ION EXCHANGERS IN THE RECOVERY OF TARTARIC ACID FROM AQUEOUS SOLUTIONS

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ABSTRACT

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Tartaric acid is a dicarboxylic acid naturally present in grapes, and has many application areas with its salts. It can be produced synthetically, manufactured as a by-product in wine industry, or can be recovered by electrodialysis and solvent extraction methods. Since, ion exchange is one of the oldest processing techniques for the recovery and purification of valuable materials, it can be applied to obtain this valuable organic acid. In this study it is aimed to investigate the effects of resin basicity, initial concentration, and initial pH of the solution on ion exchange equilibrium.

The model tartaric acid solutions were prepared for the equilibrium analysis with two different anion exchange resins in a batch type system. A shaker bath at 28 ^{o}C with 300-rpm agitation rate was used. The weakly basic resin Lewatit MP62, and strongly basic resin Lewatit M511, which are in polystyrene structure, was obtained from the producer Bayer AG. In the analysis, Shimadzu PDA Detector at 210 nm with Waters Atlantis dC_{18} column was used. 20 mM NaH_2PO_4 at pH = 2.7 was introduced to the HPLC as the mobile phase at 0.5 ml/min flow rate.

In the investigation of the resin basicity, MP62 presented better performance than M511. The equilibrium experiments were performed at three different initial acid concentrations (0.01, 0.02, and 0.10 M) for both resin, and in the pH ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, and $pK_{a2} < pH$ for weakly basic resin, and in the pH ranges $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ for strongly basic resin at each concentration. Results show that the pH of the solution is a more important parameter than the initial concentration that affects the ion exchange equilibrium. Also, Langmuir and Freundlich isotherms were plotted, and it was shown that they were in good agreement with the experimental data especially for the systems that are at low total ion concentrations.

Keywords: Tartaric acid, Ion exchange, Equilibrium, Anion Resins

ÖZ

SULU ÇÖZELTİLERDEN TARTARİK ASİTİN GERİ ELDESİNDE
İYON DEĞİŞTİRİCİLER

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Temmuz 2006, 79 sayfa

Tartarik asit, üzümlerde doğal olarak bulunan bir karboksilik asittir, ve tuzları ile birlikte pek çok kullanım alanına sahiptir. Bu asit sentetik olarak üretilebilir, şarap endüstrisinde yan ürün olarak imal edilebilir, veya elektrodiyaliz ve çözücü ekstraksiyon yöntemleri ile geri elde edilebilir. İyon değişimi, değerli materyallerin geri eldesi ve saflaştırılmasında kullanılan en eski işlem tekniklerinden biri olduğundan, yöntem bu değerli asitin geri elde edilmesinde de uygulanabilir. Bu çalışmada reçine bazikliğinin, başlangıç konsantrasyonunun, ve çözeltinin başlangıç pH düzeyinin iyon değişimi dengesine etkilerinin araştırılması hedeflenmiştir.

Denge analizleri için model tartarik asit çözeltileri, kesikli sistemde iki farklı anyon değiştirici reçine kullanılarak hazırlanmıştır. 28 ^{o}C de 300 rpm çalkalama hızında bir çalkalama banyosu kullanılmıştır. Polisitren yapıdaki zayıf baz reçinesi Lewatit MP62, ve kuvvetli baz reçinesi Lewatit M511, üretici firması olan Bayer AG’ den elde edilmiştir. Analizlerde 210 nm de Shimadzu PDA Detektör, Waters Atlantis dC$_{18}$ kolonu ile kullanılmıştır. 20 mM NaH_2PO_4 HPLC’ye, pH = 2.7 de 0.5 ml/min akış hızında mobil faz olarak verilmiştir.

Reçine bazikliği araştırmalarında MP62, M511 den daha başarılı bir performans sergilemiştir. Denge deneyleri her iki reçine için üç farklı başlangıç asit konsantrasyonunda (0.01, 0.02, and 0.10 M), ve zayıf reçine için $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, ve $pK_{a2} < pH$ aralıklarında, ve güçlü reçine için $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$ aralıklarında her konsantrasyonda gerçekleştirilmiştir. Sonuçlar çözeltinin pH’ının, iyon değişim dengesini etkileyen başlangıç konsantrasyonundan daha önemli bir parameter olduğunu göstermiştir. Ayrıca, Langmuir ve Freundlich izotermleri çizilmiş, ve bunların deneysel sonuçlar ile, özellikle de düşük toplam iyon konsantasyonundaki sistemler ile uyum içinde olduğu gösterilmiştir.

Anahtar Kelimeler: Tartarik Asit, Iyon Değişimi, Denge, Anyon Reçineler

To My Family
&
Anıl

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a	Activity
A, B	Anions in the solution or in the resin phases
C_e	Equilibrium concentration in solution phase, mol / dm^3
C_i	Ionic concentration of the i^{th} specie in both phases, mol / dm^3
C_0	Initial solution concentration, mol / dm^3
K_a	Langmuir equilibrium constant, dm^3 / mol
K_{a1}, K_{a2}	Acid 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
R-	Solid matrix of the resin
q	Resin upload, mol/g wet resin
q_e	Equilibrium concentration in adsorbent-phase, mol acid/g wet resin
q_m	Maximum exchange monolayer capacity, mol / g
q_t	Total resin capacity, mol/g wet resin
V_0	Volume of the solution, dm^3
Greek Letters	
γ_i	Activity coefficient of the i^{th} specie in the solution phase

CHAPTER 1

INTRODUCTION

Tartaric acid, $C_4H_6O_6$, is a dihydroxy dicarboxylic acid with two chiral centers, meaning that it occurs in multiple three-dimensional forms, or isomers. It is white crystalline form occurs naturally in plants, particularly grapes, and is one of the main acids found in wine. The naturally occurring form of the acid is L(+)-tartaric acid or dextrotartaric acid. The mirror-image (enantiomeric) form, levotartaric acid or D(-)-tartaric acid, and the achiral form, mesotartaric acid, can be made artificially. A rarely occurring optically inactive form of tartaric acid, DL-tartaric acid is a 1:1 mixture of the levo and dextro forms. It is distinct from mesotartaric acid and is the racemic acid.

Tartaric acid and its salts -cream of tartar (potassium hydrogen tartrate), and Rochelle salt (potassium sodium tartrate)- are beneficial chemicals, and used in many application areas. Wine making is one of the principal areas of tartaric acid use. It is added to correct acid deficiencies in wine. It is used as an acidulant in carbonated beverages. Tartaric acid is used in food industry and as an emulsifier in baking industry. It is used in the manufacture of fine drug salts, as in effervescent salts, and in cough syrups. Also, it has been utilized in photography, textile and plastics industry, in metals as a chelating agent, in ceramics, and used in electronics industry [1].

Since, tartaric acid is the major organic acid found in grapes, the commercial source of the acid is the residues from the wine industry. Turkey is ranked fourth in the world with its 3 600 000 tons of annual grape production [2]. However, only three percent of all the grapes grown in Turkey go into the production of wine. About thirty percent of the total production is consumed as table grapes; sixty seven percent is converted into raisins or processed in a grape-based Turkish delicacy pekmez, pestil and sucuk [3]. As a result of this, tartaric acid and its salts, are not produced in Turkey, but imported. The requirement for the acid and its salts are about 670 tons, and about 2 million dollars were spent in 2000 [4].

The raw materials available for the manufacture of tartaric acid and tartrates are by-products of wine making. Crude tartars are recovered from the press cakes from grape juice, from lees that are the dried slimy sediments in the wine fermentation vats, and the crystalline crusts that form in the vats in the secondary fermentation period called argols. The chemical reactions involved in tartaric acid production are summarized in Section 2.3.2.

Also, tartaric acid can be produced by bacterial fermentation, catalytic and nitric acid oxidation. Its isomer, racemic acid, is obtained synthetically by treatment of maleic acid with hydrogen peroxide in the presence of a catalyst, and meso-tartaric acid can be prepared by microbiological conversion. However, none of the foregoing processes have achieved commercial significance [1].

Ion exchange is one of the oldest processing techniques, and is subjected to various purification studies of valuable materials. This technique provides low cost, proceeds in shorter time period, has high yield and has good selectivity property. In order to purify tartaric acid by ion exchange, the selection of the resin, the determination of the operation conditions, the effect of composition ions present in the media, the efficiency of the process, and the performance of the system are of great importance. Besides the exchange capacity of the exchangers, the equilibrium properties are also necessary in designing a large-scale process. In this study, the ion exchange equilibrium, with commercially available weakly and strongly basic anion exchange resins, was studied. The effect of initial acid concentration, and pH of the acid solution were investigated.

The objective of this study was to determine the equilibrium conditions and parameters of ion exchange resins containing tertiary and quaternary amine functional groups in the recovery of tartaric acid from the solutions with different initial acid concentration and pH values. Moreover, the effect of resin basicity on the recovery of the acid was investigated.

CHAPTER 2

TARTARIC ACID

2.1 Historical Perspective

Ancient Greeks and Romans observed tartaric acid in its potassium salt form as a by-product in the production of wine. The name tartaric acid is a derivation of the medieval, alchemical term *tartarus*. However, it was first isolated from potassium tartrate, known to the ancients as tartar, circa 800 BC by the alchemist Jabir ibn Hayyan, who was also responsible for numerous other basic chemical processes still in use today [5].

The modern process, in which the acid was first obtained, was developed in 1769 by the Swedish chemist Carl Wilhelm Scheele, who boiled the raw materials such as argols or of dry sablons or of lees with chalk and decomposed the product with sulfuric acid. In 1832, a French physicist and mathematician, Jean Baptiste Biot, was discovered tartaric acid's ability to rotate polarized light. Another famous French chemist, Louis Pasteur, continued this research in 1847 by investigating the shapes of tartaric acid crystals, which he found to be asymmetric. Pasteur was the first to produce a pure sample of levotartaric acid [5]. Also, some other manufacturing methods were designed in which slaked lime was used instead of chalk [6]. In the light of these studies, in order to devise a suitable method for the production, utilizing fairly inexpensive chemicals and relatively simple operations, and thus providing economical and feasible commercial processes, many studies were conducted. The studies in literature to obtain the tartaric acid and the common production methods were investigated in Section 2.3.

The 1991's estimated total worldwide market for tartaric acid is about 58 000 tons and for potassium bitartrate is about 20 000 tons [1]. And, the requirement for this acid is increasing everyday as a result of the diversity in its usage. For Turkey, the requirement for the acid and its salts are about 670 tons, and about 2 million dollars were spent in 2000 [4].

2.2 Properties of Tartaric Acid

Tartaric acid, $C_4H_6O_6$, is a dihydroxy dicarboxylic acid with two chiral centers, meaning that it occurs in multiple three-dimensional forms, or isomers. It is white crystalline form occurs naturally in plants, particularly grapes, and is one of the main acids found in wine. The naturally occurring form of the acid is L-(+)-tartaric acid or dextrotartaric acid. The mirror-image (enantiomeric) form, levotartaric acid or D-(-)-tartaric acid, and the achiral form, mesotartaric acid, can be made artificially. A rarely occurring optically inactive form of tartaric acid, DL-tartaric acid is a 1:1 mixture of the levo and dextro forms. It is distinct from mesotartaric acid and is called racemic acid [1].

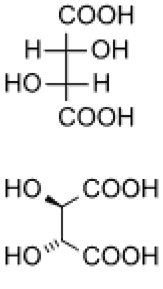
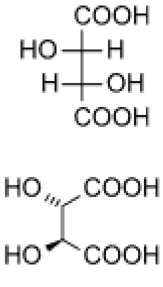
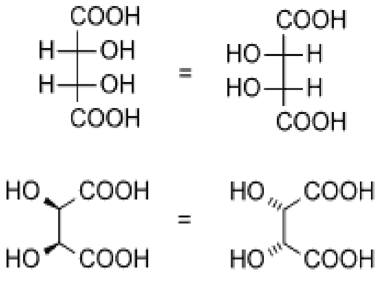
dextrotartaric acid (L-(+)-tartaric acid)	levotartaric acid (D-(-)-tartaric acid)	mesotartaric acid
		
DL-tartaric acid (racemic acid) (when in 1:1 ratio)		

Figure 2.1. Molecular structure of natural tartaric acid and its isomers.

Important derivatives of tartaric acid include its salts, cream of tartar (potassium tartrate), Rochelle salt (potassium sodium tartrate) and tartar emetic (antimony potassium tartrate).

Table 2.1. Physical Properties of Tartaric Acid [1].

Systematic name	2,3-dihydroxybutanedioic acid
Other names	2,3-dihydroxysuccinic acid threaric acid racemic acid uvic acid paratartaric acid
Molecular formula	$C_4H_6O_6$
Molecular weight	150.09 g/mol
Dissociation constants	1.04×10^{-3} (K_{a1} at 25 °C) 4.79×10^{-5} (K_{a2} at 25 °C)
Solubility in water	133 g/100 ml (20 °C)
Melting point	206°C

2.3 Production Technology

2.3.1 Synthesis

In the production of tartaric acid and its isomers, many synthesis methods were developed. For the synthesis of this valuable acid, maleic acid was used for the hydroxylation with hydrogen peroxide in the presence of tungstic acid as the catalyst [7]. Also, L(+)-tartaric acid can be produced biotechnologically either from saccharidic substrates or cis-epoxysuccinic acid. The highly selective biotransformation of cis-epoxysuccinic acid to L-tartaric acid can be performed by various species of Nocardia, Agrobacterium and Rhizobium. The activity of cis-epoxysuccinic hydrolase with the above mentioned microorganisms are stimulated by the presence of cis-epoxysuccinic acid in the culture medium. The enzyme activity can be increased also by the addition of detergents [8] and by various ions [9] during the bioconversion. In addition to these organisms the production of tartaric acid can be achieved by the action of immobilized cells of Nocardia tartaricans in pectate gel using cis-epoxysuccinic acid as the substrate in batch mode [10].

In addition to the methods mentioned above, L(+)-tartaric acid can be produced by bacterial fermentation of glucose or 5-keto-D-gluconic acid, by catalytic oxidation of 5-keto-D-gluconic acid with gaseous oxygen, and by nitric acid oxidation of carbohydrates e.g. glucose. And, its isomer, racemic acid, can be obtained synthetically by treatment of maleic acid with hydrogen peroxide in the presence of a catalyst e.g. tungstic acid. However, none of the foregoing processes have achieved commercial significance [1].

2.3.2 Manufacture

Turkey is one of the principal grape producers and exporting countries [2]. However, since only the three percent of all the grapes go into the production of wine, organic acid contents of grapes and grape juices are not qualified in Turkey [3]. In a unique study, organic acid compositions of 11 different white grape cultivars and grape juices were determined by high-pressure liquid chromatography and results are given in Table 2.2. [11].

The raw materials available for the manufacture of tartaric acid and tartrates are by-products of wine making. Crude tartars are recovered from the press cakes from grape juice, from lees that are the dried slimy sediments in the wine fermentation vats, and the crystalline crusts that form in the vats in the secondary fermentation period called argols. The chemical reactions involved in tartaric acid production are summarized in Figure 2.2.

Table 2.2. Contents of Organic Acids in White Grapes [11].

Grape Varieties	Tartaric Acid (g / l)	Malic Acid (g / l)	Citric Acid (g / l)	Total Acidity (g / l)	Titratable Acidity * (g/l)	pH
Yapıncak	7.48	2.47	0.164	10.12	6.37	3.5
Riesling	6.73	2.65	0.047	9.42	5.63	3.6
Clairette	7.28	2.19	0.062	9.53	5.66	3.6
Narince	4.98	1.87	0.045	6.90	4.01	3.6
Kabarcik	5.18	2.19	0.049	7.42	4.10	3.8
Rhazaki	5.56	2.88	0.030	8.47	4.36	3.8
Müşküle	5.48	2.76	0.074	8.32	5.85	3.6
Hafız Ali	5.46	2.77	0.054	8.28	4.80	3.8
Italian	6.23	3.40	0.062	9.65	6.23	3.7
Hasan Dede	6.25	2.14	0.055	8.44	5.32	3.8
Seedless Sultana	5.11	1.43	0.076	6.61	3.08	3.9

* Given as tartaric acid.

