic substances.
4. Purification of organic and inorganic chemicals.
5. Applications to analytical chemistry.
6. Separation of ion mixtures.

**Table 2.3: Few applications of ion exchange materials including both well developed and experimental techniques** (Zagorodni, 2007)

<p><b>Water preparation for different purposes:</b></p> <ul style="list-style-type: none"> <li>• Preparation of pure and ultrapure deionised water.</li> <li>• Water softening.</li> <li>• Potable water preparation.</li> </ul>	<p><b>Isotope separation:</b></p> <ul style="list-style-type: none"> <li>• Eu<sup>3+</sup> isotope.</li> <li>• Lithium isotopes.</li> <li>• Boron isotopes</li> <li>• Isotope analysis</li> </ul>
<p><b>Removal of specific constitutes:</b></p> <ul style="list-style-type: none"> <li>• Dealkalisation.</li> <li>• Fluoride removal.</li> <li>• Removal of organic matter, particularly colourants.</li> <li>• Oxygen removal.</li> <li>• Iron and manganese removal.</li> <li>• Cd<sup>2+</sup> removal from drinking water.</li> <li>• Nitrate removal.</li> <li>• Ammonia removal.</li> <li>• Removal of radionuclides from drinking water.</li> <li>• Removal of other harmful ions from drinking water.</li> </ul>	<p><b>Pulp and Paper industry:</b></p> <ul style="list-style-type: none"> <li>• Removal of inorganic salts from liquors.</li> <li>• Detoxification of by-products transferred for bio-cultivation.</li> </ul> <p><b>Purification of sugars and polyhydric alcohols:</b></p> <ul style="list-style-type: none"> <li>• Purification of cane, corn and beet sugars.</li> <li>• Purification of fructose.</li> <li>• Separation of monosacchirides.</li> <li>• Purification of glycerine.</li> <li>• Treatment of sorbitol.</li> <li>• Recovery of xylitol.</li> </ul>
<ul style="list-style-type: none"> <li>• Separation of radioisotopes from fission of uranium-235</li> </ul> <p><b>Nuclear Industry:</b></p> <ul style="list-style-type: none"> <li>• Waste decontamination.</li> <li>• Final storage of radioactive waste.</li> <li>• Condensate polishing.</li> </ul>	<p><b>Food Industry:</b></p> <ul style="list-style-type: none"> <li>• Removing of tasters and odours.</li> <li>• Recovery of glutamic-acid.</li> <li>• Purification of steviosides.</li> <li>• Deacidification of fruit juice.</li> </ul>
<p><b>Decontamination and recuperation of waste streams:</b></p> <ul style="list-style-type: none"> <li>• Recycling of industrial water.</li> <li>• Removal of heavy metals ions.</li> <li>• Recuperation of metals.</li> <li>• Ammonia removal.</li> <li>• Recovery of calcium aconitate.</li> </ul>	<p><b>Dairy:</b></p> <ul style="list-style-type: none"> <li>• Extraction of lactoperoxidase and lactoferrin.</li> <li>• Purification of casein.</li> </ul> <p><b>Winery:</b></p>

<ul style="list-style-type: none"> <li>• Removal of radioactive substances.</li> </ul> <p><b>Recovery and purification of biological and biochemical substances:</b></p> <ul style="list-style-type: none"> <li>• Amino acids.</li> <li>• Proteins.</li> <li>• Enzymes.</li> <li>• DNA.</li> <li>• Antibodies.</li> </ul> <p><b>Biotechnology:</b></p> <ul style="list-style-type: none"> <li>• Separation of lactic acid from fermentative broth.</li> <li>• Production of L-glutamine.</li> <li>• Production of citric acid.</li> <li>• Organic acids.</li> </ul> <p><b>Dairy:</b></p> <ul style="list-style-type: none"> <li>• Extraction of lactoperoxidase and lactoferrin.</li> <li>• Purification of casein.</li> </ul> <p><b>Recovery and purification in hydrometallurgy:</b></p> <ul style="list-style-type: none"> <li>• Uranium.</li> <li>• Thorium.</li> <li>• Rare earths.</li> <li>• Tungsten.</li> <li>• Transition metals.</li> <li>• Gold, silver, platinum and palladium.</li> </ul> <p><b>Solvent purification:</b></p> <p><b>Reagent purification:</b></p> <p><b>Preparation of inorganic salts:</b></p> <p><b>Catalysis:</b></p> <ul style="list-style-type: none"> <li>• Petroleum refining with zeolites.</li> </ul>	<ul style="list-style-type: none"> <li>• Adsorption of wine proteins in production of wines.</li> <li>• Stabilisation of wines.</li> <li>• Ethylbenzene synthesis.</li> <li>• Olefin isomerisation.</li> <li>• Catalytic reduction of nitrogen oxides.</li> </ul> <p><b>Pharmaceuticals and medicines:</b></p> <ul style="list-style-type: none"> <li>• Antibiotics.</li> <li>• Vitamins.</li> <li>• Active ingredients.</li> <li>• Taste masking.</li> <li>• Tablet disintegration.</li> <li>• Controlled and sustained drug release.</li> <li>• Immobilisation of drugs in a carrier function.</li> </ul> <p><b>Soil science and technology:</b></p> <ul style="list-style-type: none"> <li>• Artificial soils.</li> <li>• Remediation of contaminated soils.</li> <li>• Evaluation of soil properties.</li> </ul> <p><b>Buffering:</b></p> <p><b>Analysis:</b></p> <ul style="list-style-type: none"> <li>• Chromatography.</li> <li>• Sample preparation, separation, concentrating purification.</li> <li>• Replacement of analyte.</li> </ul> <p><b>Drying of different media:</b></p> <ul style="list-style-type: none"> <li>• Desiccation of solvents with zeolites.</li> <li>• Gas drying with polymeric exchangers and zeolites.</li> </ul>
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## CHAPTER 3 EXPERIMENTAL

### 3 Experimental Methods Employed

#### 3.1 Resin materials used

The comparative study was conducted with the two Dowex cation exchange resins Amberlyst 15 and Dowex Marathon MSC, and the results compared with the distribution coefficients which Strelow had obtained with BioRad AG MP-50.

#### 3.2 Volume apparatus used

All glassware used in this work was of A-grade quality. Gilsson micropipettes were used for the pipetting of millilitre quantities. The micropipettes used were calibrated at 25°C by weighing the mass of the volume dispensed. An on campus ICP-OES apparatus was used to perform and obtain the results for the comparative study.

#### 3.3 Reagents used

Analytical grade reagents were used throughout this work and were obtained from Merck (SA) Pty. Ltd or Sigma, Aldrich, Fluka and Riedel de Haen products. The AG MP-50 macroporous cation exchange resin was obtained from Bio Rad, Richmond, U.S.A. The Amberlyst 15 and Dowex Marathon MSC were purchased by Dow, Rohm and Haas Co.

Wherever water is referred to in the descriptions of the experiments indicates that de-ionized water was used. De-ionized water was obtained from a Millipore MilliQ Reagent Grade Water System at a conductivity of greater than 10 megaohm.cm<sup>-1</sup>.

#### 3.4 Preparation of resins

1. Dry resin was added to ca 100 mL deionised water in a glass beaker and stirred (using a magnetic stirrer) for approx. 30 minutes to allow the resin beads to swell.
2. The resin was then transferred into a glass column (25 cm x 3 cm).
3. The resin was washed with 5 M HCl, using a volume of HCl approximately 4 column lengths, adding small quantities at first and allowed the acid to soak into the resin. The acid was then slowly drained.
4. The procedure in step 3 was repeated, but deionised water was used instead of HCl.



5. The resin was filtered off on a Buchner funnel under vacuum.
6. The filter paper and resin were placed in a Petri dish and dried in an oven for 1hr at 100 °C, at 80 °C for the rest of the day and overnight at 60 °C.
7. The resin was stored in desiccator.

### 3.5 Sample preparation

A stock solution, containing 0.10 mmol of the monovalent (0.050 mmol of a divalent and 0.034 mmol of a trivalent element), was prepared in water.

$$\text{Mass (element)} = \frac{\text{Molecular Mass} \times \text{mmol} \times \text{Volume}}{1000}$$

In quadruplicate, 1000  $\mu\text{L}$  of the stock was pipetted in four 100 mL volumetric flasks and diluted to the mark with 0.04 M  $\text{HNO}_3$ . The stoppered flasks were shaken well. (**Reference standard**).

#### 3.5.1 Determination of the distribution coefficients for the elements

1000  $\mu\text{L}$  of the stock solution was pipetted in each of seven 50 mL plastic bottles. Respectively 1.0, 2.0, 5.0, 10.0 and 20 mL 5.0 M  $\text{HNO}_3$  were added to the first 5 plastic bottle and respectively 15 and 20 mL 10.0 M  $\text{HNO}_3$  to the other 2 plastic bottles. The calculated volume of water was added to fill the bottles to 50 mL (see Table 3.1)

**Table 3.1 Volumes of the stock solution and reagents used for the experiment**

M $\text{HNO}_3$	Mass of resin (g)	mL stock solution	mL 5.0 M $\text{HNO}_3$	mL water	Total volume mL
0.1	0.5	1.000	1.0	48.0	50.00
0.2	0.5	1.000	2.0	47.0	50.00
0.5	0.5	1.000	5.0	44.0	50.00
1.0	0.5	1.000	10.0	39.0	50.00
2.0	0.5	1.000	20.0	29.0	50.00
			mL 10.0 M $\text{HNO}_3$		
3.0	0.5	1.000	15.0	34.0	50.00
4.0	0.5	1.000	20.0	29.0	50.00

The bottles were capped and shaken overnight at 25 °C. The contents of each bottle was filtered through a column with a sinter at the bottom and the resin washed with water to remove

the non-retained element from the resin. The inside of the column was rinsed a few times with water and the filtrate collected in a 100 mL volumetric flask. The solution was diluted to the mark with water.

The portion of the element which was retained by the resin was eluted from with 40 mL 5.0 M HCl and the eluate evaporated to incipient dryness. The residue was dissolved in 4.0 mL 0.50 M HNO<sub>3</sub>, quantitatively transferred, with the aid of water, to a 100 mL volumetric flask, diluted with water to the mark and shaken well. The contents of the element in each volumetric flask was determined with ICP spectrophotometry. The distribution coefficients were calculated.

**For the filtrate (it is the mass of the element determined in the filtrate):**

$K_d = \frac{[\text{mass of the element in the reference standard (the average of the four)}] - [\text{mass of the element of the filtrate}] \times 100}{[\text{mass of the element in the filtrate}]}$

**For the resin (it is the mass of the element determined in the eluate):**

$K_d = \frac{[\text{mass of the element of the resin}] \times 100}{[\text{mass of the element of the reference standard (the average of the four)}] - [\text{mass of the element of the resin}]}$

### 3.6 Salts used

The salts used to prepare the stock solutions of the respective elements listed below were supplied by Merck. These elements were all AR grade nitrates (NO<sub>3</sub><sup>-</sup>), see Table 3.2 for the summary calculation of the salts used.

#### 3.6.1 Ag<sup>+</sup> - Monovalent element

Approximately 1.6987 g of silver nitrate (AgNO<sub>3</sub>) was weighed out and made up in a 100 ml volumetric flask to obtain a 0.10 mmol solution.

#### 3.6.2 Ni<sup>2+</sup> - Divalent element

Approximately 1.4540 g of nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.3 $Pb^{2+}$ - Divalent element

Approximately 1.6560 g of lead(II) nitrate ( $Pb(NO_3)_2$ ) was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.4 $Mn^{2+}$ - Divalent element

Approximately 0.8948 g of manganese(II) nitrate ( $Mn(NO_3)_2$ ) was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.5 $Zn^{2+}$ - Divalent element

Approximately 0.9468 g of zinc nitrate ( $Zn(NO_3)_2$ ) was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.6 $Co^{2+}$ - Divalent element

Approximately 1.4552 g of cobalt(II) nitrate hexahydrate ( $Co(NO_3)_2 \cdot 6H_2O$ ) was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.7 $Cd^{2+}$ - Divalent element

Approximately 1.1821 g of cadmium nitrate [ $Cd(NO_3)_2$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.8 $Cu^{2+}$ - Divalent element

Approximately 0.9378 g of anhydrous copper(II) nitrate [ $Cu(NO_3)_2$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.05 mmol solution.

### 3.6.9 $In^{3+}$ - Trivalent element

Approximately 1.0228 g of indium(III) nitrate [ $In(NO_3)_3 \cdot xH_2O$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution.

### 3.6.10 $Tl^{3+}$ - Trivalent element

Approximately 1.3274 g of thallium(III) nitrate [ $Tl(NO_3)_3$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution.

### 3.6.11 $Al^{3+}$ - Trivalent element

Approximately 1.2755 g of aluminium nitrate nonahydrate [ $Al(NO_3)_3 \cdot 9H_2O$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution.

### 3.6.12 $Fe^{3+}$ - Trivalent element

Approximately 1.3736 g of iron(III) nitrate nonahydrate [ $Fe(NO_3)_3 \cdot 9H_2O$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution.

### 3.6.13 $Bi^{3+}$ - Trivalent element

Approximately 1.6493 g of bismuth nitrate [ $Bi(NO_3)_3 \cdot 5H_2O$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution. Bismuth nitrate forms a suspension and takes long to dissolve, the solution was stirred until it was uniform and then transferred to the required sample sets and reference standards.

### 3.6.14 $Ga^{3+}$ - Trivalent element

Approximately 0.8695 g of gallium nitrate [ $Ga(NO_3)_3$ ] was weighed out and made up in a 100ml volumetric flask to obtain a 0.033 mmol solution.

**Table 3.2 Summary calculation of the salts used**

<b>Salt and valency</b>	<b>Mass required</b>	<b>Concentration</b>
Ag <sup>+</sup> - Monovalent element	1.6987 g	0.1 mmol
Ni <sup>2+</sup> - Divalent element	1.4540 g	0.05 mmol
Pb <sup>2+</sup> - Divalent element	1.6560 g	0.05 mmol
Mn <sup>2+</sup> - Divalent element	0.8948 g	0.05 mmol
Zn <sup>2+</sup> - <i>Divalent element</i>	0.9468 g	0.05 mmol
Co <sup>2+</sup> - <i>Divalent element</i>	1.4552 g	0.05 mmol
Cd <sup>2+</sup> - <i>Divalent element</i>	1.1821 g	0.05 mmol
Cu <sup>2+</sup> - Divalent element	0.9378 g	0.05 mmol
In <sup>3+</sup> - Trivalent element	1.0228 g	0.033 mmol
Tl <sup>3+</sup> - Trivalent element	1.3274 g	0.033 mmol
Al <sup>3+</sup> - Trivalent element	1.2755 g	0.033 mmol
Fe <sup>3+</sup> - Trivalent element	1.3736 g	0.033 mmol
Bi <sup>3+</sup> - Trivalent element	1.6493 g	0.033 mmol
In <sup>3+</sup> - Trivalent element	1.0228 g	0.033 mmol
Ga <sup>3+</sup> - Trivalent element	0.8695 g	0.033 mmol

## CHAPTER 4

### RESULTS AND DISCUSSIONS

Table 4.1 shows the distribution coefficients for the various elements in nitric acid solutions. The accumulative errors are estimated not to be higher than 1 to 3% of the results for the coefficients between 10 and 500, but are higher for very high or very low coefficients.

The main source of these errors are inhomogeneity of the coefficients for the 14 cations in nitric acid. The data will be compared against the data documented by Strelow (Strelow F.W.E., 1964) and the graphs cited by Marsch et al (Marsh, Alarid, Hammond, McLeod, Roensch, & Rein, 1978).

Although Strelow used Bio - Rad AG 50W-X8 in the study the results show the same trend of decreasing distribution coefficient values with increasing acid concentration when using Bio - Rad AG MP- 50. The two Dowex resins (i.e. Amberlyst 15 and Dowex Marathon MSC) show the same trend. Strelow's study was conducted using more than one acid medium, the writer's opinion from that study is that the elution curves demonstrated a versatility in ion exchange procedures, which means more than one cation can or may be separated in a single column through stepwise changing eluents.

Strelow argued the fact that if a sample contained multiple cations, it will be possible to elute the cations one at a time, through forming complexes with the remaining cations. These complexes can be attained by manipulating the sample solution pH value or adding an anion complex that will attach itself to a cation. The free cation will then elute and the rest will follow as they are freed stepwise.

The graphs in the study of Marsch *et al.* confirms the graphs obtained with this study that the  $K_d$  distribution coefficient decreases with increasing acid concentrations (from 0.1 – 4.0 M). Marsch's study was conducted using acid concentration range 3 to 12 M HNO<sub>3</sub>, the intention thereof was to cover previously unreported ranges as Strelow study only covered the 0.1 to 4 M range. There was thus an overlap between the two studies which would confirm each other's work.

Analytical chemists, however, prefer distribution coefficients listed in a table above graphs because graphs usually give the logarithm of the distribution coefficients vs the acid concentration and the figures are too small to read an accurate value as shown in Figure 4.1.

