ION EXCHANGERS IN THE REMOVAL OF CAFFEINE FROM AQUEOUS SOLUTIONS

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ABSTRACT

ION EXCHANGERS IN THE REMOVAL OF CAFFEINE
FROM AQUEOUS SOLUTIONS

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Caffeine is a commercially important member of a group of purine alkaloids found in coffee, tea and cacao particularly. It is an important ingredient in beverages and most important chemical element of stimulating pharmaceuticals. Caffeine is either manufactured by total synthesis or as a by-product from the decaffeinated coffee manufacturing. To investigate the equilibrium relationship of caffeine in ion exchange systems, which are widely used for recovery and purification processes, was the aim of this study. The effects of initial caffeine concentration and pH of the solution on equilibrium were also investigated.

Stock solutions of caffeine were prepared for screening of available adsorbents and cation exchange resins. A batch type operation was carried out in a shaker bath at 40 ^{o}C with 200 rpm agitation rate. After preliminary experiments, only Lewatit S100, which is a strongly acidic cation exchange

resin with s-dvb copolymer matrix, was studied. For the analysis of samples, HPLC equipment with Shimadzu PDA Detector at 254 nm and Nucleosil 100 C_{18} column was used. As mobile phase, a mixture of 8% acetonitrile, 8% 2-Propanol, and 1% acetic acid was introduced at 1.5 mL/min flow rate.

Results showed that, the caffeine uptake capacity of cation exchange resin was poor. A set of experiments were performed at three initial concentrations (0.005 M, 0.0075 M, and 0.01 M) and four different pH regions (acidic, slightly acidic, neutral, and basic). It was found that, at extreme pH conditions, the caffeine loading capacity of the resin was slightly increased. A significant effect of initial caffeine concentration, however, couldn't be observed. Due to the poor performance of gel type cation exchange resin and large molecular structure of caffeine molecule, Lewatit's SPC 112 macroporous resin was studied briefly for caffeine uptake performance. It was observed that SPC 112 has also poor but better loading capacity than S100 cation exchange resin.

Keywords: Caffeine, Ion exchange, Cation exchange resin, Equilibrium

ÖZ

KAFEİNİN SULU ÇÖZELTİLERDEN İYON DEĞİŞTİRİCİLERLE ELDESİ

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Ağustos 2006, 70 sayfa

Kafein, özellikle kahve, çay ve kakaoda bulunan pürin alkaloidler grubunun ticari olarak önemli bir üyesidir. İçeceklerin önemli bir bileşeni ve uyarıcı ilaçların en önemli etken maddesidir. Kafein, ya sentetik olarak ya da kafeinsiz kahve üretiminin yan ürünü olarak elde edilmektedir. Bu çalışmanın hedefi, kafeinin geri kazanım ve saflaştırma işlemlerinde sıkça kullanılan iyon değiştirici sistemlerdeki denge ilişkisini incelemektir. Başlangıç kafein konsantrasyonunun, ve çözeltinin başlangıç pH düzeyinin iyon değişimi dengesi üzerindeki etkileri de incelenmiştir.

Mevcut adsorbanların ve iyon değiştiricilerin elemesi için stok kafein çözeltileri hazırlanmıştır. 28 ^{o}C de 300 rpm çalkalama hızında bir çalkalama banyosunda kesikli tipte bir çalışma yürütülmüştür. Başlangıç deneylerinden sonra sadece polisitren yapıda kuvvetli asidik katyon değiştirici bir reçine olan Lewatit S100 ile çalışma yapılmıştır. Numune analizi için 254 nm de Shimadzu PDA Detektör ve Nucleosil 100 C_{18} kolonuna sahip HPLC ekipmanı kullanılmıştır. Mobil faz olarak 8% asetonitril, 8% 2-propanol ve 1% asetik asitten oluşan bi karışım verilmiştir.

Sonuçlar, katyon değiştirici reçinenin kafein alımının yetersiz olduğunu göstermiştir. Üç farklı başlangıç konsantrasyonunda (0.005 M, 0.0075 M, ve 0.01 M) ve dört farklı pH bölgesinde (asidik, az asidik, nötr, ve bazik) bir dizi deney yapılmıştır. Aşırı pH değerlerinde reçinenin kafein yükleme kapasitesinin hafifçe arttığı bulunmuştur. Başlangıç kafein konsantrasyonun ise denge ilişkisine anlamlı bir etkisi gözlenememiştir. Jel tipi katyon değitirici reçinenin düşük performansından ve kafein molekülünün moleküler yapısının büyüklüğünden ötürü, Lewatit SPC 112 makropor reçinesi ile kafein alım performansı üzerine çalışılmıştır. SPC 112 reçinesinin de düşük ama S100 reçinesine oranla daha yüksek bir yükleme kapasitesinin olduğu gözlenmiştir.

Anahtar kelimeler: Kafein, İyon değişimi, Katyon değiştirici reçine, Denge

To

My Departed Mother

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LIST OF SYMBOLS

a	Activity
A, B	Cations in the solution or in the resin phases
C_e	Equilibrium concentration in solution phase, mol / L
C_i	Ionic concentration of the i^{th} species, mol / L
C_0	Initial solution concentration, mmol / L
K_a	Langmuir equilibrium constant, dm^3 / mol
K_A, K_B	Dissociation constants
K_B^A	Selectivity coefficient
K_f	Freundlich constant
m_{Dry}	Weight of the dry resin sample, g
m_w	Weight of the hydrated resin sample, g
n	Freundlich constant
q_e	Equilibrium concentration in adsorbent-phase, mol acid/g wet resin
q_m	Maximum exchange monolayer capacity, mol / g
R-	Functional group on resin matrix
Q	Resin upload (loading), mmol/g wet resin

Greek Letters

γ_i	Activity coefficient of the i^{th} species in the solution phase

CHAPTER 1

INTRODUCTION

Caffeine, $C_8H_{10}N_4O_2$, is the most commercially important member of a group of alkaloids of which purine is the basic structure. Other important purine alkaloids are xanthine, theophylline, and theobromine. The physical properties of most alkaloids, once purified, are similar; colorless, crystalline, with definite melting points, and chiral. Caffeine is a white powder and when crystallized from water, is a monohydrate in the form of white silky needles. A saturated solution of caffeine is neutral by sensitive methods of pH measurements due to the fact that its ionization constants, K_a at 25ºC = 1.0 x 10^{-14} and K_b at 19ºC = 0.7 x 10^{-14}, are close to those of water [1].

Although caffeine is unaffected by weak acids or bases, it does have the capability of forming complexes with a number of compounds, e.g., chlorogenic acid, caffeic acid. The result of these complexes is shown by increased solubility of both components. The solubility of caffeine alone in various organic solvents and the solubility of caffeine in water at different temperatures are indicated in Appendix, Tables A.5 and A.6, respectively [1].

Caffeine occurs free and bound in a number of plants, particularly coffee, tea, guarana, mate, and kola nuts. Lesser amounts are found in cacao.

In the pharmaceutical industry, caffeine is extensively used, both as freebase and as mixtures with other ingredients. It has ability to increase mental activity and wakefulness; therefore, it is used in caffeine tablets, which are marketed to help prolong wakefulness. By far the largest use of caffeine is in popular cola beverages where it supplies a desirable flavor.

Caffeine used in various industries is supplied by either one of three types of manufacturing processes. It is either extracted from plant material as from coffee or tea, or extracted and then methylated as in cacao, or is manufactured by total synthesis from uric acid or urea and chloroacetic acid.

Manufacture of caffeine went through a change with respect to the economical conditions of the raw materials and processing costs. Until 1945, most synthetic caffeine was produced from cacao. After 1945, caffeine was obtained from tea waste. With the increasing demand of caffeine for cola beverages, decaffeinated coffee came up and caffeine was produced as a byproduct. Thus, there are two main sources of caffeine at present: from coffee as a byproduct of decaffeinated coffee manufacture and the total synthesis from urea and chloroacetic acid.

Although there are industries utilizing caffeine in the manufacture of their products in Turkey, caffeine is not manufactured by total synthesis but imported for a cost of nearly a million dollars. Turkey may not be a coffee growing country; however is one of the leading tea producers worldwide. Amount of green tea leaves produced in year 2000 is nearly 800000 tons and black tea produced is about 140000 tons. Green tea leaves contain numerous chemicals as well as caffeine up to 4% on dry basis. During the black tea manufacturing process, tons of tea leaves which are off the standard or excess, are either burned or buried. Old tea leaves which lost their economical values are pruned off and these leaves contain no less than 2% caffeine on dry basis. The possibility of the beneficiation of this caffeine potential was the motivation of this study [4].

In one process the tea waste is mixed with lime and leached with water. The extract is filtered, concentrated, and caffeine is allowed to crystallize. The crude caffeine is further purified by dissolving in a minimum of hot water,

treating with decolorizing carbon, filtering, and chilling to yield pure caffeine. In a second process, tea is made alkaline and the caffeine is extracted from the water phase by a halogenated solvent. A third process involves the direct extraction of moistened tea leaves by toluene or chloroform. However, all of the above include high solvent costs, removal and recovery difficulties, and safety problems due to the toxicity of organic solvents [5].

With a history of decades of study, ion exchange and adsorption are widely used and cheap techniques with respect to extraction. They have lower operating costs, safer operating conditions, higher yield and comparably good selectivity. Ion exchangers and adsorbents can be perfectly capable of capturing neutral molecules like caffeine from tea extract. In an ion exchange or adsorption process, equilibrium conditions are as important as the kinetics of the process. In this study, equilibrium properties of caffeine with various commercially available ion exchanger resins and adsorbents were studied [3].

This study aimed to determine the equilibrium properties of caffeine with ion exchange resins and adsorbents and investigate the effects of initial concentration and pH of aqueous caffeine solution on equilibrium.

CHAPTER 2

CAFFEINE

2.1 History

Most of the caffeine-yielding plants were discovered and used as far back as ancient times. People chewed the seeds, bark and leaves of many plants and probably associated caffeine containing plants with the resulting changes in the mood and behavior. Eventually, caffeine was cultivated and eaten to ease fatigue, to stimulate awareness, and to elevate the mood. It may have first been ground to a paste or eaten as berries; only much later was it found that by steeping it in hot water, one could get greater effects.

Tea, which has been used as a hot beverage and as a medicine, is one of the main sources of caffeine apart from coffee. Records show that it may have been used in China as early as 4700 years ago and spread to Japan, along with other aspects of the Chinese culture, in about 600 BC, but it took 700 years to fully integrate tea into Japanese daily life. After Dutch traders brought tea back to their country, its uses quickly spread throughout Europe.

The first written word on coffee is found in Arabian documents of the 10^{th} century. However, there is evidence that coffee was cultivated and the berries chewed as early as 6^{th} century in Ethiopia. At the beginning of the 11^{th} century, they began use the beans to make a hot drink called “qahwah”. As the use of the beverage spread, the word was quickly adapted to various languages.

By the end of the 17th century, the Dutch had coffee plantations in the island of Java. In the next fifty years, its cultivation spread to Caribbean colonies, Central and South America.

Caffeine was first isolated in pure form by Runge in 1820 from coffee beans. Besides that, Strecker prepared caffeine by methylating theobromine in 1861.

At the present, two main processes for the manufacture of caffeine are, from coffee as a byproduct of decaffeinated coffee manufacture and the total synthesis from urea and chloroacetic acid. These processes will be further discussed in section 2.3.

2.2 Properties of Caffeine

Caffeine, $C_8H_{10}N_4O_2$, belongs to a group of alkaloids of which purine is the basic structure. It occurs free and bound in a number of plants, particularly coffee and tea. Like most of the alkaloids it has a crystalline structure and it is chiral. A saturated caffeine solution is neutral as its ionization constants are very close to those of water. Molecular structures and ionization constants of purine alkaloids found in tea are shown in Figure 2.1.

Although caffeine is a very stable molecule, it is capable of forming complexes with a number of compounds, e.g., chlorogenic acid, caffeic acid, and benzpyrene. The result of these complexes is shown by increased solubility of both components ascribed to the induced polarization of the compounds on one another. Properties of caffeine are given in Table 2.1.

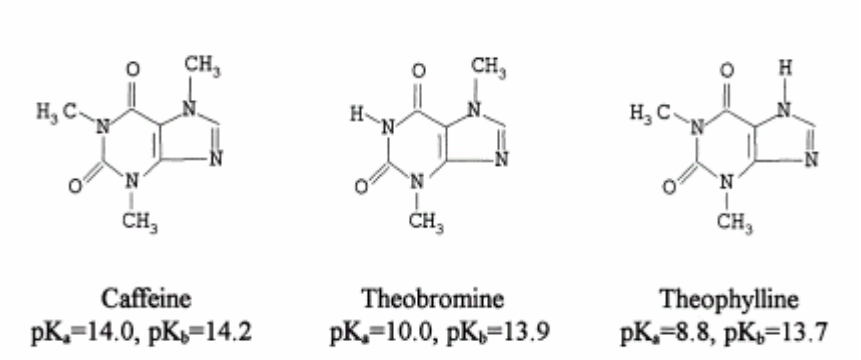


Figure 2.1 Molecular structures of purine alkaloids in tea.

Table 2.1. Properties of Caffeine [5].

Systematic name	1,3,7-trimethyl-1*H*-purine-2,6(3*H*,7*H*)-dione
Other names	1, 3, 7-trimethylxantine trimethylxanthine guaranine mateine theine methyltheobromine
Molecular formula	$C_8H_{10}N_4O_2$
Molecular weight	194.19 g/mol
Appearance	Odorless, white needles or powder
CAS number	[58-08-2]
Density and phase	1.23 g/cm^3, solid
Ionization constants	K_a = 1.0x10^{-14} at 25°C K_b = 0.7x10^{-14} at 19°C
Solubility in water	2.13 g/100 ml (25°C)
Boiling point	178 °C (sublimes)
Melting point	237°C

2.3 Manufacture of Caffeine

2.3.1 Caffeine from Tea

In one process the tea waste (3 to 4% caffeine) is mixed with lime and leached with water. The extract is filtered, concentrated, and caffeine is allowed to crystallize. The crude caffeine is further purified by dissolving in a minimum of hot water, treating with decolorizing carbon, filtering, and chilling to yield pure caffeine. In a second process, tea is made alkaline and the caffeine is extracted from the water phase by a halogenated solvent. A third process involves the direct extraction of moistened tea leaves by toluene or chloroform [1].

2.3.2 Caffeine from Coffee

The average caffeine content of the two major species of coffee, *Coffea arabica* and *Coffea canephora*, is 1 and 2% respectively. Recognition of the physiological effects of caffeine prompted the invention of a process for removing caffeine from coffee with an organic solvent in the early 1900s. Commercial decaffeination of coffee is almost always performed on green coffee beans prior to roasting where flavor and aroma are developed. Patent literature, however, cites caffeine removal from roasted beans and from roasted coffee extract.

The two major commercial decaffeination techniques are either based on solvent decaffeination or water decaffeination.

a) Solvent Decaffeination

There are numerous solvents in which caffeine may be dissolved. The choice of solvent depends on the cost of the solvent, the ease of removal and recovery, the specificity for caffeine and of course, the safety and toxicity. Originally Benzene, was used, but as chlorinated hydrocarbons became available at reasonable prices it was dropped in favor of trichloroethylene and methylene chloride. Today, another technique, supercritical fluid extraction widens the area of usage. Supercritical carbon dioxide is an excellent nonpolar solvent for caffeine (as well as many other organic compounds) also it is safer than the organic solvents that are used for caffeine extraction. The extraction process is simple: CO_2 is forced through the green coffee beans at temperatures above 31.1 °C and pressures above 73 atm. Under these conditions, CO_2 is said to be in a "supercritical" state: it has gas like properties which allow it to penetrate deep into the beans but also liquid-like properties which dissolve 97-99% of the caffeine. The caffeine-laden CO_2 is then sprayed with high pressure water to remove the caffeine. The caffeine can then be isolated by charcoal adsorption or by distillation, recrystallization, or reverse osmosis [1].

The basic steps in solvent extraction of caffeine from green beans are shown in Figure 2.2. This consists of steaming the green coffee beans for half an hour with a resulting moisture of 16 to 18% in the first column of a battery of columns. This is followed by a prewetting step to increase coffee bean moisture to above 40% by weight. The previously steamed and prewetted green coffee beans are then counter currently extracted by a solvent, methylene chloride or trichloroethylene, at temperatures between 120 and 250ºF. The column from which most of the caffeine has been removed is isolated, solvent drained, and then steam stripped to remove all residual solvent. The decaffeinated beans are discharged from the column and dried. The caffeine-rich solvent is processed to remove the caffeine and other soluble material and recycled to become the feed to the premoistened

green beans rich in caffeine.