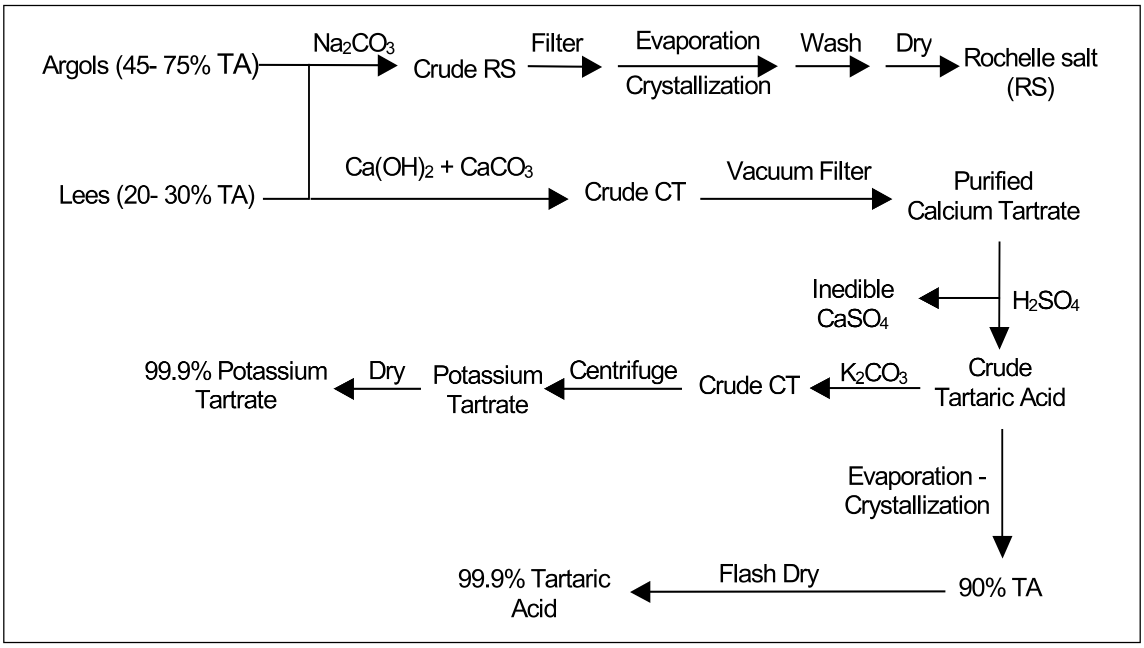


Figure 2.2. Manufacturing process for tartaric acid (TA) and its salts, calcium tartrate (CT) and potassium tartrate [1].

2.3.3 Recovery Techniques and Purification by Ion Exchange

Recovery of acids from aqueous streams or from waste sludge containing low concentrations of acids: organic/inorganic or both, is an important problem in chemical process industries. In organic acid production, the recovery and purification is a major concern from the standpoint of the cost and quality of products. Ion exchange resins in general, and weak base resins in particular, are most commonly employed methods for this purpose. The weak base resins have large capacity for acid sorption and are easy to regenerate as compared to strong base resins. Recently electrodialysis [12], and adsorption [13] have also been investigated as a means of separation and purification for organic acids.

In the early studies, the two exchange cycles, cation and anion, were considered for the recovery of tartaric acid and tartrates [14]. Synthetic resins were used, and in the case of anion exchanger, hydrochloric acid and sodium carbonate cycles were used in the process. However, it was found out that the usage of cation exchanger was useless for the recovery. And, only an anion exchanger system with a chloride-tartrate cycle was used [15]. The studies were lack of much information such as resin properties, equilibrium data and kinetics of the exchange system, but they were the pioneers of the laboratory-scale ion exchange analysis.

The uptake of some carboxylic acids and phenols rather than tartrates by an anion exchange resin is studied from aqueous solutions containing acetone or methanol. The effects of acetone, methanol, water concentration, and pH on the distribution coefficients of organic acids (butyric, benzoic, caprylic), phenols (phenol, o-nitrophenol) with some commercial resins were investigated. It was shown that the distribution coefficients of organic acids in alkaline solution were generally larger than those in acidic solution. The pH at which the uptake of an organic acid increases seems to correspond to the pK value of that acid [16].

In addition to these a number of experimental and theoretical studies have been reported on the sorption of various acids on weak base resins [17 - 20]. Adams and his co-workers observed that the uptake of sulfuric acid is fast compared with that of hydrochloric or perchloric acids as a result of valence effect [21].

Some other studies were also conducted about the fact that sorption of polybasic acids on weak base resins proceeds at a much faster rate than that of monobasic acids [22 - 23]. In addition to the effect of physical properties of the acids, the optimal basicity and structural chemistry of the basic polymer sorbent for the recovery of carboxylic acids (acetic acid) from dilute aqueous solutions was investigated [24]. Also, to develop the recovery of organic acids from aqueous solutions, macroporous resins containing tri-n-octylamine (TAO) were considered [25 - 26]. In these studies, equilibrium data were well described by the Langmuir isotherm, and the effect of the loss of the liquid ion exchanger (bleeding) was considered.

The sorption of monobasic acids on resins, in general, shows reversibility. This reversibility is due to the exclusion of H^+ from the vicinity of a positively charged resin surface as a result of electrostatic repulsion [27 - 28]. Theoretical model considering this repulsion was developed with dibasic acids on weak base resins [29]. However, in many instances, acid sorption was considered irreversible and the sorption equilibrium was interpreted in terms of simple Langmuir or Freundlich-type isotherm. The application of Langmuir- or Freundlich-type isotherm was not found satisfactory in some cases [30] and anomalous nature of sorption equilibria was also indicated with polybasic acids [31] by investigating the differences in acid separation behavior on weak base ion exchange resins [32].

The chromatographic behavior of monovalent and divalent carboxylic acids of practical importance by suppressed ion chromatography is another separation method that was studied [33]. The study was concentrated on the elution in the presence of inorganic ions, chloride and sulphate, using carbonate eluents and latex-based strong anion-exchange resin, and different types of latex-based anion-exchange columns were used for this investigation [34]. The retention model was developed, involving ion exchange equilibria of sample and eluent anions, was applied to the chromatographic data obtained.

In terms of detailed investigations on sorption of acids and differences in sorption behavior, previous studies have largely focused on the sorption dynamics of acid on weak base resins and less attention has been given to the experimental and theoretical aspects of sorption equilibria, especially with reference to the differences in the sorption behavior. Also, majority of the studies are reported on single-component monoacid, and strong polyacids. A series of studies were conducted by Takatsuji and his co-workers to investigate the adsorption of weak polyacids on weakly basic resins [35 - 38]. In these studies the single and binary equilibrium isotherms for adsorption of organic acids, acetic, malic, and citric acids, on weakly basic resin were investigated in a batch wise system. Both semi-empirical equations such as Langmuir for single systems, and Markham-Benton equations for the binary systems were correlated with the data as well as the equilibrium equations obtained from the mass-action law. The intraparticle diffusions of acetic acid and lactic acid in weakly basic ion exchangers were also investigated in these studies [39].

2.4. Determination Techniques

Grape products, such as natural fruit juices, commercial juices and nectars, and obviously wine, contain different organic acids components from the fruits used (tartaric, malic) or incorporated as additives, namely antioxidants (tartaric, malic and citric) or preservatives.

Separation, identification and quantification of the major organic acids present in a fruit juice is of considerable importance, since these compounds having important effect on quality criteria such as stability, color and flavor.

Since the simple hand titration method is not a reliable one for the determination of each component in a mixture, several methods have been developed to determine organic acids in fruit juices, including enzymatic methods, chromatographic and capillary electrophoresis [40]. Each acid may be determined enzymatically or spectrophotometrically after separating it from other components. Enzymatic analyses however require specific reagent kits for each individual organic acid, is rather time-consuming and uses large amounts of reagents. Gas chromatography (GC) has been suggested for the analysis of organic acids in the form of esters, by direct injection (acetic acid, short chain acids), by silylation and by oxidation for headspace analysis. Ion chromatographic determination is also extensively used but it requires the previous separation of sugars and polyalcohols in order to prevent interferences, or expensive on-line pretreatment procedures for the simultaneous determination of sugars and organic acids [40 - 41]. So, the HPLC method, developed in this study for the determination of tartaric acid in the solution at equilibrium with the ion exchange resin, is an acceptable and a reproducible procedure.

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. Inorganic and organic 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. By this means exchangers are able to interact with ions from the liquid phase. There are a large variety of such interactions: they may be due to electrostatic and van der Waals forces, heteropolar and covalent binding, or coordination forces [42]. 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 exchange has been described as one of the oldest scientific phenomenon known to humanity, but the first truly scientific allusion to ion exchange is attributed to two English agricultural chemists in 1850. These were J. T. WAY and H. S. THOMPSON, who independently observed the replacement of calcium in soils by ammonium ions. This discovery was the precursor to the study of inorganic materials capable of ‘base’ exchange, and it was shown that natural zeolite minerals (chabazite and natrolite) could reversibly exchange cations. H. GANS recognized the importance of this property in water softening, and in 1905 patented a series of synthetic amorphous aluminosilicates for this purpose [43].

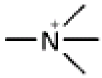
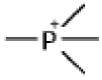
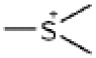
Ion exchanger production was radically altered by the discovery of synthetic resin exchangers by B. A. ADAMS and E. L. HOLMES in 1935. They used a condensation polymerization reaction to create a granular material able to be used in columns. The first polystyrene-based resin was invented by D'ALELIO in 1944. Two years later, MCBURNEY produced polystyrene anion-exchange resins by chloromethylation and amination of the matrix. After that, three manufacturers invented resins with a high degree of cross-linking 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. These invented resins in which the polymer is artificially expanded by the addition of a nonpolymerizable compound that is soluble in the monomer are known as macroporous or macroreticular *resins*. Other naturally porous resins are known as *gel resins.* Between 1970 and 1972, a new type of anion-exchange resin with a polyacrylic matrix appeared on the market. This possesses exceptional resistance to organic fouling and a very high mechanical stability due to the elasticity of the polymer. In the 1980s and 1990s, several producers developed new manufacturing technologies aimed at producing resins with particles of almost identical size [43].

Sophisticated developments of novel resin exchangers (and inorganic materials), together with improvements in properties of commercial products, continue to be heightened by the extensive area that modern ion exchange interests cover. The process governs ion separations important to analytical techniques, large-scale industrial water purification, pharmaceutical production, protein chemistry, wastewater treatment (including nuclear waste) and metals recovery (hydrometallurgy) [43]. In addition it has a critical role in life processes, soil chemistry, sugar refining, catalysis and in membrane technology.

3.2. Structures of Ion-Exchange Resins

An ion exchanger consists of the polymer matrix and the functional groups that interact with the ions. Organic ion exchangers mainly have the polystyrene and polyacrylic matrices; where inorganic ion exchangers are primarily layer silicates and zeolites, are of relatively minor importance for this thesis. Also, other types of matrices phenol-formaldehyde, and polyalkylamine resins are available in the market. Table 3.1 shows the most used acid and base functional groups on organic ion exchangers.

Table 3.1. Types of Ion Exchangers and Their Functional Groups.

Type	Name of fixed functional group	Chemical structure of functional group
Cation exchangers		
Strong acid	Aryl sulfonic	$-C_6H_5-SO_3H$
Weak acid	Carboxylic acid	$-COOH$
	Phenolic hydroxyl	$-C_6H_5-OH$
Intermediate acid	Phosphonic	$-P(O)(OH)_2$
	Phosphonous	$-P(O)H(OH)$
	Phosphoric	$-O-P(O)(OH)_2$
Anion exchangers		
Strong base	Quaternary ammonium	
	Phosphonium	
	Sulfonium	
Weak base	Primary amine	$-NH_2$
	Secondary amine	$-NHR$
	Tertiary amine	$-NR_2$
Amphoteric exchangers	Mixture of acid and base groups	

3.3. General Properties

3.3.1. Degree of Cross-Linking and Porosity

The degree of cross-linking in ion exchangers can be explained as the weight percentage of DVB related to the total amount of monomer prior to polymerization. An increase in the degree of cross-linking (e.g. above 10 – 12 % DVB) produces harder, less elastic resins. On the other hand, resins with higher degrees of cross-linking show more resistance to oxidizing conditions that tend to de-cross-link the polymer [44].

Activation (i.e., chemical transformation of the inert copolymer into an ion-exchange resin) becomes difficult with the increase in the degree of cross-linking because the high density of the matrix hinders access to the interior of the bead. In addition, osmotic stress cannot be absorbed by the elasticity of the structure, which causes the bead to shatter. Finally, the rate of exchange increases in proportion to the mobility of the ions inside the exchanger bead: if the structure is too dense, ionic motion is slowed down, thus reducing the operating capacity of the resin.

The greater the ionic mobility in the resin, the poorer is the differentiation between the adsorption of ionic species with the same charge. Consequently, the degree of cross-linking in the resin must be increased when greater differences in ionic affinity are required.

Cross-linking reduces the retention of water in ion-exchange resins. The volume occupied by this water is a measure of the resin's porosity.

Macroporous resins are made by mixing the monomers with a compound (e.g., heptane, saturated fatty acids, $C_4 – C_{10}$ alcohols or polyalcohols, or low molecular mass linear polystyrene) 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.

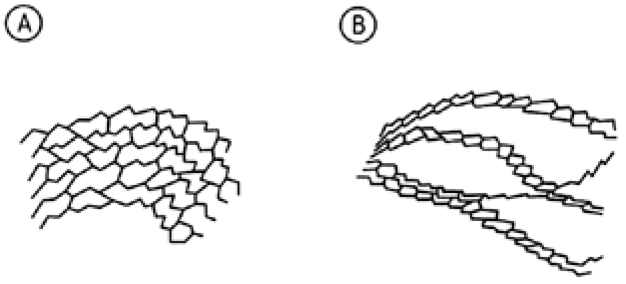


Figure 3.1 Arrangement of structural units in gel (A), macroporous (B) resins [44].

3.3.2. Exchange Capacity

Capacity and related data are primarily used for characterizing ion exchange materials and for use in the numerical calculation of the exchange operations.
The total capacity (total exchange capacity, maximum capacity) of a resin, expressed in equivalents per unit weight (or per unit volume), represents the number of active sites available. In polystyrene exchangers, the maximum number of active sites corresponds to the “grafting” of one active group per benzene ring.

The operating capacity (apparent capacity, effective capacity) is defined as the proportion of total capacity used during the exchange process. It can amount to a large or small proportion of the total capacity and 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, type, concentration, and quantity of regenerant.

3.3.3. Stability

The chemical, thermal and mechanical stability and the ion exchange behavior of the resins depend chiefly on the structure, the degree of the cross linking of the matrix, on the nature and number of fixed ionic groups [18].

Chemical stability of the matrix is affected by highly oxidizing conditions (presence of chlorine or chromic acid) that can attack the matrix and destroy cross-linking. The sulfonic group of cation-exchange resins has high thermal stability. Anion-exchange resins, on the other hand, are temperature-sensitive. Polycondensation-type resins that are manufactured in bulk and broken up into irregular grains are comparatively fragile, so have low mechanical stability and used only in fixed beds. Polystyrene and polyacrylic resins made by suspension polymerization are perfect spheres and suffer little damage when used in continuous moving-bed ion-exchange plants. Gel-type anion resins are generally weaker than cation materials and are particularly poor at withstanding compression. 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 [44].

3.3.4. Density

Resin density is an important property because it determines the hydrodynamic behavior in counterflow systems. Resin density normally lies in the following ranges (figures in parentheses are the most common values for standard resins):

Table 3.2. Density Properties of Common Resins [44].

Strongly acidic cation exchangers	1.18 – 1.38 (1.28)
Weakly acidic cation exchangers	1.13 – 1.20 (1.18)
Strongly basic anion exchangers	1.07 – 1.12 (1.10)
Weakly basic anion exchangers	1.02 – 1.10 (1.05)

3.3.5. Particle Size

For industrial use, particle size is a compromise between the speed of the exchange reaction (which is greater with small beads) and high flow rates (which require coarse particles to minimize the head loss). 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.

3.3.6. Moisture Content

Ion-exchange resins carry both fixed and mobile ions, which 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 moisture content is defined as:

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

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

3.4. Ion-Exchange Equilibrium and Selectivity

Ion exchange equilibrium can be characterized by the adsorption isotherm. The distribution of the ions is frequently expressed by one of the common sorption isotherms, either Langmuir or Freundlich.

The simplest, and the most widely used theoretical model was developed first by Langmuir. It describes the adsorption of one component as a monolayer. The Langmuir model was originally developed to represent chemisorption on the distinct localized adsorption sites. The basic assumptions on which the model based 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.

So, the Langmuir equation,

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

where q_e is the solid phase equilibrium concentration and c_e the corresponding solution phase concentration, can be derived from both kinetic and thermodynamic considerations.

The other most common empirical isotherm is the Freundlich isotherm. The expression of the Freundlich equation is,

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

which K_f and n are the parameters that can be determined experimentally. It was empirical at the time of its proposal, can also be derived both kinetically and thermodynamically if certain assumptions are made concerning the nature of the surface and mechanism of adsorption. The Freundlich equation implies surface heterogeneity. This means, unlike Langmuir isotherm, Freundlich isotherm does not assume that all active sites are uniform. Also, in Freundlich, q falls logarithmically as the heat of adsorption increases and assumed uptake capacity of the adsorbent is infinite [45].

When plotted on log-log scale, the isotherm gives a straight line with a slope of n, which is an approximation of the sorption intensity. The intercept k (at $C_e = 1$) approximates the sorption capacity.

As mentioned above, conventional models for ion exchange are based on a number of simplifications and limiting assumptions. A basic assumption is that the maximum uptake of ions by an ion exchange resin is constant and determined by the number of functional groups on the resin matrix. The other one is a strict stoichiometric coupling among different components involved in the ion exchange process. This implies that each ion released from the resin phase has to be replaced by another component from the liquid phase with an equivalent charge. Furthermore, it is assumed that only counter ions, with a charge opposite to that of the functional groups, can enter the resin phase. Co-ions are assumed to be excluded from the resin phase due to the strong repulsive forces between like charges. The electroneutrality condition determines the quantity of counterions that will enter the resin; in any case, their total number of charge equivalents must equal the resin capacity [46].