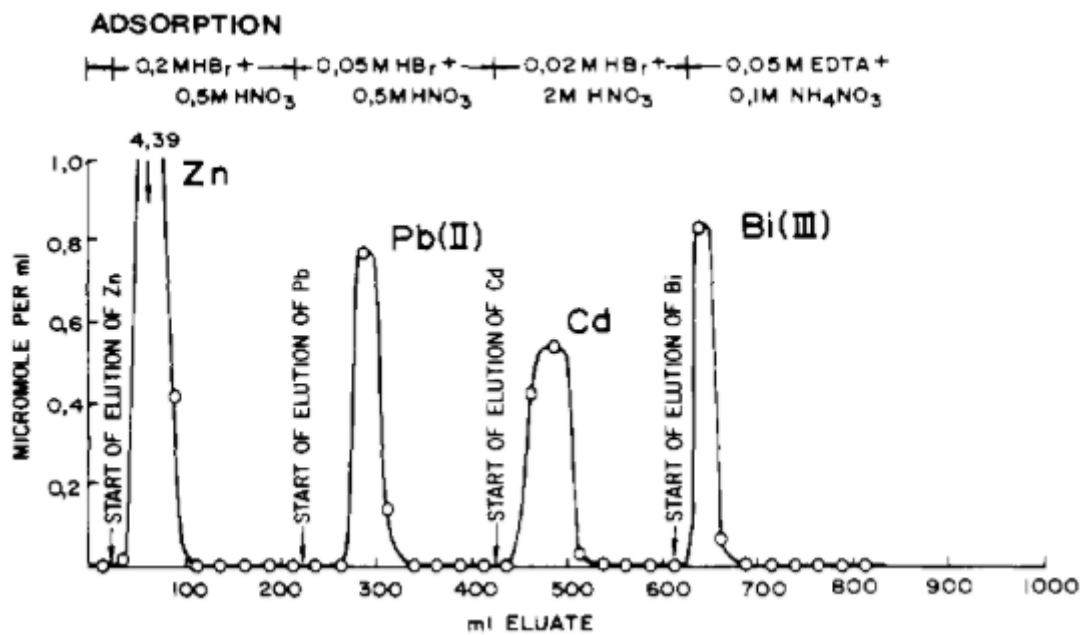


Figure 4.1 Elution curve Zn-Pb(II)-Cd-Bi(III), column of 11.5ml (5g) AG1 – X8 resin, 200 – 400 mesh (65 x 15 mm). Flow-rate  $2.5 \pm 0.5$  mL/min (Strelow F. W., 1978)

Girardi *et al* used circles to show whether the element had been retained, slightly retained or not at all retained by the resin (Figure 4.2) but these results does not help an analyst at all to plan a proper separation of elements.

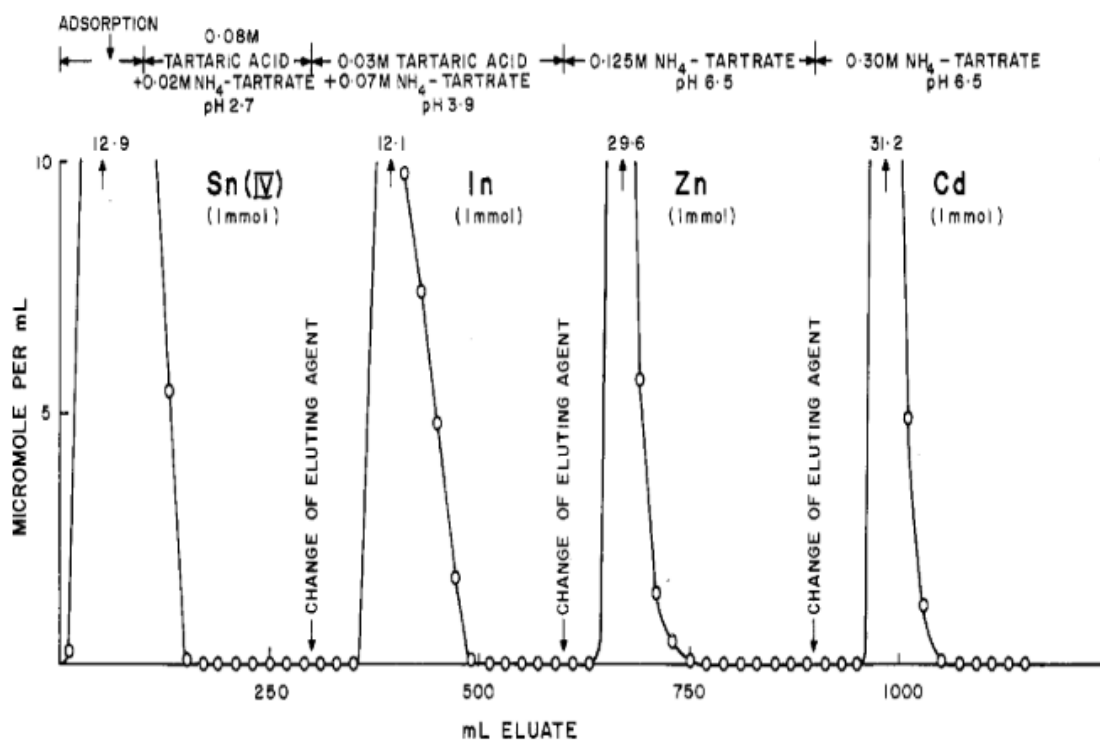


Figure 4.2 Elution curve Sn(IV) – In – Zn – Cd: 60 mL (20g) AG 50W – 8X resin, 200 – 400 mesh; column length 145 nm, Ø 23 mm; low rate  $4.0 \pm 0.5$  mL, column in NH4 form (Strelow & van der Walt, 1982)

The  $K_d$  coefficient was calculated and expressed in units using the formula below:  $K_d = \frac{[\text{mass of the element of the resin}] \times 100}{\{[\text{mass of the element of the reference standard (the average of the four)}] - [\text{mass of the element of the resin}]\}}$

**Table 4.1 Distribution coefficients for elements on the three macroporous cation exchangers in nitric acid solutions**

Element	Resin	Molarity of HNO <sub>3</sub> [M]						
		0.1	0.2	0.5	1.0	2.0	3.0	4.0
Ag <sup>+</sup>	Amberlyst 15	1605	603	221	98	43.5	29.2	25.8
	Bio Rad AG MP-50	156	86	36.0	18.1	7.9	5.4	4.0
	Dowex Marathon MSC	218	120	75	58	38.5	17.6	16.9
Cd <sup>2+</sup>	Amberlyst 15	7068	1796	290	77	33.4	25.2	24.6
	Bio Rad AG MP-50	1500	392	91	32.8	10.8	6.8	3.4
	Dowex Marathon MSC	2542	568	115	40.1	20.3	19.4	18.3
Co <sup>2+</sup>	Amberlyst 15	3871	847	158	41.4	18.0	16.8	15.4
	Bio Rad AG MP-50	1260	392	91	28.2	10.1	6.1	4.7
	Dowex Marathon MSC	2413	535	114	35.6	20.0	16.0	16.0
Cu <sup>2+</sup>	Amberlyst 15	3902	968	162	48.1	23.4	16.9	19.1
	Bio Rad AG MP-50	1080	356	84	26.8	8.6	4.8	3.1
	Dowex Marathon MSC	1974	470	98	34.7	23.3	2.04	18.0
Mn <sup>2+</sup>	Amberlyst 15	7629	1876	305	90	30.5	18.2	15.8
	Bio Rad AG MP-50	1240	389	89	28.4	11.4	7.1	3.0
	Dowex Marathon MSC	2578	748	117	33.5	15.3	12.5	12.0
Ni <sup>2+</sup>	Amberlyst 15	9492	407	149	46.6	23.0	18.8	17.9
	Bio Rad AG MP-50	1140	384	91	28.1	10.3	8.6	7.3
	Dowex Marathon MSC	3170	657	130	33.0	19.5	17.5	13.0
Pb <sup>2+</sup>	Amberlyst 15	>10 <sup>4</sup>	9200	2344	310	59	22.4	12.6
	Bio Rad AG MP-50	>10 <sup>4</sup>	1420	183	35.7	8.5	5.5	4.5
	Dowex Marathon MSC	4883	1802	187	33.4	12.3	11.2	7.8
Zn <sup>2+</sup>	Amberlyst 15	3672	913	160	63	39.7	37.5	33.7
	Bio Rad AG MP-50	3568	857	182	54	43.7	42.4	38.2
	Dowex Marathon MSC	1980	559	120	50	42.4	34.5	31.3
Al <sup>3+</sup>	Amberlyst 15	> 10 <sup>4</sup>	> 10 <sup>4</sup>	739	163	61	42.9	26.5
	Bio Rad AG MP-50	> 10 <sup>4</sup>	> 10 <sup>4</sup>	1623	185	63	48.3	48.3
	Dowex Marathon MSC	> 10 <sup>4</sup>	> 10 <sup>4</sup>	161	146	67	45.3	42.3
Bi <sup>3+</sup>	Amberlyst 15	> 10 <sup>4</sup>	5353	171	152	941	19.1	16.8
	Bio Rad AG MP-50	> 10 <sup>4</sup>	8228	985	57	22.7	17.5	12.0
	Dowex Marathon MSC	>10 <sup>4</sup>	333	41.1	21.3	16.6	10.1	5.2
Fe <sup>3+</sup>	Amberlyst 15	> 10 <sup>4</sup>	> 10 <sup>4</sup>	2046	227	60	40.7	27.1
	Bio Rad AG MP-50	> 10 <sup>4</sup>	> 10 <sup>4</sup>	1961	162	50.4	28.5	12.2
	Dowex Marathon MSC	> 10 <sup>4</sup>	> 10 <sup>4</sup>	675	117	34.8	21.9	22.2
Ga <sup>3+</sup>	Amberlyst 15	> 10 <sup>4</sup>	> 10 <sup>4</sup>	1356	180	27.4	18.6	17.6
	Bio Rad AG MP-50	> 10 <sup>4</sup>	> 10 <sup>4</sup>	1521	138	31.6	19.0	16.4
	Dowex Marathon MSC	> 10 <sup>4</sup>	> 10 <sup>4</sup>	786	67	19.9	13.8	13.7
In <sup>3+</sup>	Amberlyst 15	> 10 <sup>4</sup>	> 10 <sup>4</sup>	3862	439	90	20.9	6.7
	Bio Rad AG MP-50	> 10 <sup>4</sup>	> 10 <sup>4</sup>	1580	296	58	24.7	21.7
	Dowex Marathon MSC	> 10 <sup>4</sup>	> 10 <sup>4</sup>	956	120	30.2	15.4	14.6
Tl <sup>3+</sup>	Amberlyst 15	2606	1051	310	98	29.4	14.7	11.4
	Bio Rad AG MP-50	1776	635	191	65	22.0	10.1	9.7
	Dowex Marathon MSC	311	116	37.4	10.6	4.3	3.0	1.8



The data shown in Table 4.1 was used to plot the following graphs:

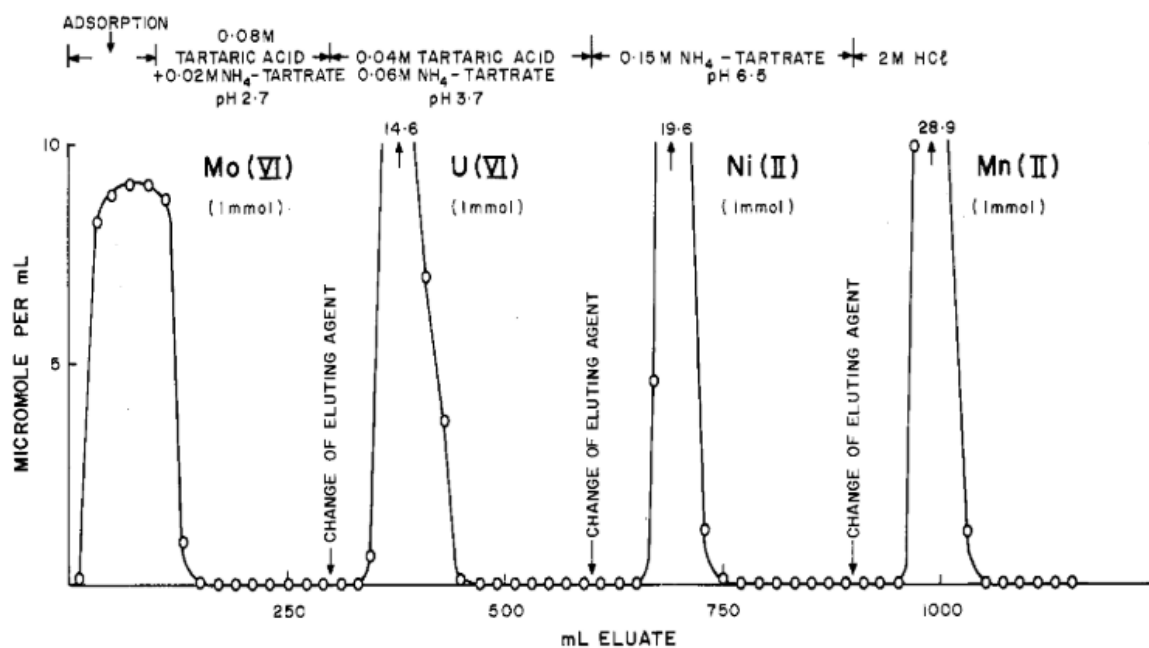


Figure 4.3 Elution curve Mo(IV) – U(VI) – Ni(II) – Mn(II): 60 mL (20g) AG 50W – 8X resin, 200 – 400 mesh; column length 145 cm, Ø 23 mm; low rate  $4.0 \pm 0.5$  mL, column in NH<sub>4</sub> form (Strelow & van der Walt, 1982)

Cleveland (Cleveland, 1971) states that nitrate complexes are stronger than chloride complexes, whereby the researcher found to elute silver ( $\text{Ag}^+$ ), lead ( $\text{Pb}^{2+}$ ) and nickel ( $\text{Ni}^{2+}$ ), with 5 M hydrochloric acid yielded poor results as the chlorides in their respective solutions formed a stronger complex but yielded good results when eluted with 5 M nitric acid.

From the Table 4.1, one will notice that the distribution coefficients in the 0.1 – 0.5 M  $\text{HNO}_3$  follows the following trend on Amberlyst 15 > Dowex Marathon MSC > Bio Rad AG MP – 50 for the elements silver ( $\text{Ag}^+$ ), cadmium ( $\text{Cd}^{2+}$ ), cobalt ( $\text{Co}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), manganese ( $\text{Mn}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ) and lead ( $\text{Pb}^{2+}$ ). From this information the researcher formed the following opinion that Bio Rad AG MP-50 would be the ideal ion exchange material to be used as this resin retained the elements the least.

However, we noticed that zinc ( $\text{Zn}^{2+}$ ) the distribution coefficient order was Amberlyst 15  $\approx$  Bio Rad AG MP-50 > Dowex Marathon MSC. This divalent element was the exception to the opinion raised above, where Bio Rad AG MP-50 ion exchange material retained the zinc cation strongly. Also in 0.1 M  $\text{HNO}_3$  the distribution coefficients are all >  $10^4$  for the elements, aluminium ( $\text{Al}^{3+}$ ), bismuth ( $\text{Bi}^{3+}$ ), iron ( $\text{Fe}^{3+}$ ), gallium ( $\text{Ga}^{3+}$ ) and indium ( $\text{In}^{3+}$ ). All three cation exchange resins that were used retained these elements strongly at the diluted state (i.e. 0.1 M) of the solutions.

Also from Table 4.1 it seems that thallium ( $Tl^{3+}$ ) can probably be separated from all the other elements on Dowex Marathon MSC in 1.0 M  $HNO_3$  in a 10 ml resin column and in 2.0 M hydrochloric acid on a 20 mL resin column.

A further observation was noted from the results (Table 4.1) and the graphs in Appendix A that the cations in the higher concentrations were not retained by the ion exchange resins. At the lower concentrations the cations was strongly retained.

This resin material can be cleaned by elution of the cations with high acid concentrations followed by water and be re-used making it a cheaper product to use in the long term if it can be re-used. If one consider it being commonly used in the water treatment facilities for treating water, when water could be filtered with resin material that is rejuvenated and reused for more than once. This means the cost of drinkable water will be reasonable, and also the removing of pollutants (example  $Cd^{2+}$ ) from drinking water.

However filter systems that uses resin material should be monitored and maintained to prevent break-through, as noted that that at low concentrations (especially nano concentrations), it becomes difficult to remove sorbed cations through the normal filter or backwash methods, and can only remove it through eluting the sorbed cation from the resin through washing it with 4 M hydrochloric acid.

With proper record keeping and maintenance one can prevent resin material to be spent and replace it with “fresh” material just before pollutants break through.

Some authors preferred to use graphs to show the effect of the acid's concentrations (or the organic solvent's concentrations) on the distribution coefficient values. They use a linear-logarithmic paper and plotted the acid concentration (or the solvent concentrations) on the linear-axis and the distribution coefficient values on the logarithmic axis. Figure 4.1 is a copy of graphs published by Strelow (1978) and show the actual size of the graphs in the paper. One can see the effect of the hydrochloric acid concentration on the distribution coefficient values but one cannot read the values of the distribution coefficients accurately because the figures are too small to read an accurate value.

Tables that show the distribution coefficients vs the acid concentration are more useful for an analytical chemists because the separation factor,  $\alpha_A^B$ , for elements B and A can be calculated more accurately.

Girardi *et al* (Girardi, Pietra, & Sabbioni, 1970) used circles to show whether the element had been retained, slightly retained or not at all retained by the resin (Figure 4.2) but these results does not help an analyst at all to plan a proper separation of elements.

Van der Meulen determined the equilibrium distribution coefficients of 42 selected elements in 0.1 M and 0.25 M citric acid at various concentrations of nitric acid, namely, 0.2 M, 0.5 M and 1.0 M, respectively. The distribution coefficients are shown in Table 1, p68 – 69 in Van der Meulen's thesis (van der Meulen, 2003).

## CHAPTER 5 CONCLUSION

Separation techniques using ion exchangers cannot be made obsolete, as we find footprints in every sphere of the biosphere that it is being used. Although it is extensively documented for use on the lithosphere, we do find work done also on the hydrosphere (examples making seawater potable) and lithosphere (example adsorbing heavy metals from air).