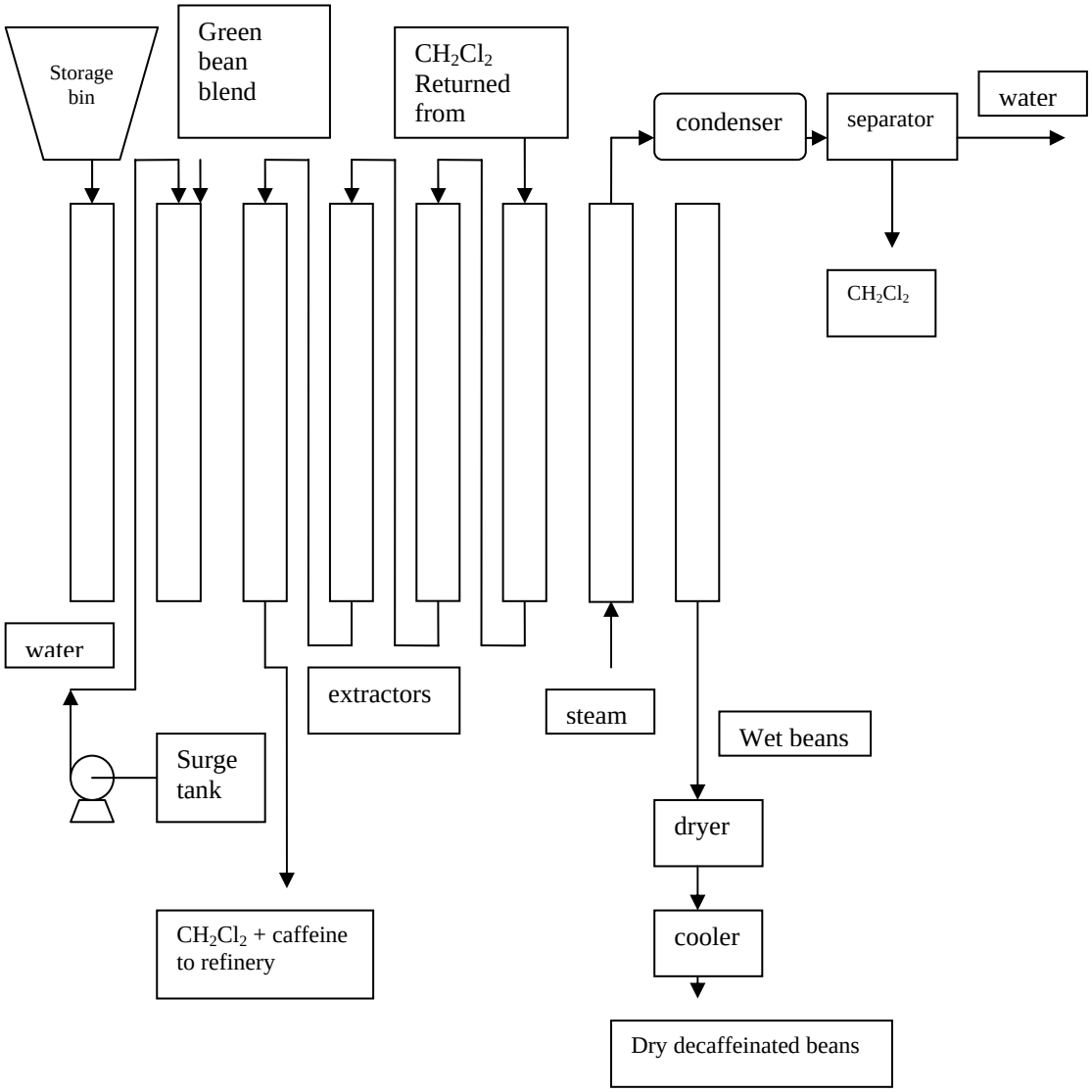


Figure 2.2. Solvent decaffeination.

b) Water Decaffeination

In 1941 a decaffeination invention was filed by Berry and Walters of General Foods using water extract from green coffee beans in equilibrium with the green beans, except for caffeine. Advantages claimed are higher extraction rates, elimination of water-insoluble waxes extracted by the solvent, purer caffeine in a caffeine recovery system and less heat treatment of coffee bean by the elimination of the solvent stripping step because there is no direct solvent contact with the beans. A flow sheet of the water decaffeination process is shown in Figure 2.3 [1].

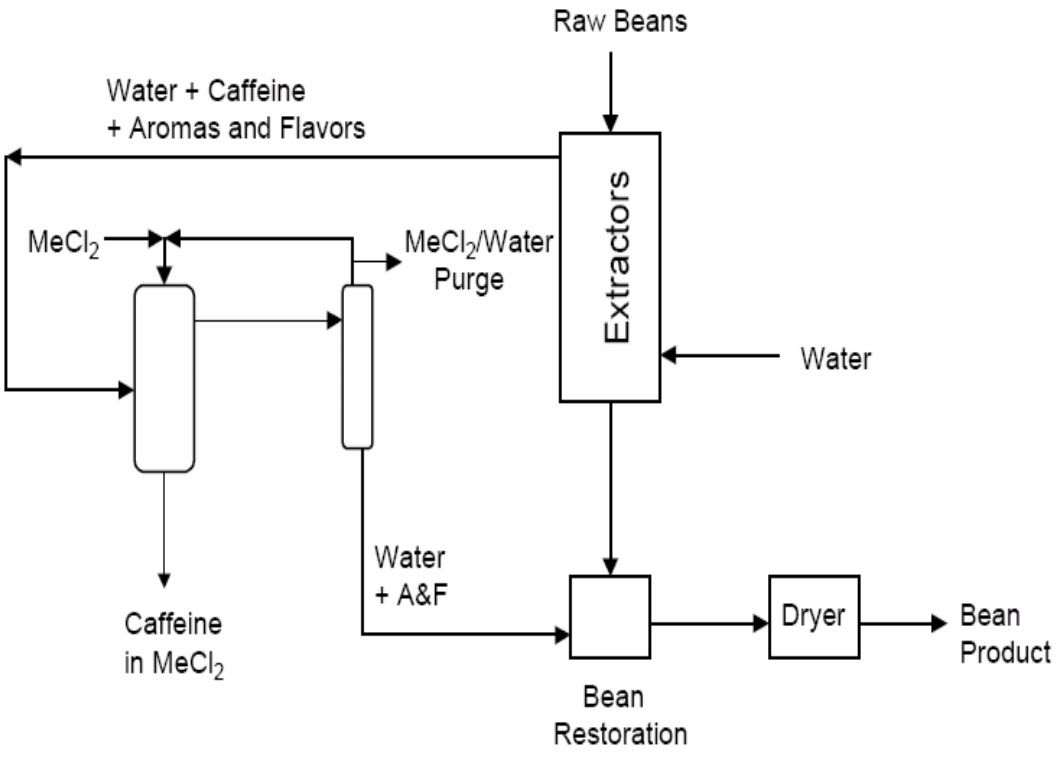


Figure 2.3 Water decaffeination.

Again a battery of columns is used in which green coffee beans are contacted countercurrently with water extract. As the extracting liquid moves through the extraction zone, water is preferentially absorbed by the beans. The water extract removes about 98% of the caffeine in about 8 hours of residence in the column. Finally, the decaffeinated green coffee beans are air dried and processed in the conventional manner to produce decaffeinated instant coffee. Extract, rich in caffeine (0.5% by weight), after centrifuging to remove suspended solids such as coffee chaff, is contacted with a solvent to selectively transfer caffeine. The solvent, rich in caffeine, is regenerated in the caffeine refining system.

CHAPTER 3

ION EXCHANGE

3.1. Introduction

In ion exchange, ions of a given charge (either cations or anions) in a solution are adsorbed on a solid material (*the ion exchanger*) and are replaced by equivalent quantities of other ions of the same charge released by the solid. Ion exchangers consist of either a crystalline or a polymeric matrix and functional groups. Depending on the pH value of the liquid phase, these groups can either be protonated or dissociated. Due to this, exchangers are able to interact with ions from the liquid phase. There are a large variety of such interactions where electrostatic and van der Waals forces, heteropolar and covalent binding, or coordination forces are involved [6]. The various types of matrices and their degree of crosslinking translate into different selectivities for given species and into different mechanical and osmotic stability [8]. Ion exchange forms the basis of a large number of chemical processes, which can be divided into three main categories: substitution, separation, and removal of ions.

Ion exchangers are classified according to their functionality and the physical properties of the support matrix. Cation and anion exchangers are classified in terms of their ability to exchange positively or negatively charged species. Strongly acidic and strongly basic ion exchangers are ionized and thus are effective at nearly all pH values. Weakly acidic exchangers are typically effective in the range of pH 5-14. Weakly basic resins are effective in the

range of pH 0-9. Weakly acidic and basic exchangers are often easier to regenerate, but leakage due to incomplete exchange may occur. The achievable ion exchange capacity depends on the concentration of ionogenic groups and their availability as an exchange site. The latter is a function of the support matrix [7].

Polymer-based, synthetic ion exchangers known as resins are commercially available in gel type or truly porous forms. Gel type resins are not porous in the usual sense of the word, since their structure depends upon swelling in the solvent in which they are immersed. When crosslinked polymers are used as the support matrix, the internal porosity so defined varies in inverse proportion to the degree of crosslinking, with swelling. The ion held by the exchanger also influences the resin swelling. Thus, the size of the resin particles is changed during the ion exchange process as the resin is changed from one form to another and this effect is more dramatic for resins with lower degree of crosslinking. The choice of degree of crosslinking is dependent on several factors including: the extent of swelling, the exchange capacity, the intraparticle diffusivity, the ease of regeneration, and the physical and chemical stability of the exchanger under chosen operating conditions [7]. The concentration of ionogenic groups determines the capacity of the resin.

Truly porous, synthetic ion exchangers are also available. These materials retain their porosity even after removal of the solvent and have measurable surface area and pore size. Since higher degrees of crosslinking are typically used to produce truly porous ion exchange resins, these materials tend to be more stable under highly oxidative conditions, more attrition-resistant, and more resistant to breakage due to osmotic shock than their gel-type counter parts. Moreover, since their porosity does not depend entirely on swelling, they can be used in solvents with low dielectric constant where gel-type resins can be ineffective. Porous ion exchange resins are

also useful for the recovery and separation of high-molecular-weight substances such as proteins or colloidal particles [7].

3.2. Historical Aspects

The first usage of ion exchange dates back to the middle of the nineteenth century when Thomson and Way noticed that ammonium sulfate was transformed into calcium sulfate after percolation through a tube filled with soil. In 1905, Gans softened water for the first time by passing it through a column of sodium aluminosilicate that could be regenerated with sodium chloride solution. In 1935, Liebknecht and Smit discovered that certain types of coal could be sulfonated to give a chemically and mechanically stable cation exchanger. In addition, Adams and Holmes produced the first synthetic cation and anion exchangers by polycondensation of phenol with formaldehyde and a polyamine, respectively. D'Alelio invented the first polystyrene-based resin in 1944. In 1946, McBurney produced a polystyrene anion-exchange resin by chloromethylation and amination of the matrix. Following these inventions, resins with a high degree of cross-linking were produced to cope with the fouling of the resin by natural organic acids present in surface waters and the mechanical stress imposed by plants operating at high flow rates [9]. There resins are also known as macroporous resins. By 1970, a new type of anion-exchange resin with a polyacrylic matrix was developed which possessed exceptional resistance to organic fouling and a very high mechanical stability due to the elasticity of the polymer. Later developments on ion exchange technologies in 1980s and 1990s were mainly on the production of uniform particle size distribution.

At present, ion exchangers have become a novel topic with a wide range of applicability in various areas such as water purification (for both domestic

and industrial uses), hydrometallurgy (recovery of metals), drug production in pharmaceutical industries, wastewater treatment, sugar refining, etc [9].

3.3. Structures of Ion-Exchange Resins

An ion exchanger consists of a polymer matrix and the functional groups that interact with the ions. Organic ion exchangers mainly have the polystyrene and polyacrylic matrices (Figure 3.1), whereas inorganic ion exchangers are primarily layer silicates and zeolites and are of relatively minor importance. Besides these major types, there are other types of matrices including phenol – formaldehyde resins (phenolic resins) which show interesting adsorption properties and polyalkylamine resins, obtained from polyamines by condensation with epichlorohydrin, which gives an anion exchanger directly in a single step.

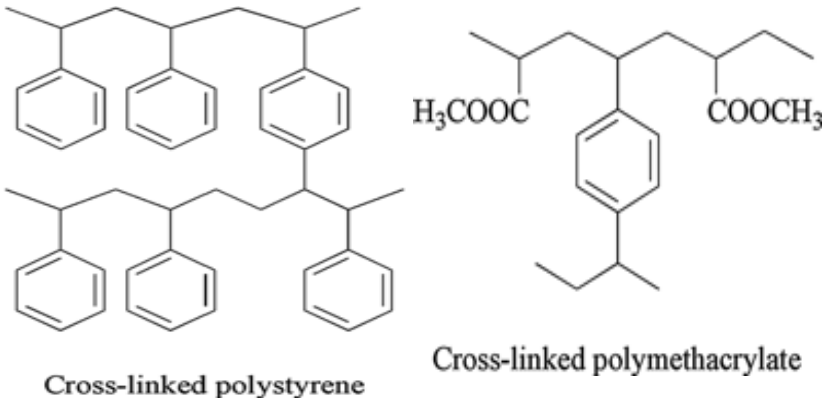
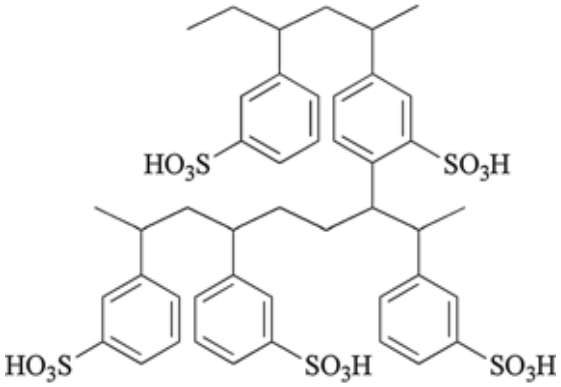


Figure 3.1 Polystyrene and polyacrylic matrices of organic ion exchangers.

Cation-exchange resins in current use can be separated into two classes according to their active groups: strongly acidic (sulfonic groups) and weakly acidic (carboxylic groups). The most widely used strongly acidic cation exchange resin is the cross-linked polystyrene 3-sulfonic acid. Figure 3.2 shows the structure of a strongly acidic cation exchange resin.



Cross-linked polystyrene 3-sulfonic acid

Figure 3.2 Strongly acidic cation exchange resin with cross-linked polystyrene 3-sulfonic acid as the functional group.

Weakly acidic resins are almost always obtained by hydrolysis of polymethylacrylate or polyacrylonitrile to give a poly (acrylic acid) matrix. The structure of a weakly acidic cation exchange resin is shown in Figure 3.3.

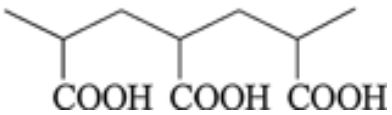


Figure 3.3 Weakly acidic cation exchange resin with carboxylic acid as the functional group.

For anion exchangers, resins with quaternary ammonium groups are strongly basic. Those with benzyl-trimethyl-ammonium groups are known as type 1 and are the most strongly basic, whereas those with benzyl-dimethyl-ethanol-ammonium groups are known as type 2 and are slightly less basic. Figure 3.4 shows the polyacrylic type structure of a strongly basic anion exchange resin.

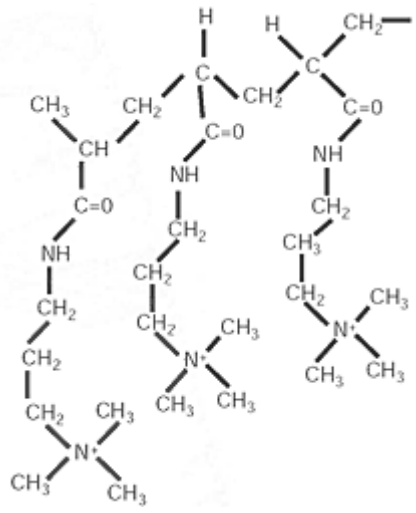


Figure 3.4 Structure of a polyacrylic type strongly basic anion exchange resin.

Resins whose active group is an amine are generally denoted as weakly basic, although their basicity may vary considerably. Tertiary amines are sometimes called medium-base or intermediate-base resins, whereas primary amines are very weakly basic and are rarely used.

By using polymerization and activation methods analogous to those described above, a wide variety of functional groups can be grafted onto a

given polymer. Some of these groups can be used for selective uptake of ions, principally metals. Table 3.1 summarizes various functional groups used in organic ion exchangers.

Table 3.1. Types of Ion Exchangers and Their Functional Groups [8].