So, in general the ion exchange equilibrium reaction between ions in solution and ions on the resin is a reversible reaction described by the equation

$$n(R^+)B^- + A^{n-} \Leftrightarrow n\,B^- + (R^+)_n\,A^{n-} \qquad \text{(Eq. 3.4)}$$

for an anion exchange resin (R^+) represents the fixed functional group of the resin. The equilibrium condition between the resin phase and and the solution phase can be described by the selectivity coefficient. The law of mass action defines the selectivity coefficient for the above reaction as

$$K_B^A = \frac{(a_B)^n\,(a_{R_nA})}{(a_A)\,(a_{RB})^n} \qquad \text{(Eq. 3.5)}$$

where a_A and a_B are the activities of A and B in solution, a_{R_nA} and a_{RB} are the activities in the resin phase. Since;

$$a_i = C_i\,\gamma_i \qquad \text{(Eq. 3.6)}$$

here C_i is the ionic concentration, and γ is the activity coefficient of the i^{th} species, both the resin and solution phase can be described in terms of activity coefficients and concentrations. Under dilute solution conditions, the activity coefficient γ is assumed to be unity and the solution phase is described by the concentration term only. However, this assumption cannot be made for the resin phase where ion concentrations in the pores are very high. But, since the activity coefficients in the resin cannot be measured, the selectivity coefficient is practically calculated as

$$K_B^A = \frac{[B^-]^n\,[R_nA]\cdot\gamma_{R_nA}}{[A^-][RB]^n\cdot\gamma_{RB}} \qquad \text{(Eq. 3.7)}$$

where $[A^-]$ and $[B^-]$ are the concentrations of A^- and B^- in solution, and $[R_nA]$, $[RB]$ are the resin phase concentrations of A and B. The quantities $[RB]\cdot\gamma_{RB}$ and $[R_nA]\cdot\gamma_{R_nA}$ can also be expressed as the equivalent ionic fractions, x_{RB} and x_{RnA}.

3.5. Exchange Kinetics Principles

Mass action equations apply only to systems in equilibrium. In industrial practice where a solution flows through the resin, equilibrium is not necessarily reached and the results are influenced by kinetic considerations.

The ion exchange process involves seven steps upon which the rate of exchange can depend. These are:

1. Transport of exchanging ions in the bulk solution
2. Film diffusion – transport through the film layer at the resin surface

3. Pore diffusion – transport within the resin particle
4. Reaction rate kinetics
5. Pore diffusion of the exchange ions outward
6. Film diffusion of the exchange ions outward
7. Transport of these ions outward in the bulk solution

In fully ionized systems, the rate-determining step of ion exchange is the diffusion of the mobile ions toward, from, and in the resin phase, rather than the chemical reaction between fixed ions of the resin and mobile counterions. If a cation-exchange resin with negative fixed ions is used as an example, the cation concentration in the resin is much greater than that in solution. However, any cations diffusing out of the resin into the dilute solution create a net negative charge in the solid phase and a net positive charge in solution. The resulting potential difference is called the *Donnan potential*; it prevents anions from penetrating the (negatively charged) resin. This phenomenon is called *Donnan exclusion.* Therefore, the co-ion does not participate in the ion-exchange process. Diffusion through the film and in the solid phase occurs at different rates and two steps may be rate determining [44]:

1. Diffusion of ions within the resin (*particle diffusion*).
2. Diffusion in the Nernst film (*film diffusion*)

The slower step controls the overall ion-exchange rate.

CHAPTER 4

EXPERIMENTAL WORK

4.1. Materials

4.1.1. Ion Exchange Resins

In the present study two different ion exchange resins were used. A weakly basic anion exchanger of tertiary amine functional group with crosslinked polystyrene matrix (Lewatit MP62), and a strongly basic anion exchanger of quaternary amine functional group, again with crosslinked polystyrene matrix (Lewatit M511). The producer of the both resins is Bayer AG. The weakly basic resin (MP62) was converted into free base form, and the strongly basic resin (M511) into hydroxide form, as explained in 4.2. The properties of these commercially available resins are given in Table 4.1.

Table 4.1. Properties of Anion Exchange Resins Used in This Study [47].

General Description	Weak Base	Strong Base
	MP62	M511
Ionic form, as shipped	Free base	Cl^-
Functional group	Tertiary amine	Quaternary amine
Matrix	Crosslinked polystyrene	Crosslinked polystyrene
Structure	Macroporous	Macroporous
Appearance	Beige, opaque	Light yellow
Operating temperature, max. ^oC	70	70
Operating pH range	0 - 8	0 - 12

4.1.2. Chemicals

All the chemicals used in the study was analytical or HPLC grade. The tartaric acid used in the experiments was purchased from Acros Organics. NaH_2PO_4 solution, used as the mobile phase in HPLC analysis, and 20 mM H_3PO_4, that was used to set the pH of the solution to 2.7, was from Merck.

The pH of the solutions in Erlen- myer flasks, for the equilibrium analysis on weakly basic anion exchange resin (MP62), was adjusted with 10 N sodium hydroxide (Merck). The solutions were daily prepared by using ultra pure water obtained from Milli-Q (Millipore) system.

4.2. Resin Preparation and Characterization

The ion exchangers used in the experiments were Lewatit MP62 and Lewatit M511 (Bayer, Germany). The Lewatit M511 resin was obtained from a pilot fermentation process carried out at METU, and the Lewatit MP62 was obtained from the manufacturer (Bayer, Germany) in free base form.

The pretreatment of the resins was performed in a batch system by washing with 2.0 N hydrochloric acid, deionized water and 2.0 N sodium hydroxide in turn and finally the swollen resins were washed with ultrapure water, obtained from Milli-Q system (Millipore), until the pH value decreased to 7. Conditioning served to remove soluble impurities and low molecular weight polymers from the resin. The weakly basic exchanger was in free base form, and the strongly basic exchanger was in hydroxide form after this pretreatment. The pretreated resins were drained, filtered to remove excess water and stored in containers for further use.

The water retention capacity, bulk density, and the total exchange capacities of the ion exchanger resins were determined in accordance with ASTM D 2187-92a [48]. The test methods B - Water retention capacity, test method C - Settled density, and test method M - Total anion capacity of anion-exchange resins, were used for the characterization of the resins. The results are presented in Table 4.2.

Table 4.2. Characteristics of Resins Used in the Experiments

Resin	Density (g / L)	Bulk density (g / L)	Moisture content	Total Exchange Capacity	
				q_t (mmol / g wet resin)	q_t' (eq / L resin)
Lewatit MP62	1020	660	% 50	2.55	1.68
Lewatit M511	1070	700	% 42	1.93	1.35

4.3. Method

4.3.1. Preliminary Experiments

After the preparation of the ion exchanger resins, initial experiments were carried out to investigate the equilibrium time by the batch method. For the determination, known weights of ion exchangers (2.5 g resins) were contacted with the model solutions, 0.03 M tartaric acid concentration, at 4500-ppm. The Erlenmeyer's were placed on a shaker bath at 28 ^{o}C and 200 rpm for approximately 82 hours for weakly basic resin, MP62, and approximately 12 hours for strongly basic resin. These contact times were chosen to make sure that equilibrium was reached. The samples were prepared for two sets and analyzed in duplicate. And each set was checked for the attainment of equilibrium at certain times by injecting 20 µl aliquots to the HPLC for the analysis.

The results of the equilibrium time analysis are tabulated in Appendix A.1, and as presented in Figures 5.1 and 5.2 the equilibrium was reached at 9 hours for MP62, and at 3 hours for M511.

4.3.2. Concentration Analysis

Three different concentrations of tartaric acid solutions in 250 ml were prepared for the concentration analysis. The initial concentration values were 0.01 M, 0.02 and 0.10 M. The solutions at 0.01 M concentration were treated with 0.25 – 5.42 g weakly basic resins in 250 ml. Erlenmeyer flasks. The solutions at 0.02 M were treated with 0.50 - 10.25 g resins, and the solutions at 0.10 M with 3.20 - 67.81 g resins. The resins and tartaric acid solutions were brought to equilibrium at 28 ^{o}C by shaking at 200 rpm. Samples of 1 ml were collected after the equilibrium was reached and diluted with ultra pure water, and injected with the samples of 20 µl to the HPLC system for the analysis. This procedure was applied throughout all experiments.

The single component system of tartaric acid with two different anion exchange resins, weakly - MP62, and strongly - M511, were selected to investigate the effect of initial acid concentration on equilibrium. In previous studies the tartaric acid content of grapes, grape juices, lees, wines, and industrial wastes was defined between the ranges of 0.017 M to 0.174 M [11], [49 - 51]. So, in this study, the effect of initial tartaric acid concentrations was investigated at three different concentrations, 0.01, 0.02, and 0.10 M of model solutions.

All the experiments were carried out in duplicate. The 250 ml solutions at 0.01 M concentration were treated with 0.25 – 5.42 g weakly basic resins in. 300 ml Erlenmeyer flasks sealed with foil-lined caps. The solutions at 0.02 M were treated with 0.50 - 10.25 g resins, and the solutions at 0.10 M with 3.20 - 67.81 g resins. The vials were placed on a shaker bath at 28 ^{o}C and 200 rpm for approximately 11 hours for MP62, and 5 hours for M511. After the attainment of equilibrium, the samples were taken from the vials, diluted by 1/10, and injected to the HPLC system for the analysis. The results were discussed in Section 5.3, and experimental data were tabulated in Appendix A.

4.3.3. pH Analysis

For the investigation of the effect of pH upon sorbent capacity, or in general, ion exchange equilibrium, 0.01, 0.02 and 0.10 M aqueous tartaric acid solution were adjusted to the pH values of: $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, and $pK_{a2} < pH$, for weakly basic resin (MP62), and to the pH values of: $pH < pK_{a1}$, $pK_{a1} < pH < pK_{a2}$, for strongly basic resin (M511).

For the pH values lower than the first acid dissociation constant of tartaric acid (pK_{a1}), initial concentrations of the tartaric acid solutions were taken. In order to increase the initial pH values of the solution to the values higher then pK_{a1}, 10 N NaOH was used. This high concentration of NaOH was prepared in order to keep the initial concentration of the acid solution unchanged. So, the higher pH values were set to 3.47, and to 4.52 for the MP62, and 3.50 for the M511.

All the experiments in this part also were carried out in duplicate. The weighed resins, and the tartaric acid solution were contacted until they reach equilibrium in 300 ml Erlenmeyer sealed with foil-lined caps. And, to attain the equilibrium the vials were placed on a shaker bath at 28 ^{o}C and 200 rpm for approximately 11 hours for MP62, and 5 hours for M511. The samples were analyzed by HPLC. The results of these experiments were discussed in Section 5.4, and data were tabulated in Appendix A.

4.3.4. Isotherms

The experiments for the equilibrium isotherm investigation were conducted in batch mode for MP62, and M511 resins at 28 ^{o}C. The concentration of tartaric in model solutions varied from 0.01 M to 0.10 M. All reactions were carried out in a shaker bath, in Erlenmeyer flasks, sealed with foil-lined caps at 200rpm.

The initial (C_0) and equilibrium concentrations (C_e) of tartaric acid were determined in each run by using HPLC, and sorbed tartaric acid amounts per gram of hydrated resin (q_e) at equilibrium with the solution were calculated from the mass balance. Equilibrium ion exchange isotherms were prepared by plotting the amount of tartaric sorbed per unit mass of hydrated resins as a function of residual concentration of lactic acid at equilibrium. The mean values of duplicates of each concentration were plotted and fitted to the both Langmuir and Freundlich equations by using a computer program, SigmaPlot, and the parameters of these equations were evaluated by non-linear regression applied by the program. These graphs are given in Chapter 5, and data are presented in Appendix A.

4.4. HPLC Analysis

Tartaric acid analyses were performed by using HPLC, and two samples were analyzed in duplicate for each treatment. The mobile phase used in the system was 20 mM NaH_2PO_4 solution at pH 2.7 with a flow rate of 0.5 ml/min. It was daily prepared by using ultra pure water obtained from Milli-Q system (Millipore). The pH of the mobile phase was set to 2.7 by using H_3PO_4 (Merck), and determined with an Inolab WTW Series pH 720 pH meter.

The mobile phase was filtered through 45 µm cellulose acetate filter papers after solution preparation and degassed. The standard and unknown solutions were prepared in different concentrations with ultra pure water. The acid used in the study was obtained from Acros Organics, and 20 µl aliquots of samples or standards were injected to HPLC.

The HPLC system was equipped by Shimadzu PDA detector. Tartaric acid was detected at 210 nm. And, during the analyses the temperature of the column was kept at 30 ^{o}C in a column oven.

The parts of the HPLC system used in this study, and the properties of the column with the analysis conditions are given in Table 4.3 and Table 4.4.

Table 4.3. The Parts of the HPLC System.

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

Table 4.4. The Properties of the Column and Analysis Conditions for HPLC Measurement.

Property	Specifications
Type of Analysis	L(+) Tartaric Acid
Retention Time	L(+) Tartaric Acid: 4.67 min
Column	Waters - Atlantis^{TM} dC_{18}
Column Length	150 mm
Column Diameter	4.6 mm
Particle Size	5 µm
Guard Cartridge	Waters - SenrtyTM Guard Column (4.6 x 20 mm)
Mobile Phase	20 mM NaH_2PO_4 @ pH = 2.7
Flow Rate	0.5 ml/min
Injection Volume	20 µl
Column Temperature	30 ^oC
Elution Type	Isocratic Elution

4.5. Summary of the Experimental Studies

In this study the investigation of the ion exchange equilibria of a weak polyprotic acid, tartaric acid, with the commercially available weakly, and strongly basic anion resin, Lewatit MP62 and M511 was conducted, respectively. To extend the information about the equilibrium conditions, the effects of initial acid concentration, and pH were considered. Also, in the light of these experiments, the effect of resin basicity on ion exchange equilibrium was observed. A summary of essentials of the experiments performed is presented in Table 4.5.

Table 4.5. Summary of Conditions for Batch Experiments.

Resin Type	Parameters	
	Initial Concentration, C_0	Initial pH
Lewatit MP62	0.01 M	2.58
		3.47
		4.52
	0.02 M	2.42
		3.47
		4.52
	0.10 M	2.04
		3.47
		4.52
	Conditions	
	Contact time	11 h
	Temperature	28 ^oC
	Agitation speed	200 rpm
Resin Type	Parameters	
	Initial Concentration, C_0	Initial pH
Lewatit M511	0.01 M	2.58
		3.50
	0.02 M	2.42
		3.50
	0.10 M	2.04
		3.50
	Conditions	
	Contact time	5 h
	Temperature	28 ^oC
	Agitation speed	200 rpm

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Preliminary Experiments

Preliminary experiments were conducted for the evaluation of equilibrium times with weakly and strongly basic resins in 0.03 M tartaric acid solutions. It was found that the weakly basic anion exchange resin – Lewatit MP62 reaches equilibrium completely after 9 hours, and the strongly basic resin – Lewatit M511 reaches equilibrium completely after 3 hours. The concentration changes in tartaric acid solutions with two different resins can be seen in Figure 5.1. and in Figure 5.2.

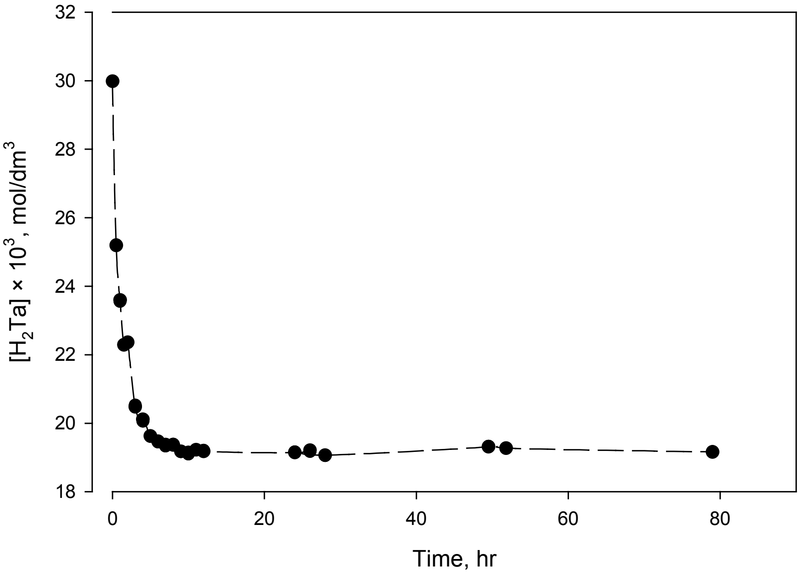


Figure 5.1. Experimental data for the equilibrium time analysis on Lewatit MP62 – weakly basic resin with tartaric acid.

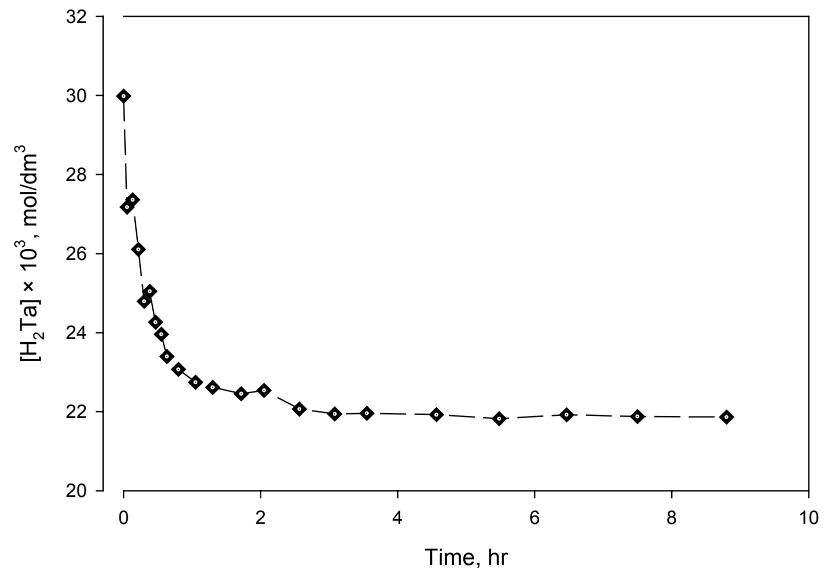


Figure 5.2. Experimental data for the equilibrium time analysis on Lewatit M511 – strongly basic resin with tartaric acid.