Within the mining sector chelates are used extensively in ion exchange chromatographic procedures for the extraction of heavy metals, the recovery of metal ions from low grade ore and the purification of plating baths. Research at tertiary institutions is ongoing in synthesising and evaluating chelates.

The future of ion exchangers within research is therefore bright as it contributes positively to business and society. So the need for ion exchangers will always be there, however how we will deal with the ever increasing cost of these ion exchange resins.

It is obvious that there are high income manufacturers that need specialised ion exchanged technology and there are low income manufacturers that need the same or a generic ion exchange material.

The research results show that all three ion exchange resins perform the same, yet there is a big difference in prices. There is therefore no difference in product quality as the ion exchangers performed the same. The difference would therefore be the difference in exchange rates when purchasing from USA (US\$) and Europe (Euros) or locally (Rands).

The type of ion exchange resin that should be considered for research should be based on the research budget or funds available. A locally supplied Dowex Marathon MSC ion exchange gel, are considered cheap (i.e. less than R 400 / 500 g), as compared to the US based macro reticular ion exchange resin, Bio-Rad AG MP 50 (R 20 000 / 500 g).

The gel type resin is widely used in the water industry. The macroporous ion exchange resin are more used in specialised separation, such as the separation of radioisotopes from the target material.

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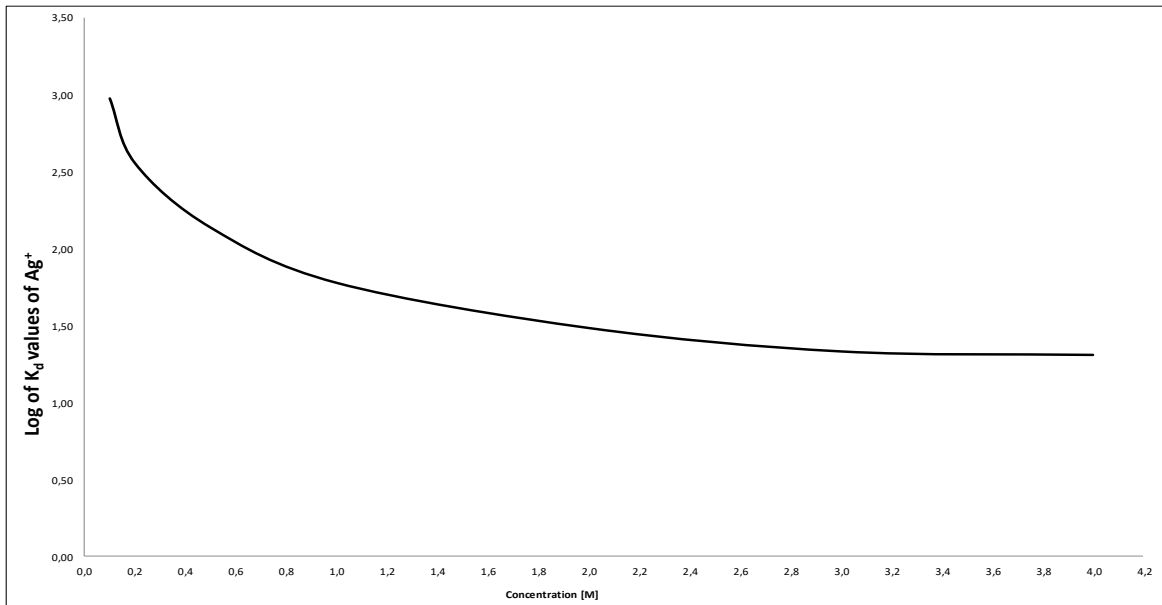
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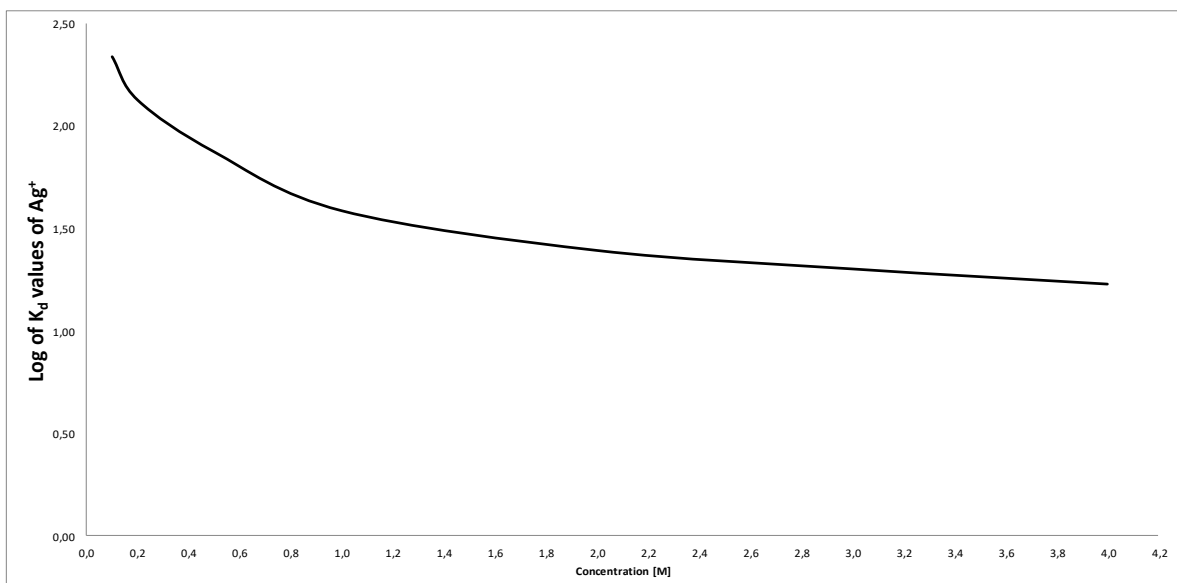
## APPENDIX / APPENDICES

**$K_d$  values graphs for the fourteen trace elements obtained on Amberlyst 15, Bio Rad AG MP 50 and Dowex Marathon MSC vs. the nitric acid ( $\text{HNO}_3$ ) concentration (M)**

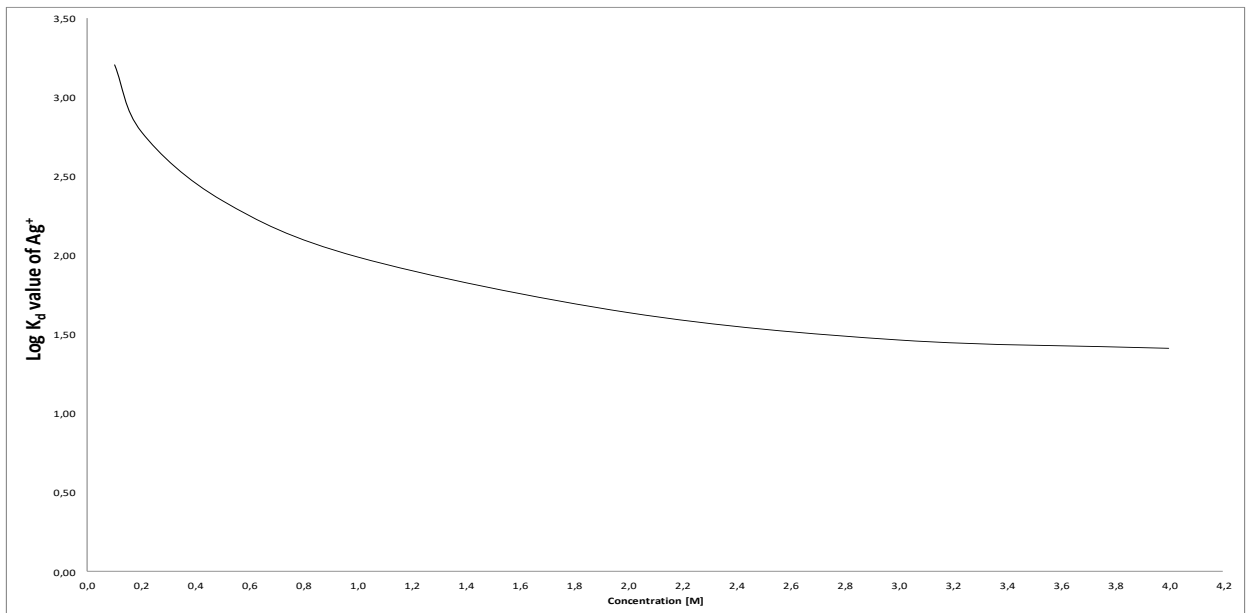
**A.1  $K_d$  values for Ag obtained on Bio Rad AG MP 50 vs the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



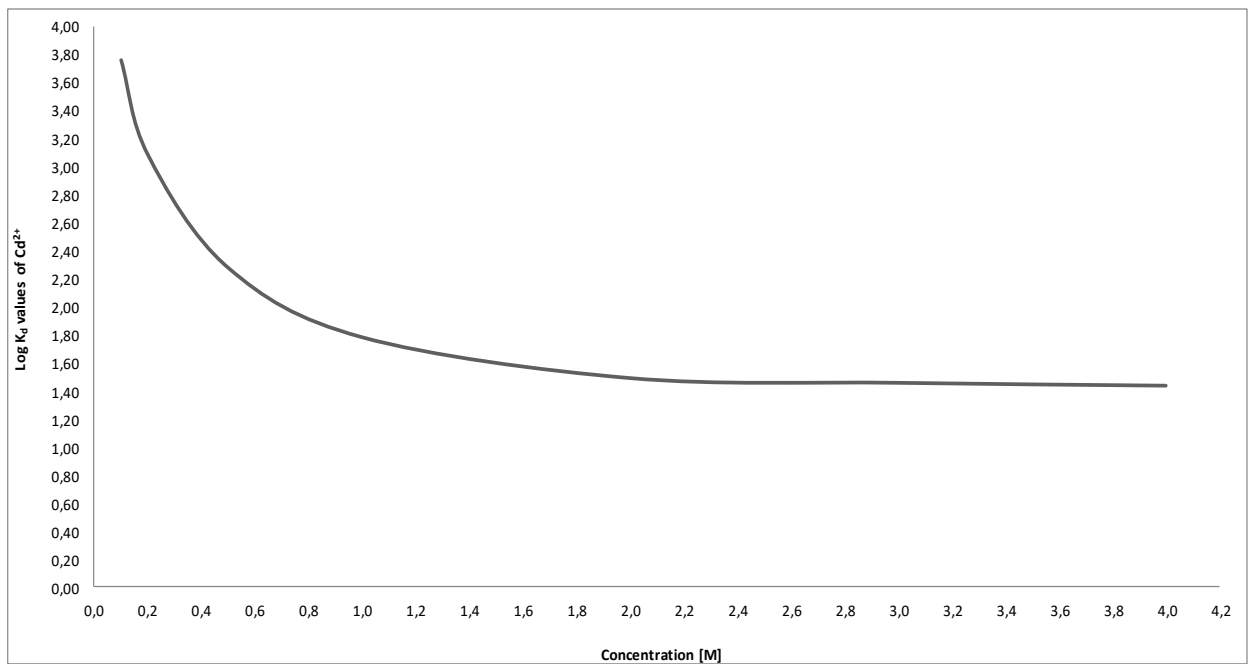
**A.2  $K_d$  values for Ag obtained on Dowex Marathon MSC vs the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



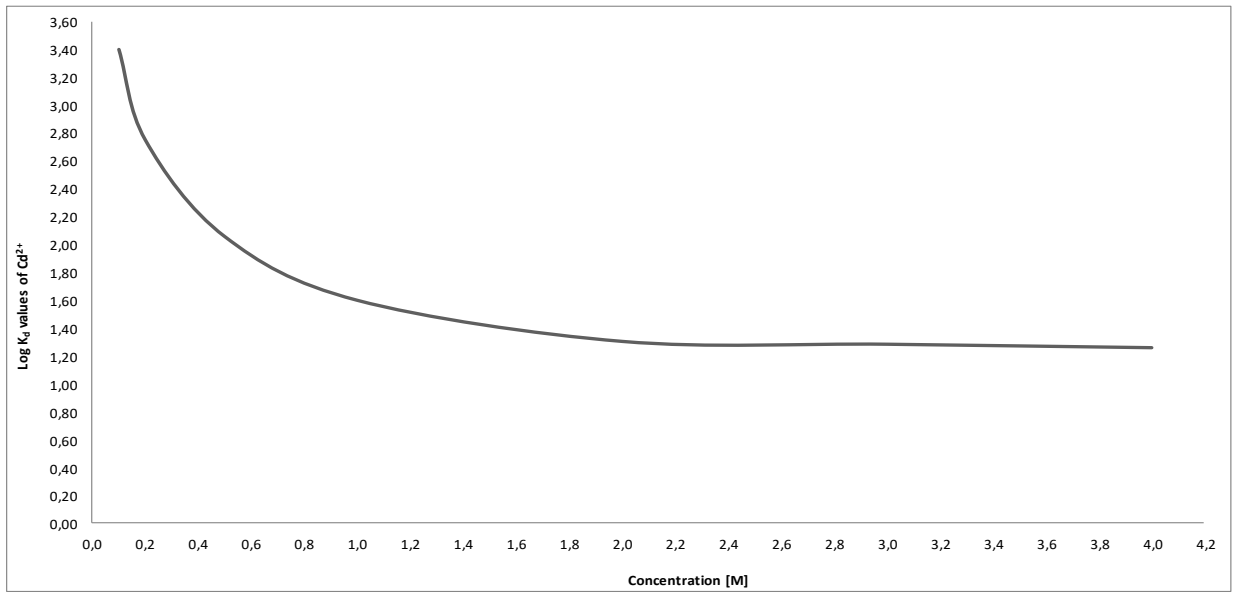
**A3  $K_d$  values for Ag obtained on Amberlyst 15 vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



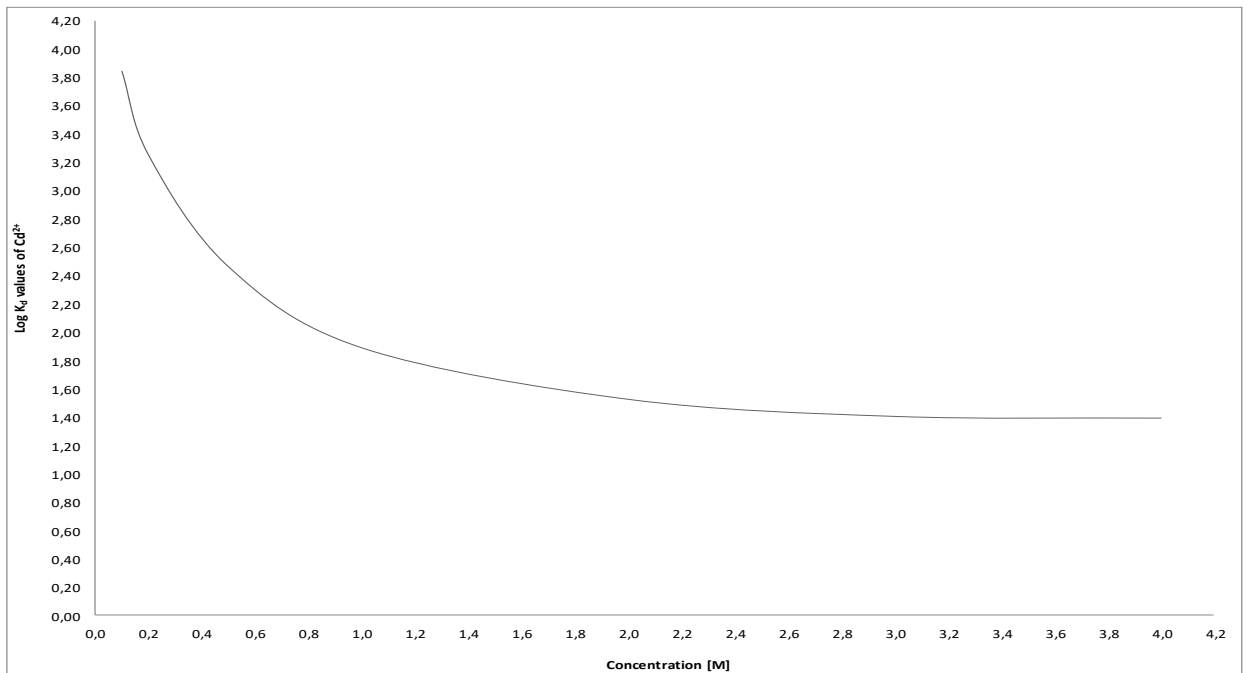
**B1  $K_d$  values for Cd obtained on Bio Rad AG MP 50 vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