Active groups	Structure	Type of resins
Sulfonic	$R\text{-}SO_3\ H$	Strong acid cation (SAC)
Carboxylic	R-COOH	Weak acid cation (WAC)
Ammonium	$R\text{-}N + (CH\ 3\ )_3\ Cl\ -$ $R\text{-}N + (CH\ 3\ )_2\ (CH\ 2\ )_2\ OH\ Cl^-$ $R\text{-}N + (CH\ 3\ )_2$	Strong base anion (SBA) type I Strong base anion (SBA) type II Weak base anion (WBA)
Chelating	R-SH $R\text{-}CH_2\ N(CH_2\ COOH)_2$ $R\text{-}CH_2\ NHCH_2\ CH_2\ PO_3\ H$	Chelating resins

Apart from the ion exchangers, there are also so called inert exchangers or adsorbent resins. Adsorbent resins are not ion exchangers but resemble them very closely. They have a high porosity and are used for the adsorption of nonionic or weakly ionized species complementary to ion exchangers. They may have cation or anion exchange groups or no ion-exchange groups at all. The latter are inert ionically. In order of decreasing polarity, adsorbent resins can be classified as ionized adsorbents, phenolic adsorbents and inert adsorbents.

3.4. General Properties

3.4.1. Degree of Cross-Linking and Porosity

As the degree of cross linking increase that is as the weight percentage of DVB related to the total amount of monomer prior to polymerization increase, harder, less elastic resins are produced. Higher degree of cross linking provides more resistance to oxidizing conditions that tend to de-cross-link the polymer. Above 10 – 12% DVB, however, the structure becomes too hard and dense. Activation of the inert copolymer becomes difficult because access to the interior of the bead is hindered by the high density of the matrix. Moreover, osmotic stress cannot be absorbed by the elasticity of the structure, therefore may cause the shattering of the resin bead. Finally, as the mobility of the ions within the bead which is related to the density of the structure is increased, the rate of exchange is increased. If the structure is too dense, ionic motion is slowed down resulting in the reduction of the ion exchange capacity.

For sulfonic resins, maximum operating capacity is obtained with approximately 8% DVB [3].

An increased ion mobility within the resin bead results in a poorer differentiation between the adsorption of ionic species with the same charge. As a result, the degree of cross-linking in the resin must be increased when greater differences in ionic affinity are required.

Moisture content of the resin is also related to the degree of cross-linking. Cross linking reduces the retention of water in the resins. The water hold up in the resin is a measure of the porosity.

Macroporous resins are made by mixing the monomers with a compound, which expands the resin. Channels are formed inside the beads, producing an artificially high porosity. Resins containing such channels are described as *macroporous*, whereas other resins with natural porosity are known as *gel resins* [3].

Finally, macroporous resins are used when reversible uptake of large molecules is necessary, without fouling the resin. The adsorbent resins or inert exchangers described in section 3.3 have a macroporosity that allows selective retention of various molecules.

3.4.2. Exchange Capacity

The total exchange capacity of a resin, expressed in equivalents (eq) per kilogram of dry resin (the weight capacity C_p) or equivalents per liter of wet settled resin (the volume capacity C_V)., represents the number of active sites available.

The operating capacity is defined as the proportion of total capacity used during the exchange process. It depends on a number of process variables such as; concentration and type of ions to be absorbed, rate of percolation, temperature, depth of resin bed, and type, concentration, and quantity of the regenerant. Capacity is essential for the classification of the ion exchange materials and the evaluation of the experimental data and the calculations following.

3.4.3. Stability and Service Life

Ion exchange resins are expected to serve for several years therefore the stability of the resin beads are of primary importance.

Although industrially available resins have a degree of cross linking high enough to make them insoluble, highly oxidizing conditions (presence of chlorine or chromic acid) can attack the matrix and destroy cross-linking. When oxidizing agents are present, highly cross-linked resins with a greater resistance to oxidation, such as the macroporous resins, should be used. The thermal stability of sulfonic group of cation exchange resins is very high. Anion exchange resins, however, are temperature sensitive. Polystyrene and polyacrylic resins made by suspension polymerization are perfect spheres and suffer little damage when used in continuous moving-bed ion-exchange plants; however, mechanical strength can vary considerably from one product to another. Acrylic resins are more elastic than polystyrene materials and can normally withstand any mechanical stress encountered in practice. Macroporous resins are often the strongest of all and are used widely for the most severe stress conditions. Resins for industrial use must be able to withstand hundreds of cycles of exhaustion and regeneration. Higher mechanical and osmotic strengths are obtained with resins whose matrix is sufficiently strong to withstand physical shock (attrition) but sufficiently flexible and porous to deform without breaking under the effect of osmotic shock [3].

3.4.4. Density

In terms of hydrodynamic behavior in counterflow systems, the density of the

resin plays an important role. The standard density ranges for different types of resins are given in Table 3.2.

Table 3.2 Standard Density Ranges of Common Resins in g/mL (figures in parentheses are the most common values for standard resins) [3].

Exchanger type	Density (g/mL)
Strongly acidic cation exchanger	1.18 – 1.38 (1.28)
Weakly acidic cation exchanger	1.13 – 1.20 (1.18)
Strongly basic anion exchanger	1.07 – 1.12 (1.10)
Weakly basic anion exchanger	1.02 – 1.10 (1.05)

3.4.5. Particle Size

The particle size of the resin beads affects the speed of the exchange reaction (which is greater with small beads) and the amount of head loss (which require coarse particles to minimize the head loss). Therefore, the particle size distribution should be optimized for the desired property of operation. The size of the polymer droplets formed during polymerization, and hence the size of the resin beads, is determined by the polymerization technology, the suspension medium and, the monomer concentration. Many producers now, offer ion-exchange resins with a very uniform particle size distribution, which gives closer uniformity coefficients to unity, hence smaller range of particle size.

3.4.6. Moisture Content

Both fixed and mobile ions within the ion exchange resin are always surrounded by water molecules located in the interior of the resin beads. The water retention capacity governs the kinetics, exchange capacity, and mechanical strength of ion-exchange resins. The water retention capacity or moisture-holding capacity (MHC) of a resin is defined as:

$$\mathrm{MHC} = \frac{m_w - m_{Dry}}{m_w} \qquad \text{(Eq. 3.1)}$$

where m_w is the weight of the hydrated resin sample and m_{Dry} the weight of the same sample after drying.

The MHC of an ion-exchange resin is an inverse function of the degree of cross-linking unless the porosity or degree of cross-linking in the polymer is artificially increased (as in macroporous resins).

3.5. Ion-Exchange Equilibrium and Selectivity

Ion exchange and adsorption phenomena can be characterized in a similar fashion as their mechanisms have a lot of resemblances. Many models have been proposed for adsorption and ion exchange equilibria. The simplest relationship between solid phase and the fluid phase concentrations is the linear isotherm. Apart from that, the most common nonlinear sorption isotherms used in both adsorption and ion exchange equilibrium expressions are either, Langmuir or Freundlich isotherms.

Langmuir isotherm is the classical isotherm for a homogeneous flat surface, and most popular of all. It's based on several assumptions, which are:

1. Monolayer coverage. Molecules are adsorbed at a fixed number of monolayer well-defined localized sites.

2. Each active site can adsorb one molecule.

3. There is no interaction between molecules adsorbed on neighboring sites.

4. The heat of adsorption is constant, and all sites are energetically equivalent. The same energy at each surface site.

Thus, the Langmuir equation can be derived as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \qquad \text{(Eq. 3.2)}$$

where q_e is the solid phase concentration and C_e is the fluid phase concentration.

For a heterogeneous flat surface, a classical isotherm is the Freundlich isotherm:

$$q_e = K_f C_e^n \qquad \text{(Eq. 3.3)}$$

where K_f and n are empirical constants. Apart from the heterogeneous surface assumption, in Freundlich equation, uptake capacity of the

adsorbent is assumed to be infinite and solid phase concentration, q_e, decreases logarithmically as the heat of adsorption increases [11].

Several isotherms combine aspects of both the Langmuir and Freundlich equations. One that has been shown to be effective in describing data mathematically for heterogeneous adsorbents is the Tóth isotherm. Other well-known isotherms include the Radke-Prausnitz isotherm and the Sips isotherm [7].

As mentioned earlier, the most common models for adsorption and ion exchange are based on several assumptions and limiting conditions. The basic assumption in these models is that the maximum amount of ions that can be uptaken by the ion exchange resin is constant and it is limited by the amount of functional groups within the resin matrix. Another basic assumption is that the exchange reactions occur stoichiometrically that is equivalent charges are exchanged between phases. In addition to these, only ions that have an opposite charge with respect to the charge of the functional group are assumed to be allowed within the resin phase. However, the total number of ions let into the resin is limited by their total equivalent charge equal to the maximum capacity of the resin.

The exchange equilibrium between the ions in solution and resin phases can be described by an equilibrium reaction as follows:

$$n(R^-)A^+ + B^{n+} \Leftrightarrow n\,A^+ + (R^-)_n B^{n+}$$

Where *R* represents the functional group of the resin, and *n* is the number of ions. The equilibrium between the ions A and B can be defined by introducing a selectivity coefficient, K_B^A based on the law of mass action:

$$K_B^A = \frac{(a_A)^n (a_{R_nB})}{(a_B)(a_{RA})^n} \quad \text{(Eq. 3.4)}$$

Where a_A and a_B are the activities of ions A and B in solution phase, and a_{RnB} and a_{RA} are the activities within the resin phase, respectively.

Activities can be related to concentrations by activity coefficients as:

$$a_i = \gamma_i C_i \quad \text{(Eq. 3.5)}$$

Where γ is the activity coefficient and C_i is the concentration of the i^{th} species in the same phase. Activities can be defined in terms of activity coefficients and concentrations in both resin and solution phases. Ideally, dilute solutions have an activity coefficient of unity and activities are taken as the concentrations. However, as the resin phase ion concentration is never dilute, it cannot be assumed that the activities of ions in the resin phase converges unity. Since there is no way to measure resin phase activity coefficients, Selectivity coefficients are generally calculated in the following fashion:

$$K_B^A = \frac{\left[A^+\right]^n \left[R_nB\right] \cdot \gamma_{R_nB}}{\left[B^{n+}\right]\left[RA\right]^n \cdot \gamma_{RA}} \quad \text{(Eq. 3.6)}$$

or

$$K_B^A = \frac{\left[A^+\right]^n x_{R_nB}}{\left[B^{n+}\right] x_{RA}} \quad \text{(Eq. 3.7)}$$

Where $[A^+]$ and $[B^{n+}]$ are the solution phase concentrations and $[R_nB]$ and $[RA]$ are the resin phase concentrations of A and B, and x_{RnB} and x_{RA} are the equivalent ionic fractions.

CHAPTER 4

EXPERIMENTAL WORK

4.1. Materials

4.1.1. Cation Exchange Resins and Adsorbents

Several cation exchange resins and adsorbents were used throughout the preliminary studies as they were screened for best performance. Table A.7 in Appendix summarizes the materials screened. Two cation exchange resins, a strongly acidic cation exchanger having sulfonic acid as functional group with cross-linked s-dvb copolymer matrix (Lewatit$^{(R)}$ S100) and a weakly acidic cation exchange resin having carboxylic acid as functional group with crosslinked polyacrylate matrix (Lewatit$^{(R)}$ CNP80) were used. Strong cation exchange resin was used in two ionic forms, H^+ and Na^+, whereas weakly acidic one was used in only H^+ form. Both resins are manufactured by Bayer, Germany. In addition, 4 adsorbents; reversed phase silica (Merck), silica gel (Riedel), cellulose (Riedel) and magnesium silicate (Merck) were used in the preliminary studies. S100 cation exchange resin was available in wasted form; therefore it was regenerated and characterized as explained in part 4.2. The properties of the commercially available cation exchange resins are given in Table 4.1.

At the end of the studies, due to the very low capacity of the cation exchange resin, S100, it was decided that a macroporous cation exchange

resin should be observed for caffeine uptake performance. Therefore, a strongly acidic, highly cross-linked cation exchange resin (Lewatit$^{(R)}$ SPC 112) was used. The properties of SPC 112 are also given in Table 4.1.

Table 4.1. Properties of Cation Exchange Resins Used in This Study [19].

Cation exchange resin	strong acid	weak acid	Strong acid
	S100	CNP80	SPC 112
Ionic form	H^+ and Na^+	H^+	H^+
Functional group	sulfonic acid	carboxylic acid	sulfonic acid
Matrix	s-dvb	crosslinked polyacrylate	s-dvb
Structure	gel type beads	macroporous	macroporous
Appearance	brown, translucent	yellow white, opaque	Dark grey, opaque
Operating Temperature, max. ^oC	120	70	120
Operating pH range	0 - 14	5 - 14	0 - 14

4.1.2. Chemicals

All the chemicals used in the study was analytical or HPLC grade. Caffeine used in the preparation of stock solutions and standard solutions was purchased from Acros Organics. Acetic acid and propan-2-ol used in the preparation of the mobile phase in HPLC analysis and hydrochloric acid and sodium hydroxide used for pH adjustment in equilibrium studies, was from Merck. Acetonitrile used in mobile phase preparation in HPLC analysis and

sodium chloride used in the pretreatment of cation exchange resin was from J.T.Baker. All the solutions were freshly prepared on the day of experiment using deionized water obtained from Milli-Q plus water treatment system with millipore purification pak.

4.2. Resin Preparation and Characterization

All the exchange resins and adsorbents except for S100H were available as shipped in the department laboratory. A considerable amount of S100 was available in wasted form. Following a regeneration and characterization process, strong cation exchange resin in H^+ form was obtained with convenient characteristics.

The cation exchange resin was pretreated in a batch operation. Resin was washed with 6 M sodium chloride followed by deionized water and then 2N hydrochloric acid. The swollen resin beads were rinsed with deionized water until excess hydrogen ions in resin phase solution were carried away and pH value was increased to 7. This way, a strong cation exchange resin in H^+ form, S100H, was obtained. The pretreated resin was drained and filtered. After removal of excess water, wet resin was stored in glass containers for further use in characterization tests.

Water retention capacity, bulk density and total ion capacity of the pretreated cation exchange resin were determined according to the ASTM standards [10] following test methods B, C and F. Characteristics of regenerated and pretreated cation exchange resin together with weak cation exchange resin and macroporous strong cation exchange resin are given in Table 4.2.

Table 4.2. Characteristics of Cation Exchange Resins Used in the Experiments.

Resin	Density	Bulk density	Water retention	Total capacity
	g / L	g / L	%	eq / L resin
Lewatit S100H	1200	820	53	1.78
Lewatit S100Na	1280	850	45	2.00
Lewatit CNP80H	1190	750	47	4.30
Lewatit SPC 112H	1210	840	50	1.60

4.3. Method

4.3.1. Preliminary Experiments

After the characterization of S100H, preliminary experiments were carried out in a batch system in order to both determine the time required for the corresponding resins and adsorbents and caffeine to reach equilibrium and to screen the uptaking capabilities of the resins and adsorbents. A gram of each resin and adsorbent was contacted with 100 mL of 0.0025 M caffeine in an Erlenmeyer flask for one day. Flasks were placed in a constant temperature shaker bath (GFL 1083) at 40^{o}C with 200 rpm. To investigate the attainment of equilibrium, samples were taken at times and 20 µl aliquots of diluted samples were analyzed by HPLC.

The results of screening experiments are given in Appendix A.1. As shown in figures 5.1, 5.2 and 5.3, the time required to reach equilibrium for S100H, RP silica and magnesium silicate are 3, 2, 2 hours, respectively. However, to assure that equilibrium is reached, experiments are performed with an hour added to the obtained times.

In the light of the screening experiments, it is decided that the effect of initial concentration and pH on equilibrium will be investigated using the resin having the best prospect as a start, S100H.

At the end of the studies, additional experiments were carried out with macroporous cation exchange resin, SPC 112, in order to observe the equilibrium relationship of caffeine in strongly acidic macroporous cation exchange resin within a preliminary range. The procedure followed to investigate the effect of initial pH on the equilibrium in the previous experiments was also followed in the experiments involving SPC 112 macroporous resin.

4.3.2. Effect of Initial Concentration

To determine the effect of initial concentration on equilibrium and resin capacity, 250 mL volumes of caffeine solutions with three different initial concentrations were contacted with a range of resin mass without adjusting the pH of the solution. Initial concentrations were selected as 0.005, 0.0075 and 0.01 M. 0.005 M solution was contacted with cation exchange resin with masses changing from 0.32 to 13.36 g. 0.0075 M solution was contacted with a resin mass range of 1.07 to 19.59 g and 0.01 M solution with a range of 0.68 to 20.39 g. erlenmeyer flasks were placed in a shaker bath at 40 ^{o}C

with 200 rpm shaking speed for four hours where equilibrium is expected to be attained. At the end of four hours 1 mL samples were taken using a micropipette and diluted with deionized water to suit the HPLC operating conditions and 20 µL aliquots were injected to separation column for HPLC analysis. The pH measurements of the remaining solution in the erlenmeyer flasks were carried out right after sampling. The results of the initial concentration analysis are tabulated in Appendix A.