In literature, for other commercial ion exchanger resins, the sorption equilibrium time for the recovery of acids show large variations with each other. The fastest time to reach the equilibrium was obtained as 1 h with a 93 % recovery of acetic acid (monobasic acid), with weakly basic resin [20]. However, this fast equilibration period and high recovery rate was not observed in any other studies. In the studies conducted by Bhandari et al., the equilibrium for the adsorption of strong (HCl, HNO_3, and H_2SO_4), and weak (formic acid, monochloroacetic acid) acids with different commercial weak base resins was fully reached after about 48 h [27 - 29], [31 - 32]. In the studies that were concentrated on the recovery of carboxylic acids on weak base resins, the equilibrium was reached completely after 5 days with a 68 % recovery [35 - 36].

Preliminary kinetic experiments performed in this study show that, the equilibrium of tartaric acid with the anion exchanger Lewatit M511 occurred more rapidly, 6 h earlier than Lewatit MP62. In a large-scale production, rather than batch reactions, since the contact time of resin with the solution would be considerably shorter, the equilibrium time would play an important role for the process. So, the strongly basic resin, M511, looks like a better alternative than the weak one, MP62, with respect to the equilibrium times. However, percent recovery and loading of tartaric acid on resin are important criterion for the resin selection. The loadings of tartaric acid on weakly basic, and strongly basic resins are shown as a function of reaction time in Figure 5.3, and in Figure 5.4 respectively. In Table 5.1, loading of acid on the resins is shown for the preliminary experiments. The comparisons of loading of acid with the total capacities of the resins show that, the resins were not fully loaded at the initial experiments, and the percentages of loading for each resin are close to each other.

The effects of initial acid concentration, pH of the solution on the recovery of tartaric acid with weakly and strongly basic resins are considered in Section 5.3, and in Section 5.4 respectively. In addition to these, the recoveries of tartaric acid on these resins are also investigated. Since the recovery is affected with the conditions of the ion exchange systems (C_o, pH), it should be investigated separately. This means that efficiency term should taken into account especially during the decision for the selection of ion exchange systems, and for the design of the scale-up processes.

Table 5.1. Recovery of Tartaric Acid on Two Different Ion Exchange Resins.

Type of resin	Loading of tartaric acid on resin q (mmol/g wet resin)	Resin capacity q_t (mmol/g wet resin)	Percent loading on resin (%)
Lewatit MP62	1.30	2.55	52
Lewatit M511	0.97	1.93	51

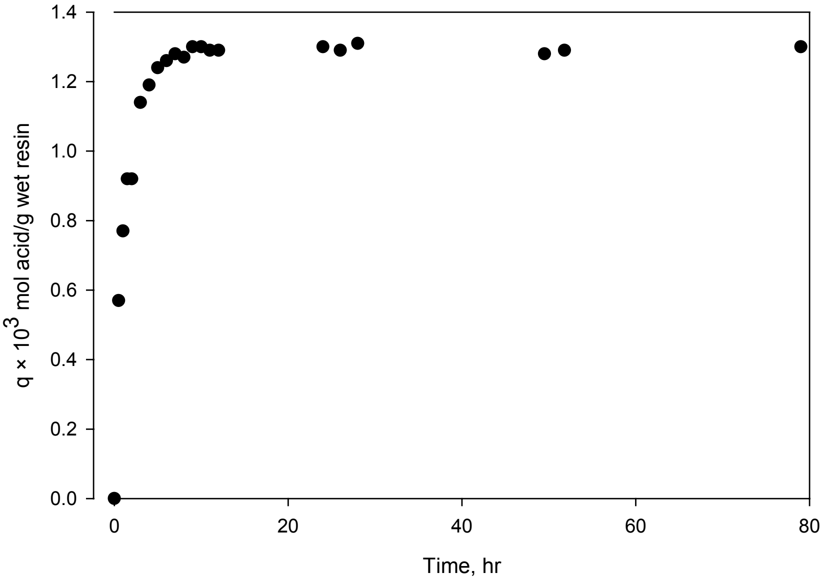


Figure 5.3. Kinetics for loading of tartaric acid with weakly basic resin, Lewatit MP62.

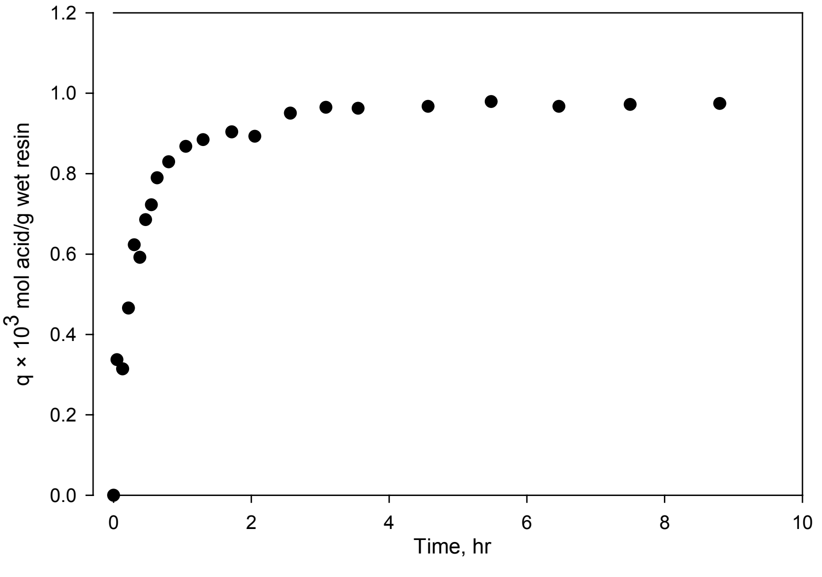


Figure 5.4. Kinetics for loading of tartaric acid with strongly basic resin, Lewatit M511.

5.2. Comparison of Resin Basicity

Resin basicity has significant impact on sorption equilibria. It may not be just sufficient to select a resin for the removal of acids on the basis of its high theoretical capacity for sorption. The pH of the solution, and the acid type that will be recovered also play important role for the selection of the resin type.

Normally, the weak base resins have large capacity, and most commonly employed for the removal of acids from aqueous streams. In addition to the capacity, weak base resins are easy to regenerate as compared to strong resins. However, the prediction of equilibria related with the resin basicity is a difficult task and for the selection of resin, experiments should be carried out.

The equilibrium conditions for the adsorption of tartaric acid on two different, weakly (Lewatit MP62) and strongly (Lewatit M511) basic, anion exchange resins were investigated in this study as well as the effect of initial concentration and pH. The resin properties were tabulated in Table 4.2. The known amount of resins were treated with 250 ml, 0.01, 0.02, and 0.10 M tartaric acid solutions in a batch system, keeping the temperature constant at 28 ^{o}C in a shaker bath with a shaker speed of 200 rpm. The sorption data are plotted in terms of the adsorbent-phase concentration (q_e, mol acid/g wet resin) and the solution concentration (C_e, mol acid/dm^3) at equilibrium.

As shown in Figure 5.5, the ability of adsorbing tartaric acid is higher with MP62 than M511 under the pH conditions $pH < pK_{a1}$. At these conditions for all three different initial acid concentrations, the loading of tartaric acid on weakly basic anion exchange resin is higher than the strongly basic resin.

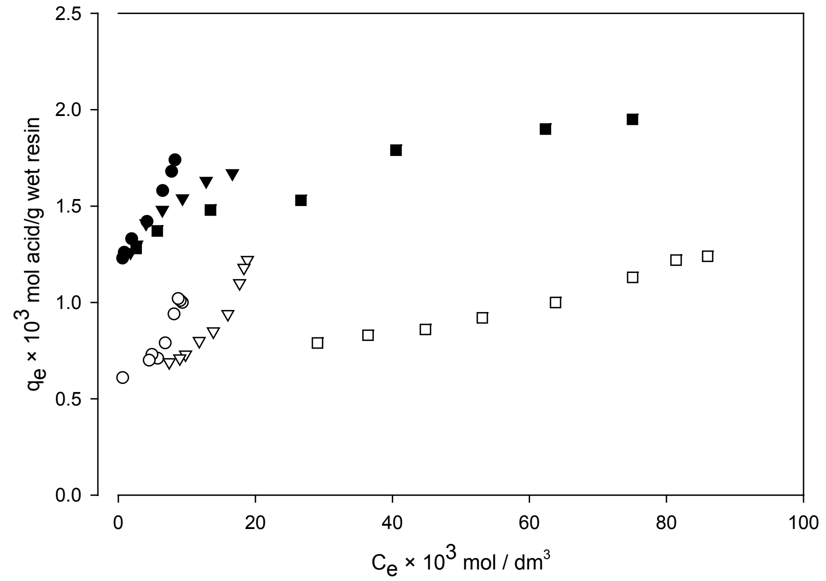


Figure 5.5. Effect of resin basicity on recovery of tartaric acid at initial pH condition, pH < pK_{a1}, at 28 °C: ● MP62 C_0= 0.01M, ○ M511 C_0= 0.01M, ▼ MP62 C_0= 0.02M, ∇ M511 C_0= 0.02M, ■ MP62 C_0= 0.10 M, □ M511 C_0= 0.10M.

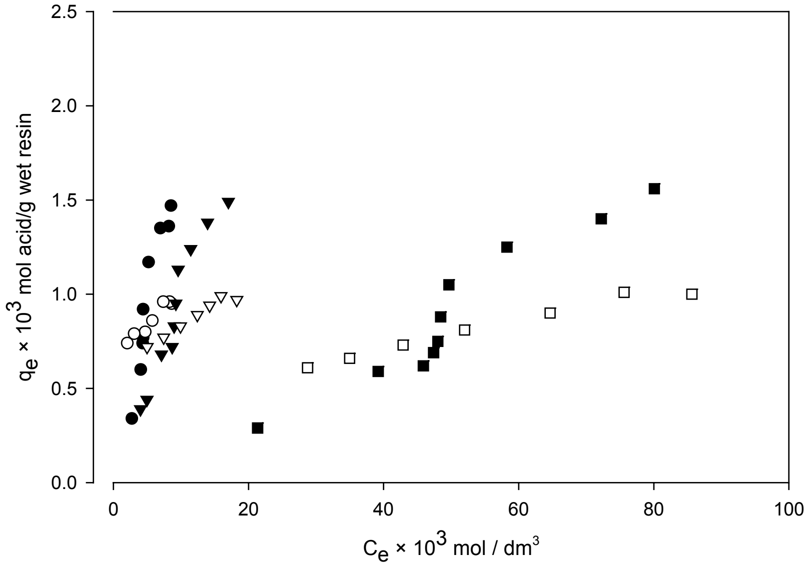


Figure 5.6. Effect of resin basicity on recovery of tartaric acid at pH condition, pK_{a1} < pH < pK_{a2}, at 28 °C: ● MP62 C_0= 0.01M, ○ M511 C_0= 0.01M, ▼ MP62 C_0= 0.02M, ∇ M511 C_0= 0.02M, ■ MP62 C_0= 0.10 M, □ M511 C_0= 0.10M.

A similar result was obtained for the acid concentration at $pK_{a1} < pH < pK_{a2}$ condition. However, in Figure 5.6 it can be seen that resin basicity doesn't show such a significant difference for the adsorption of acid on the resins as in the case that was presented in Figure 5.5. It is evident from the figures that, the capacity of weakly basic resin was affected more than the strongly basic resin. This affect can be observed more dramatically as the amount of resin increased in the batch system (it can be seen at lower C_e values). At these conditions, the amount of tartaric acid recovered by the strongly basic resin was exceeds the amount that was recovered by the weak one.

5.3. Effect of Initial Concentration on Equilibrium

The effects of different tartaric acid concentrations on uptake of tartaric acid by two different ion exchangers were investigated. Figures 5.7 - 5.11 and Figures 5.13 - 5.14 show the results of equilibrium values of tartaric acid in the resin phase and solution phase.

5.3.1 Weakly Basic Resin – Lewatit MP62

Figure 5.7 shows the equilibrium isotherms for the adsorption of tartaric acid dissolved in pure water. From the graph it can be seen that the exchange of tartaric acid with the weakly basic resin at the condition $pH < pK_{a1}$, is not affected significantly by the initial concentration of the acid in the solution. However, since the high acid concentration, 0.10 M >> 0.01 & 0.02 M, causes a higher protonation to the resin's active sites, the adsorbent phase equilibrium concentration (q_e) is slightly higher ($q_e \approx 1.9\times10^{-3}$ mol/g) than the resin particles that are in the solution at low concentrations ($q_e \approx 1.7\times10^{-3}$ mol/g). The similar results were observed in literature for the removal of organic acids by adsorption on weakly basic resins [35]. Another result observed from the figure below is that, the adsorption of tartaric acid on MP62 can be considered favorable for all these three initial acid concentrations at given conditions.

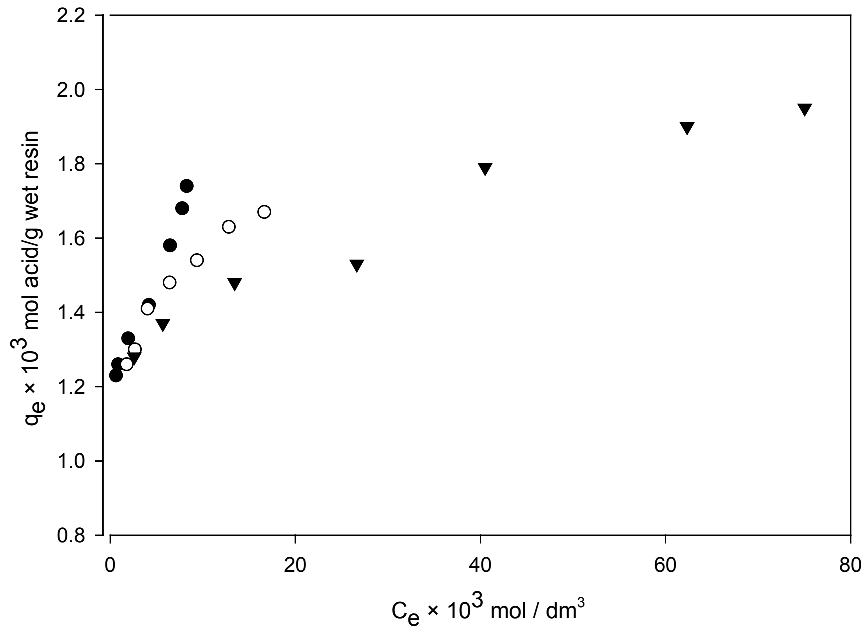


Figure 5.7. Effect of initial concentration on equilibrium for weakly basic anion-exchange resin (MP62) with H_2Ta solution at initial pH and at three different initial concentrations: C_0: ● 0.01 M, ○ 0.02 M, and ▼ 0.10 M at 28 °C.

The effect of the initial concentration of tartaric acid in the solution can be also neglected for the low values of concentrations (0.01, 0.02 M) at the conditions $pK_{a1} < pH < pK_{a2}$. However, as the concentration of the acid is increased, in this pH range, the effect of initial concentration on loading on adsorbent phase becomes significant. At low concentrations, the isotherms show favorable behavior, where at high concentration value, both favorable and unfavorable conditions begin to occur. This behavior can be observed in Figure 5.8. The isotherms obtained at 0.01, and 0.02 M are resemble concave down curves which means favorable reaction, where the isotherm at 0.01 M look like as a S-shaped curve, means the reaction has both have favorable and unfavorable behavior. This is because; the active sites of the weakly basic resin are affected more in a negative manner, as the total ion concentration of the solution increases at this pH and temperature conditions. On the other hand, the adsorbent phase equilibrium concentration (q_e) does not show significant difference for this system at different initial concentrations, $q_e \approx 1.50\times10^{-3}$ mol/g.