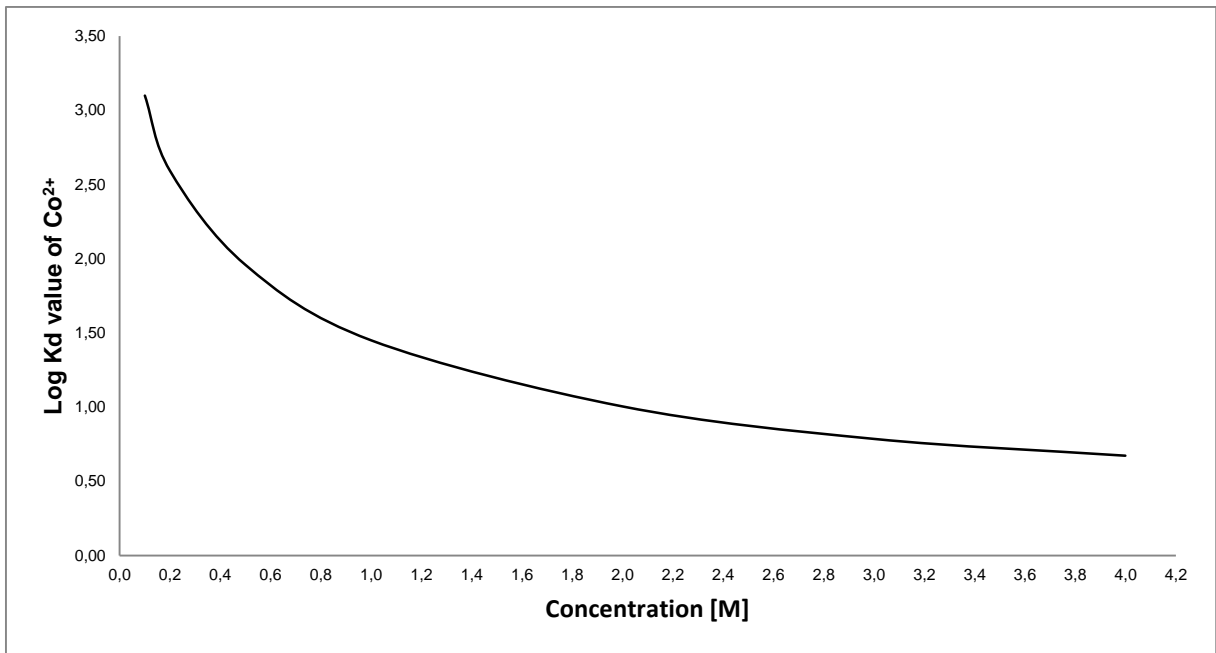
**B2  $K_d$  values for Cd obtained on Dowex Marathon MSC vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



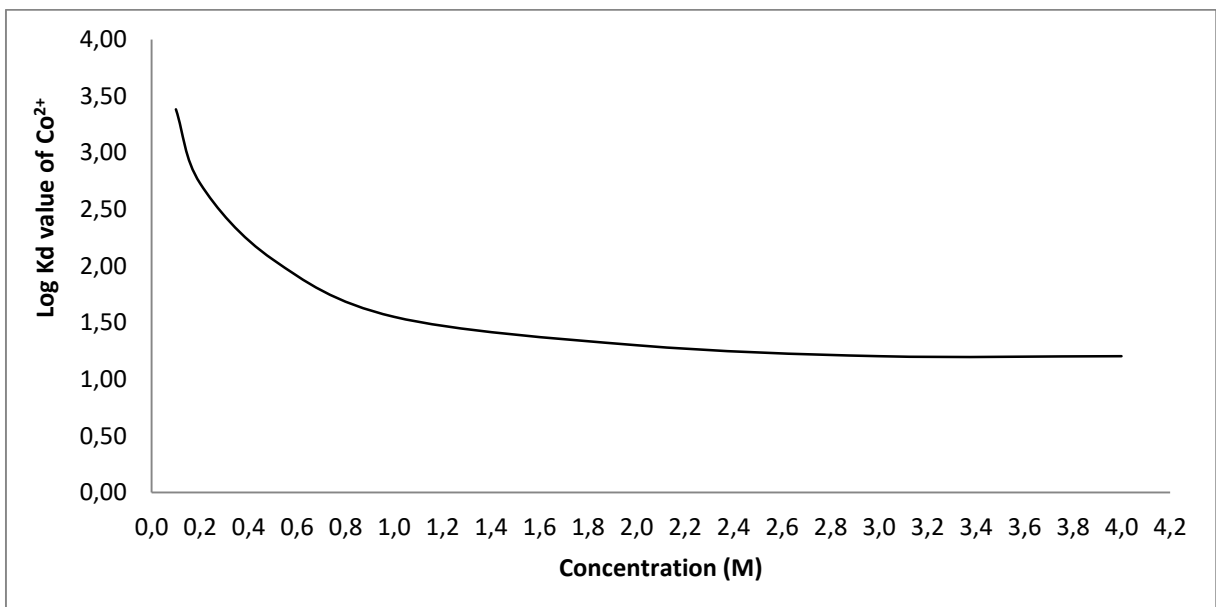
**B3  $K_d$  values for Cd obtained on Amberlyst 15 vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



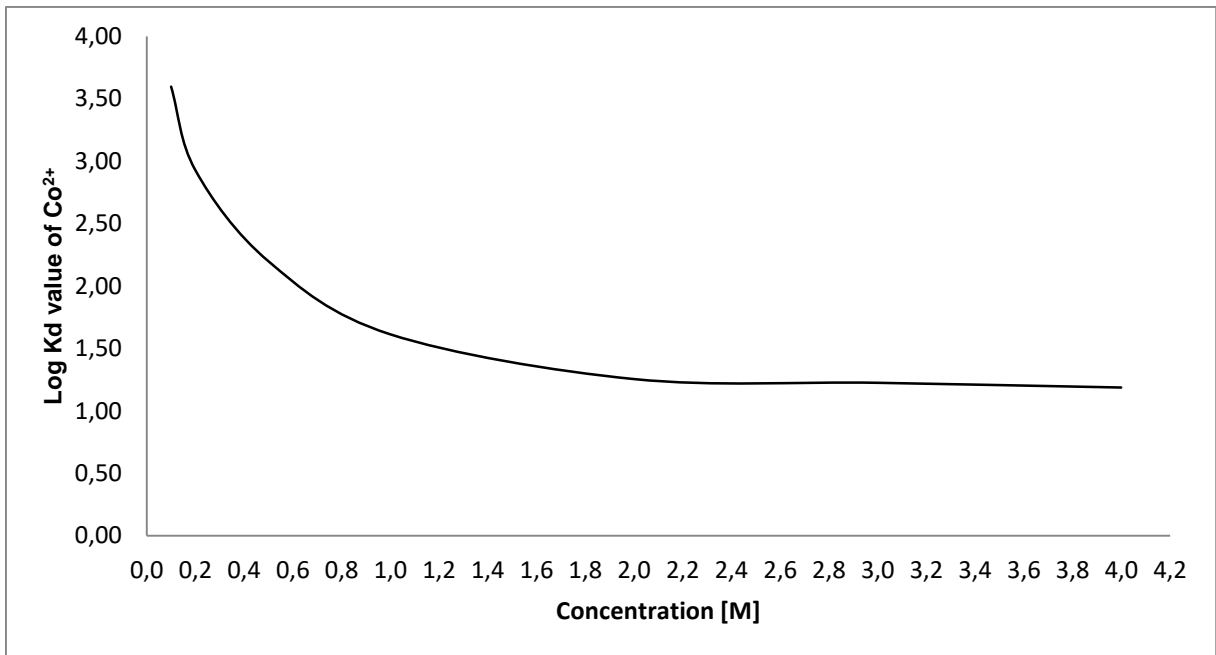
**C1  $K_d$  values for Co obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



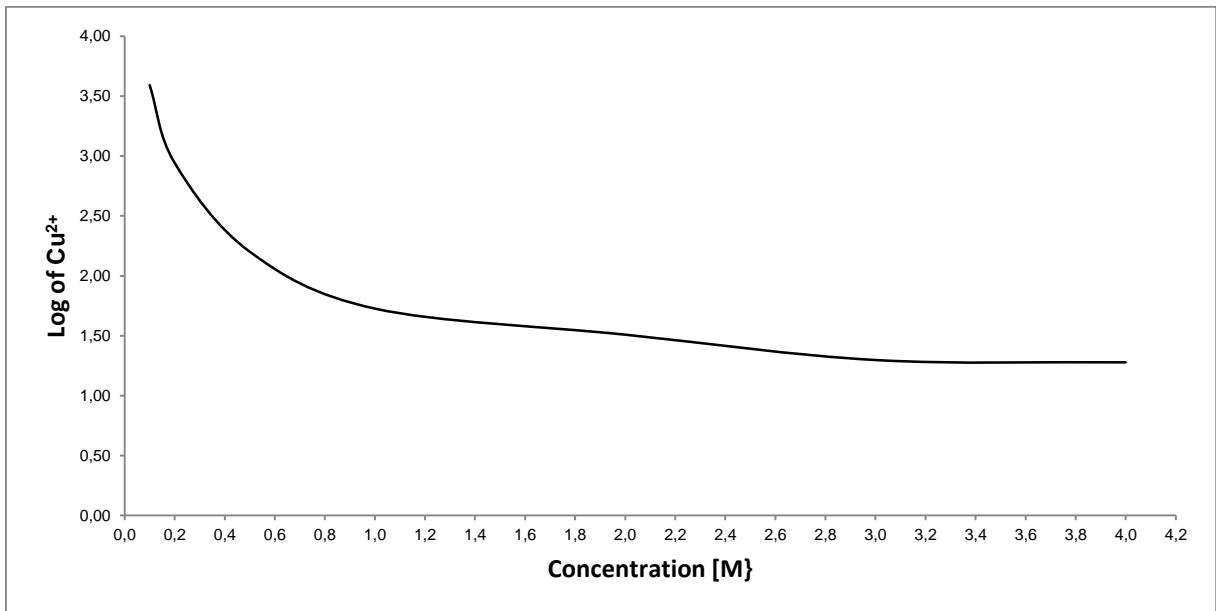
**C2  $K_d$  values for Co obtained on Dowex Marathon MSC vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



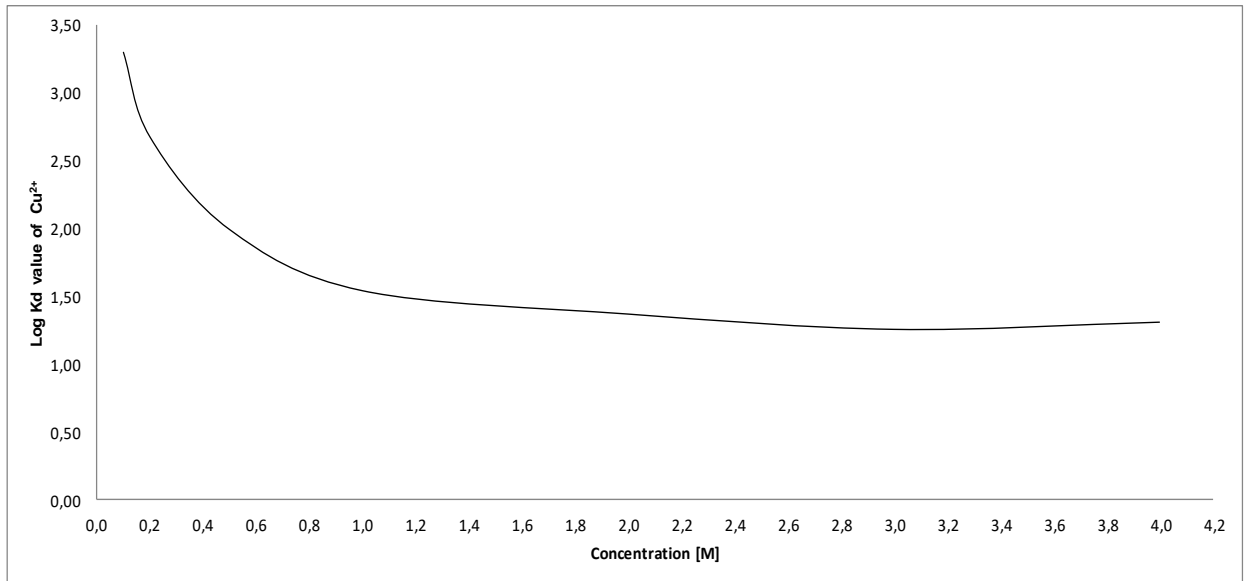
**C3  $K_d$  values for Co obtained on Amberlyst 15 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



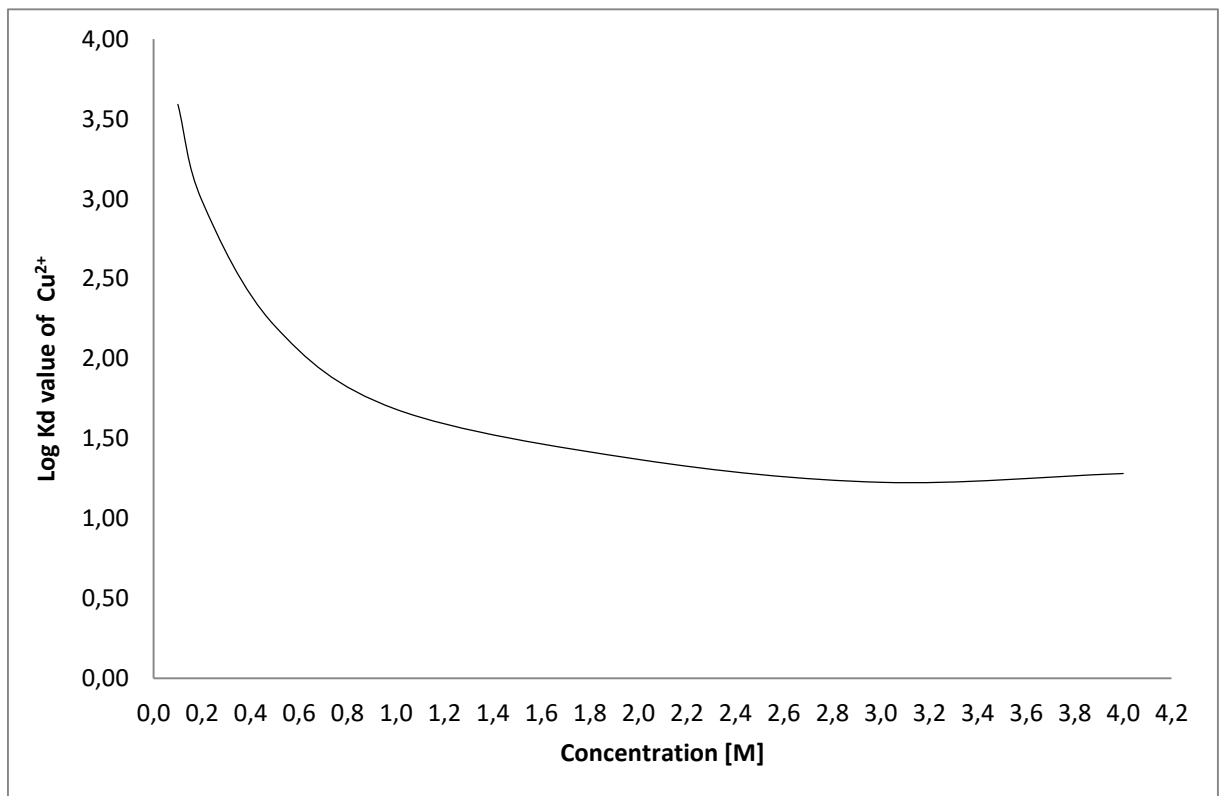
**D1  $K_d$  values for Cu obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



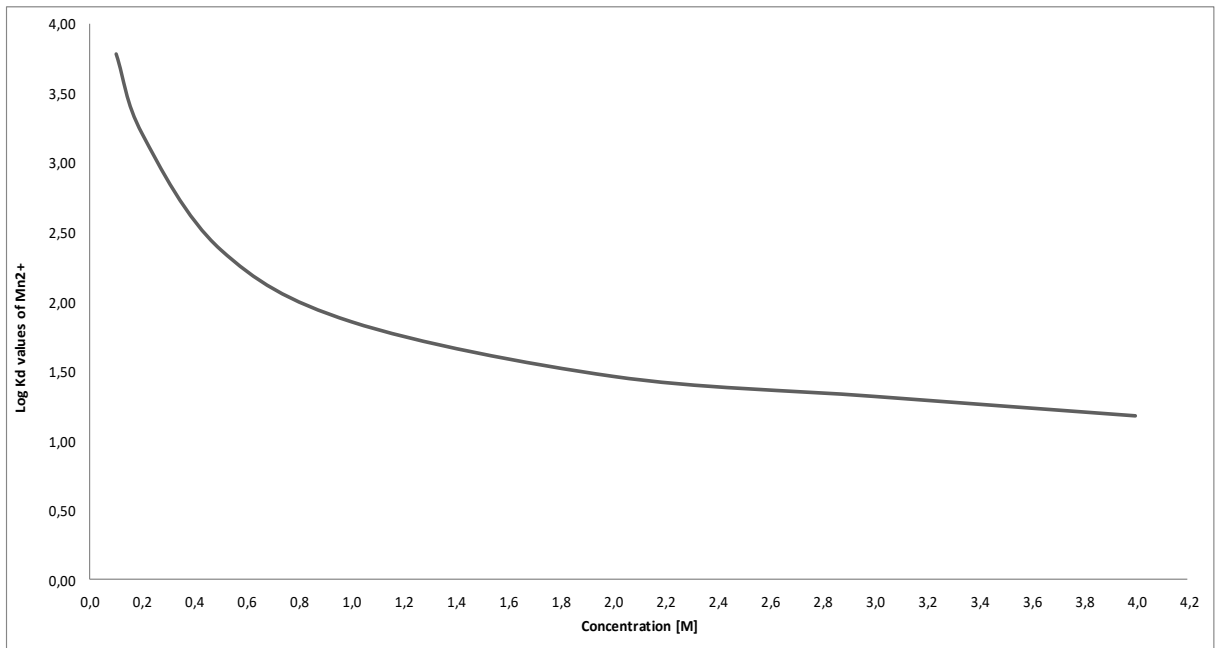
**D2  $K_d$  values for Cu obtained on Dowex Marathon MSC vs. the Nitric Acid ( $HNO_3$ ) concentration (M)**