4.3.3. Effect of Initial pH

To express the effect of pH on the exchange capacity, previously investigated initial concentrations were each adjusted to pH regions of acidic, slightly acidic and slightly basic using hydrochloric acid and sodium hydroxide. This way, pH parameter was investigated in four regions with pH values of 3, 5, 7 and 9. To adjust the pH to 3, 2 mL of 1 N hydrochloric acid was used. For pH of 5, 2 mL of 0.01N hydrochloric acid was used. For pH of 9, 0.25 mL of 0.2N sodium hydroxide was used. The additions of such low volumes were assumed to have negligible effect on any property under investigation. pH adjusted solutions of three initial concentrations were contacted with corresponding values of resin masses following the procedure described previously. As equilibrium concentrations were analyzed by HPLC, change in pH of solution was measured also. The results of the pH analysis are tabulated in Appendix A.

4.4. HPLC Analysis

All the concentration analyses were carried out by an HPLC unit equipped

by Shimadzu. Standard and unknown samples of caffeine solutions were given once on each run, since the experiments were checked for reproducibility later. Among a number of methods listed in catalogs, an easily applicable method regarding mobile phase and analysis time was selected and customized for more efficient analysis. The mobile phase used in HPLC analysis was a mixture of 1% acetic acid, 8% acetonitrile and 8% 2-propanol prepared with deionized water on the day of analysis. The mixture was filtered through 0.45 μm mixed cellulose ester filter papers by a vacuum pump and degassed in ultrasound water bath (Branson 2200) before feeding to HPLC unit. Standard samples of caffeine solution were prepared before each set of experiment. Standard and unknown samples of caffeine were injected consecutively through a manual injector valve (Rheodyne). Caffeine was detected at 254 nm. Column temperature was kept constant at 40^{o}C.

The HPLC analysis identification tag is given in Table 4.3. The column properties and operating conditions are summarized in Table 4.4. The calibration curve used to determine solution phase caffeine concentration is given in Figure A.1 of Appendix.

Table 4.3. Components of the HPLC Unit.

Pump	Shimadzu LC-20AD Solvent Delivery Unit
Detector	Shimadzu SPD-M20A Photodiode Array Detector
Degasser	DGU-20A5 Degassing Unit
Controller	Shimadzu CBM 20Alite System Controller
Column Oven	CTO-20AC Column Oven
Mobile Phase Reservoir	1L glass container
Interface	7725i Manuel Injector
Software	LC - Solution

Table 4.4. Properties of Column and Operating Conditions of HPLC Analysis.

Property	Specifications
Type of Analysis	Caffeine
Retention Time	Caffeine: 4.18 min
Column	Teknokroma – Nucleosil 100 C_{18}
Column Length	25 cm
Column Diameter	0.46 cm
Particle Size	5 µm
Mobile Phase	1% Acetic acid, 8% Acetonitrile, 8% 2-Propanol
Flow Rate	1.5 ml/min
Injection Volume	20 µL
Column Temperature	40 ^{o}C
Elution Type	Isocratic

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Preliminary Experiments

As no information could be found in literature about the equilibrium relations between caffeine and ion exchangers and adsorbents, a simple screening procedure was put into practice. A number of cation exchange resins and adsorbents were used in order to figure out which materials have the potential for caffeine uptake. Among the tried materials S100 cation exchange resin, magnesium silicate and RP silica had better performances compared to others.

All of the experiments were performed at 40ºC. The reason for that is very high solubility of caffeine in hot water. Compared to the organic solvents water is much more abundant, cheap and safe. However, at room temperature, the solubility of caffeine in water is 2.13 g/L. That of caffeine in water at 40ºC on the other hand is 4.64 g/L. Therefore, to obtain a higher solubility, temperature is selected as 40ºC.

Considering the acidities of the cation exchange resins used in preliminary experiments, it is seen that weakly acidic cation exchange resins, which are in Na^+ form, have completely failed to uptake caffeine. Due to the chemical nature of the caffeine molecule and its large molecular structure, weakly acidic resins were not able to adsorb caffeine. The data obtained from the preliminary experiments are tabulated in Table A.1 of Appendix A.1. Figures

5.1, 5.2 and 5.3 show the times required to reach equilibrium for S100 cation exchange resin, magnesium silicate and RP silica, respectively. RP silica was excluded due to the difficulties encountered in the preparation of the experimental set up.

From Figure 5.1, it is seen that after 3 hours of operation, solution phase concentration is constant. To be on the safe side, the equilibrium time for S100 cation exchange resin is taken as 4 hours in the following set of experiments involving S100 cation exchange resin. In figures 5.2 and 5.3, the equilibrium is reached after 2 hours and in a similar fashion to S100 cation exchange resin, experiment times are taken as one hour more, 3 hours for following set of experiments.

Comparing the exchange kinetics of the cation exchange resin and adsorbents, it is seen that the adsorbents require more or less the same time to reach equilibrium whereas the cation exchange resin needs slightly more time. The rapid adsorption of caffeine on magnesium silicate and RP silica can be explained by smaller particle size of the adsorbent beads compared to the resin beads. As mentioned in section 3.4.5 earlier, as the particle size gets smaller, the adsorption or exchange reaction becomes more rapid. Since continuous operation is more preferred than batch operation in industrial applications of ion exchangers or adsorbents, rapid uptake, hence, smaller particles can be advantageous rather than coarse particles. The payoff for using small particles on the other hand, would be greater head loss. Therefore, depending on the preferences, exchange material with smaller particle size distribution can be used so that the contact time in the packed column is shorter.

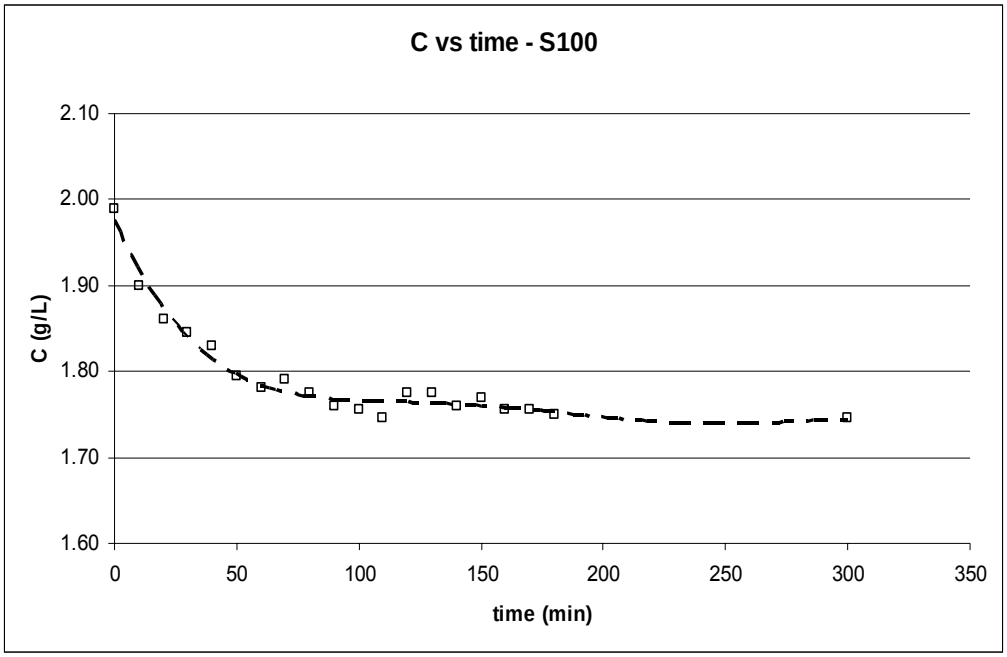


Figure 5.1 Solution phase equilibrium concentration vs. time plot for 2 grams of S100 cation exchange resin in 250 mL 0.01 M caffeine solution at 40^{o}C.

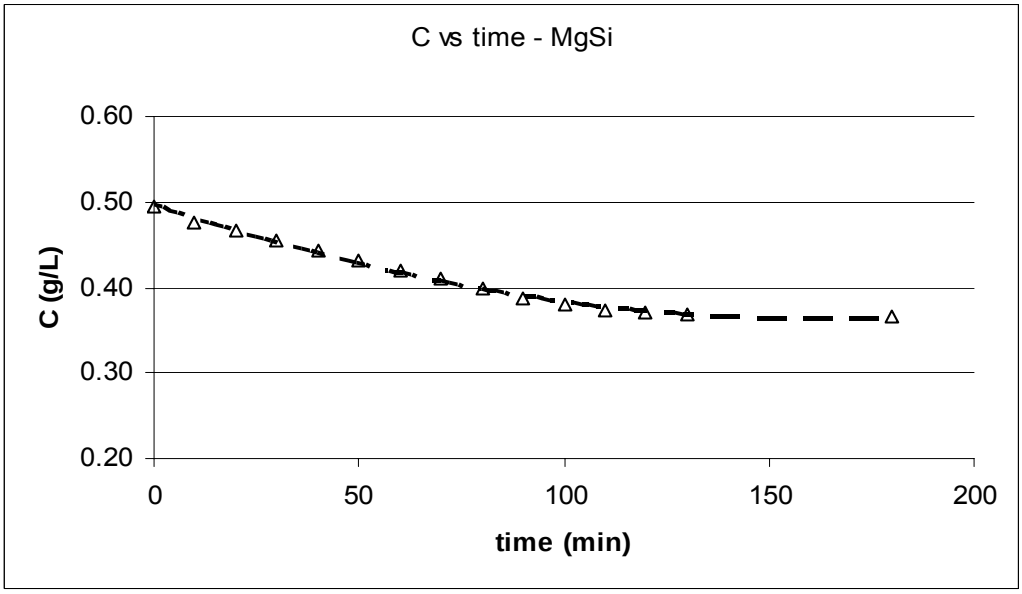


Figure 5.2 Solution phase equilibrium concentration vs. time plot for 2 grams of magnesium silicate in 250 mL 0.0025 M caffeine solution at 40^{o}C.

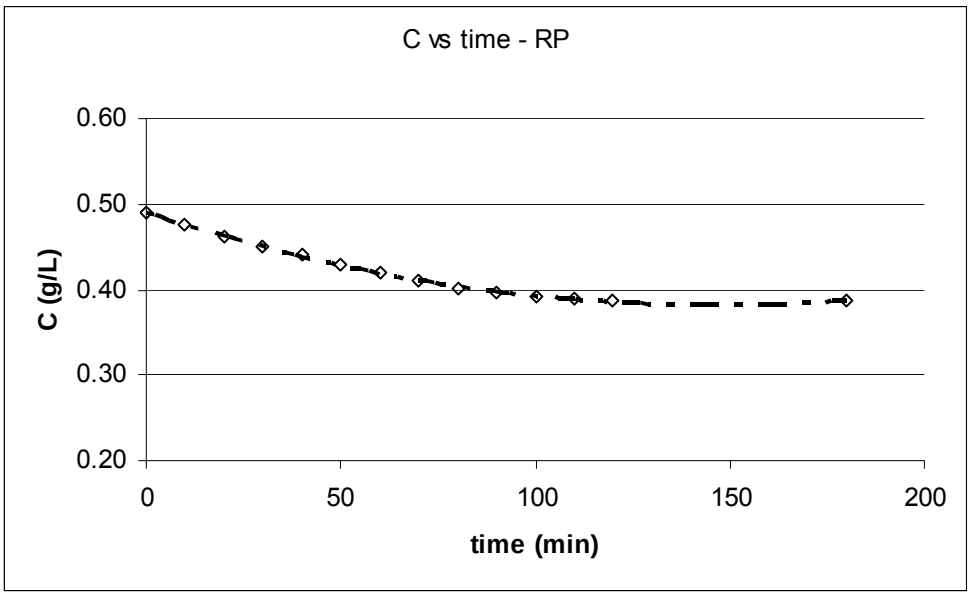


Figure 5.3 Solution phase equilibrium concentration vs. time plot for 2 grams of RP silica in 250 mL 0.0025 M caffeine solution at 40^{o}C.

Another consideration in a large-scale continuous operation would be the recovery ratio of the material used. Mass action law can be used in order to determine caffeine loading in the resin phase using the equilibrium concentration of solution phase. Unfortunately, when the resin phase equilibrium concentrations were calculated using mass action law, the recovery capacities of all three materials were found to be very low. Comparing the caffeine loading of S100, magnesium silicate and RP silica, as seen in Figure 5.4, S100 cation exchange resin had the greatest loading of caffeine followed by magnesium silicate and RP silica.

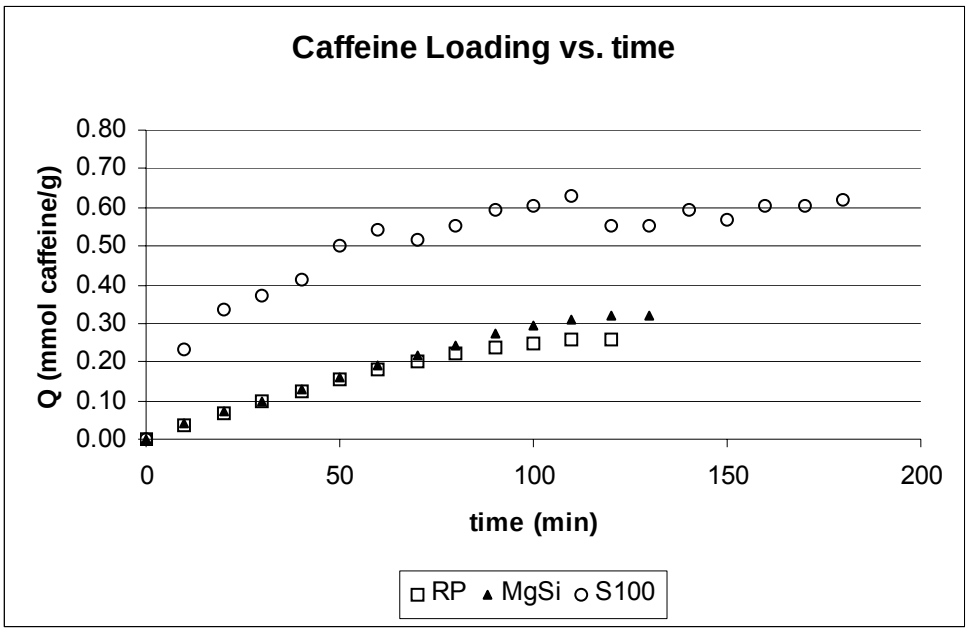


Figure 5.4 Caffeine loading per unit mass of materials plotted against time.

After the evaluation of the preliminary results, it was decided that the future experiments involving the investigation of the effect of initial concentration, C_0, and initial pH of the solution (as these have individual effects on the uptake of caffeine) on the equilibrium and uptake of caffeine, will be carried on with S100 cation exchange resin as it had fair but the best performance over the three.

5.2. Effect of Initial Concentration on Equilibrium

Initial concentration was one of the two parameters that are investigated for their effects on equilibrium. The selected initial concentrations were 0.005 M, 0.0075 M and 0.010 M. The point in selecting these initial concentrations

was that as the preliminary experiments showed, the efficiency of the resin for caffeine uptake was very low and the amount of resin available at hand was limited. Therefore, without a reasonable piece of information about the equilibrium relationships of caffeine with cation exchange resins, there was no reason to work with concentrated solutions of caffeine.

Figures 5.5 to 5.8 show the effect of initial concentration on caffeine loading at four different pH regions. Acidic pH region corresponds to pH of 3.0 and slightly acidic, neutral and basic pH regions correspond to pH values of 5.0, 7.0, and 9.0, respectively. The experimental data are tabulated in Appendix section in Tables A.11 to A.14. All the experiments were performed at 40^{o}C, with 200rpm agitation speed.

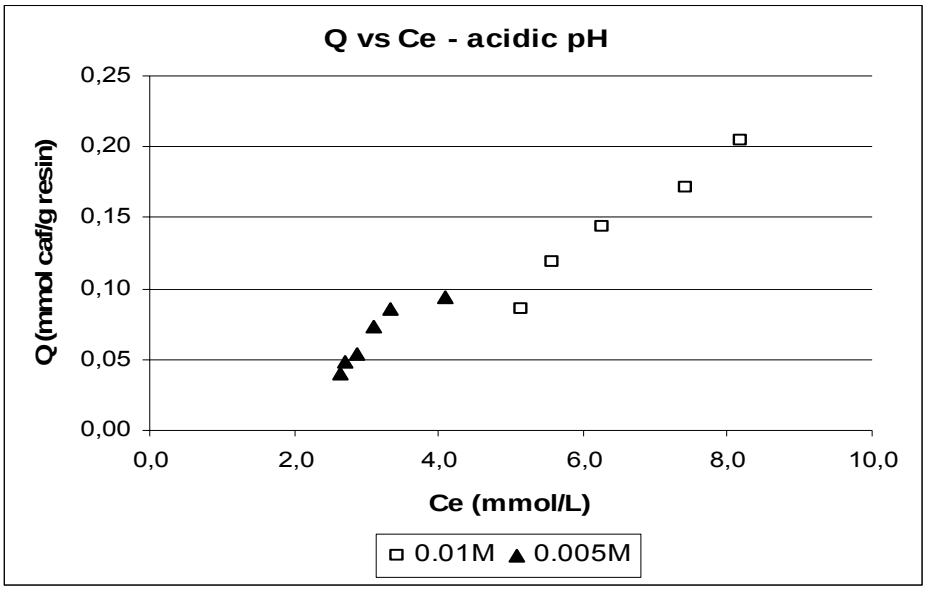


Figure 5.5 Effect of initial concentration on caffeine loading at acidic pH at 40^{o}C.