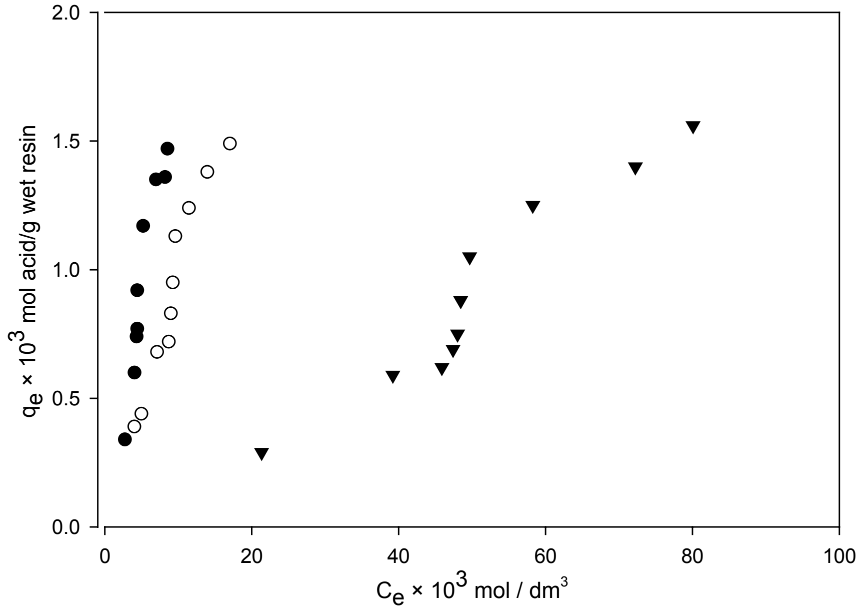


Figure 5.8. Effect of initial concentration on equilibrium for weakly basic anion-exchange resin (MP62) with H_2Ta solution at pH 3.47 and three different initial concentrations: C_0: ● 0.01 M, ○ 0.02 M, and ▼ 0.10 M at 28 °C.

The most dramatic result about the effect of initial acid concentration was observed at solution condition, $pK_{a2} < pH$. As shown in Figure 5.9 - 5.11, the ion exchange isotherms show unfavorable behavior for the solution at high acid concentration, 0.10 M. This is because of the increase in total ion concentration of the solution. Both high acid concentration in the solution, and high amount of base used to set the pH of the solution higher than pK_{a2} value, affected the adsorption of acid on weak resin negatively. It was mentioned in the previous paragraph, as the amount of competing ions increase in the solution, the adsorption of counter ions on the active sites of the weakly basic resin decrease. Also, when the Figure 5.9, Figure 5.10, and Figure 5.11 is compared with the Figures 5.7, and 5.8, it is the first time that the adsorbent phase equilibrium concentration becomes lower ($q_e=1.03\times10^{-3}$ mol/g) at high initial acid concentration, 0.10 M, than the more dilutes ones, 0.01 and 0.02 M ($q_e \approx 1.25\times10^{-3}$ mol/g). To observe the unfavorable behavior of three different initial acid concentrations for the case $pK_{a2} < pH$ (4.52), the concentrations 0.01, 0.02, and 0.10 are presented separately by the Figures 5.9 – 5.11 below.

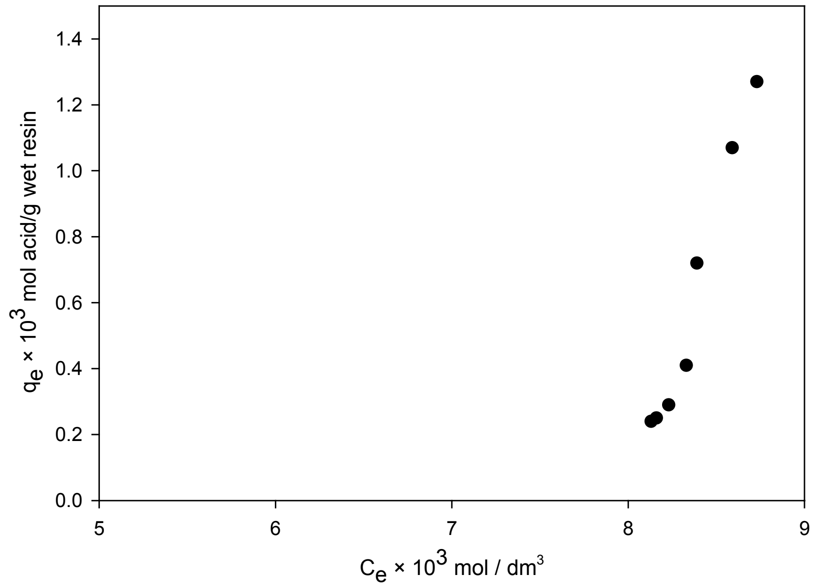


Figure 5.9. Effect of initial H_2Ta concentration (C_0: ● 0.01 M) on equilibrium for weakly basic anion-exchange resin at solution pH 4.52, and temperature 28 °C.

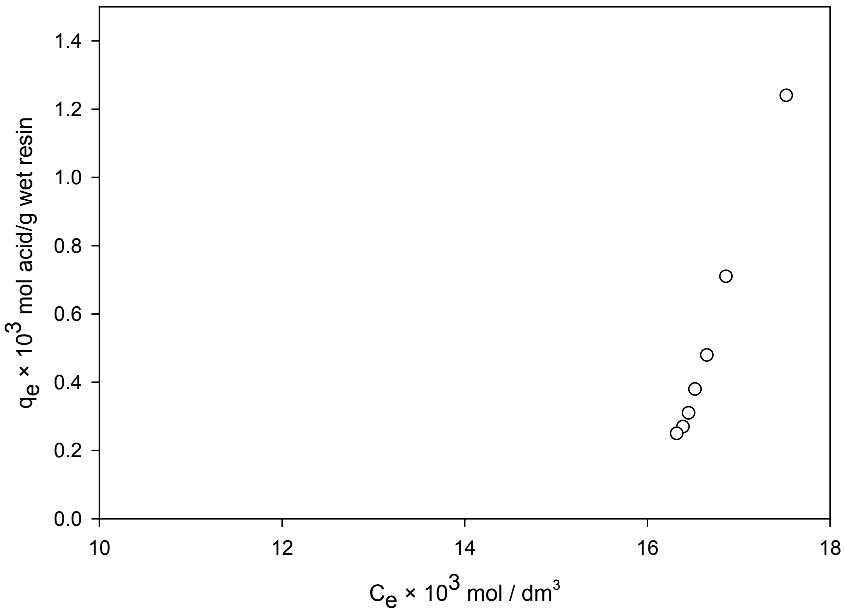


Figure 5.10. Effect of initial H_2Ta concentration (C_0: ○ 0.02 M) on equilibrium for weakly basic anion-exchange resin at solution pH 4.52, and temperature 28 °C.

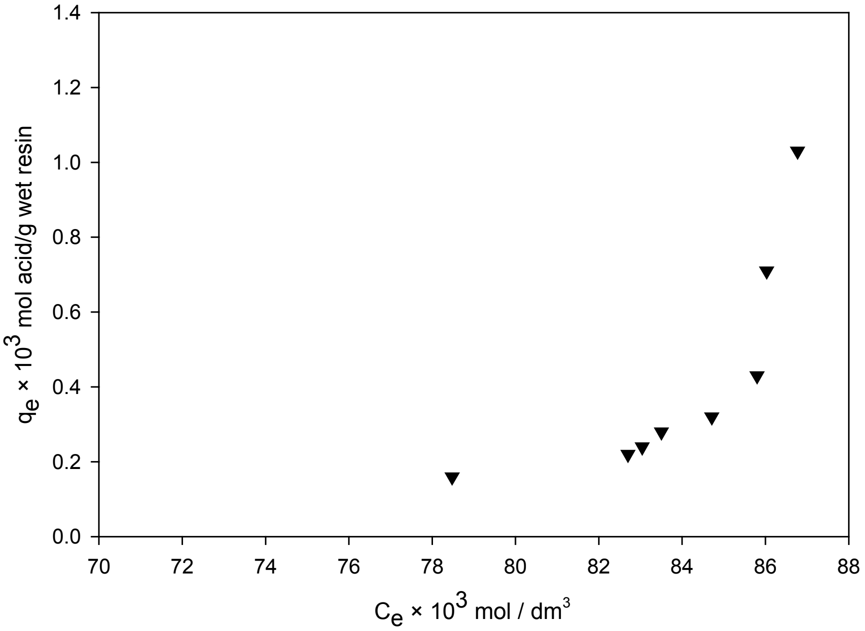


Figure 5.11. Effect of initial H_2Ta concentration (C_0: ▼ 0.10 M) on equilibrium for weakly basic anion-exchange resin at solution pH 4.52, and temperature 28 °C.

A final comment on the results obtained in this part is about the acid removal percentages of the weakly basic resin. The effect of initial concentration on tartaric acid removal by MP62 can be seen in Figure 5.12. Initial acid concentration showed significant effect not on the equilibrium but on the removal efficiencies of the resin. The acid removal by Lewatit MP62 was found to be higher than the literature values [20], [35], [36]. As presented in Figure 5.12, maximum H_2Ta removal percentage was obtained at initial concentration of 0.01 M. The percentage decreased with increasing concentration. MP62 had the highest H_2Ta removal percentage with 93.7% at initial conc. 0.01 M and at pH < pK_{a1}, and the lowest value 13.2% at initial concentration of 0.10 M at pK_{a2} < pH. Another result that can be seen from this figure is that, acid removal percentages were also negatively affected by increase in solution pH. As seen in Figure 5.12, the increase of pH from pH < pK_{a1} to pK_{a2} < pH decreased percent removal from 93.7% to 24.3% for 0.01 M initial acid concentration. But the effect of initial pH will be considered in detail in Section 5.4.

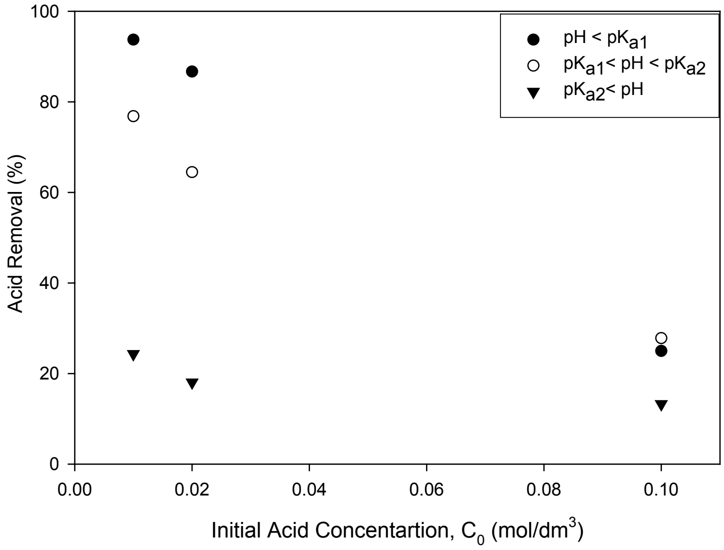


Figure 5.12. Effect of initial concentration on H_2Ta removal for Lewatit MP62.

5.3.2. Strongly Basic Resin – Lewatit M511

A similar approach, which was followed for the weakly basic resin, was also used to investigate the effect of the initial acid concentration on strongly basic resin, M511. Three different tartaric acid solutions at initial concentrations of 0.01, 0.02, and 0.10 M, were prepared for the analysis at pH < pK_{a1}, and pK_{a1} < pH < pK_{a2} conditions. As presented in Figures 5.13, and 5.14, initial acid concentration does not have a significant effect on the adsorption of acid by the resin. The adsorbent phase equilibrium concentration (q_e) was obtained about 1.22×10^{-3} mol/g in the first case (pH < pK_{a1}), and 0.97×10^{-3} mol/g in the second case (pK_{a1} < pH < pK_{a2}). The adsorbent phase concentrations for strongly basic resin are much more lower than the ones found for the weakly basic resin. One of the reasons for this difference is the total capacity of each resin. As mentioned in Section 4.2, the capacity of weakly basic resin is 32 % higher than the strongly basic one. The other reason for the higher values of acid loading by weakly basic resin compared to the strongly basic one can be explained by the selectivity. The strongly basic resin, M511, seems to have a higher selectivity for the tartaric acid than the weakly one.

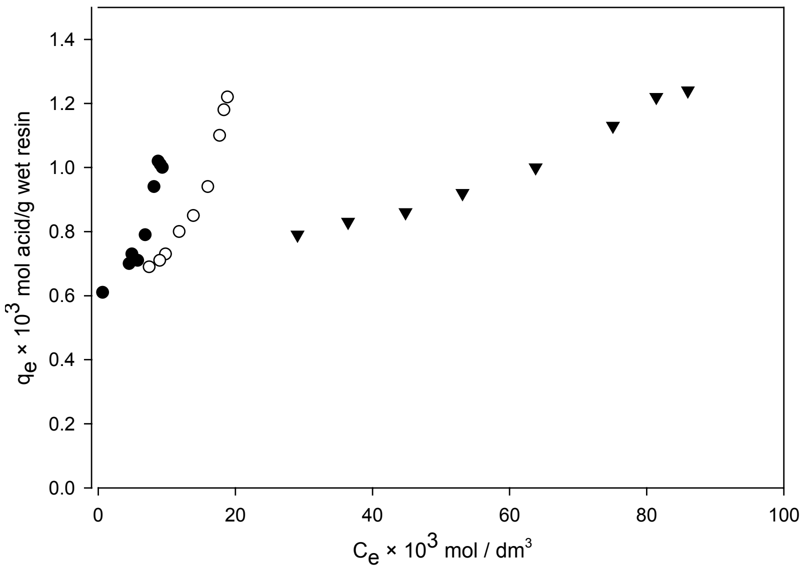


Figure 5.13. Effect of initial concentration on equilibrium for strongly basic anion-exchange resin (M511) with H_2Ta solution at pH < pK_{a1} at three different initial concentrations: C_0: ● 0.01 M, ○ 0.02 M, and ▼ 0.10 M at 28 °C.

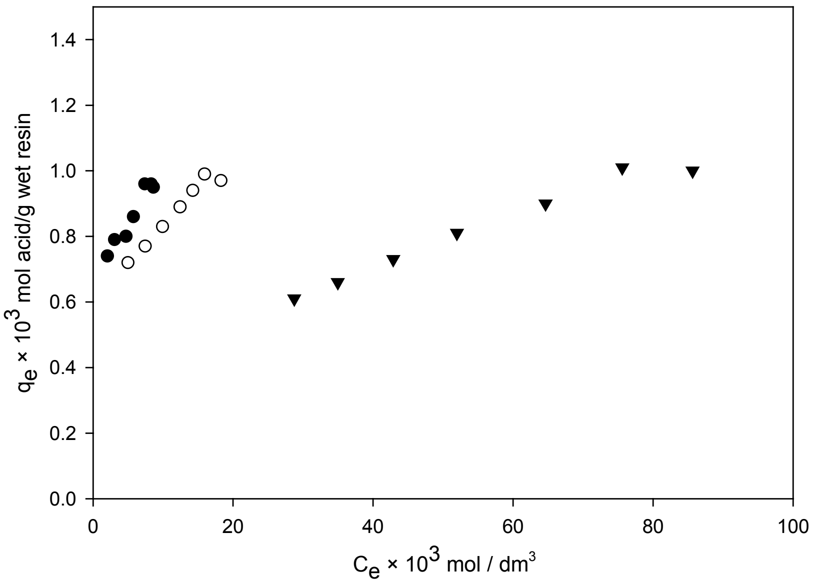


Figure 5.14. Effect of initial concentration on equilibrium for strongly basic anion-exchange resin (M511) with H_2Ta solution at pH 3.50 at three different initial concentrations: C_0: ● 0.01 M, ○ 0.02 M, and ▼ 0.10 M at 28 °C.

The results obtained for the acid removal percentages by the strongly basic resin are close to the ones for the weakly basic resin. The effect of initial concentration on tartaric acid removal by M511 can be seen in Figure 5.15. Initial acid concentration showed significant effect on the removal efficiencies of the resin. The acid removal by Lewatit M511 was found to be higher than the literature values [20], [35], [36]. As presented in Figure 5.15, maximum H_2Ta removal percentage was obtained at initial concentration of 0.01 M. The percentage decreased with increasing concentration. M511 had the highest H_2Ta removal percentage with 88 % at initial conc. 0.01 M and at $pH < pK_{a1}$, and the lowest value 14.4% at initial concentration of 0.10 M at $pK_{a1} < pH < pK_{a2}$. Another result that can be seen from this figure is that, acid removal percentages were not affected much with the increase in solution pH (from initial pH to 3.47). As seen in Figure 5.15, the increase of pH from $pH < pK_{a1}$ to $pK_{a1} < pH < pK_{a2}$ decreased percent removal from 88% to 86% for the initial acid concentration 0.01M. The effect of initial pH on recovery will be considered in detail in Section 5.4.

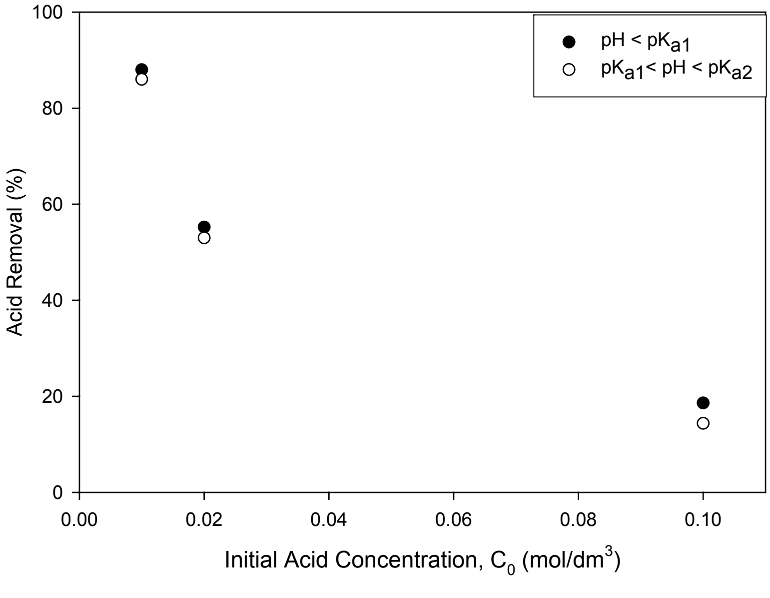


Figure 5.15. Effect of initial concentration on H_2Ta removal for Lewatit M511.