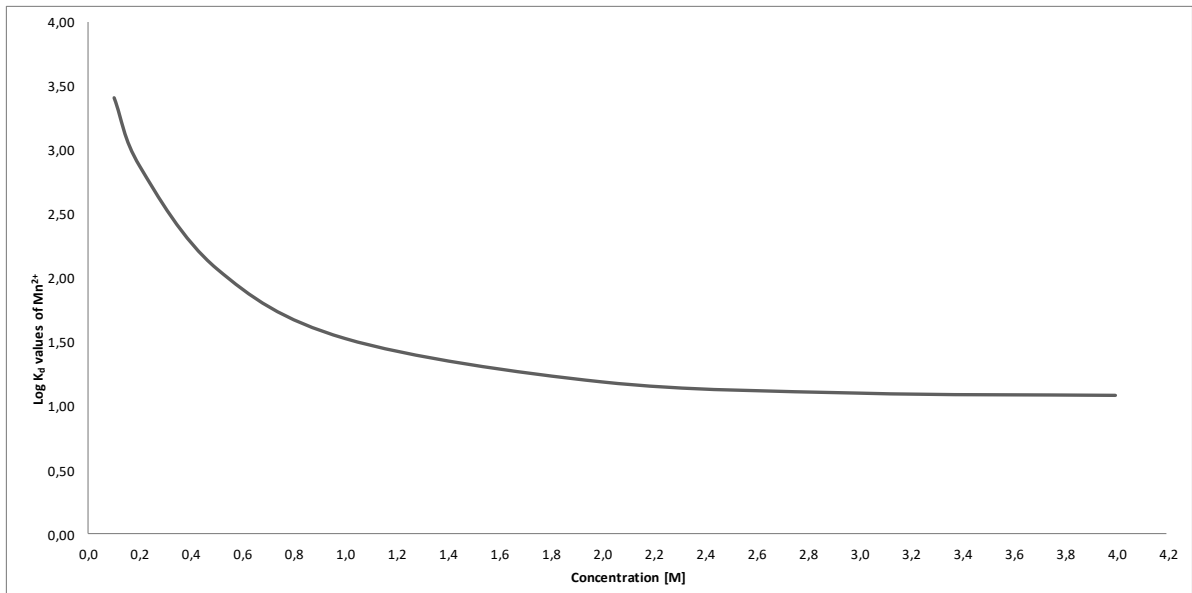
**D3  $K_d$  values for Cu obtained on Amberlyst 15 vs. the Nitric Acid ( $HNO_3$ ) concentration (M)**



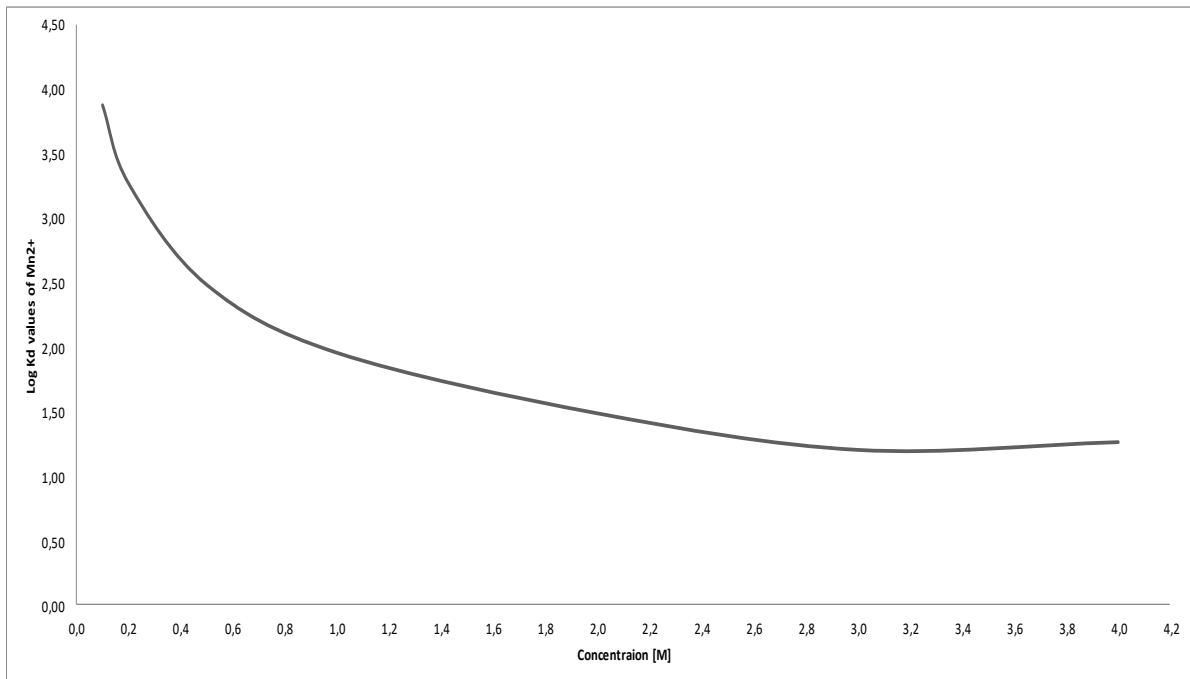
**E1  $K_d$  values for Mn obtained on Bio Rad AG MP 50 vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



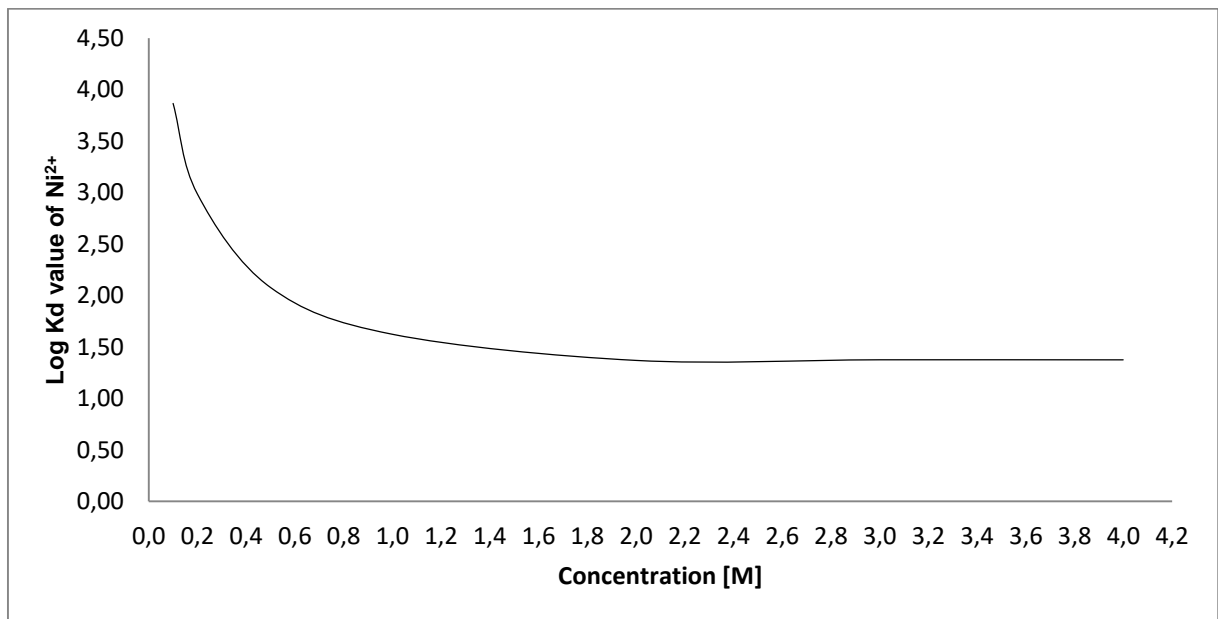
**E2  $K_d$  values for Mn obtained on Dowex Marathon MSC vs. the Nitric Acid ( $\text{HNO}_3$ ) concentration (M)**



**E3  $K_d$  values for Mn obtained on Amberlyst 15 vs. the Nitric Acid ( $HNO_3$ ) concentration (M)**

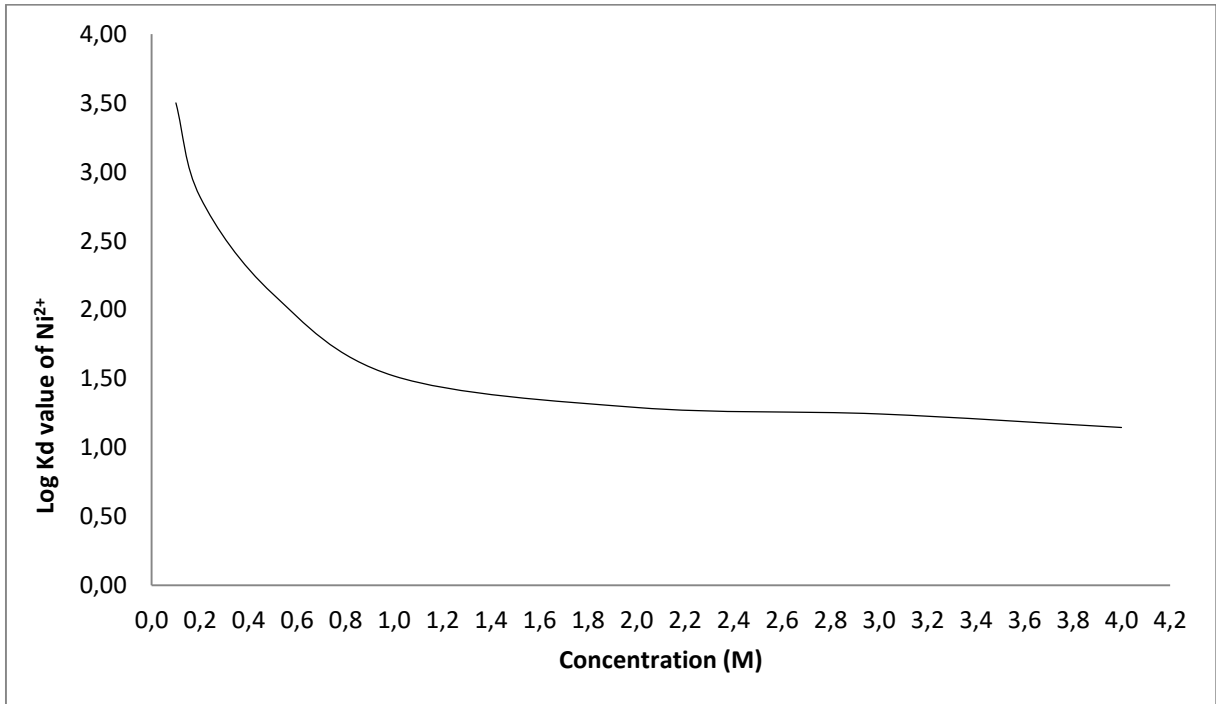


**F1  $K_d$  values for Ni obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**

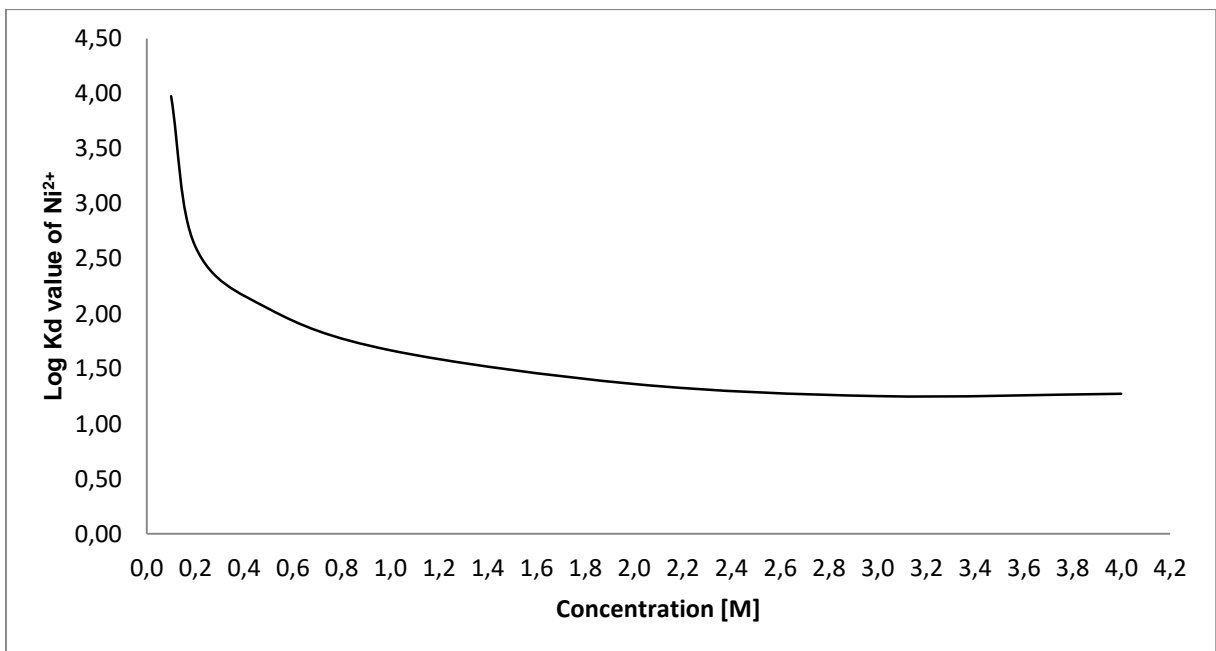




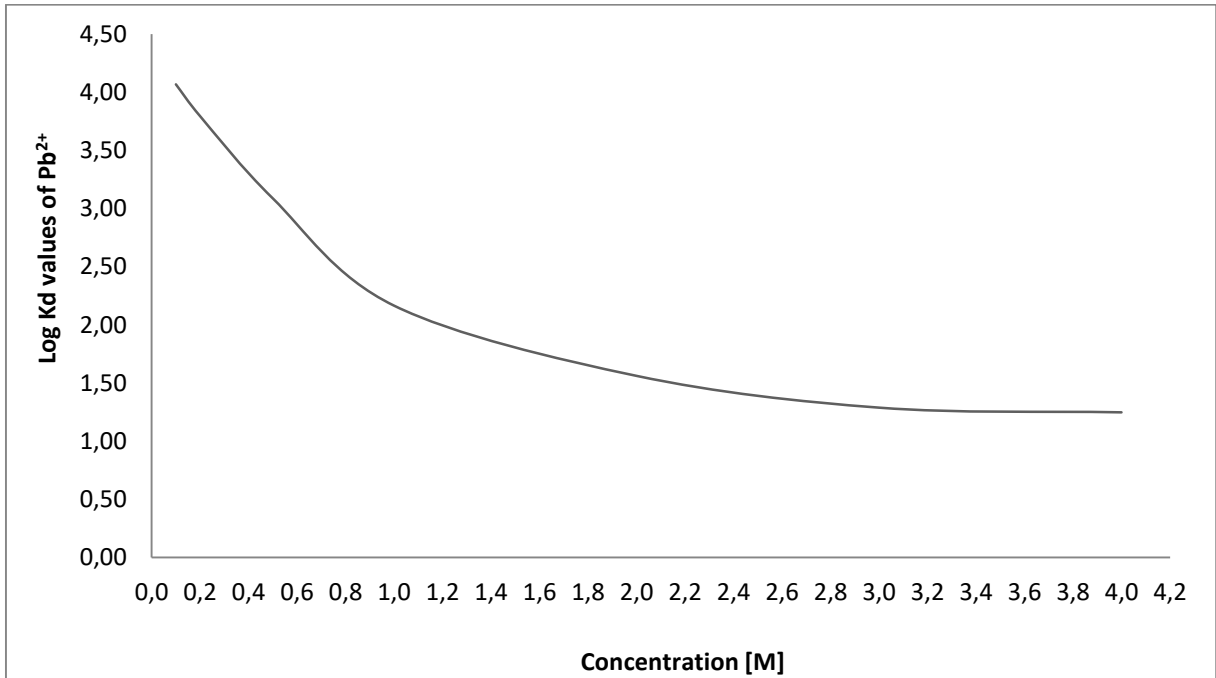
**F2  $K_d$  values for Ni obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



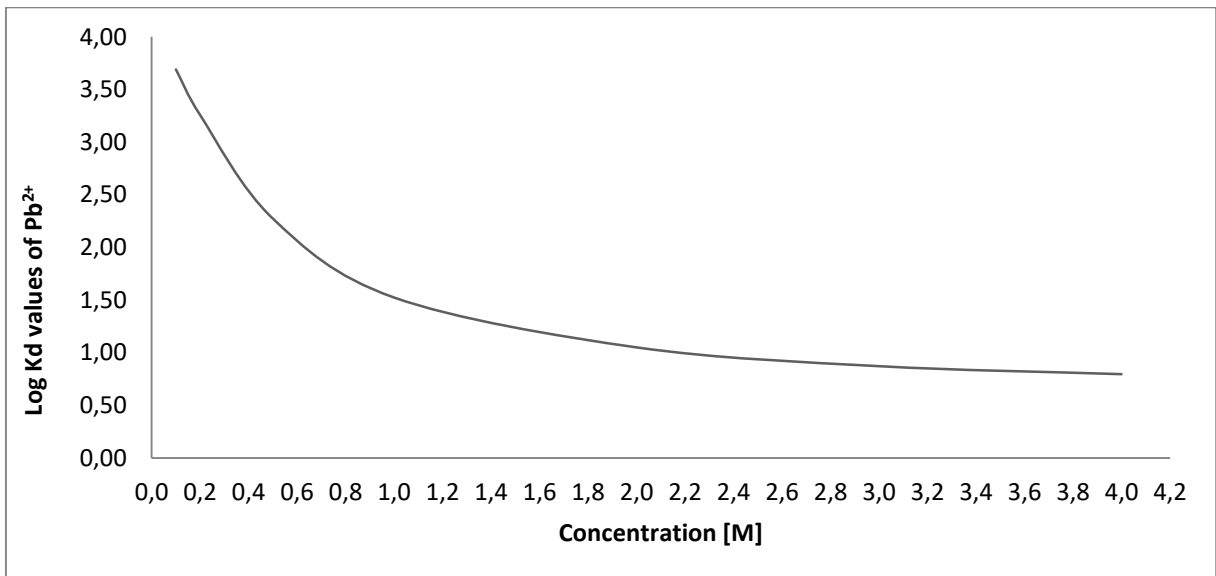
**F3  $K_d$  values for Ni obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



