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ADSORPTION OF MALIC ACID IN AQUEOUS
SOLUTION BY AMBERLITE XAD-4

Dissertation submitted in partial fulfillment for the
Degree of Bachelor of Science (Health) in Forensic Science

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2009

CERTIFICATE

This is to certify that the dissertation entitled

'Adsorption of malic acid acid in aqueous solution by Amberlite XAD-4'

Is a bonafide record of research work done by

Ms. Nor Diyana bt. Md. Sani

during the period of 16th December to 30th April 2009

under my supervision.

Signature of Supervisor: ....[signature]...........................

Name and address of supervisor: Assoc. Prof. Dr. Syed Waliullah Shah
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Date: ...11/05/09......................

Dedicated to my beloved parents,

Dr. Hj. Md.Sani bin Ibrahim

And

Dr. Hjh. Junaidah bt. Osman

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In the name of Allah, the Most Gracious and Most Merciful, I thank Thee for giving me this opportunity to successfully finish this project and dissertation. Without Your divine guidance I would not have been able to complete it.

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TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

ABSTRACT

The adsorption of malic acid onto XAD-4 was studied. The effect of shaking time, pH, temperature, concentration of malic acid and amount of adsorbent on the adsorption of malic acid was investigated by batch process. It was found that the adsorption process works best at lower pH (pH 2.0) and shaking time of 75 min. The equilibrium data could be described well by Langmuir and Freundlich isotherms but the best fit is the Freundlich model based on the higher correlation coefficient (R^2) value. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were calculated. The results showe that the adsorption is endothermic, spontaneous and entropy driven respectively.

INTRODUCTION

Organic acids are organic compounds which are a class of weak acids that do not dissociate completely in water. Most organic acids are soluble in organic solvents. Examples include citric acid, tartaric acids, lactic acid, succinic acid, malic acid, fumaric acid and many more.

Organic acids are found in fruits. However, the amount may vary depending on the stage of ripening of the fruits whereby the stage before the fruit ripens has the highest amount of organic acids as demonstrated in peaches and plums (Martinex-Madrid, 2000; Garcia-Marino, 2008). They are also available in commercialized boxed juices, cordial, concentrate and wines. A study on Brazilian wines found that the wines contains several organic acids including tartaric, malic, lactic, succinic, acetic and citric acid where the concentration range of these acid vary from 300 to about 2000 mg/L (Peres *et al.*, 2009). These acids provide nutritional value to wine as well as flavor and taste to the wines. Acids like L-lactic, citric, malic and D-glucuronic acids that contain hydroxyl or carboxyl groups are produced by biological systems in animals.

Simple organic acids like formic acids or acetic acids are preferred for oil and gas stimulation treatments. This is because they are less reactive to metals since they are needed to be in contact with metal pipes for a longer time at high temperatures. Conjugate bases of organic acid like citrate and lactate are used in biologically-compatible buffer solutions. Due to the organic acids' 'weak acid nature', citric acid and oxalic acid have been used to remove rust.

Organic acids or carboxylic acids determine the acidity of fruits. These acids are responsible in giving a fruit's flavor, colour and aroma. They also inhibit the actions of enzymes and chelate metals resulting in the inhibition of chemical precipitation and oxidation (Heranandez et al., 2008). Organic acids have also been used as food preservatives. This is because organic acids are non-ionized and so are able to penetrate the bacterial cell wall and disrupt the normal physiology of certain types of bacteria that are sensitive to certain pH. Once the acid enter the bacteria, it will create a low internal pH that will subsequently impair or cease the growth of the bacteria (Brul & Coot, 1999).

Malic acid can be classified as an organic acid as well as a carboxylic acid. It has the formula $HO_2CCH_2CHOHCO_2H$ and in salt or ester form is called malate. Malic acid has the molecular weight of 134.09 g/mol. Perhaps the most popular role of malic acid or malate is as an intermediate in the citric-acid cycle. Malic acid gives the sour and tart or sharp taste to foods. Malic acid is present in many fruits and vegetables and more abundant in unripe fruits.
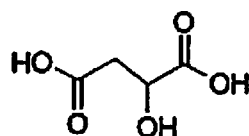

Fig.1.1. Chemical structure of malic acid

The most popular fruit to contain malic acid is apple (Rodbotten et al., 2009). Other fruits include elderberry (Sambucus nigra L.) (Veberic et. al, 2008), pineapple (356 mg/100g FW) and papaya (209 mg/100g FW) (Hernandez et al., 2009), grapes and cranberries (Volscenk et al, 2006), Damson plums (2-6 mg/g FW) (Garcia-Marino et al., 2008) and

apricots (Bureau *et al.*, 2008). Malic acid is also present in other food and drinks like wine, beer and maple syrup (Tremblay & Paquin, 2007). Malic acid provides the acidicity in wines which determines the physical, biochemical and microbial stability of wine (Volscenk *et al.*, 2006; Peres *et al.*, 2009). It is also present in beer as a result of the fermentation process during the beer manufacturing process (Nord *et al.*, 2007).