5.4. Effect of pH on Equilibrium

5.4.1. Weakly Basic Resin – Lewatit MP62

Sorption of tartaric acid on weak base resin essentially follows a two-step mechanism. In the first step, the free ionogenic groups of the resin (denoted by R) are protonated by the H^+ ions of the acid. So, the protonation mechanism can be presented as:

$$\overline{R} + \overline{H^+} \Leftrightarrow \overline{RH^+} \qquad \text{(Eq. 5.1)}$$

Protonation results the formation of positively charged surface within the pore walls of resin. The second step is the interaction of the positively charged pore surface of the resin ($\overline{R}\overline{H}^+$), with the negatively charged anions of the resin:

$$\overline{RH^+} + \overline{A}_s \Leftrightarrow \overline{RHA} \qquad \text{(Eq. 5.2)}$$

These electrostatic interactions between ions and the functional group of the resin are affected by some factors. One of the most important factors is the liquid phase pH, especially if polyprotic acids are concerned. The reason is that pH of the solution governs the dissociation reactions of the poylprotic acids. Also, the solution pH dominates the strength of the ionic interaction between the ions and the functional group of the resin, which also directly affects the uptake of acid.

In the investigation of the effect of pH on tartaric acid uptake with the weakly basic anion exchange resins, MP62, three different points were selected: initial pH of the solution ($pH < pK_{a1}$), 3.50 ($pK_{a1} < pH < pK_{a2}$), and 4.52 ($pK_{a2} < pH$). After preparing 0.01, 0.02, and 0.10 M tartaric acid solutions, the pH values were set to the required points by using 10 N NaOH.

As shown in Figures 5.16 - 5.18, the uptake of the acid affected significantly with the changes in pH of the solution. For all three initial acid concentrations, 0.01, 0.02, and 0.10 M, in the pH range, pH < pK_{a1}, the adsorption of tartaric acid on weak resin is favorable. However, as the amount of resin in the solution increases the exchange reaction becomes less favorable at pH 3.47. And, as represented in all figures, for the concentrated solution, p K_{a2} < pH, 4.52, the adsorption is unfavorable for all three different concentrations.

In the previous page it was explained that, the adsorption of tartaric acid on MP62 occurs with two-step mechanism. In the first step, the active sites of the resin are protonated with the H^+ ions. These H^+ ions are obtained from the dissociation of the tartaric acid. However, as the pH of the solution increased, the amount of hydrogen ions in the solution, that is responsible for the protonation of the active sites, decreases. This effect explains the unfavorable behavior of the ion exchange mechanism for high pH values (pK_{a1} < pH).

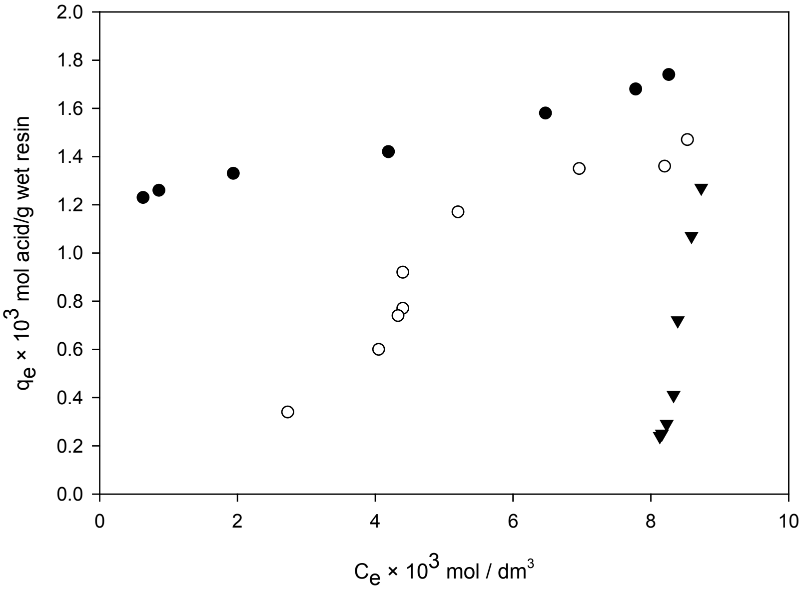


Figure 5.16. Effect of pH on equilibrium for weakly basic anion-exchange resin (MP62) with 0.01 M H_2Ta solution at three different initial pH values: ● 2.58, ○ 3.47, and ▼ 4.52 at 28 °C.

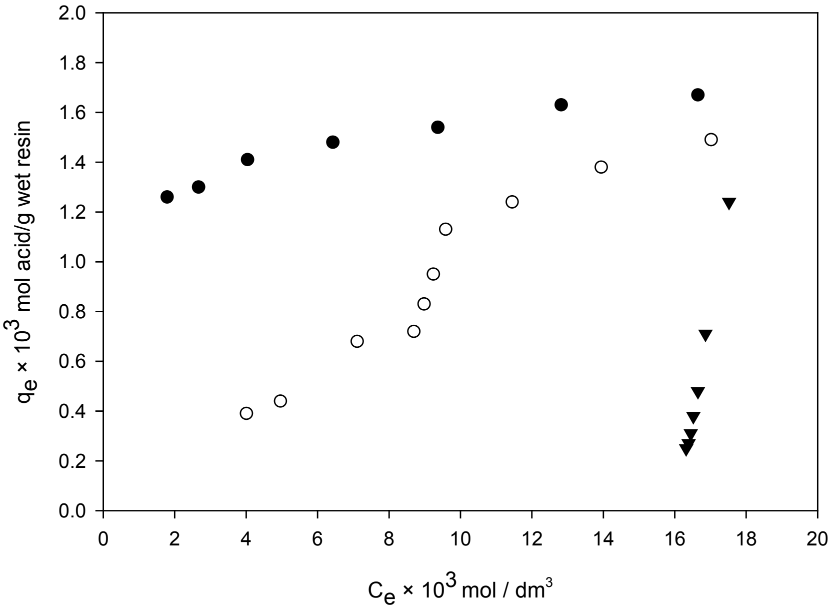


Figure 5.17. Effect of pH on equilibrium for weakly basic anion-exchange resin (MP62) with 0.02 M H_2Ta solution at three different initial pH values: ● 2.42 ○ 3.47, and ▼ 4.52 at 28 °C.

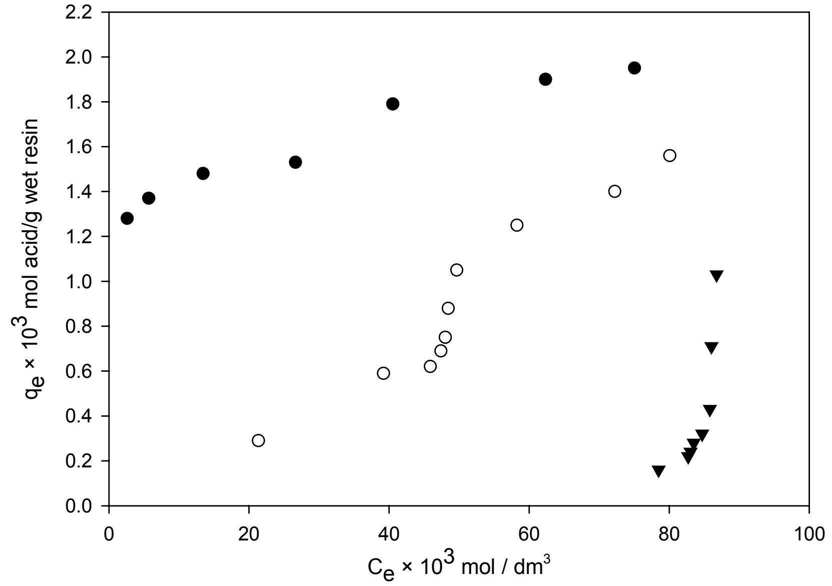


Figure 5.18. Effect of pH on equilibrium for weakly basic anion-exchange resin (MP62) with 0.10 M H_2Ta solution at three different initial pH values: ● 2.04, ○ 3.47, and ▼ 4.52 at 28 °C.

The effect of pH on the percent removal of tartaric acid by MP62 can be seen in Figure 5.19. Since the protonation of the weak base resin is an important parameter for the exchange reaction, the highest percentages were obtained for the low pH values (high H^+ concentrations). In other words, adsorption of H^+ ions, in the first step, on suitable active sites led to the removal of high amount of tartaric acid from the solution per gram resin [53]. As the initial pH of the solution increases, the percent removal of acid by the weak resin decrease [36], [37], [54]. The percent removal of acid from the solutions at 0.01, and 0.02 M concentrations are very close compared to the one at 0.10 M. For 0.01 M initial acid concentration, the percent acid removal decreased from 93.7% to 57% by the pH change 2.58 to 3.47, and 57% to 19% by the pH change 3.47 to 4.52. The similar values were obtained for the 0.02 M initial acid concentration. There is still a decrease in the percent removal of acid by MP62 for the initial acid concentration 0.10 M. However, this decrease is not as much as the ones at low concentrations. At this concentration, the acid removal decreased from 59.5% to 41.7% by the pH change 2.04 to 3.47, from 41.7% to 14.2% by the pH change of 3.47 to 4.52.

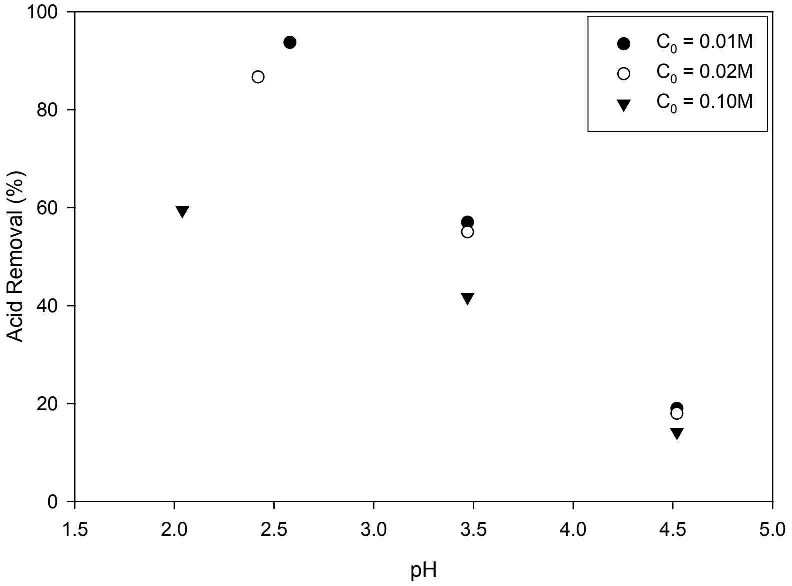


Figure 5.19. Effect of pH on tartaric acid adsorption by MP62.

5.4.2. Strongly Basic Resin – Lewatit M511

The same approach in the previous part was also followed for the investigation of the effect of pH on adsorption, for strongly basic anion exchange resin, M511. For strongly basic resin the ion exchange mechanism is different from the weak one. In strongly basic one, the active sites of the resin contain OH$^-$ ions, and these ions were exchanged with the anion of the acid in the solution.

$$\overline{R-OH} + \overline{A_s^-} \Leftrightarrow \overline{R-A} + \overline{OH_s^-} \qquad \text{(Eq. 5.3)}$$

So, as shown in the previous equation, the initial OH$^-$ concentration of the solution determines the direction of the exchange reaction for the acid-resin system. For high values of pH, the exchange reaction will shift its position to decrease the concentration of OH$^-$ ions, shift backward, to balance the effect of change in pH. As a result of this effect, the uptake of resin would decrease significantly for high values of pH. By considering these, the investigation of pH effect for strongly basic resin was performed for pH < pK_{a2}. In Figures 5.20 - 5.22 it can be seen that the M511 resin was not affected significantly as much as the weakly basic resin by the conditions pH < pK_{a1}, and pK_{a1} < pH < pK_{a2}.

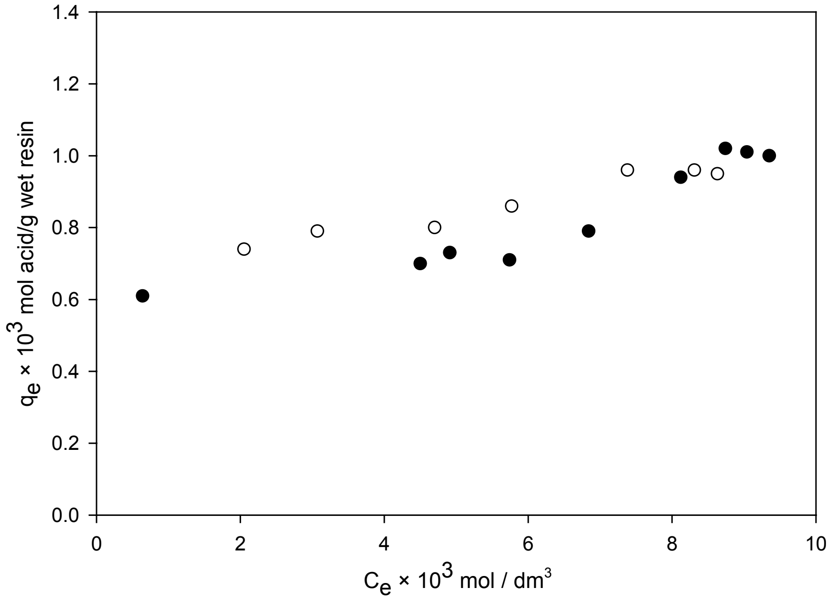


Figure 5.20. Effect of pH on equilibrium for strongly basic anion-exchange resin (M511) with 0.01 M H_2Ta solution at two different initial pH values: ● 2.58, ○ 3.47, at 28 °C.

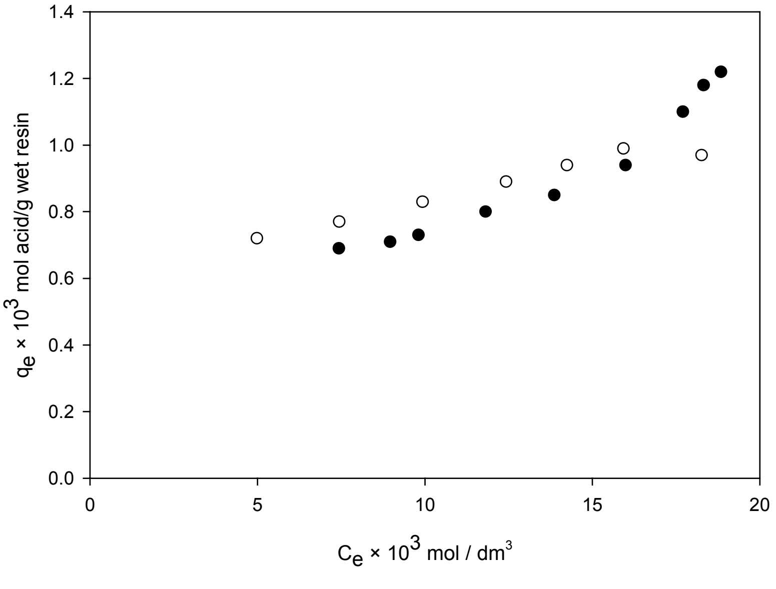


Figure 5.21. Effect of pH on equilibrium for strongly basic anion-exchange resin (M511) with 0.02 M H_2Ta solution at two different initial pH values: ● 2.42, ○ 3.47, at 28 °C.

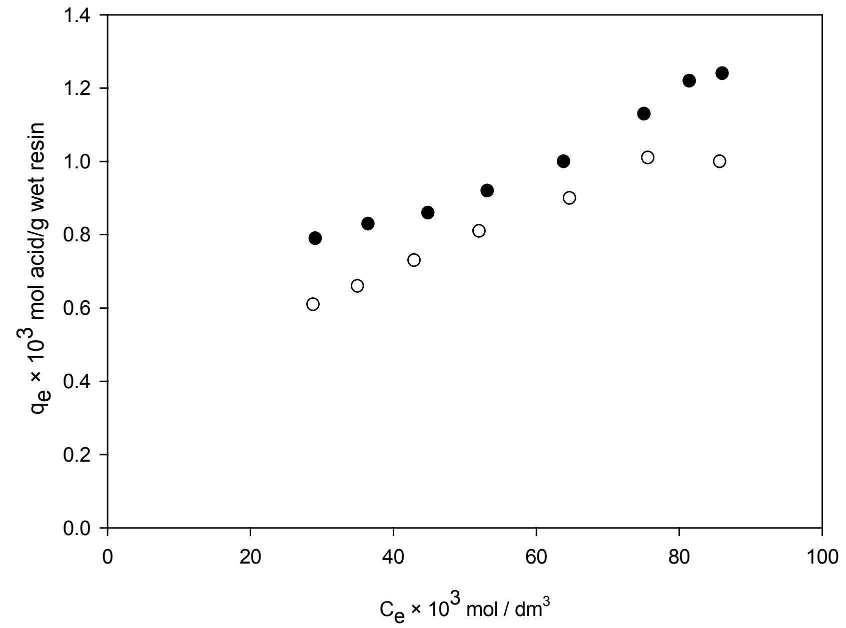


Figure 5.22. Effect of pH on equilibrium for strongly basic anion-exchange resin (M511) with 0.10 M H_2Ta solution at two different initial pH values: ● 2.04, ○ 3.50, at 28 °C.