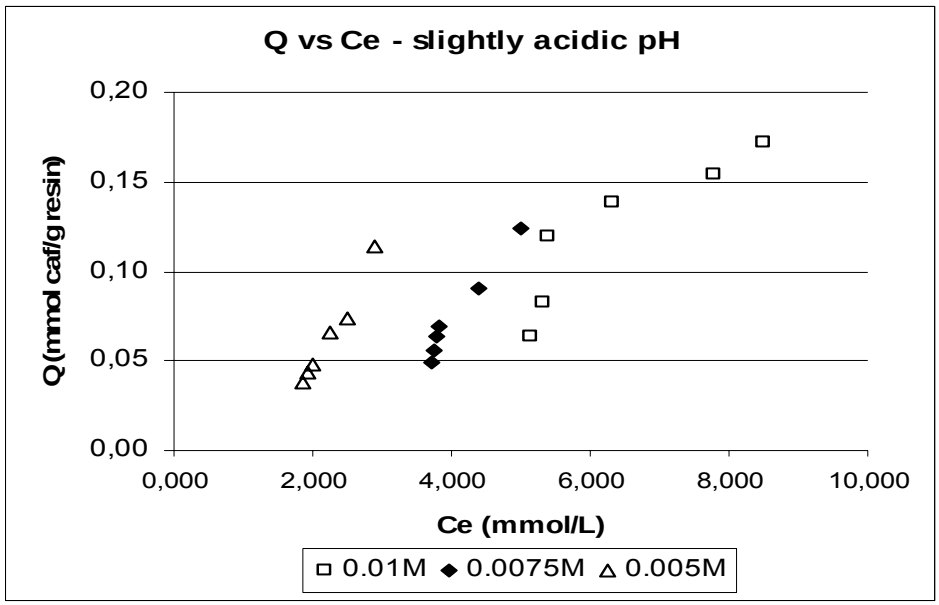


Figure 5.6 Effect of initial concentration on caffeine loading at slightly acidic pH at 40°C.

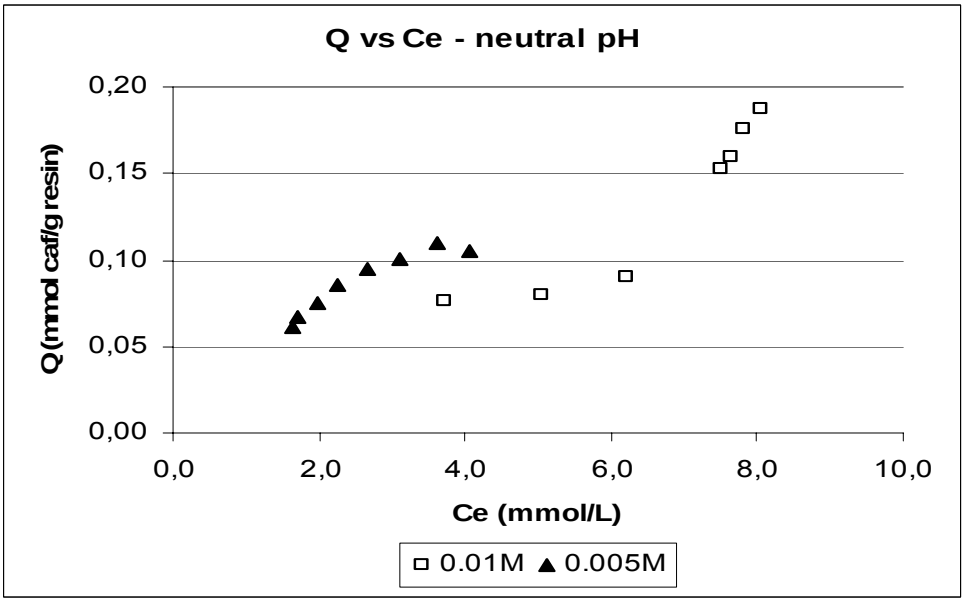


Figure 5.7 Effect of initial concentration on caffeine loading at neutral pH at 40°C.

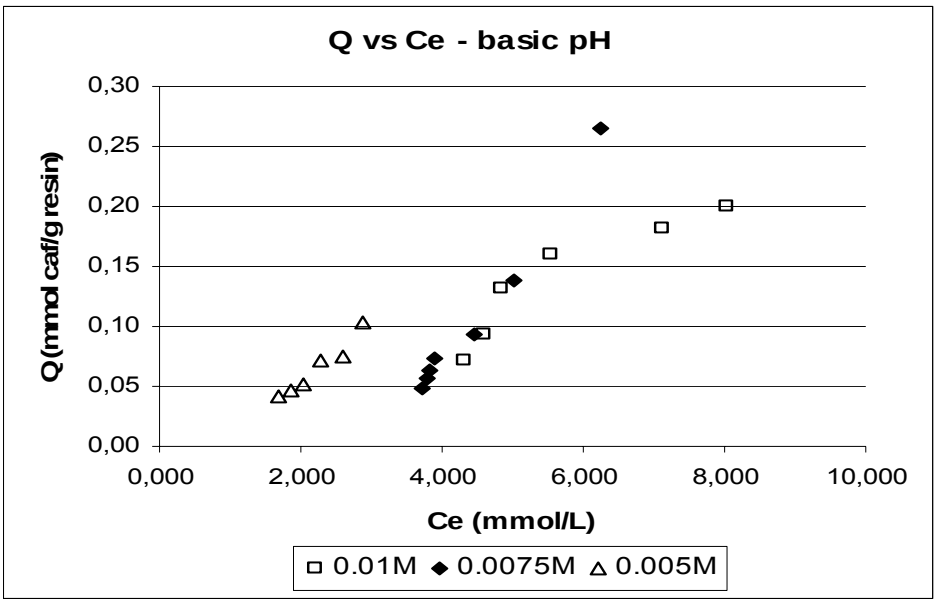


Figure 5.8 Effect of initial concentration on caffeine loading at basic pH at 40^{o}C.

From two sets of experiments, where the initial concentration of the caffeine solution was 0.0075 M, much deviated results were obtained in majority of the data points. In spite of having reproducibility higher than 90%, which were the lowest of this part, the behavior of the isotherms couldn't be explained and therefore, for the acidic and neutral pH regions, 0.0075 M data were all discarded. The reproducibility was checked for all sets by repeating 2 of the data points each time and is given in Table 5.1. The change in the concentration of the samples was never below 94%. Therefore, it can be assumed that the experiments were reproducible.

Table 5.1 Reproducibility Information (Q_1 and Q_2 are caffeine loadings (mmol caffeine / g resin))

	Q_1	Q_2	%	Q_1	Q_2	%	Q_1	Q_2	%
	0.005 M			0.0075 M			0.01 M		
Acidic pH	0.0858	0.8250	96.1	0.1329	0.1261	94.9	0.1709	0.1659	97.1
	0.0533	0.0515	96.6	0.0848	0.0807	95.2	0.1184	0.1146	96.8
Slightly acidic pH	0.0733	0.0703	95.9	0.0909	0.0864	95.0	0.1541	0.1479	96.0
	0.0475	0.0462	97.2	0.0631	0.0598	94.8	0.1389	0.1324	95.3
Neutral pH	0.1095	0.1116	98.1	0.0781	0.0825	94.7	0.1753	0.1686	96.2
	0.0853	0.0876	97.4	0.0875	0.0926	94.5	0.1522	0.1476	97.0
Basic pH	0.0748	0.0723	96.7	0.1382	0.1328	96.1	0.1820	0.1756	96.5
	0.0514	0.0493	96.0	0.0735	0.0699	95.1	0.1311	0.1257	95.9

As can be seen from the figures 5.5 to 5.8, it is hard to discuss any significant effect of initial concentration on the isotherms. To define a behavior for the isotherms obtained is also not possible since the end regions of the isotherms were not completely reached. Although as large amount of resin as possible was used to observe maximum loading of caffeine, due to the poor exchange and adsorption performance of the resin, the region closer to the origin stayed unknown. On the other hand, very low quantities of resin were used to obtain data points near the other end of the isotherms. However, some data points had to be discarded due to the inconsistency of the analysis results. In some points, it seemed that resin phase which didn't have caffeine initially, released caffeine where it should have removed caffeine from solution. Therefore, those extreme points were discarded.

Another observation was achieved when percent removal per unit mass of resin was plotted against initial concentration. As seen in Figure 5.9, the

percent removal of a unit mass of resin is slightly increased with increased initial concentration. For the most dilute initial concentration experiments data points are a little deviated from expected results, however, due to dilution of the samples where the concentration is already dilute, such error can be accepted. The HPLC equipment had to be operated by injecting aliquots of very dilute concentrations.

Nevertheless, it is seen that increasing initial concentration results in a slight increase in percent removal per unit mass, which can be explained by stronger driving force and therefore incoming of more molecules to the active sites. Hence the caffeine removal from solution phase is increased.

Consequently, the percent removal results per gram of resin are disappointing. Not more than 15% of the caffeine present in solution phase is removed in any case. The main reason for that would be the chemical stability and large molecular size of caffeine molecule causing poor ion exchange and adsorption performances, respectively.

A final comment on the results of this section will be about the ratio of the two mechanisms carried out to uptake caffeine. In literature, although studied as a separation method, it is stated that both ion exchange and adsorption takes place when ion exchanger resins are used to retain nonionic solutes such as caffeine [15]. Therefore, after final sampling, the caffeine solutions left in the erlenmeyer flasks were each measured for pH change. Calculating the amount of hydrogen ions released into the solution, and assuming one to one exchange, it was found that the dominant mechanism in caffeine uptake was adsorption. The percent removal of caffeine from solution phase by ion exchange mechanism has never exceeded 2%.

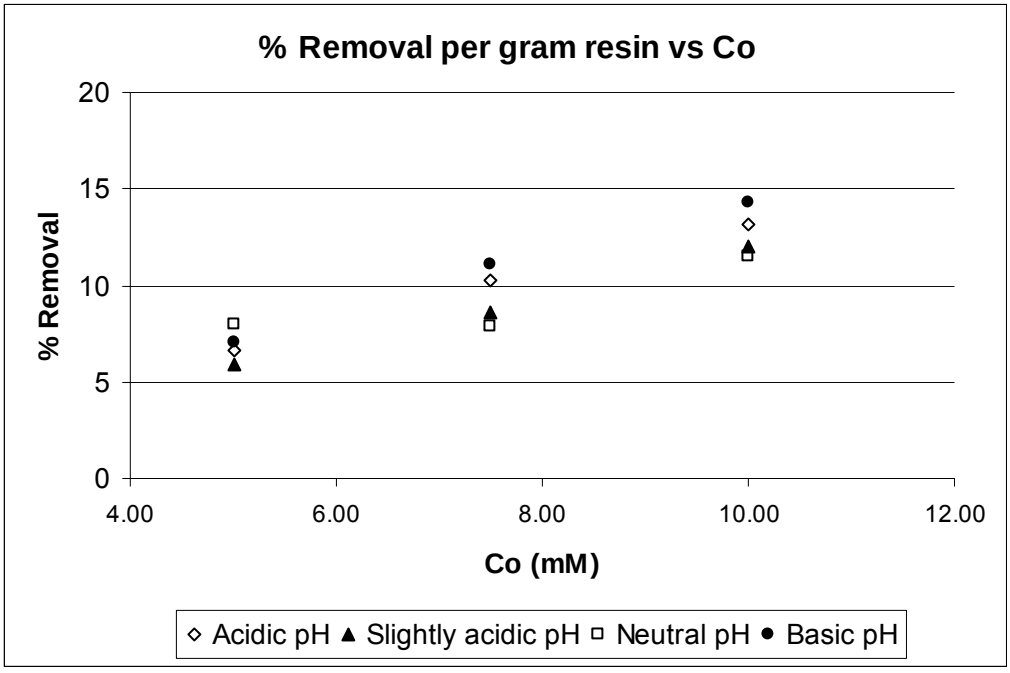


Figure 5.9 Percent removal per gram of S100 resin vs. initial concentration graph at four different pH regions.

Figures 5.10 to 5.12 show the effectiveness of ion exchange mechanism for the removal of caffeine. Leaving the results of the set where 0.0075 M initial solution was studied aside, it can be seen from the figures that the percent removal of caffeine by ion exchange mechanism slightly increased by increasing resin mass. The explanation of this behavior would be the increased chances of the encounter of caffeine molecules with resin phase functional groups at the active sites reserved for ion exchange. With less resin amounts, the caffeine loading capacity of the resin would be largely occupied by the caffeine removed by adsorption.

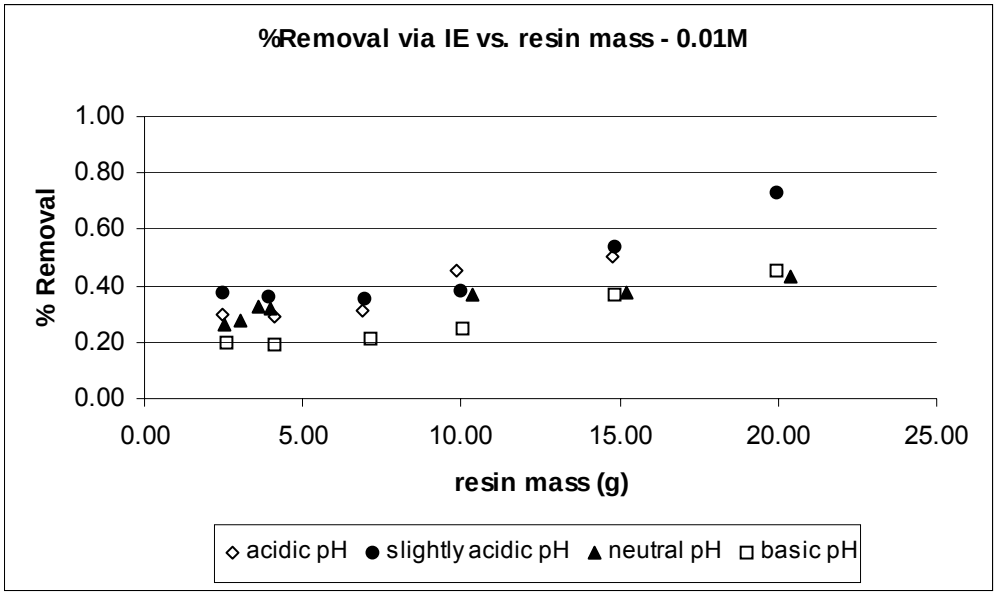


Figure 5.10 Percent of dominance of ion exchange for removal of caffeine vs. resin mass for 0.01 M caffeine solution.

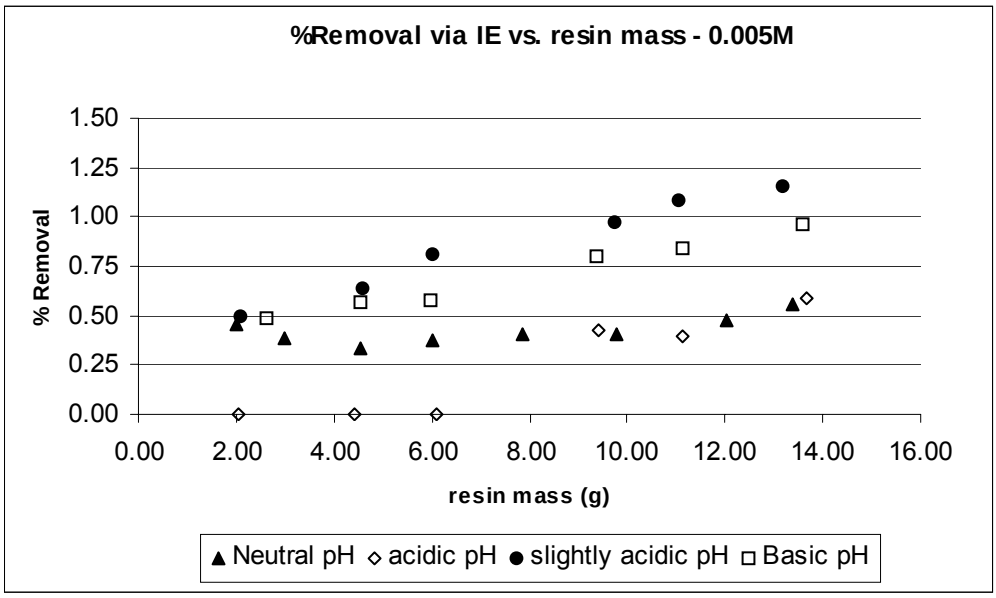


Figure 5.11 Percent of dominance of ion exchange for removal of caffeine vs. resin mass for 0.005 M caffeine solution.