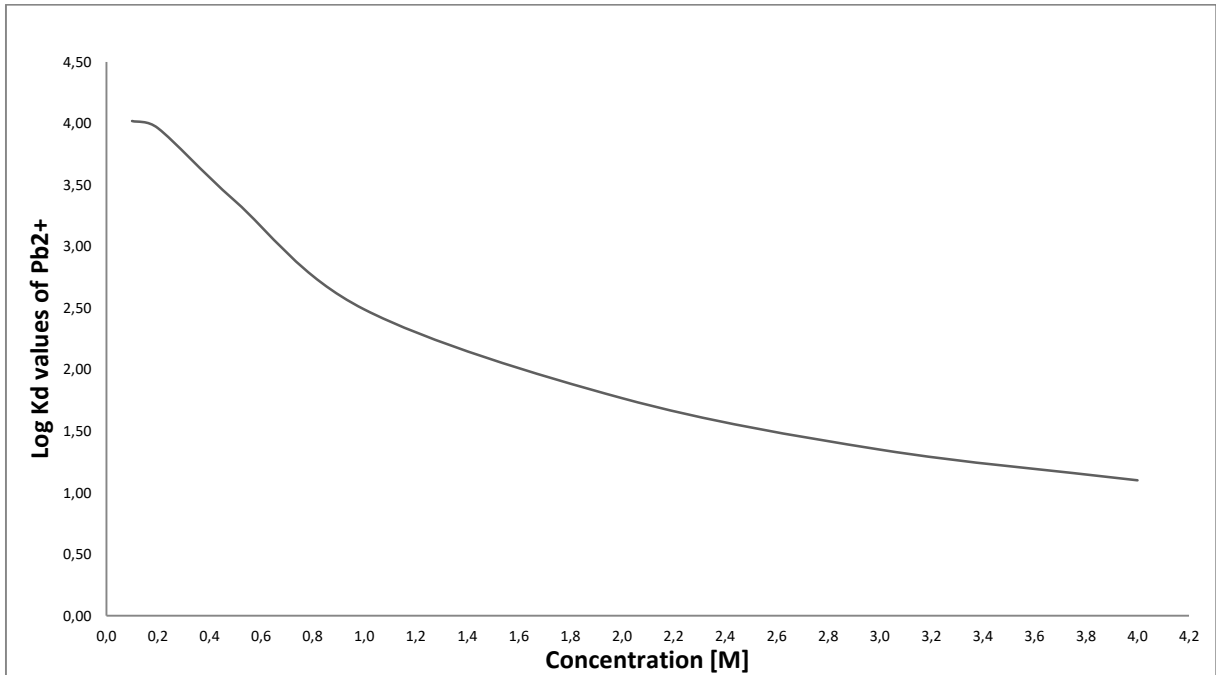
**G1**  $K_d$  values for Pb obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



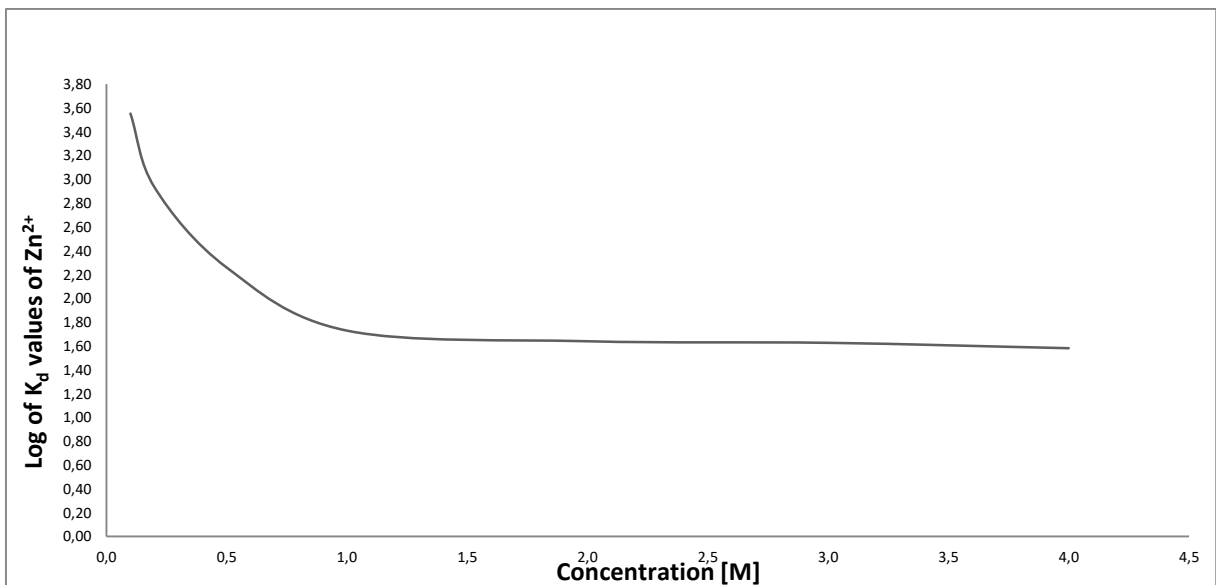
**G2**  $K_d$  values for Pb obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



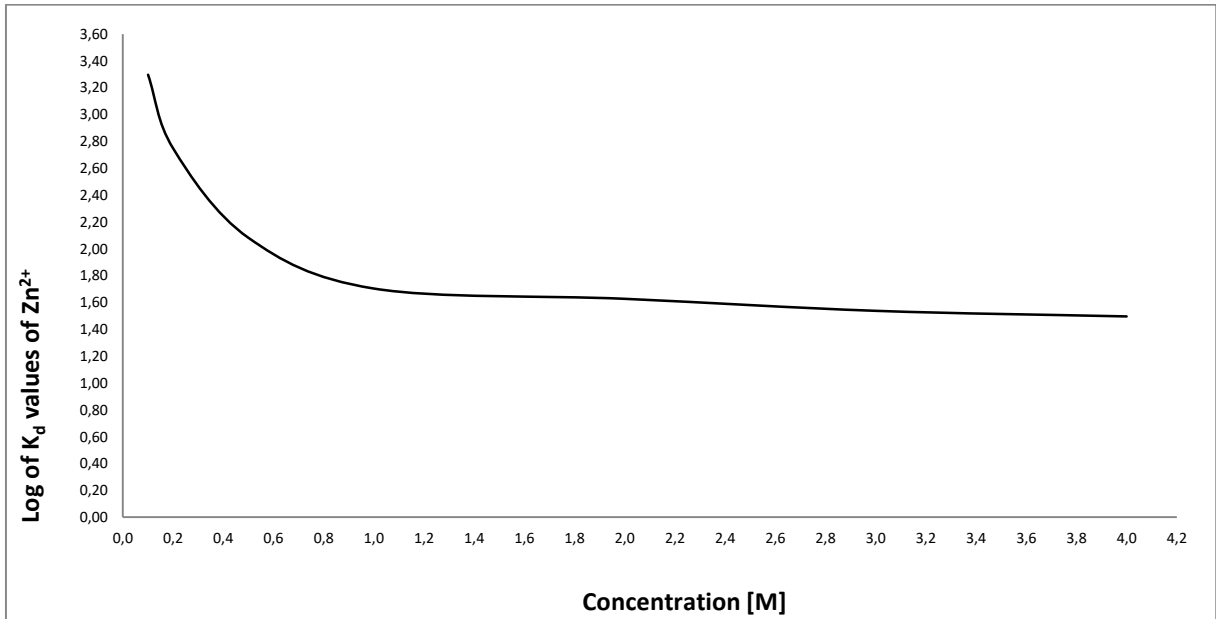
**G3**  $K_d$  values for Pb obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



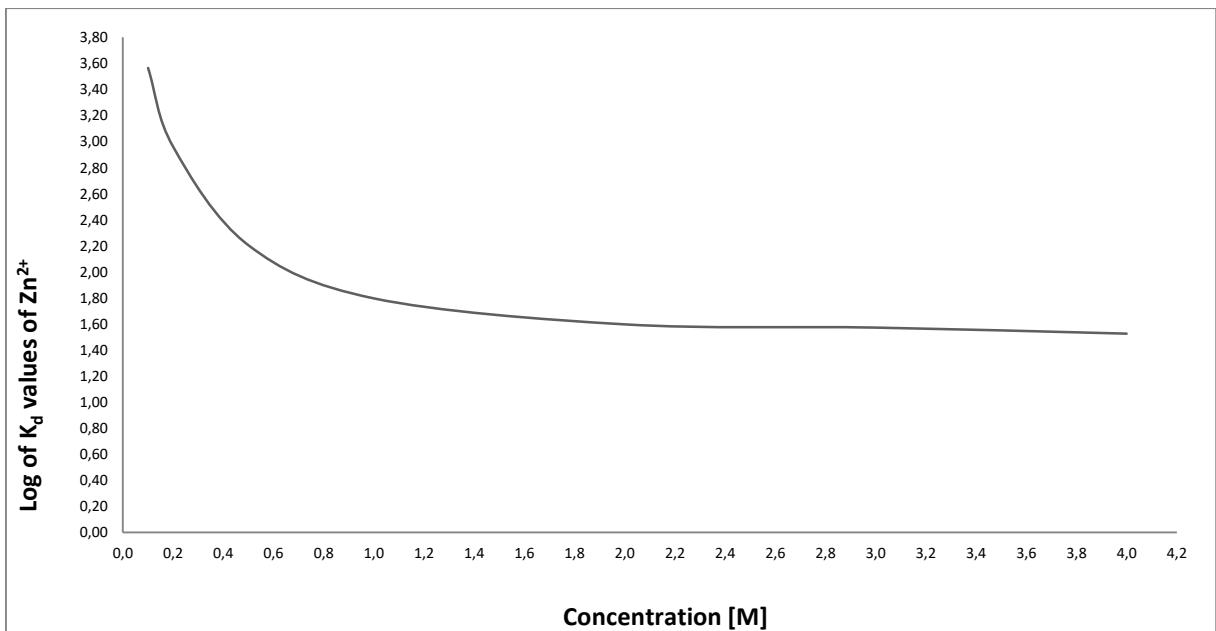
**H1**  $K_d$  values for Zn obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



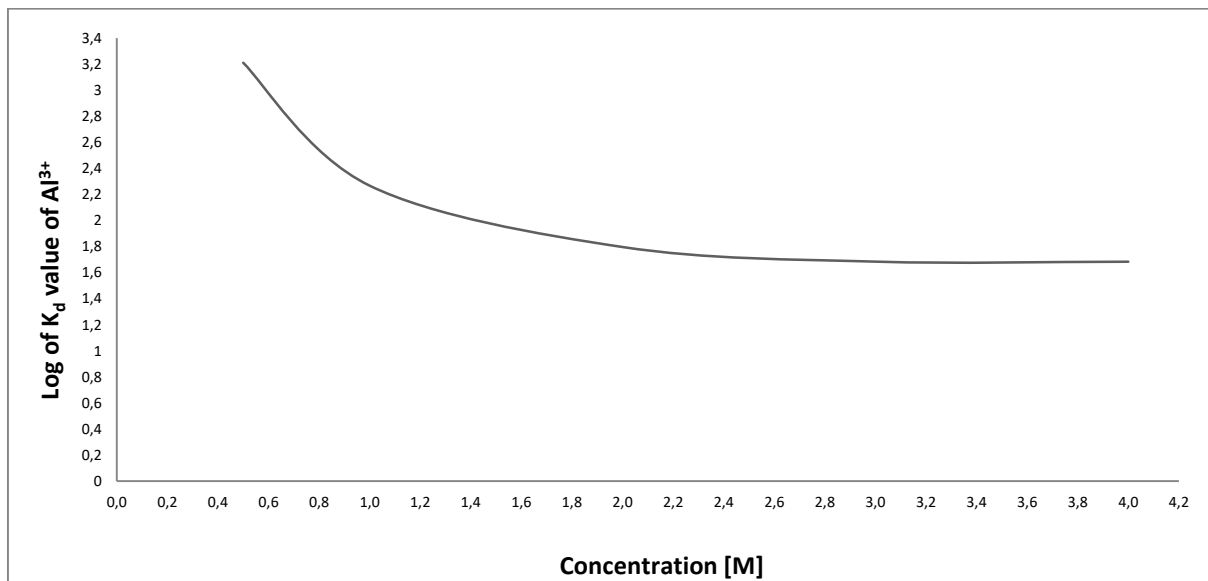
**H2  $K_d$  values for Zn obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



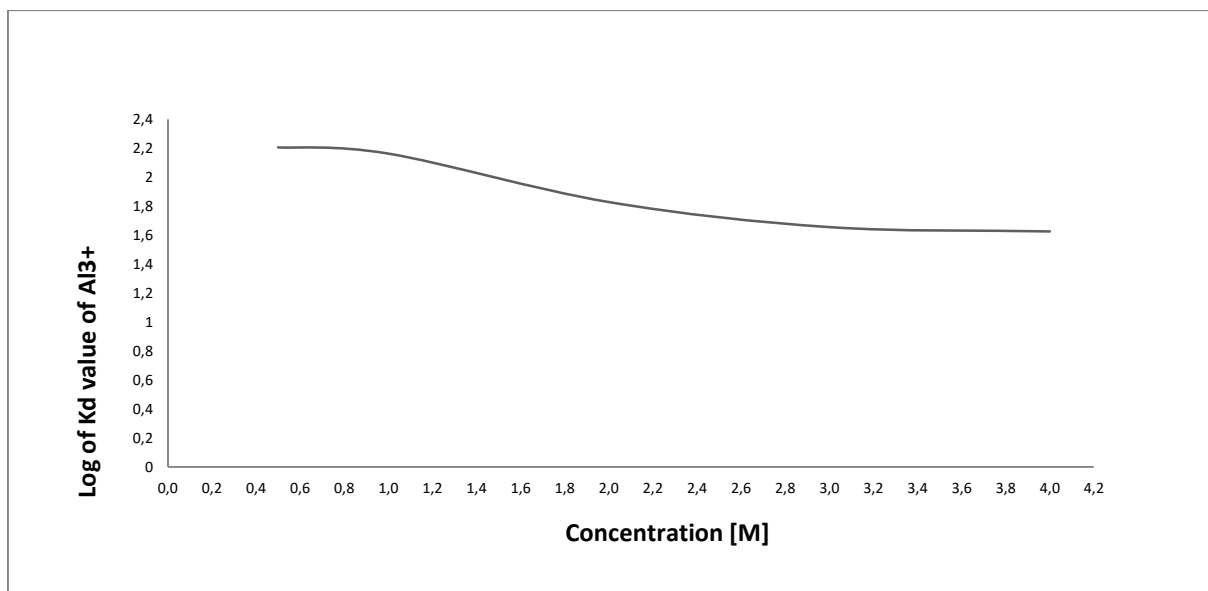
**H3  $K_d$  values for Zn obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



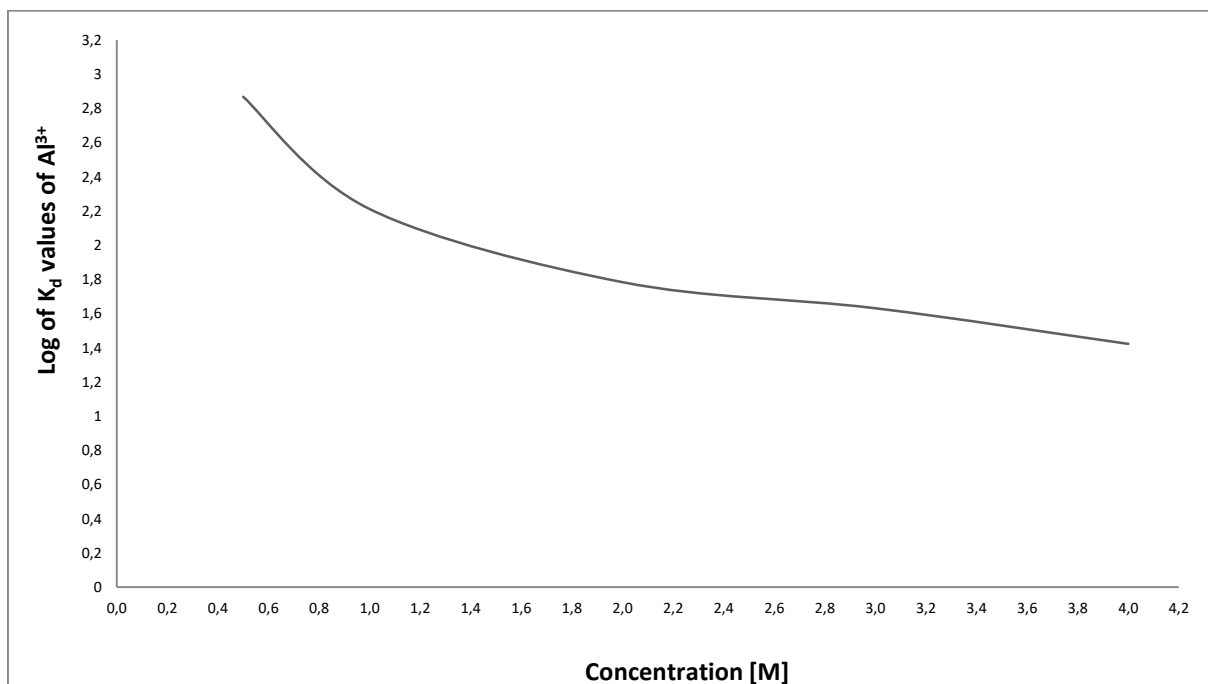
**I1  $K_d$  values for Al obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