As mentioned at the beginning of this section, the equilibrium of tartaric acid and M511 was not affected significantly by the initial pH value, for pH < pK_{a2}, of the tartaric acid solution. This means, M511 resin is less sensitive to the pH changes compared to the MP62 resin. In addition to the equilibrium isotherms, the effect of pH on the percent removal of the acid was also investigated. As shown in Figure 5.23, pH has different effect on tartaric acid adsorption by M511 rather than the MP62. The main difference is that, for M511 resin, acid removal was increased as the initial pH of the 0.01, and 0.02 M solutions increased from pH 2.58 and 2.42 to 3.50. And, higher percent removal was obtained not in the lowest acid concentration but for the initial concentration 0.02 M. The recovery increased from 55% to 63%, and reached the maximum value.

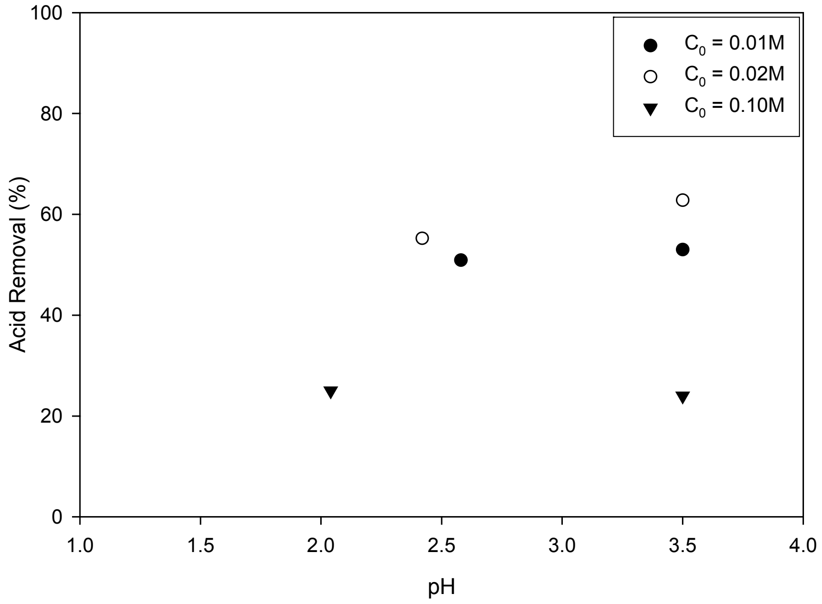


Figure 5.23. Effect of pH on tartaric acid adsorption by M511.

5.5. Isotherms

The ion exchange isotherms and the conformity to the Langmuir and Freundlich equations were verified for tartaric acid in model solutions at initial pH values (pH < pK_{a1}) and at constant temperature, 28 °C, are shown in Figures 5.24 - 5.26. The rest of the plots of the isotherms, obtained for 0.01, 0.02, 0.10 M initial tartaric acid solutions at pK_{a1} < pH, for strongly basic resins were given in Figures 5.27 - 5.29.

The conformation of isotherms with the semi-emprical models was performed by using software, SigmaPlot^{TM}, and the parameters, e.g. q_m (maximum exchange monolayer capacity), of these equations were obtained by non-linear regression applied by the program. The parameters of these semi-empirical equations for weakly and strongly basic resins are tabulated in Table 5.2, and in Table 5.3 respectively. It is apparent that the conformity for the weakly basic resin, MP62, both to the Langmuirian and Freundlichian behavior is much better at initial pH values of the solution (2.58, 2.42, 2.04). So, for the other pH values the fitting of the experimental data for these semi-empirical models are not valid and were not investigated. On the other hand, for strongly basic resin, M511, the conformity to the semi-empirical equations is much better than MP62 at initial pH values of the solution (2.58, 2.42, 2.04, and 3.50) for all initial concentrations as observed from the curve-fit correlation coefficient, R^2.

Table 5.2. Isotherm Equations.

	Langmuir Equation	Freundlich Equation
Equation	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$q_e = K_f C_e^n$

In Langmuir equation, as mentioned before, q_m is the monolayer capacity approached at large concentrations, and K_a is an equilibrium constant. The derivation of the isotherm from the experimental data assumes negligible interaction between the adsorbed molecules [52].

On the other hand, Freundlich isotherm is the classical for a heterogeneous surface. In this equation, n is a positive number and generally not an integer. For the reactions in which the ion exchange is favorable, $n < 1$, and for the ones in which the exchange is unfavorable, $n > 1$ [52]. The other isotherms used in literature, combine aspects of both the Langmuir and Freundlich equations. So, in this study these two isotherms were used for the equilibrium analysis.

Figures 5.24 - 5.26, show the Langmuir and Freundlich isotherms, also calculated model parameters and the regression coefficients are tabulated in Table 5.3 - 5.4.

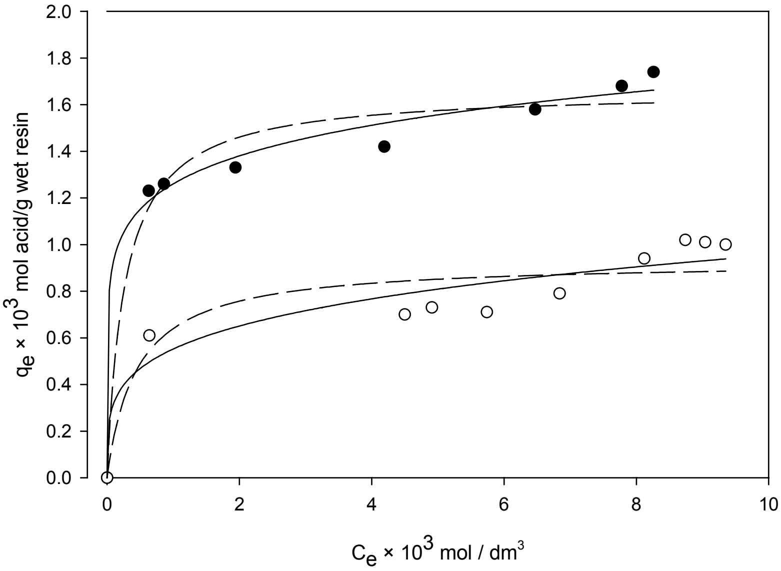


Figure 5.24. Equilibrium isotherms for adsorption of tartaric acid on ●MP62, and ○M511 resins in a 0.01 M tartaric acid solution at pH 2.58, T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

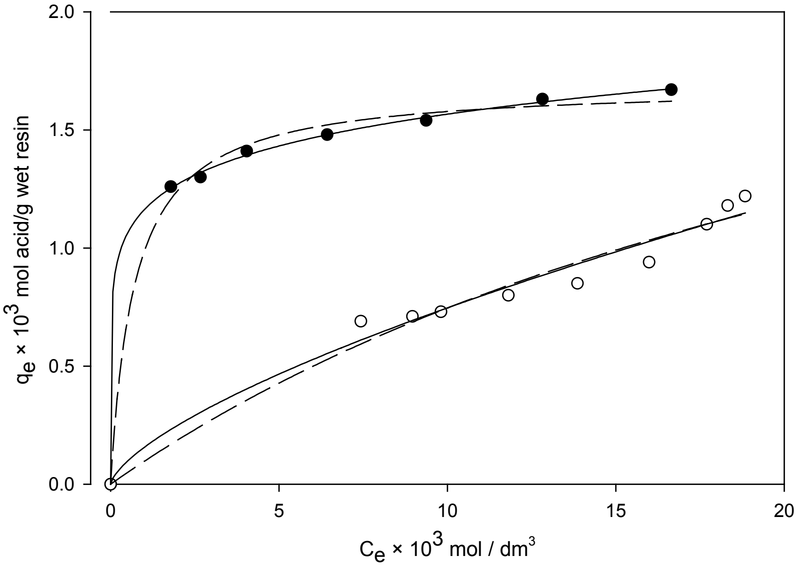


Figure 5.25. Equilibrium isotherms for adsorption of tartaric acid on ●MP62, and ○M511 resins in a 0.02 M tartaric acid solution at pH 2.42, T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

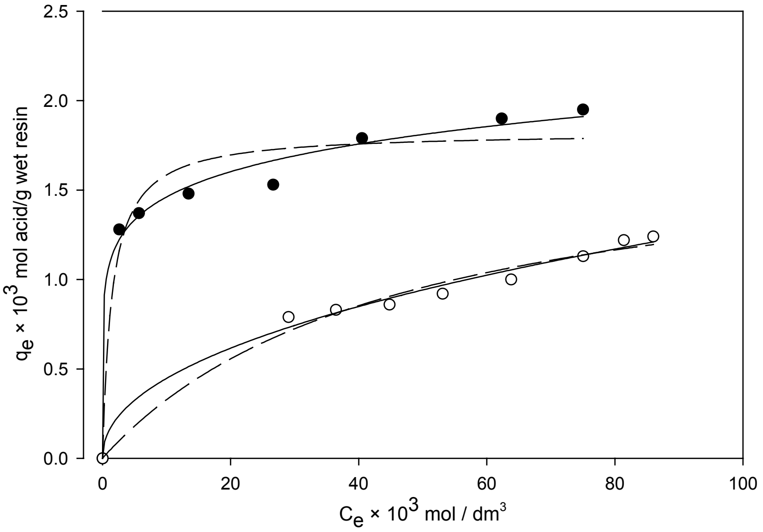


Figure 5.26. Equilibrium isotherms for adsorption of tartaric acid on ●MP62, and ○M511 resins in a 0.10 M tartaric acid solution at pH 2.04, T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

Table 5.3. Equilibrium Data of Langmuir and Freundlich Isotherms for Weakly Basic Resin – MP62.

$C_0 \times 10^3$ (mol/dm^3)	Initial PH	Freundlich			Langmuir		
		R^2	K_f	n	R^2	q_m (mol/g)	K_a (dm^3/mol)
10	2.58	0.988	1.26	0.13	0.968	1.66	3.65
20	2.42	0.999	1.16	0.13	0.995	1.69	1.39
100	2.04	0.989	1.08	0.13	0.949	1.82	0.66

When the parameters for the Freundlich and Langmuir isotherms investigated in Table 5.3, it can be seen that at low pH conditions (2.58, 2.42, 2.04) both isotherms fit well to the semi-empirical models at three different initial acid concentrations. However, when the R^2 values compared, Freundlich equation show a better representation than Langmuir equation. The n values in three different acid concentrations at low pH values show that, $n = 0.13 < 1$, the ion exchange reaction is favorable under these conditions. On the other hand, as the initial pH value of the solution increased the n values in Freundlich equation approach to unity, which means the exchange reactions became less favorable. For these unfavorable conditions for weakly basic resin at pH values higher than pK_{a1}, Langmuir and Freundlich equations did not fit to the equilibrium data as it can be observed in Table 5.3. This is because of the deviation from the ideality. So, for the MP62 resin it can be said that, the experimental data correlated with the semi-emprical equations at low total ion concentrations rather than non-ideal conditions.

The similar investigation was performed for the strongly basic ion exchange resin, M511, and the results are presented in Table 5.4. In these analyses, it can be said that the semi-empirical equations show better representation for M511 when compared with MP62. As seen in Table 5.4, the n values in Freundlich equation show that the ion exchange reactions are favorable, $n < 1$, for the given conditions. And this behavior can be observed in Figures 5.27, 5.28, and 5.29. It is also good to observe that the maximum exchange monolayer capacities, q_m, are almost same with the total capacity of M511. It can be said that the model equations for M511 gave better results when compared with the parameters obtained for MP62.

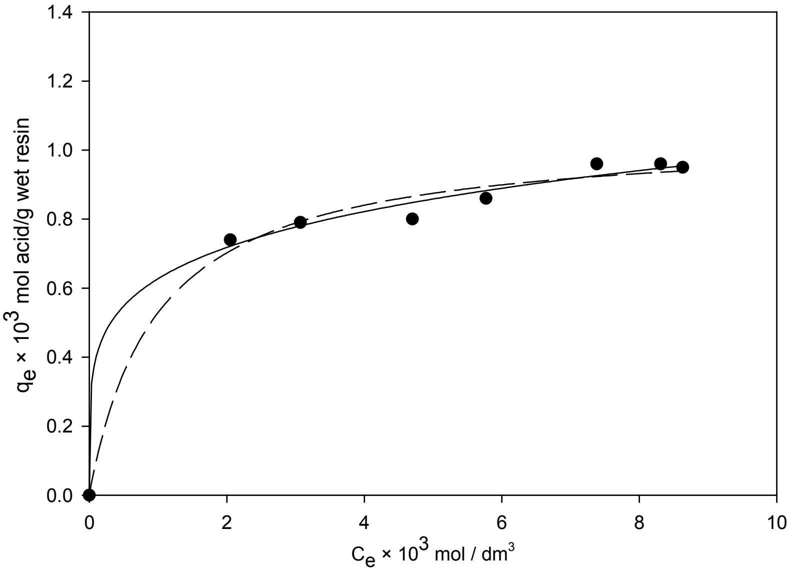


Figure 5.27. Equilibrium isotherms for adsorption of tartaric acid on ●M511 in a 0.01 M tartaric acid solution at pH 3.50, and T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

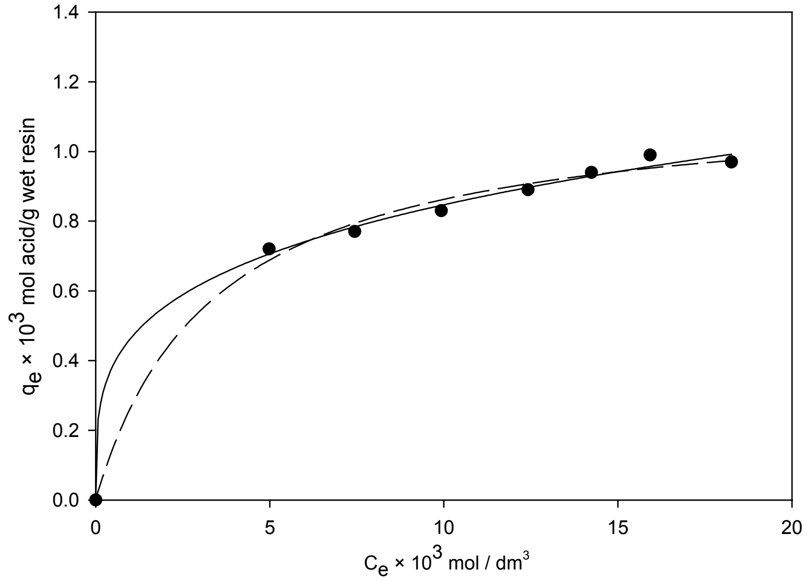


Figure 5.28. Equilibrium isotherms for adsorption of tartaric acid on ●M511 in a 0.02 M tartaric acid solution at pH 3.50, and T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

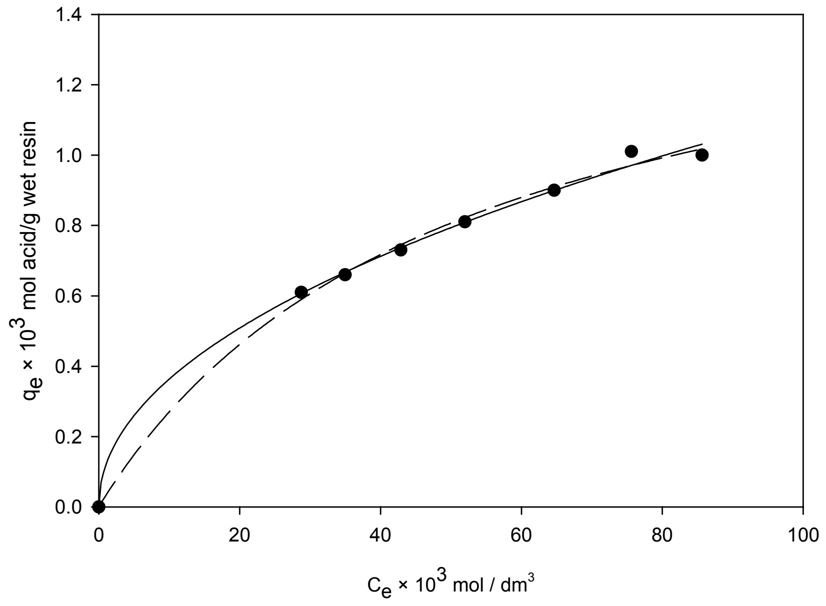


Figure 5.29. Equilibrium isotherms for adsorption of tartaric acid on ●M511 in a 0.10 M tartaric acid solution at pH 3.50, and T = 28 °C. – – Langmuir isotherm, — Freundlich isotherm.

Table 5.4. Equilibrium Data of Langmuir and Freundlich Isotherms for Strongly Basic Resin – M511.