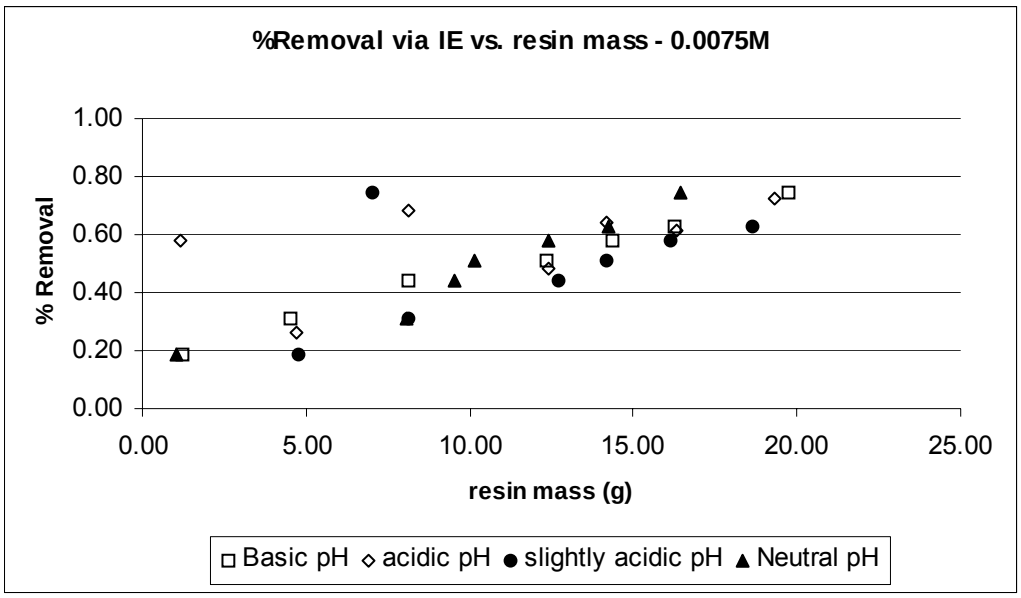


Figure 5.12 Percent of dominance of ion exchange for removal of caffeine vs. resin mass for 0.0075 M caffeine solution.

The effect of initial concentration on equilibrium couldn't be observed as hoped. The reason for that would be the selection of the initial concentration values for investigation due to the lack of information and adequate time and material. Dilute solutions, although having different concentrations, converge to ideality and their behaviors cannot be separated significantly. However, the most important set back while evaluating the effect of initial concentration on equilibrium was the lack of information in literature. Caffeine is not just unstudied for observing the effect of initial concentration on equilibrium but also hasn't been studied at all in terms of its equilibrium relationship with ion exchangers and adsorbents considering industrial scale operations. The articles found in literature are mainly related to the determination of caffeine with different analysis methods. The main reason for not studying caffeine – ion exchange equilibrium would be adequate manufacturing performance of the present techniques and also the introduction of supercritical fluid extraction of caffeine from aqueous

solutions as an alternative process to other manufacturing techniques. Information related to caffeine is usually encountered in studies where analysis methods are developed and therefore are useless in terms of comparison of figures.

5.3. Effect of pH on Equilibrium

The second parameter investigated for its effects on equilibrium relationship of caffeine with cation exchange resin was initial pH of the solution. In order to observe an effect, four pH regions were selected and initial pH values were set in each set of experiments correspondingly as 3.0, 5.0, 7.0 and 9.0 for acidic, slightly acidic, neutral and basic pH regions, respectively. For each initial concentration previously studied, these four pH regions were studied and figures 5.13 to 5.15 were obtained. Data for these isotherms are tabulated in Appendix section in Tables A.8 to A.10.

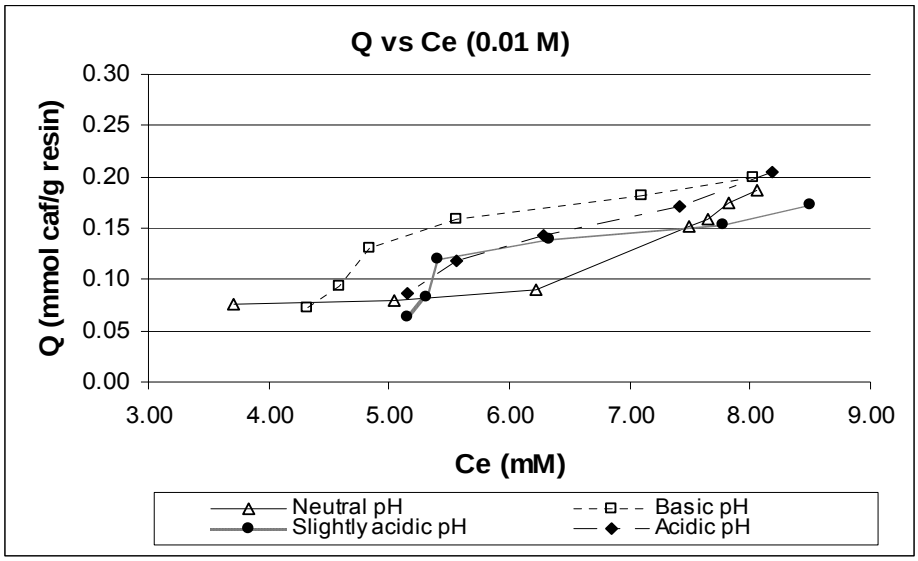


Figure 5.13 Effect of pH on equilibrium for 0.01 M caffeine solution at 40^{o}C.

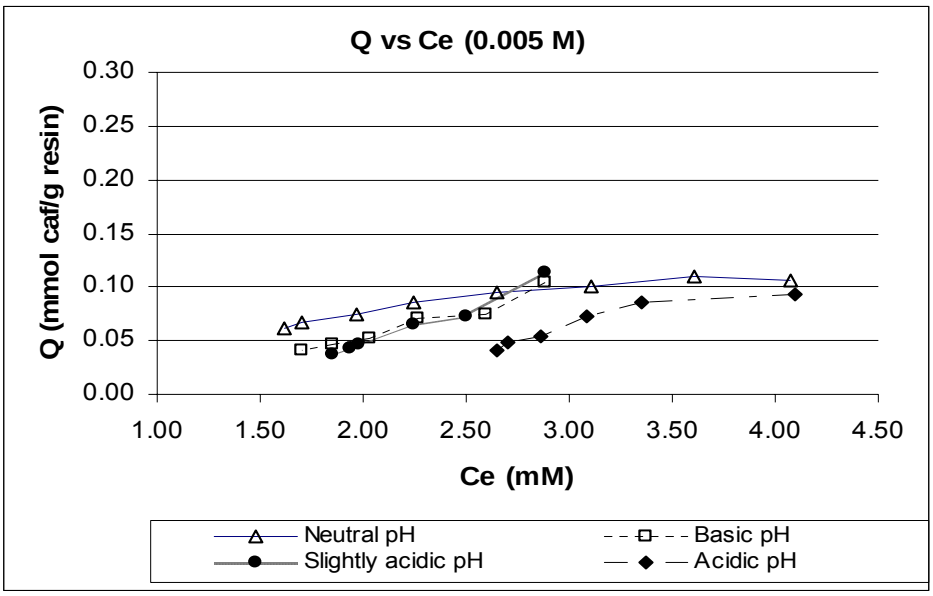


Figure 5.14 Effect of pH on equilibrium for 0.005 M caffeine solution at 40^{o}C.

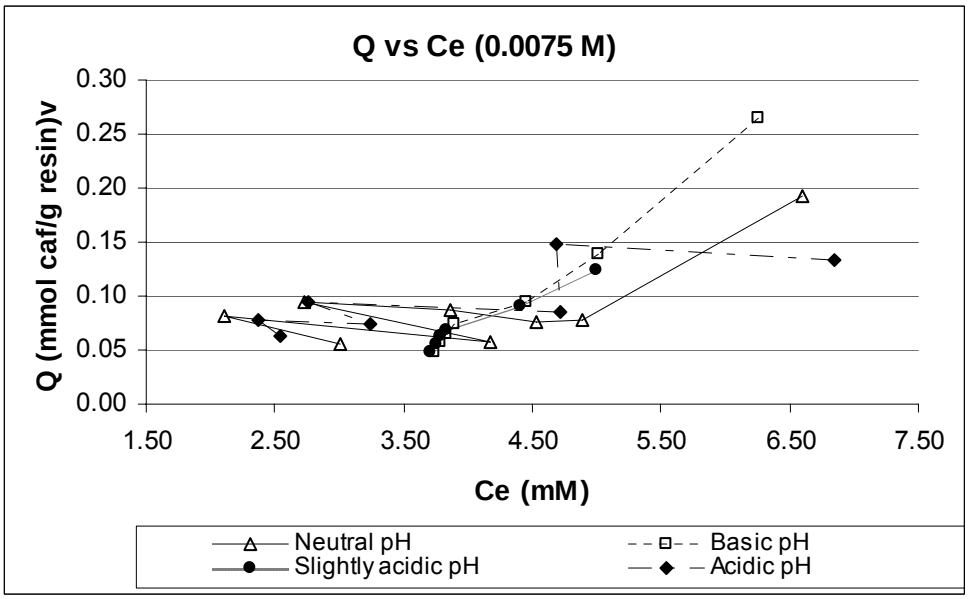


Figure 5.15 Effect of pH on equilibrium for 0.0075 M caffeine solution at 40^{o}C.

The investigation for the effect of initial pH on equilibrium aimed to determine the potential chemical nature of the caffeine molecule. As pH is one of the major factors affecting the ion exchange process in general, it would also have a major effect on the uptake of caffeine. Due to the nitrogen molecules within the molecular structure, caffeine molecules can be expected to cationize in extreme pH conditions. Due to strong chemical stability of caffeine molecule, pH condition should be extreme. However, since the ion exchange mechanism plays a negligible role in the uptake of caffeine, the effect of initial pH on the uptake of caffeine to resin phase was only slightly observed.

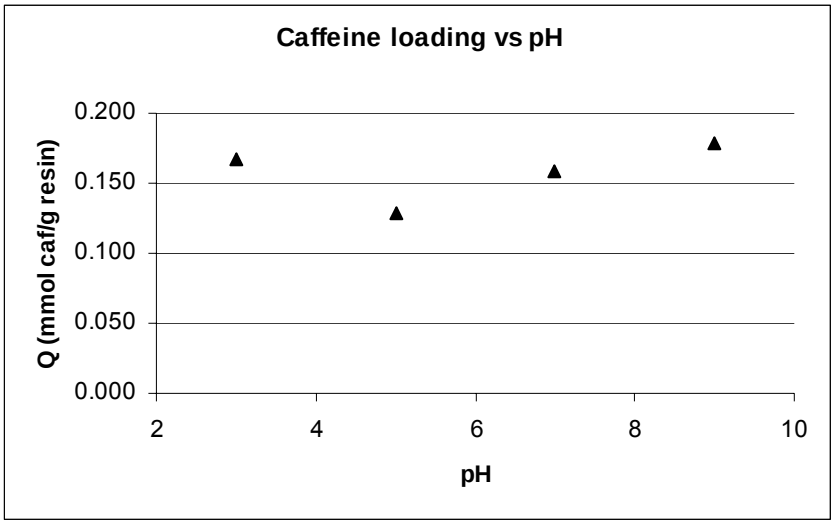


Figure 5.16 Effect of initial pH on caffeine loading with 0.01 M initial caffeine concentration.

One of the comments about the results of this section would be related to the caffeine loading at different pH regions. Figures 5.16 to 5.18 show the

caffeine loading values plotted against initial pH of the solution. In all three graphs, the highest caffeine loading was achieved at acidic and basic pH regions, which is consistent with one of the already rare studies in literature, a study related to simultaneous determination of various species in food and pharmaceutical preparations by ion chromatography where it is stated that at extreme pH values, caffeine can be adsorbed and/or exchanged more easily [17]. However, for 0.005 M solution of caffeine, this result is observed as less significantly.

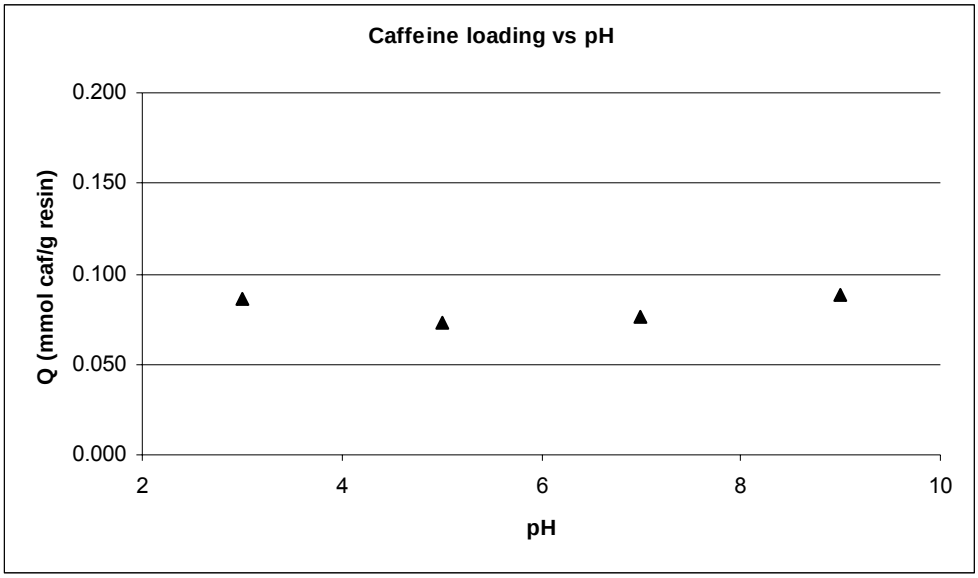


Figure 5.17 Effect of initial pH on caffeine loading with 0.005 M initial caffeine concentration.

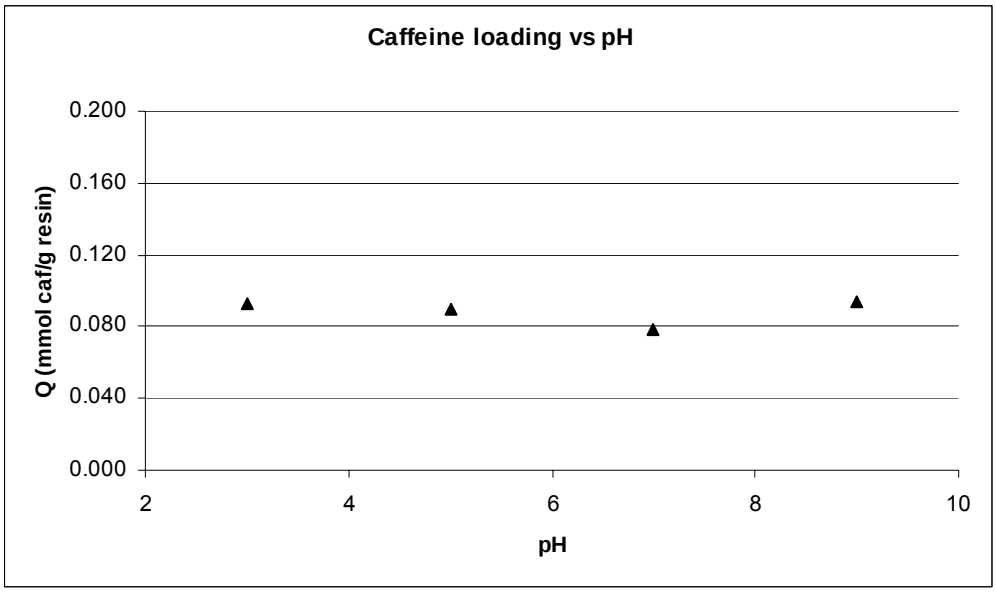


Figure 5.18 Effect of initial pH on caffeine loading with 0.005 M initial caffeine concentration.