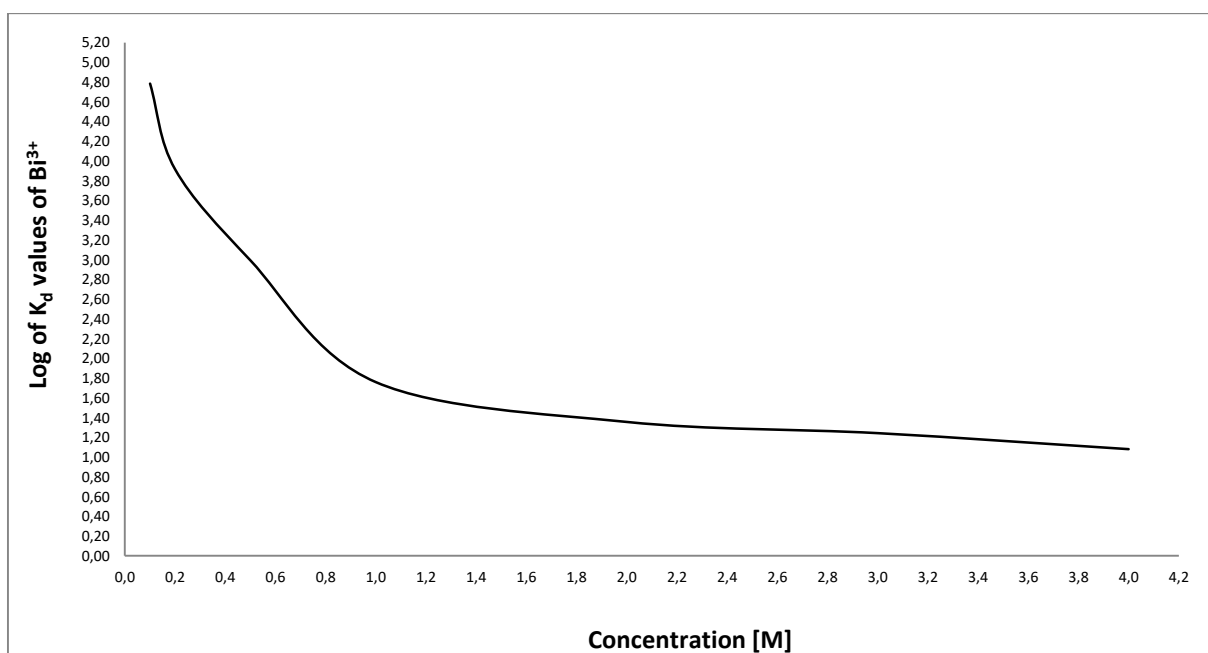
**I2  $K_d$  values for Al obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



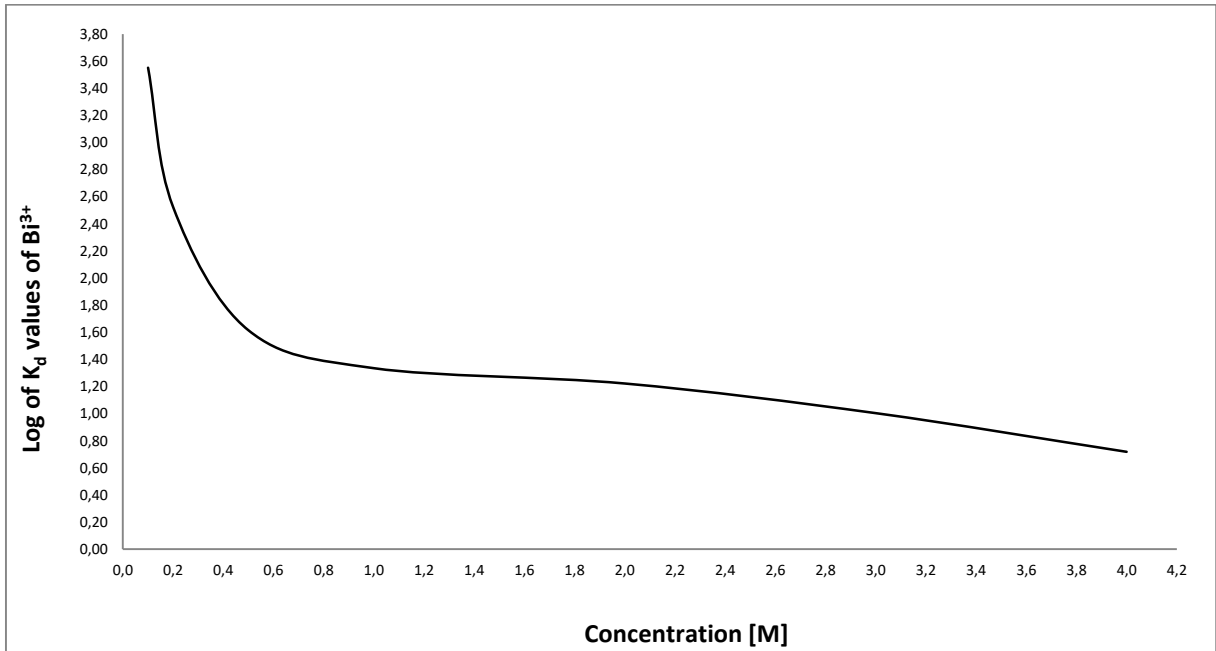
**I3**  $K_d$  values for Al obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



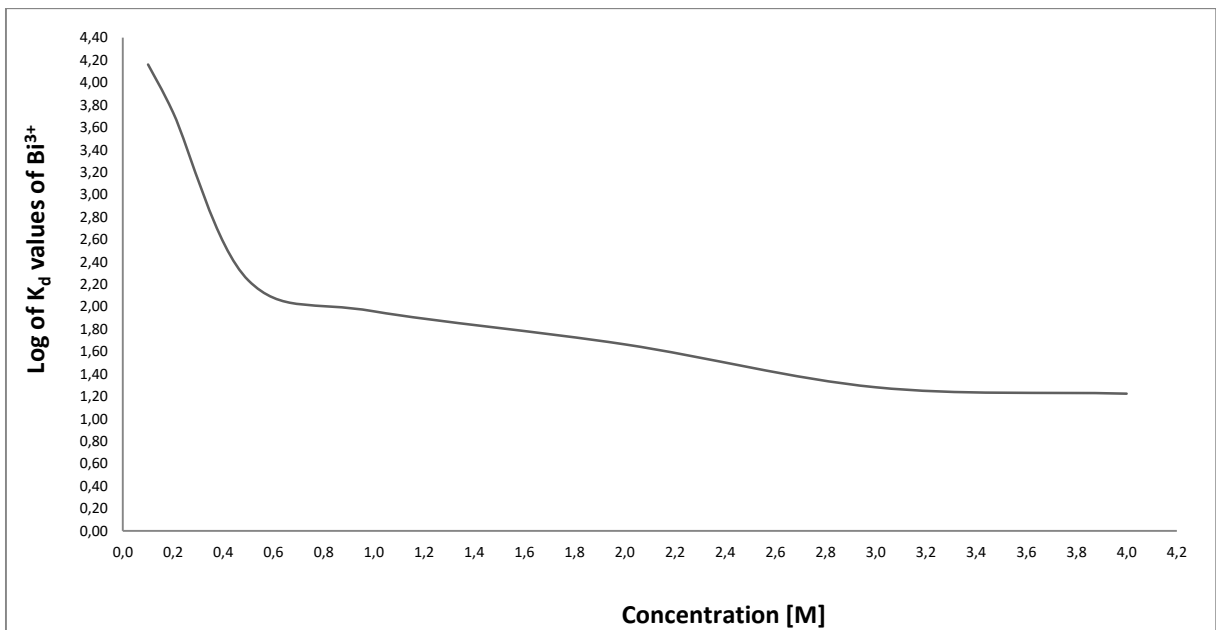
**J1**  $K_d$  values for Bi obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)



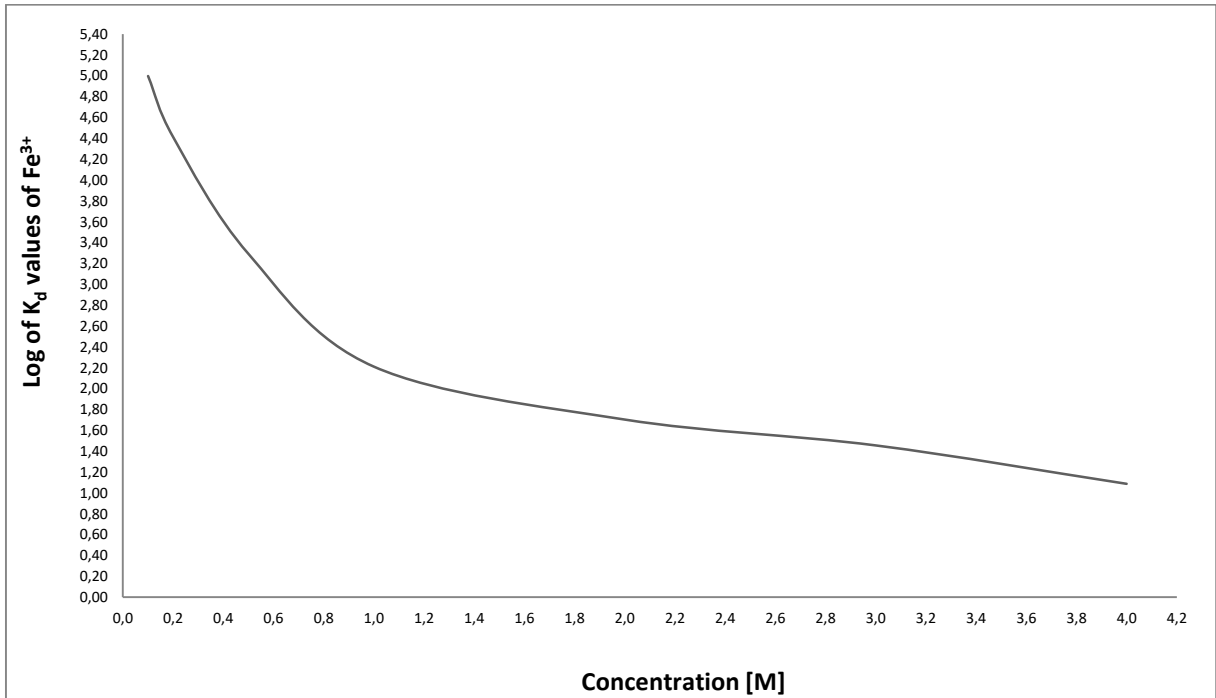
**J2  $K_d$  values for Bi obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



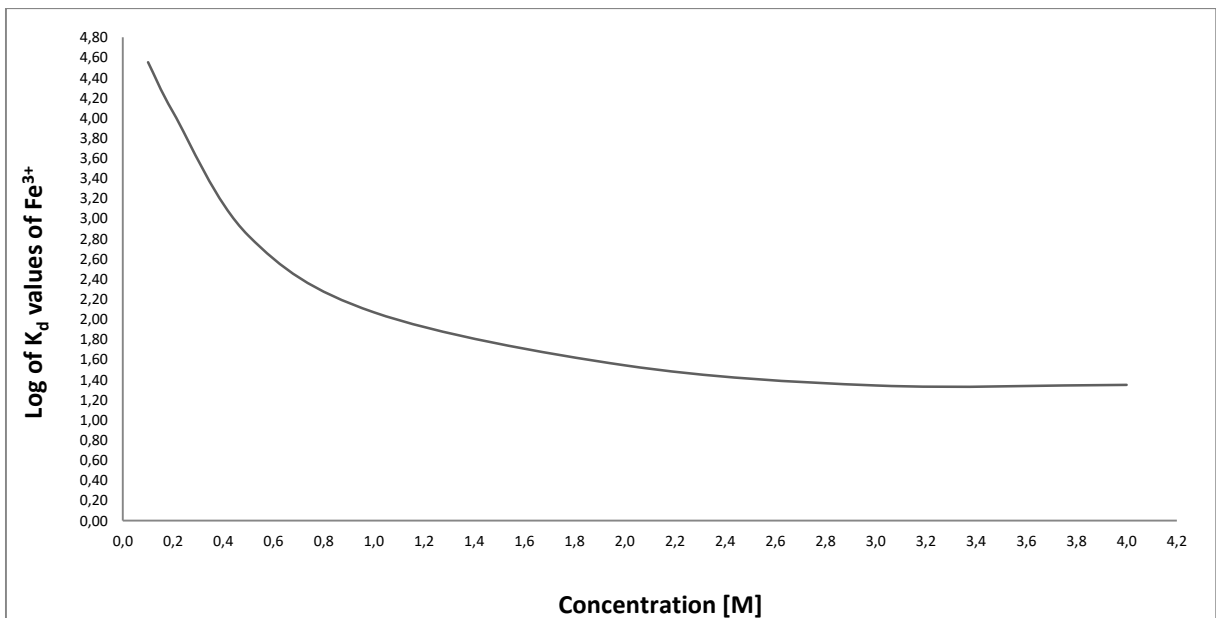
**J3  $K_d$  values for Bi obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