		Freundlich			Langmuir		
$C_0 \times 10^3$	Initial pH	R^2	K_f	n	R^2	q_m (mol/g)	K_a (dm^3/mol)
10	2.58	0.911	0.55	0.28	0.846	0.93	2.21
10	3.50	0.993	0.63	0.19	0.987	1.05	1.02
20	2.42	0.971	0.16	0.68	0.964	2.89	0.04
20	3.50	0.996	0.46	0.26	0.993	1.15	0.30
100	2.04	0.988	0.15	0.46	0.980	1.84	0.02
100	3.50	0.996	0.12	0.49	0.996	1.60	0.02

CHAPTER 6

CONCLUSIONS

The single recovery of tartaric acid from the model solution by weakly, Lewatit MP62, and strongly, Lewatit M511, basic ion exchangers was investigated. The preliminary experiments showed that strongly basic resin reaches equilibrium faster than the weakly basic resin. It is 9 hours for MP62, while it is only 3 hours for M511. On the other hand, the weak resin exhibited significantly higher total capacity, q_t, than the strong one. For MP62, the total capacity was obtained 2.55 mol / g wet resin, and for M511 it was obtained 1.93 mol / g wet resin. These commercially available resins have been screened for the equilibrium analysis by considering the effect of resin basicity, initial acid concentration, and pH of the solution.

It is concluded from the experimental findings that the resin basicity has an impact on sorption equilibria. This impact becomes significant for the low pH values of the tartaric acid solutions, $pH < pK_{a1}$. At this acidity of the solution, the amount of tartaric acid that is adsorbed by the unit amount of resin was higher for MP62 than M511 for all initial acid concentrations. However, as the acidity of the solution increases, $pK_{a1} < pH < pK_{a2}$, the impact of resin basicity on equilibrium becomes less significant at different acid concentrations.

The equilibrium isotherms for single component system of tartaric acid were little affected by the low initial concentrations (C_0 = 0.01, 0.02 M) than the high initial concentration (C_0 = 0.10 M) for both of the resins. The equilibrium capacities that were obtained at low initial concentrations are nearly same for each resin, and only slightly lower than the capacities obtained at higher concentration. The ability to adsorb tartaric acid was in the order MP62 > M511 at these three concentrations.

When the percent removal of acid, at 0.01, 0.02, and 0.10 M initial concentrations, are compared with each other and with literature values, the adsorption of tartaric acid on MP62, and M511 appeared technically feasible for the given conditions. Another result of this study indicates that probably the most important parameter that affects the ion exchange equilibria is the initial pH of the solution, especially for the weakly basic resin. Since the protonation of the active sites of MP62 is the primary mechanism in the adsorption of tartaric acid, at low initial pH values ($pH < pK_{a1}$), the isotherms were found to be favorable. And, in these favorable conditions, high percent recoveries were obtained. However, as the initial pH of the solution had increased ($pK_{a1} < pH < pK_{a2}$, and $pK_{a2} < pH$), the adsorption of acid on weak resin became unfavorable at given conditions.

On the other hand, for the strongly basic resin, the ion exchange isotherms showed favorable behavior at both $pH < pK_{a1}$, and $pK_{a1} < pH < pK_{a2}$ systems. And, a decrease, on the percent removal of tartaric acid from the solution, was not observed for M511 at high initial acidity of the acid solutions.

Finally, both Langmuir and Freundlich models were able to describe the adsorption of tartaric acid on weakly basic resin for all initial concentrations (0.01, 0.02, and 0.10 M) only at $pH < pK_{a1}$, and isotherms can be expressed by these equations only at these conditions. For strongly basic resin, Langmuir and Freundlich models show better representation for the removal of acid than the weakly basic one. Especially, at these concentrations, the models fit better at $pK_{a1} < pH < pK_{a2}$ conditions.

6.1. Suggestions for Future Work

In the light of the gained experiences and findings in the present study, future research of the work can be extended with the following recommendations.

- For weakly basic resin, at high pH conditions, different semi-empirical equations can be used for the equilibrium analysis.

- A complex model starting from the mass-action law can be developed for each resin.
- Findings in this research can be used as a supplement for the experiments that could be performed with actual grape juices.

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APPENDIX A

EXPERIMENTAL DATA FOR THE TARTARIC ACID REMOVAL

Equilibrium experiments were carried out with two different: weakly basic, Lewatit MP62, and strongly basic, Lewatit M511, anionic resins. The equilibria of tartaric acid with these ion exchangers were investigated by considering three parameters; the effect of resin basicity, the total initial tartaric acid solution concentration, and pH of this solution. The solution concentrations of 0.01 M, 0.02M, and 0.10 M at their initial pH values (2.58, 2.42, and 2.04 respectively), at pH 3.57, and at pH 4.52 were prepared for the studies. Using the same amount of resins and solution volume in each run, and keeping the temperature at 28 ^{0}C in a shaker bath with an agitation rate of 200 rpm, nine equilibrium points were obtained for each resin.

A.1. Data of the Preliminary Experiments

Table A.1. Data for Equilibrium Time Analysis of MP62.

Time (h)	$[H_2Ta]\times10^3$ (mol/dm^3)	$[H_2Ta]\times10^3$ (mol/dm^3)	Average conc. (mol/dm^3)	Acid taken by the resin $\times10^3$ (mol/g wet resin)
0	29.98	29.98	29.98	0
0.50	25.19	25.21	25.20	0.57
1.00	23.60	23.55	23.58	0.77
1.50	22.28	22.29	22.29	0.92
2.00	22.36	22.35	22.35	0.92
3.00	20.47	20.52	20.50	1.14
4.00	20.11	20.06	20.09	1.19
5.00	19.63	19.61	19.62	1.24
6.00	19.47	19.45	19.46	1.26
7.00	19.37	19.33	19.35	1.28
8.00	19.36	19.38	19.37	1.27
9.00	19.17	19.17	19.17	1.30
10.0	19.14	19.10	19.12	1.30
11.0	19.22	19.22	19.22	1.29
12.0	19.18	19.21	19.19	1.29
24.0	19.14	19.16	19.15	1.30
26.0	19.21	19.17	19.19	1.29
28.0	19.07	19.05	19.06	1.31
49.5	19.31	19.32	19.32	1.28
51.8	19.27	19.27	19.27	1.29
79.0	19.16	19.17	19.16	1.30

Table A.2. Data for Equilibrium Time Analysis of M511.

Time (h)	$[H_2Ta]\times10^3$ (mol/dm^3)	$[H_2Ta]\times10^3$ (mol/dm^3)	Average conc. (mol/dm^3)	Acid taken by the resin $\times10^3$ (mol/g wet resin)
0	29.98	29.98	29.98	0
0.05	27.22	27.13	27.17	0.34
0.13	27.35	27.37	27.36	0.31
0.22	26.11	26.10	26.10	0.47
0.30	24.77	24.82	24.79	0.62
0.38	25.04	25.05	25.05	0.59
0.47	24.24	24.29	24.27	0.69
0.55	23.93	23.99	23.96	0.72
0.63	23.38	23.42	23.40	0.79
0.80	23.07	23.07	23.07	0.83
1.05	22.72	22.77	22.75	0.87
1.30	22.58	22.65	22.61	0.88
1.72	22.46	22.45	22.45	0.90
2.05	22.55	22.52	22.54	0.89
2.57	22.04	22.09	22.06	0.95
3.08	21.95	21.94	21.94	0.96
3.55	21.96	21.96	21.96	0.96
4.57	21.94	21.91	21.92	0.97
5.48	21.80	21.84	21.82	0.98
6.47	21.91	21.93	21.92	0.97
7.50	21.87	21.89	21.88	0.97
8.80	21.85	21.88	21.86	0.97

A.2. Weakly Basic Anion Exchange Resin – Lewatit MP62

The amount of tartaric acid that was adsorbed in the resin phase, qe, was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V_0}{m_w} \qquad \text{(Eq. A.1)}$$

where C_0 is the initial acid concentration in the solution, C_e is the equilibrium concentration, V_0 is the initial volume of the solution, and finally m_w is the amount of wet resin in the system.

The experimental data for the exchange reactions and the parameters derived from these data at nine equilibrium points, for weakly basic resin, are presented in Tables A.3 to A.5. The isotherms of each equilibrium points are presented in Chapter 5. The same procedure for the presentation of data was followed for the strongly basic resin in Section A.3.

A.2.1 Experimental Data

Table A.3. Raw and Calculated Data for Equilibrium Studies of 0.01 M Tartaric Acid Solution with MP62 Resin at pH 2.58, 3.47, and 4.52.

m_W	Initial pH	Final pH	V_0	$C_0 \times 10^3$	$C_e \times 10^3$	$q_e \times 10^3$
0.25	2.58	2.65	0.25	10	8.26	1.74
0.33	2.58	2.67	0.25	10	7.78	1.68
0.56	2.58	2.71	0.25	10	6.47	1.58
1.02	2.58	2.82	0.25	10	4.19	1.42
1.52	2.58	3.03	0.25	10	1.94	1.33
1.81	2.58	3.26	0.25	10	0.86	1.26
1.91	2.58	3.39	0.25	10	0.63	1.23
0.25	3.47	3.51	0.25	10	8.53	1.47
0.33	3.47	3.60	0.25	10	8.20	1.36
0.56	3.47	3.79	0.25	10	6.96	1.35
1.02	3.47	4.01	0.25	10	5.20	1.17
1.52	3.47	4.37	0.25	10	4.40	0.92
1.81	3.47	4.75	0.25	10	4.40	0.77
1.91	3.47	4.82	0.25	10	4.33	0.74
2.46	3.47	5.79	0.25	10	4.05	0.60
5.42	3.47	6.11	0.25	10	2.73	0.34
0.25	4.52	5.16	0.25	10	8.73	1.27
0.33	4.52	5.27	0.25	10	8.59	1.07
0.56	4.52	6.05	0.25	10	8.39	0.72
1.02	4.52	6.66	0.25	10	8.33	0.41
1.52	4.52	6.94	0.25	10	8.23	0.29
1.81	4.52	7.03	0.25	10	8.16	0.25
1.91	4.52	7.12	0.25	10	8.13	0.24

Table A.4. Raw and Calculated Data for Equilibrium Studies for 0.02 M Tartaric Acid Solution with MP62 Resin at pH 2.42, 3.47, and 4.52.

m_W	Initial pH	Final pH	V_0	$C_0 \times 10^3$	$C_e \times 10^3$	$q_e \times 10^3$
0.50	2.42	2.48	0.25	20	16.65	1.67
1.10	2.42	2.55	0.25	20	12.82	1.63
1.73	2.42	2.65	0.25	20	9.37	1.54
2.30	2.42	2.73	0.25	20	6.43	1.48
2.82	2.42	2.88	0.25	20	4.04	1.41
3.33	2.42	2.99	0.25	20	2.67	1.30
3.61	2.42	3.10	0.25	20	1.79	1.26
0.50	3.47	3.71	0.25	20	17.02	1.49
1.10	3.47	3.99	0.25	20	13.94	1.38
1.73	3.47	4.36	0.25	20	11.45	1.24
2.30	3.47	5.04	0.25	20	9.59	1.13
2.82	3.47	5.51	0.25	20	9.24	0.95
3.33	3.47	5.96	0.25	20	8.98	0.83
3.87	3.47	6.15	0.25	20	8.70	0.72
4.74	3.47	6.19	0.25	20	7.11	0.68
8.54	3.47	6.47	0.25	20	4.96	0.44
10.25	3.47	6.97	0.25	20	4.01	0.39
0.50	4.52	5.18	0.25	20	17.52	1.24
1.10	4.52	6.36	0.25	20	16.86	0.71
1.73	4.52	6.71	0.25	20	16.65	0.48
2.30	4.52	6.95	0.25	20	16.52	0.38
2.82	4.52	7.12	0.25	20	16.45	0.31
3.33	4.52	7.18	0.25	20	16.39	0.27
3.61	4.52	7.30	0.25	20	16.32	0.25

Table A.5. Raw and Calculated Data for Equilibrium Studies for 0.10 M Tartaric Acid Solution with MP62 Resin at pH 2.04, 3.47, and 4.52.

m_W	Initial pH	Final pH	V_0	$C_0 \times 10^3$	$C_e \times 10^3$	$q_e \times 10^3$
3.20	2.04	2.09	0.25	100	75.05	1.95
4.95	2.04	2.13	0.25	100	62.35	1.90
8.31	2.04	2.23	0.25	100	40.52	1.79
12.00	2.04	2.34	0.25	100	26.64	1.53
14.59	2.04	2.51	0.25	100	13.45	1.48
17.20	2.04	2.73	0.25	100	5.68	1.37
19.00	2.04	2.96	0.25	100	2.60	1.28
3.20	3.47	3.78	0.25	100	80.09	1.56
4.95	3.47	3.93	0.25	100	72.22	1.40
8.31	3.47	4.38	0.25	100	58.27	1.25
12.00	3.47	5.53	0.25	100	49.67	1.05
14.59	3.47	6.33	0.25	100	48.44	0.88
17.20	3.47	6.38	0.25	100	48.03	0.75
19.00	3.47	6.56	0.25	100	47.40	0.69
21.80	3.47	6.74	0.25	100	45.89	0.62
25.80	3.47	6.95	0.25	100	39.21	0.59
67.81	3.47	7.17	0.25	100	21.34	0.29
3.20	4.52	6.18	0.25	100	86.77	1.03
4.95	4.52	6.78	0.25	100	86.03	0.71
8.31	4.52	7.18	0.25	100	85.80	0.43
12.00	4.52	7.55	0.25	100	84.71	0.32
14.59	4.52	7.68	0.25	100	83.50	0.28
17.20	4.52	7.83	0.25	100	83.04	0.24
19.00	4.52	7.93	0.25	100	82.70	0.22
33.64	4.52	8.68	0.25	100	78.48	0.16

A.3 Strongly Basic Anion Exchange Resin – Lewatit M511

A.3.1 Experimental data

Table A.6. Raw and Calculated Data for Equilibrium Studies of 0.01 M Tartaric Acid Solution with M511 Resin at pH 2.58, and 3.50.

m_W	Initial pH	Final pH	V_0	$C_0 \times 10^3$	$C_e \times 10^3$	$q_e \times 10^3$
0.17	2.58	2.59	0.25	10	9.35	1.00
0.24	2.58	2.60	0.25	10	9.04	1.01
0.31	2.58	2.61	0.25	10	8.74	1.02
0.50	2.58	2.64	0.25	10	8.12	0.94
1.00	2.58	2.70	0.25	10	6.84	0.79
1.49	2.58	2.79	0.25	10	5.74	0.71
1.75	2.58	2.80	0.25	10	4.91	0.73
1.97	2.58	2.82	0.25	10	4.50	0.70
3.86	2.58	2.91	0.25	10	0.64	0.61
0.36	3.50	3.55	0.25	10	8.63	0.95
0.44	3.50	3.60	0.25	10	8.31	0.96
0.68	3.50	3.67	0.25	10	7.38	0.96
1.23	3.50	3.76	0.25	10	5.77	0.86
1.65	3.50	3.97	0.25	10	4.70	0.80
2.19	3.50	4.30	0.25	10	3.07	0.79
2.69	3.50	5.62	0.25	10	2.05	0.74

Table A.7. Raw and Calculated Data for Equilibrium Studies of 0.02 M Tartaric Acid Solution with M511 Resin at pH 2.42, and 3.50.

m_W	Initial pH	Final pH	V_0	$C_0 \times 10^3$	$C_e \times 10^3$	$q_e \times 10^3$
0.22	2.42	2.42	0.25	20	18.84	1.22
0.35	2.42	2.44	0.25	20	18.32	1.18
0.52	2.42	2.45	0.25	20	17.70	1.10
1.10	2.42	2.47	0.25	20	15.99	0.94
1.82	2.42	2.50	0.25	20	13.86	0.85
2.58	2.42	2.53	0.25	20	11.81	0.80
3.48	2.42	2.59	0.25	20	9.81	0.73
3.90	2.42	2.69	0.25	20	8.96	0.71
4.55	2.42	2.80	0.25	20	7.43	0.69
0.45	3.50	3.56	0.25	20	18.26	0.97
1.03	3.50	3.62	0.25	20	15.93	0.99
1.54	3.50	3.70	0.25	20	14.24	0.94
2.14	3.50	3.77	0.25	20	12.42	0.89
3.03	3.50	4.00	0.25	20	9.93	0.83
4.10	3.50	4.32	0.25	20	7.44	0.77
5.24	3.50	5.90	0.25	20	4.98	0.72

Table A.8. Raw and Calculated Data for Equilibrium Studies of 0.10 M Tartaric Acid Solution with M511 Resin at pH 2.04, and 3.50.

m_W	Initial pH	Final pH	V_0	$C_0\times10^3$	$C_e\times10^3$	$q_e\times10^3$
1.70	2.04	2.04	0.15	100	86.00	1.24
3.80	2.04	2.06	0.25	100	81.41	1.22
5.51	2.04	2.07	0.25	100	75.06	1.13
9.02	2.04	2.09	0.25	100	63.81	1.00
12.70	2.04	2.13	0.25	100	53.13	0.92
16.00	2.04	2.15	0.25	100	44.82	0.86
19.14	2.04	2.20	0.25	100	36.45	0.83
22.57	2.04	2.24	0.25	100	29.07	0.79
3.58	3.50	3.58	0.25	100	85.64	1.00
6.05	3.50	3.69	0.25	100	75.60	1.01
9.84	3.50	3.87	0.25	100	64.66	0.90
14.73	3.50	4.16	0.25	100	51.99	0.81
19.68	3.50	4.66	0.25	100	42.88	0.73
24.78	3.50	6.33	0.25	100	34.96	0.66
29.27	3.50	9.02	0.25	100	28.74	0.61