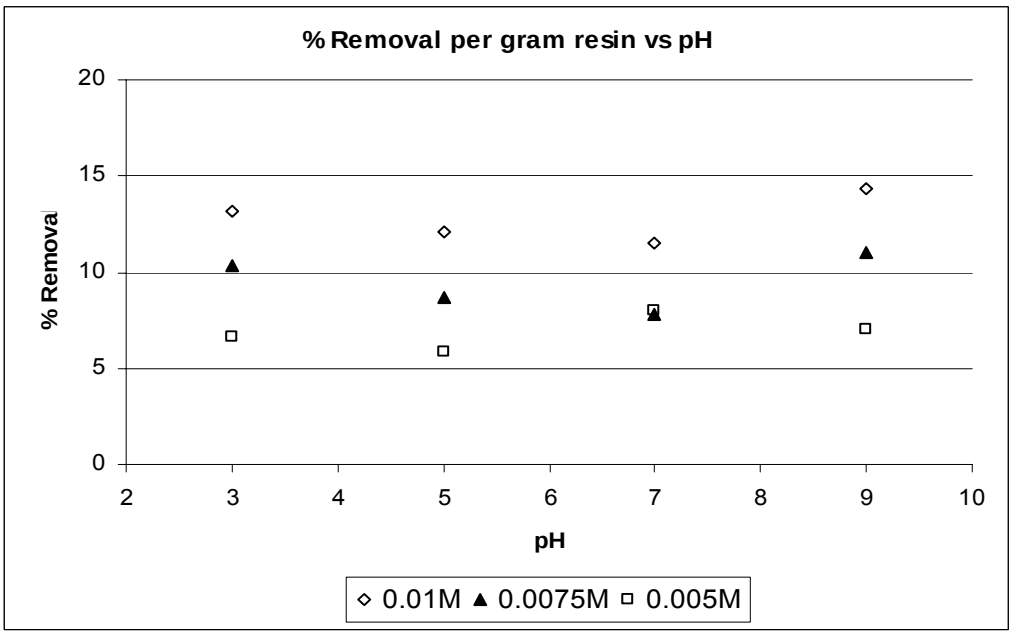


Figure 5.19 Percent removal per gram of resin vs. pH graph for three initial concentrations of caffeine.

Percent removals of caffeine per gram of resin were also determined in correspondence to the caffeine loading versus pH graphs and the effect of pH on this property is shown in Figure 5.19. The highest removal occurs at acidic and basic initial pH conditions. The percent removal values are again very low as it was in the previous section and although the performance of the cation exchange resin is poor for caffeine uptake, it is consistent within the study.

5.4. Macroporous Resin Studies

After many sets of experiments, the results obtained related to the equilibrium relationship of caffeine with cation exchange resin, S100, were discouraging for future studies. Therefore, considering the large molecular size of caffeine, it was decided that a macroporous type of strongly acidic cation exchange resin, SPC112, could be studied in the same manner. For removal of large molecules by adsorption, macroporous resins are preferred. Having larger pore size, a better removal of caffeine was expected.

In order to perform similar set of experiments, the equilibrium time needed was determined at 40^{o}C. Figure 5.20 shows the change in concentration with respect to time for 4.49 grams of SPC112 resin. It is seen that after four and a half hours of agitation at 200 rpm speed, the solution phase concentration becomes constant. Therefore, with a safety margin of half an hour, following experiments were carried out with an operating time of five hours.

This preliminary experiment also contributed in the evaluation of the macroporous resin in terms of caffeine loading capacity. In Figure 5.21, a comparative presentation of the caffeine loading performances of S100 and SPC112 resins are given. It is observed that although the kinetic rate of

caffeine uptake is higher in S100, the overall caffeine loading performance of SPC112, the macroporous resin is better. However, similar to the gel type cation exchange resin, the performance of the macroporous resin for caffeine removal was far beyond satisfying.

The increased caffeine loading achieved by the macroporous cation exchange resin can be explained by larger pore size of the resin. Having larger pores must have enabled more caffeine uptake since as larger cavities need more molecules to occupy. In other words, the theoretical exchange capacity of the macroporous resin was used with a better efficiency than that of gel type cation exchange resin.

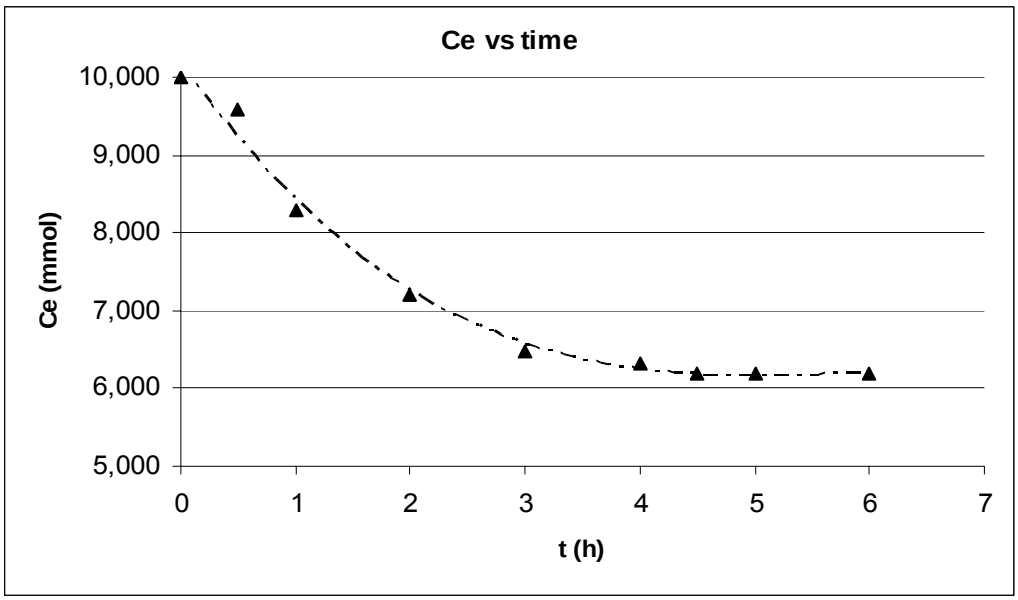


Figure 5.20 Equilibrium concentration vs. time graph for SPC 112 macroporous resin in 0.01 M caffeine solution.

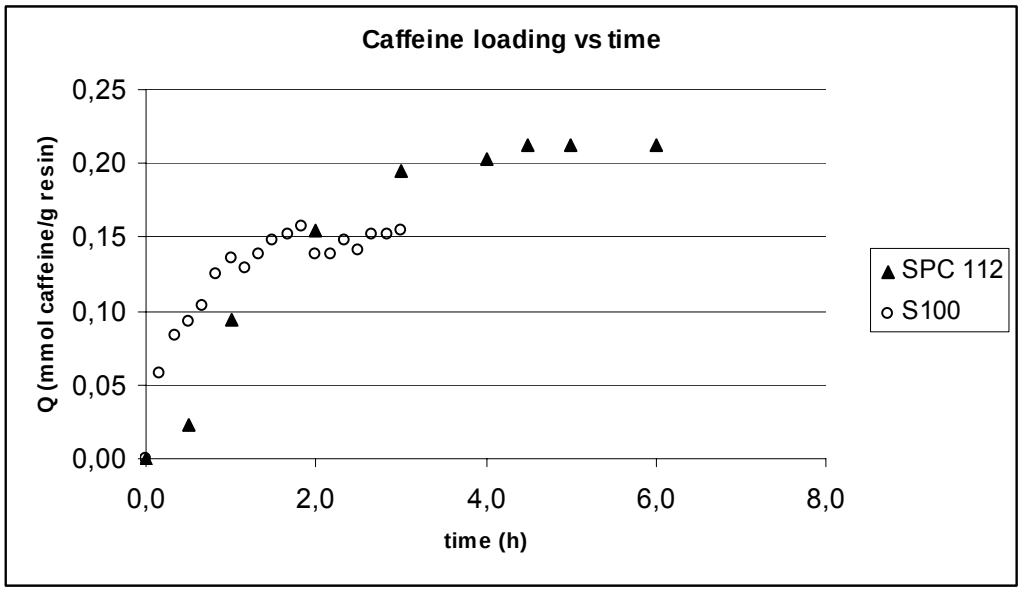


Figure 5.21 Caffeine loading versus time plot for SPC 112 and S100 resins with 0.01 M caffeine solution.

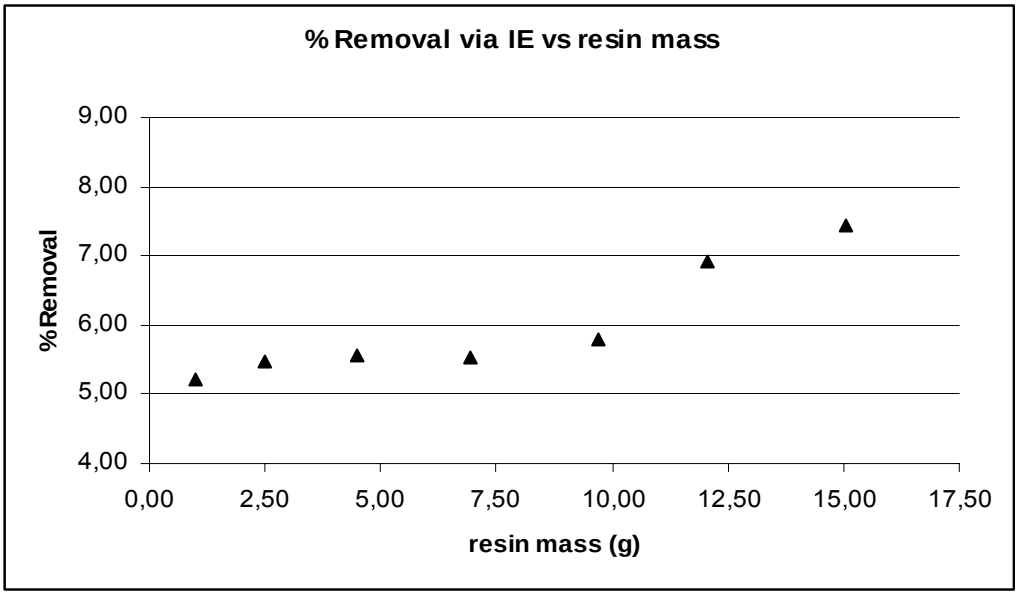


Figure 5.22 Percent of dominance of ion exchange for removal of caffeine vs. resin mass for 0.01 M caffeine solution with initial pH of 3.0.

Figure 5.22 shows the effectiveness of ion exchange mechanism in the uptake of caffeine. Having the significance of ion exchange mechanism for gel type cation exchange resin in mind, we observe that ion exchange mechanism plays a far more significant role in macroporous resin. Going up to 8%, it can be noted that both mechanisms are contributing to the uptake of caffeine.

Since only preliminary studies were to be carried out for the macroporous resin, only two pH values were studied with the most concentrated initial concentration of caffeine. pH regions were selected as acidic and basic regions, corresponding to pH values of 3.0 and 10.0 for this individual part. Figure 5.23 below shows the isotherms obtained for 0.01 M caffeine solution at acidic and basic pH values. As seen from the figure, both isotherms can be considered as favorable. Figures 5.24 and 5.25, on the other hand show the comparison of the isotherms of the two resins at both pH values.

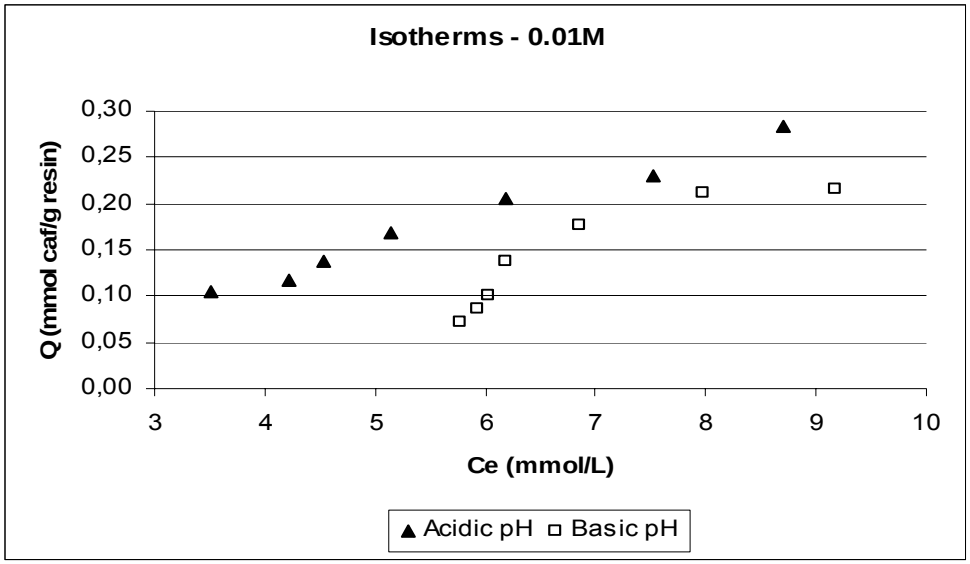


Figure 5.23 Effect of pH on equilibrium for SPC112 macroporous resin in 0.01 M caffeine solution.

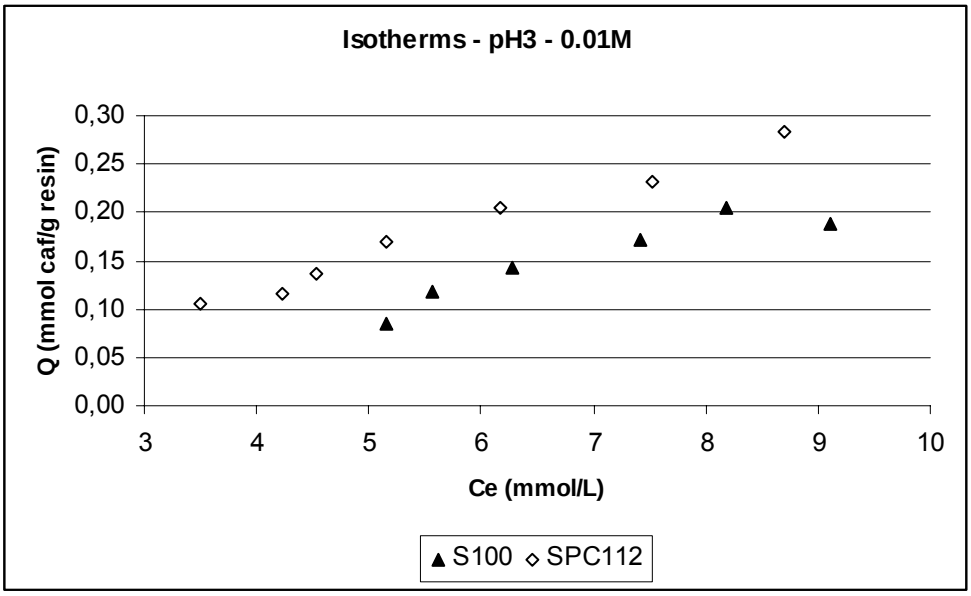


Figure 5.24 Comparison of S100 and SPC 112 resins for caffeine loading capacities with 0.01 M initial concentration at acidic pH.

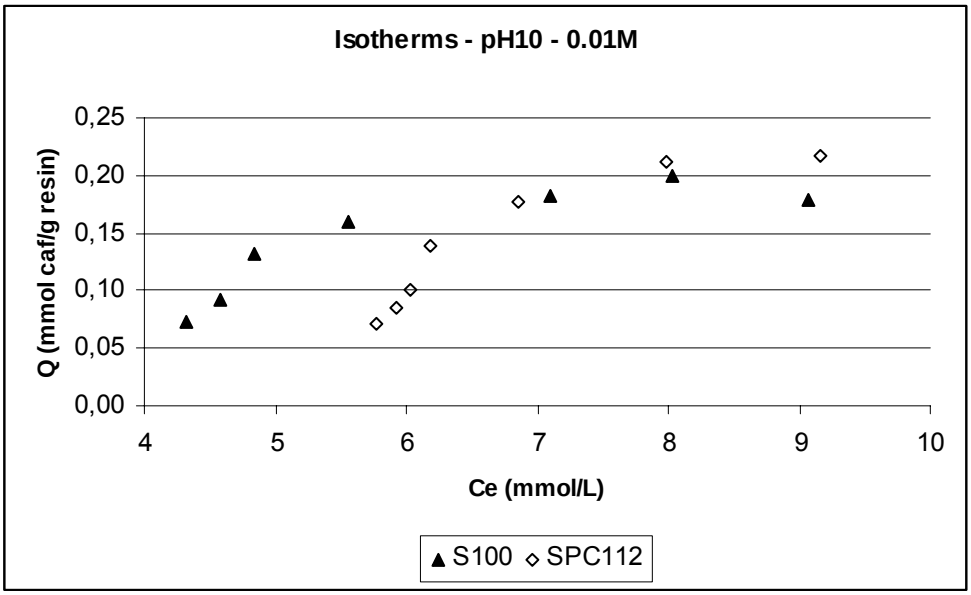


Figure 5.25 Comparison of S100 and SPC 112 resins for caffeine loading capacities with 0.01M initial concentration at basic pH.

As seen from Figure 5.25, both isotherms can be considered as favorable, however, it should be noted that a more detailed investigation at the end regions of the isotherms must be carried out for better evaluation of results.

CHAPTER 6

CONCLUSIONS

The single recovery of caffeine from a model solution by gel type strongly acidic cation exchange resin, Lewatit S100, and macroporous cation exchange resin, Lewatit SPC112, was studied. Preliminary experiments were carried out in order to screen the available resins and adsorbents. Time required for reaching equilibrium was observed for all resins and adsorbents. It was seen that the exchange reaction or adsorption where materials having smaller particle sizes were used was more rapid and they have reached equilibrium faster. On the other hand, the caffeine loading capacities of all the materials were very poor. S100 cation exchange resin was further investigated for the effects of initial caffeine concentration and initial pH values on equilibrium. Three initial concentrations and four pH values were studied. Preliminary studies for macroporous cation exchange resin were also carried out.