**K1  $K_d$  values for Fe obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**

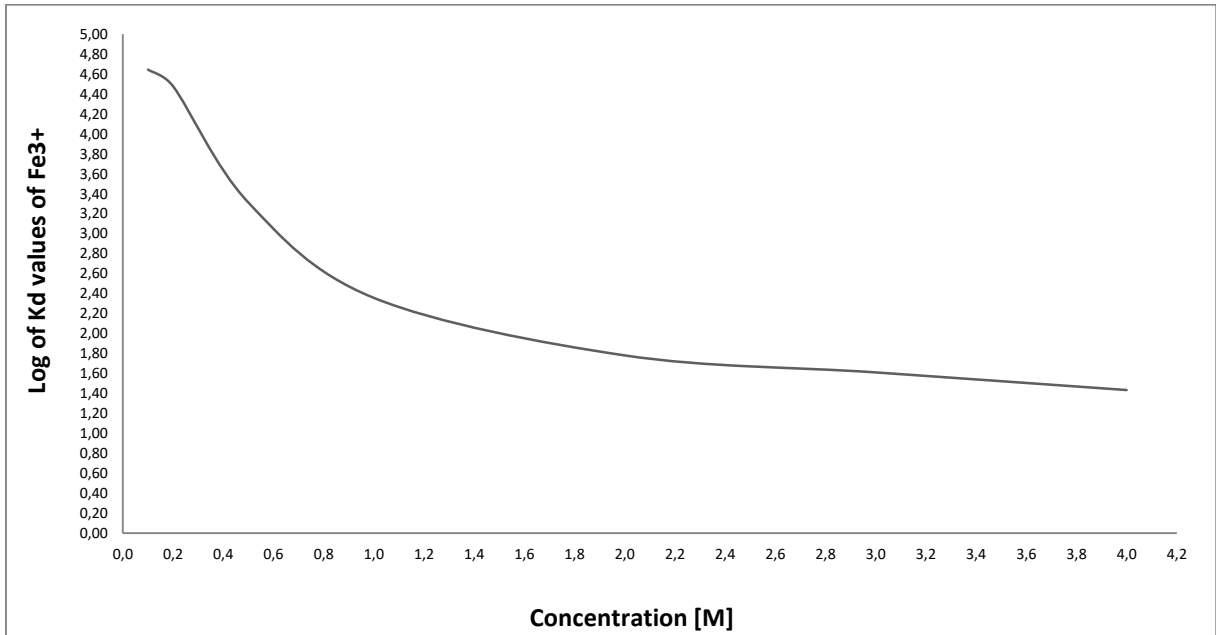


**K2  $K_d$  values for Fe obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**

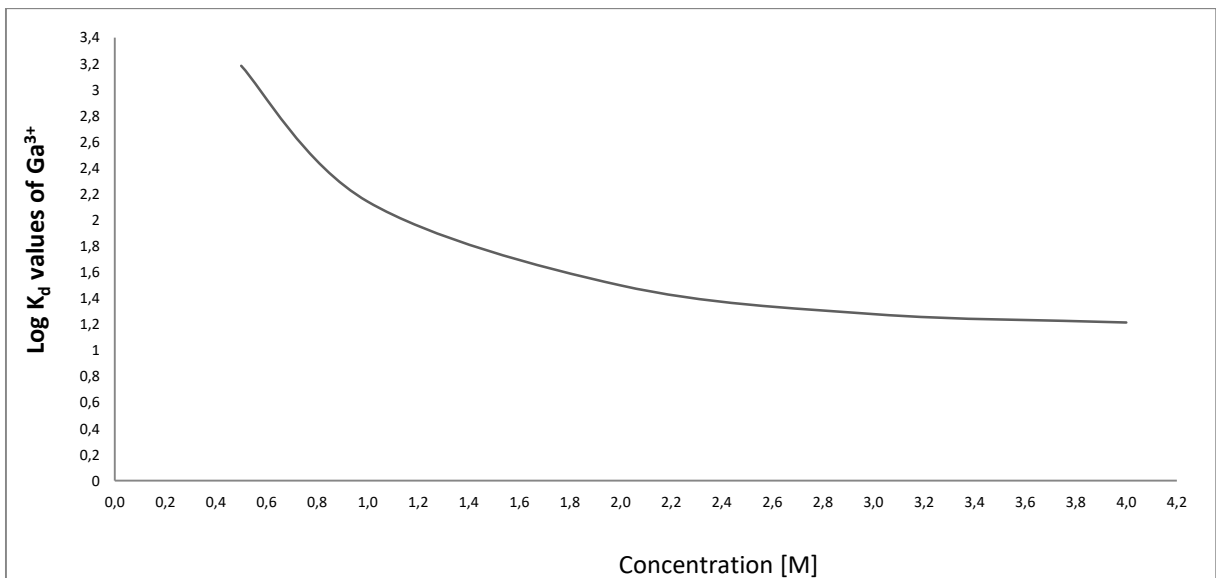




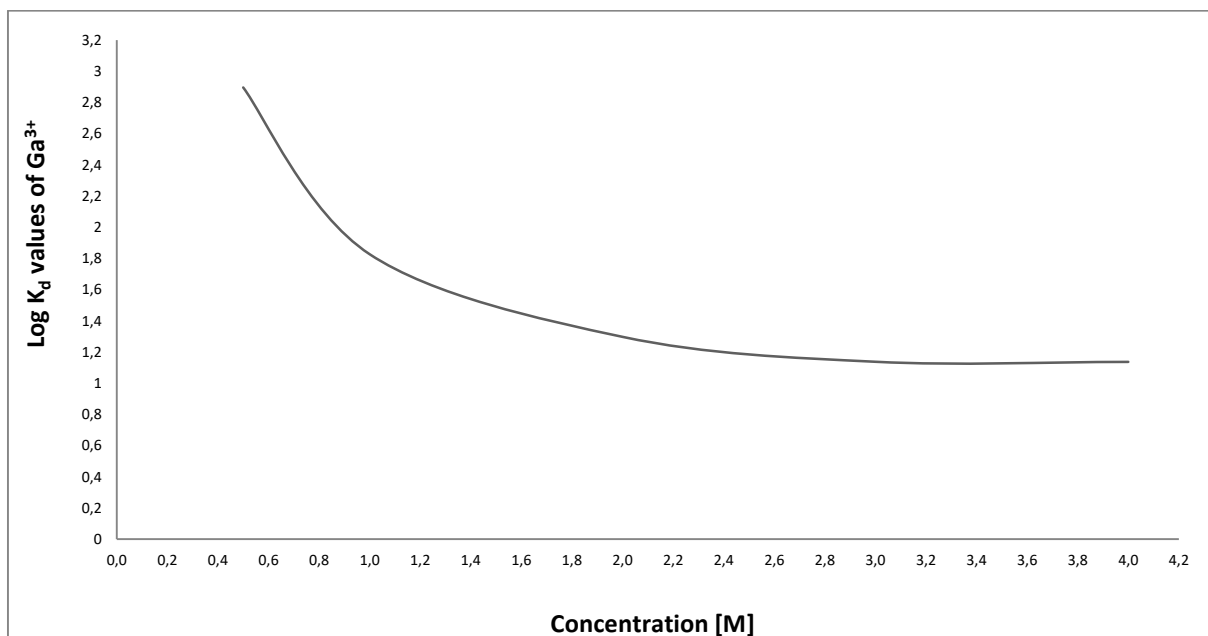
**K3  $K_d$  values for Fe obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



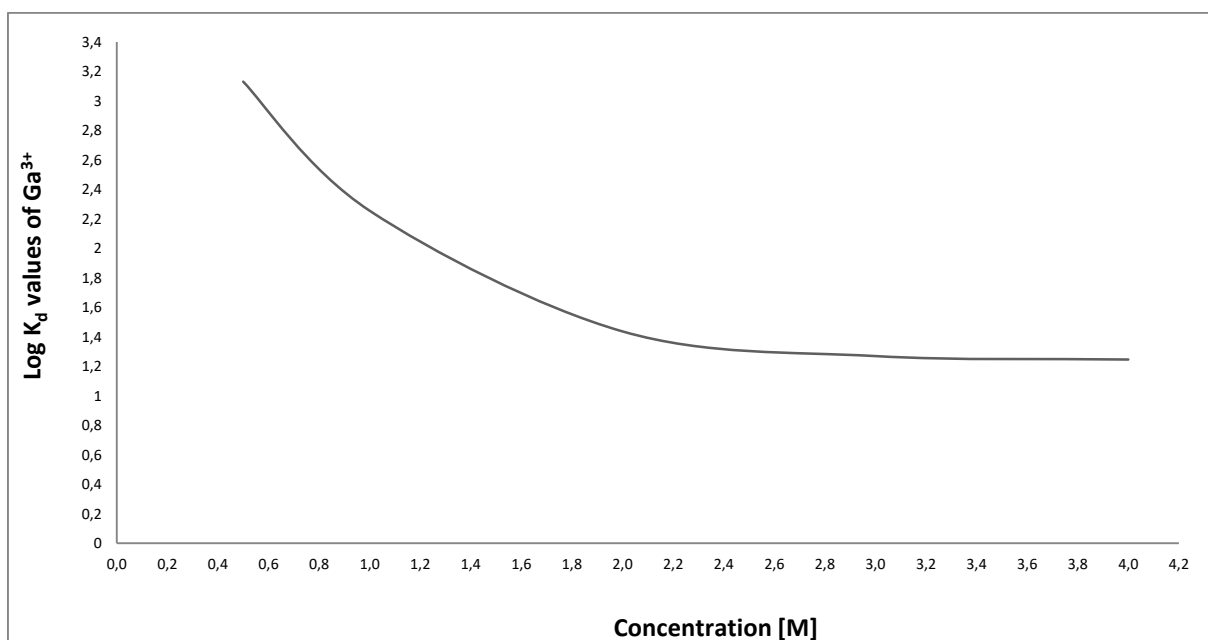
**L1  $K_d$  values for Ga obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



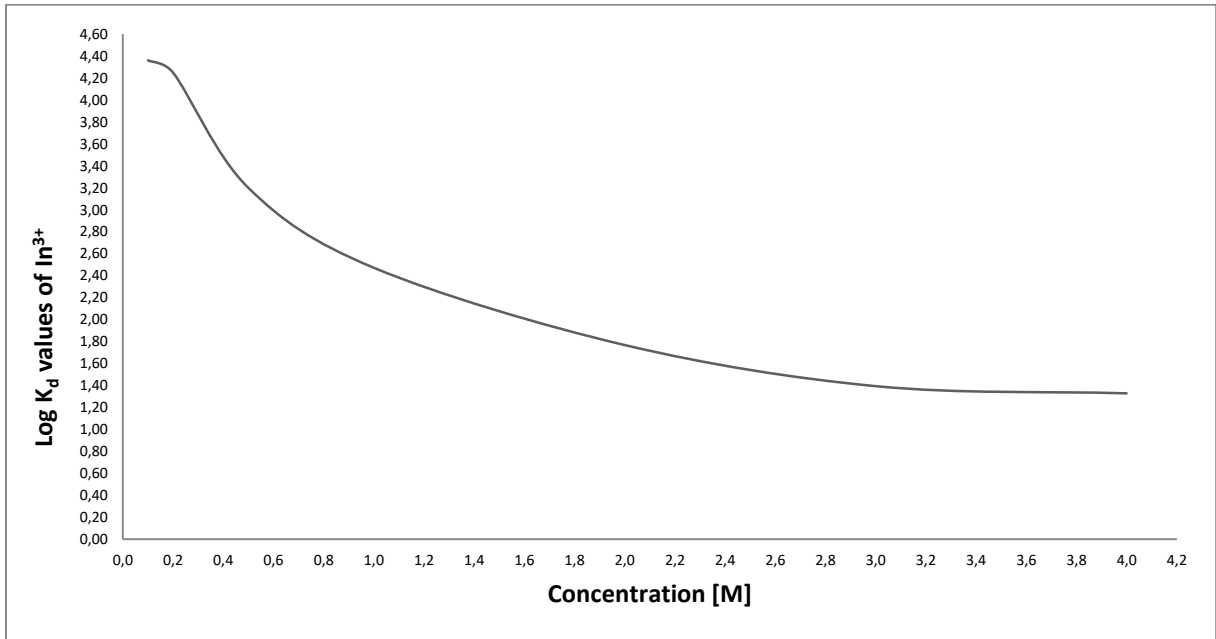
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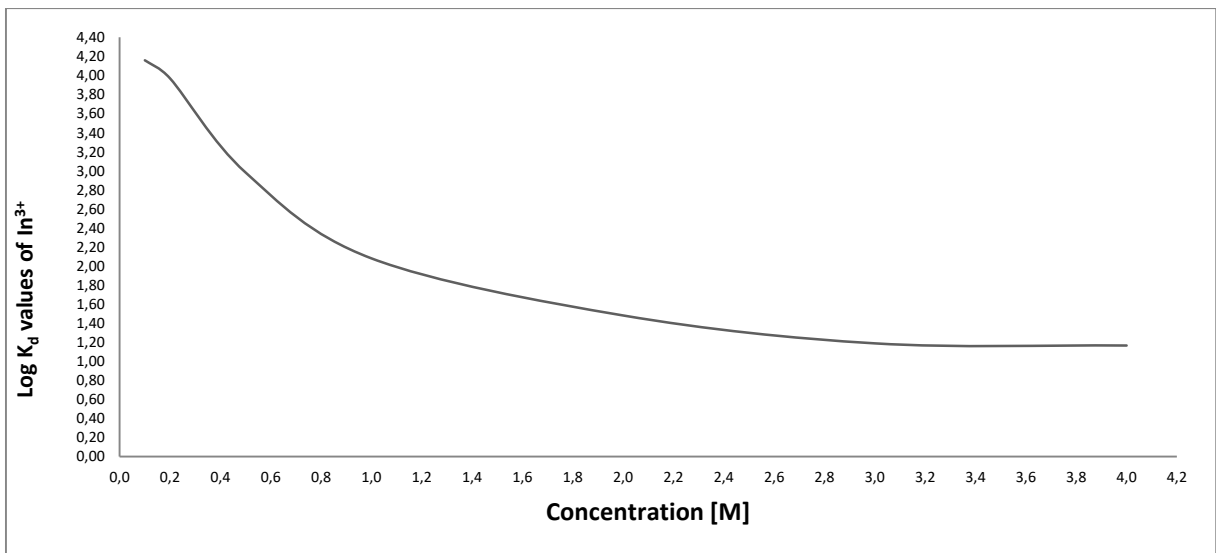
**L3  $K_d$  values for Ga obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



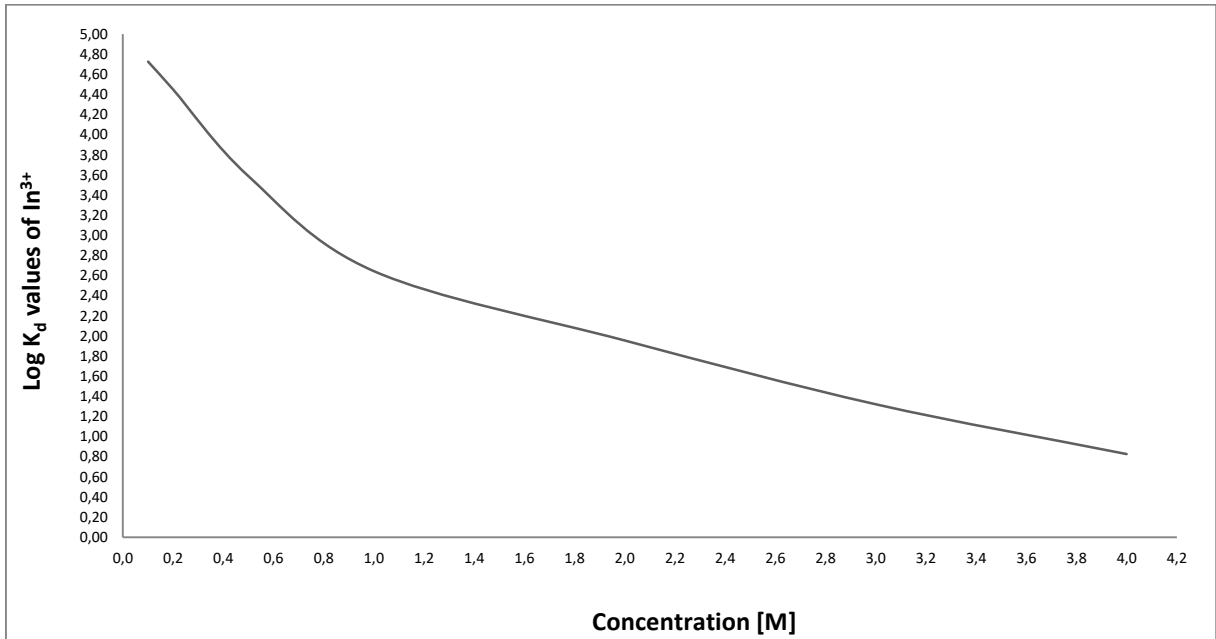
**M1  $K_d$  values for In obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



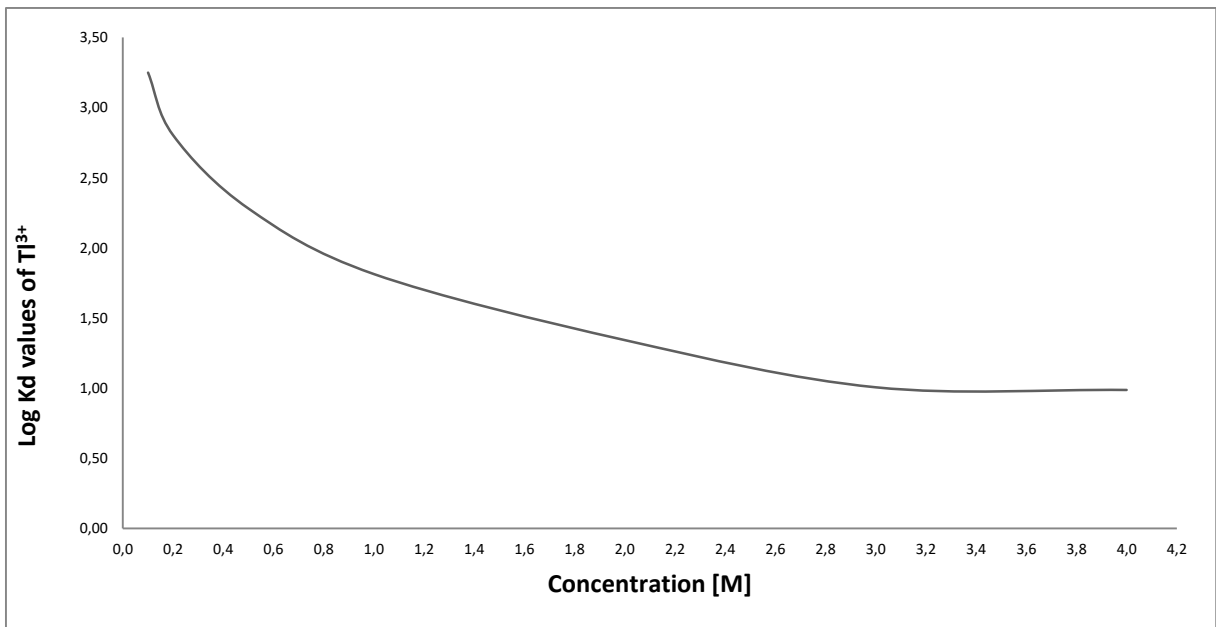
**M2  $K_d$  values for In obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



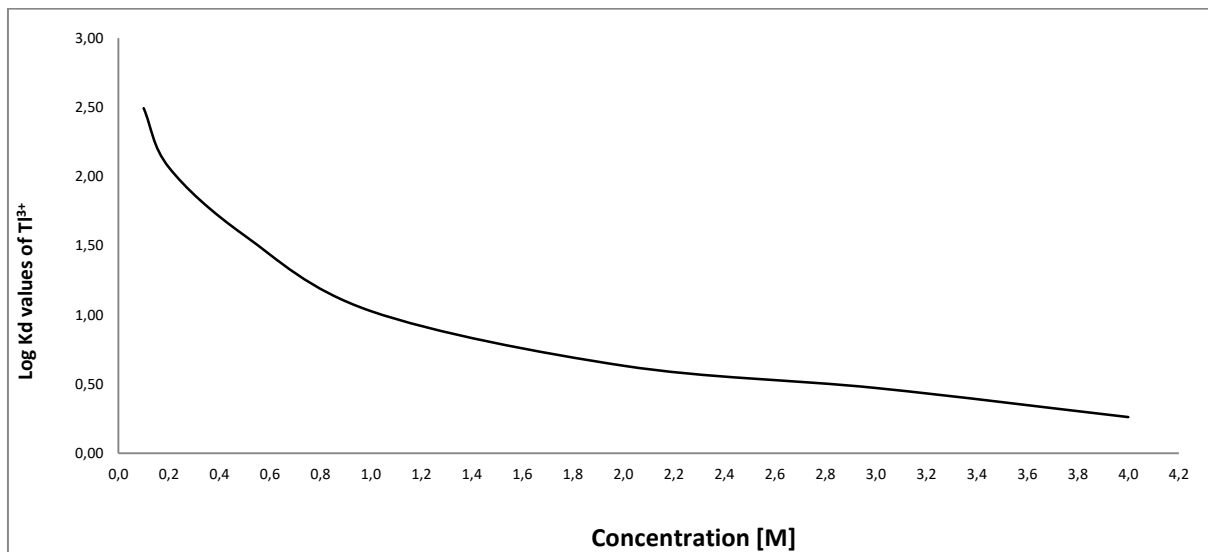
**M3  $K_d$  values for In obtained on Amberlyst 15 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



**N1  $K_d$  values for Tl obtained on Bio Rad AG MP 50 vs. the Nitric acid ( $HNO_3$ ) concentration (M)**



**N2  $K_d$  values for TI obtained on Dowex Marathon MSC vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**



**N3  $K_d$  values for TI obtained on Amberlyst 15 vs. the Nitric acid ( $\text{HNO}_3$ ) concentration (M)**