It can be concluded that changing the initial caffeine concentration would have no significant effect on equilibrium. Although the obtained isotherms can be considered as favorable, the removal performances are poor. However, for extreme pH values the caffeine loading capacity of S100 cation exchange resin was slightly increased.

With pH measurements before and after the experiments at hand, it is concluded that the dominant mechanism in caffeine uptake by cation exchange resins is adsorption. In neither set of experiments, the ratio of caffeine uptaken via ion exchange exceeded 2%. For the macroporous resin

however, the contribution of ion exchange to the removal of caffeine was much greater compared to S100 resin. The ratio of contribution of ion exchange gets as high as 8% when macroporous resin was used. On the other hand, although adsorption was the dominant mechanism, the preliminary experiments of magnesium silicate and RP silica had also poor performance for caffeine removal, which states that the main reason beyond these performances would be the chemical and physical nature of the caffeine molecule.

The loading capacity and removal ratio of ion exchange resins and adsorbents for caffeine was very poor. However, they were positively affected by extreme pH conditions. Acidic and basic solutions of caffeine gave the best results in terms of caffeine removal.

To sum up, the equilibrium studies of caffeine with cation exchange resins showed that, with its large molecular structure and strong chemical stability, the removal of caffeine from aqueous solutions was not feasible as the removal ratios and total exchange capacities were very low. Though, more detailed research on the utilization of macroporous cation exchange resins may be a good idea, since only preliminary studies were carried out in this study. In spite of having very low capacities for caffeine removal, more concentrated caffeine solutions can be studied also, for better investigation of the effect of initial concentration on equilibrium. On the other hand, an empirical model equation can be developed to describe the competeing ion exchange and adsorption mechanisms especially in macroporous resin. However, one should note that the experiments carried out in this study involved single component solutions. Considering the complexity of a real tea extract, the performance of cation exchange resins or adsorbents would be far worse than expected.

REFERENCES

1. McKett, J.J., "Encyclopedia of Chemical Processing and Design", Vol. 5, pp. 425 – 439, Marcel Dekker Inc., 1977.

2. Kirk-Othmer, '*Kirk-Othmer Encyclopedia of Chemical Technology*', 4th Edition, Vol. 13, pp. 1071-1081, Wiley, 1991

3. Elvers, B., '*Ullmann's Encyclopedia of Industrial Chemistry*', 5th Edition, Vol. 14, pp. 393-459, VCH Publishers, 1991

4. DİE, '*Türkiye İstatistik Yıllığı*', 2000

5. Wikipedia contributors, 'Caffeine, Wikipedia, The Free Encyclopedia, 26th June 2006.
http://en.wikipedia.org/wiki/Caffeine

6. Höll, W. H., Horst, J., '*Surface Complexation Theory: Multispecies Ion Exchange Equilibria*', Academic Press, pp. 1640-1651, 2000

7. Perry, R. H., Green, D. W., '*Perry's Chemical Engineers' Handbook*', Sec. 26, 7th Edition, McGraw-Hill, 1997.

8. Novasep Technologies, "Ion Exchange", 3rd July 2006.
http://www.novasep.com/technologies/ion-exchange.asp

9. Dyer, A., '*Ion Exchange*', Academic Press, pp. 156-173, 2000

10. ASTM D 2187-92a, Annual Book of ASTM Standards, USA, 1992

11. Adamson, A. W., '*Physical Chemistry of Surfaces*', 5 th Edition, Wiley,

1990

12. Naik, J.P., Nagalakshmi, S., "Determination of Caffeine in Tea Products by an Improved High Performance Liquid Chromatography Method", Journal of Agric. Food Chemistry, 45, 3973 – 3975, 1997.

13. Goldberg, A.P., "Comparison of Columns for Reversed Phase Liquid Chromatography", Analytical Chemistry, 54, 342 – 345, 1982

14. Naik, J.P., "Improved High Performance Liquid Chromatography Method to determine Theobromine and Caffeine in Cocoa and Cocoa Products", Journal of Agric. Food Chemistry, 49, 3579 – 3583, 2001.

15. Pesek, J.J., Frost, J.H., "Adsorption as a Mechanism for Separation of Nonionic Solutes by Pellicular Ion Exchange Chromatography", Analytical Chemistry, Vol.45, No.9, 1973.

16. Adamson, A. W., '*Physical Chemistry of Surfaces*', 5 th Edition, Wiley, 1990

17. Chen, Q., Wang, J., "Simultaneous Determination of Artificial Sweeteners, Preservatives, Caffeine, Theobromine and Theophylline in Food and Pharmaceutical preparations by Ion Chromatography", Journal of Chromatography A, 937, 57 – 64, 2001.

18. Helfferich, F. G., '*Ion Exchange*', McGraw-Hill, 1962

19. Lewatit Ion Exchange Resins – Product Information Sheets

20. Harland, C. E., '*Ion Exchange: Theory and Practice*', 2nd Edition, The Royal Society of Chemistry, 1994

APPENDIX A

A.1. Data of the Experiments

Table A.1. Screening of Ion Exchange Resins and Adsorbents in Terms of Their Caffeine Uptake

Solid phase	mass (g)	Solution Concentration (M)	Equlibrium Concentration (M)	Caffeine Uptaken (mg Caf / g solid)
S100H	1	0.0025	0.0016	1.7478
S100Na	1	0.0025	0.0024	0.1942
CNP80H	1	0.0025	0.0022	0.5826
RP Silica	1	0.0025	0.0020	0.9710
Magnesium silicate	1	0.0025	0.0019	1.1652
Cellulose	1	0.0025	0.0024	0.1942
Silica gel	1	0.0025	0.0024	0.1942

Table A.2. Concentration vs. Time Data for S100 in 0.01M Caffeine Solution

Time (min)	Concentration (g/L)	Time (min)	Concentration (g/L)
0	1,990	100	1,755
10	1,900	110	1,745
20	1,860	120	1,775
30	1,845	130	1,775
40	1,830	140	1,760
50	1,795	150	1,770
60	1,780	160	1,755
70	1,790	170	1,755
80	1,775	180	1,750
90	1,760		

Table A.3. Concentration vs. Time Data for Magnesium Silicate in 0.0025M Caffeine Solution

Time (min)	Concentration (g/L)
0	0,494
10	0,477
20	0,466
30	0,456
40	0,444
50	0,432
60	0,420
70	0,410
80	0,399
90	0,388
100	0,380
110	0,373
120	0,370
130	0,369

Table A.4. Concentration vs. Time Data for RP Silica in 0.0025M Caffeine Solution

Time (min)	Concentration (g/L)	Time (min)	Concentration (g/L)
0	0,489	70	0,410
10	0,475	80	0,402
20	0,463	90	0,396
30	0,451	100	0,392
40	0,440	110	0,389
50	0,429	120	0,388
60	0,419		

Table A.5. Solubility of Caffeine in Organic Solvents

Solvent	Solubility (grams Caffeine / 100 g Solvent)	Temperature (°C)
Ethyl Alcohol (95%)	1,32	25
Ethyl Alcohol (Absolute)	1,88	25
	5,85	60
Ethyl acetate	0,73	18
	4,2	Bp*
Methyl alcohol	1,14	25
Acetic acid (99.5%)	2,6	21,5
Acetone	2,32	30,5
Aniline	29,4	30,5
Benzaldehyde	13,1	30,5
Benzene	0,91	18
	1,16	25
	1,23	30,5
	5,29	80
Carbon tetrachloride	0,26	20
	0,70	Bp
Chloroform	12,9	17
	12,3	25
	11,92	25
	15,63	Bp
Ether	0,12	18
	0,27	25
	0,30	Bp
Trichloroethylene	0,76	15
Dichloroethylene	1,82	15
Pyridine	34,39	20-25
Quinoline	3,56	20-25
Toluene	0,58	25
Xylene	1,13	32,5

* Bp: Boiling point

Table A.6. Solubility of Caffeine in water, 0º to 80 ºC

Temperature (ºC)	Solubility (grams Caffeine / 100 g H_2O)
0	0,60
15	1,00
20	1,46
25	2,13
30	2,80
40	4,64
50	6,75
60	9,70
70	13,50
80	19,23

Table A.7. Material Performances in Screening Studies

Material	Type	Relative Caffeine Uptake
S100H	Strong cation exchange resin	Very good
S100Na	Strong cation exchange resin	Average
CNP80H	Weak cation exchange resin	Average
CNP80Na	Weak cation exchange resin	Poor
RP Silica	Sorbent	Good
Silica Gel	Sorbent	Poor
Cellulose	Sorbent	Average
Mg Silicate	Sorbent	Good

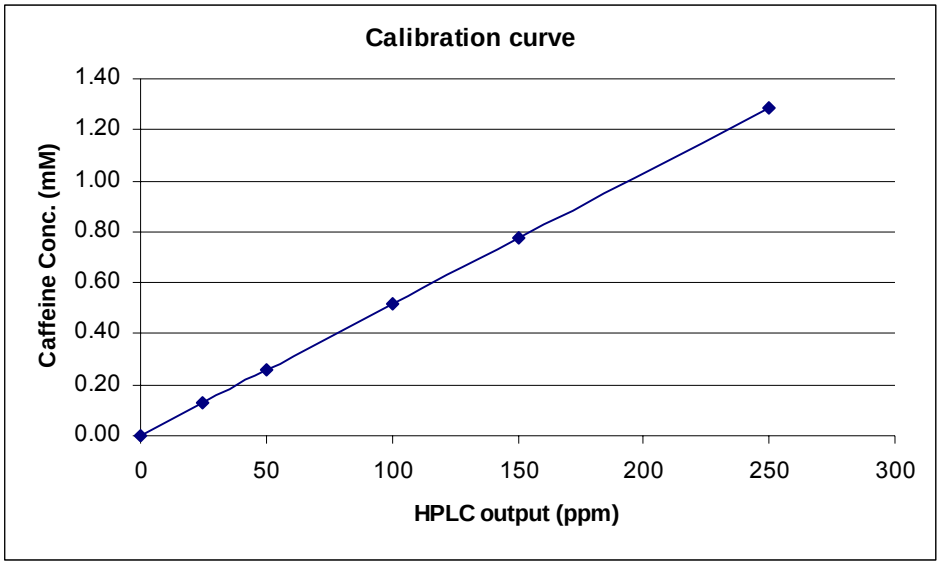


Figure A.1 Calibration curve that is used to determine solution phase concentration of caffeine.

Table A.8 Isotherm data for 0.01 M caffeine solution at different pH values.

0.01M		pH 7	0.01M		pH 9
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.509	8.0587	0.1873	2.583	8.0330	0.1994
3.010	7.8270	0.1753	4.103	7.1061	0.1820
3.593	7.6468	0.1594	7.103	5.5613	0.1595
4.008	7.4974	0.1522	10.014	4.8404	0.1311
10.326	6.2204	0.0900	14.856	4.5829	0.0927
15.237	5.0463	0.0803	19.944	4.3254	0.0723
20.385	3.7075	0.0764			
0.01M		pH 3	0.01M		pH 5
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.484	8.1874	0.2047	2.468	8.4964	0.1722
4.105	7.4150	0.1709	3.928	7.7755	0.1541
6.882	6.2822	0.1431	6.952	6.3337	0.1389
9.837	5.5613	0.1184	9.998	5.4068	0.1198
14.795	5.1493	0.0857	14.863	5.3038	0.0823
			19.953	5.1493	0.0632

Table A.9 Isotherm data for 0.005 M caffeine solution at different pH values.

0.005M		pH 7	0.005M		pH 9
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.002	4.0731	0.1055	2.600	2.8836	0.1040
3.000	3.6045	0.1095	4.559	2.6004	0.0748
4.536	3.1030	0.1000	5.978	2.2657	0.0711
6.012	2.6519	0.0942	9.390	2.0340	0.0514
7.850	2.2400	0.0853	11.137	1.8538	0.0474
9.778	1.9670	0.0754	13.570	1.6993	0.0417
12.013	1.6993	0.0670			
13.362	1.6220	0.0617			
0.005M		pH 5	0.005M		pH 3
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.0840	2.8836	0.1142	2.0580	4.0937	0.0938
4.5640	2.4974	0.0733	4.4240	3.3471	0.0858
6.0320	2.2400	0.0661	6.0970	3.0896	0.0728
9.7540	1.9825	0.0475	9.4170	2.8579	0.0533
11.0550	1.9310	0.0431	11.1210	2.7034	0.0486
13.1840	1.8538	0.0376	13.6820	2.6519	0.0405

Table A.10 Isotherm data for 0.0075M caffeine solution at different pH values.

0.0075M		pH 7	0.0075M		pH 9
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
1.0680	6.5911	0.1929	1.1920	6.2564	0.2646
8.0780	4.8919	0.0781	4.5180	5.0206	0.1382
9.5110	4.5314	0.0758	8.1410	4.4542	0.0941
10.1520	3.8620	0.0875	12.3400	3.8877	0.0735
12.3830	2.7291	0.0946	14.3760	3.8363	0.0640
14.2430	4.1710	0.0569	16.2380	3.7848	0.0575
16.4150	2.1112	0.0808	19.7260	3.7333	0.0480
19.5850	3.0124	0.0562			
0.0075M		pH 5	0.0075M		pH 3
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
4.7620	4.9949	0.1244	1.1630	6.8486	0.1329
8.1410	4.4027	0.0909	4.7000	4.6859	0.1479
12.7130	3.8363	0.0694	8.1210	4.7116	0.0848
14.1730	3.7848	0.0631	12.3950	2.7549	0.0950
16.1410	3.7590	0.0558	14.2000	3.2441	0.0743
18.6490	3.7075	0.0490	16.3060	2.3687	0.0782
			19.2880	2.5489	0.0637

Table A.11 Isotherm data for acidic caffeine solution (pH 3) at different initial concentration values.

pH 3		0.01M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.4840	8.1874	0.2047
4.1050	7.4150	0.1709
6.8820	6.2822	0.1431
9.8370	5.5613	0.1184
14.7950	5.1493	0.0857
pH 3		0.005M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.0580	4.0937	0.0938
4.4240	3.3471	0.0858
6.0970	3.0896	0.0728
9.4170	2.8579	0.0533
11.1210	2.7034	0.0486
13.6820	2.6519	0.0405

Table A.12 Isotherm data for neutral caffeine solution (pH 7) at different initial concentration values.

pH 7		0.01M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.5085	8.0587	0.1873
3.0100	7.8270	0.1753
3.5926	7.6468	0.1594
4.0080	7.4974	0.1522
10.3260	6.2204	0.0900
15.2370	5.0463	0.0803
20.3850	3.7075	0.0764
pH 7		0.005M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.0020	4.0731	0.1055
3.0000	3.6045	0.1095
4.5360	3.1030	0.1000
6.0120	2.6519	0.0942
7.8500	2.2400	0.0853
9.7780	1.9670	0.0754
12.0130	1.6993	0.0670
13.3620	1.6220	0.0617

Table A.13 Isotherm data for slightly acidic caffeine solution (pH 5) at different initial concentration values.

pH 5		0.01M	pH 5		0.005M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.4680	8.4964	0.1722	2.0840	2.8836	0.1142
3.9280	7.7755	0.1541	4.5640	2.4974	0.0733
6.9520	6.3337	0.1389	6.0320	2.2400	0.0661
9.9980	5.4068	0.1198	9.7540	1.9825	0.0475
14.8630	5.3038	0.0823	11.0550	1.9310	0.0431
19.9530	5.1493	0.0632	13.1840	1.8538	0.0376
pH 5		0.0075M			
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)			
4.7620	4.9949	0.1244			
8.1410	4.4027	0.0909			
12.7130	3.8363	0.0694			
14.1730	3.7848	0.0631			
16.1410	3.7590	0.0558			
18.6490	3.7075	0.0490			

Table A.14 Isotherm data for basic caffeine solution (pH 9) at different initial concentration values.

pH 9		0.01M	pH 9		0.005M
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)	resin mass (g)	Ce (mM)	Q (mmol caf/g resin)
2.5830	8.0330	0.1994	2.6000	2.8836	0.1040
4.1030	7.1061	0.1820	4.5590	2.6004	0.0748
7.1030	5.5613	0.1595	5.9780	2.2657	0.0711
10.0140	4.8404	0.1311	9.3900	2.0340	0.0514
14.8560	4.5829	0.0927	11.1370	1.8538	0.0474
19.9440	4.3254	0.0723	13.5700	1.6993	0.0417
pH 9		0.0075M			
resin mass (g)	Ce (mM)	Q (mmol caf/g resin)			
1.1920	6.2564	0.2646			
4.5180	5.0206	0.1382			
8.1410	4.4542	0.0941			
12.3400	3.8877	0.0735			
14.3760	3.8363	0.0640			
16.2380	3.7848	0.0575			
19.7260	3.7333	0.0480			