Although certain fruits may be rich in malic acid, the levels of malic acid in the fruits may vary depending on the season in which they are grown, for example, the malic acid level for white grapes cultivated in western countries for the purpose of wine production is 10 g/L in cool climates while in warmer climates the level decreases to 3 g/L. This is because malic acid level tends to decrease faster as the fruit ripens especially in warmer climates. However, this problem can be put to use as it helps to determine the best time to harvest the fruits by determining the malic acid levels in the fruits (Henick-Kling *et al.*, 1994).

Other food types that may contain malic acid include carbonated drinks, vegetable drinks, dairy beverages, sports energy drinks, iced teas, chewing gums, some types of candies, muffin, cereal, fruit bars, jams, jellies, fruit fillings, frozen desserts and ice cream. In these foods, malic acid enhances the flavour and gives them a more natural taste, prevents turbidity, balances the sweet to sour taste, masks any unpleasant taste from other ingredients, boosts aromatic flavor intensity and reduces the weight and cost of the products in general.

Malolactic fermentation is a method used to decrease the acidity of wine. This is done through the reduction of total titritable acidity and raising the pH of the wine by

changing the concentrations of L-malic and L-lactic. This process results in the softening of the wine as well as developing mellowness and full-bodiedness of the wine all of which increases the quality and taste of wine. Besides improving the taste of wine, malolactic fermentation also helps to boost the microbial stability of wine especially for stored wine (Nielson *et al.*, 1999).

Malic acid has many important benefits. These health benefits have been used by food and health product manufacturers to come up with marketable items that feature the goodness of malic acid. Malic acid has been demonstrated to be good antioxidants (Veberic *et al.*, 2008). In one study, malic acid has been added in chicken feed to maintain the intestinal activity and health of poultry (Moharrery & Mahzonieh, 2002). This is important as the animals have very limited immunity against pathogenic bacteria. By adding malic acid to the diet of poultry, it will yield healthy birds that are good to eat. Most often it is used as standards in many experiments regarding the detection of organic acids in plants and fruits (Tremblay & Paquin, 2007).

Malic acid plays an important role in human metabolism. It helps in reversing the negative effects of hypoxia. Other than being derived from various food sources mentioned earlier, malic acid is also produced in human bodies by the Citric Acid Cycle or also known as Krebs Cycle. This cycle occurs in the mitochondria which utilizes oxygen for cellular respiration and thus produces energy in anaerobic and aerobic conditions. This aerobic sequence converts lactic and pyruvic acids from anerobic glycolysis through a series of steps to carbon dioxide and water. This cycle uses oxygen transported to the cells by haemoglobin.

During the complete oxidation of one molecule of glucose, 36 molecules of ATPs are produced (Sackheim & Lehman, 1994).

Malic acid's key role is the production of energy in the form of NADH or the equivalent of 2.5 ATPs through the malate-aspartate redox shuttle in the electron transport chain. In anaerobic conditions, malic acid removes the accumulation of reducing equivalents through its reduction to succinate and oxidation to oxaloacetate. This allows it to reverse the inhibition of glycolysis by hypoxia (Chang & Tong, 2003).

After endurance training, an athlete's muscles were found to contain 50% increase in malate-aspartate redox shuttle enzymes where malate plays the key role. In eukaryotes, when there is a demand for energy in the form of ATPs, there is also a high stipulate for malic acid (Russel et al., 1995). Therefore, various products have been manufactured which contain malic acid or people who want to maximize their energy production so that they can perform better in sports and exercise. There are also studies which indicate that malic acid together with magnesium will combat problems with hypoxia. Consequently, scientists have found a correlation between malic acid and magnesium deficiencies with fibromyalgia which is characterized by chronic widespread pain to the muscles and connective tissues whereby a simple touch to the skin would bring extreme pain to the sufferer (Abraham & Flechas, 1992).

Extensive research has been done on malic acid and found that it is non-toxic, non-mutagenic and even showed to be able to bind and remove aluminum from the brain. Malic acid has been described as having a clean, smooth, mellow and persistent tart taste. When

added in commercialized beverages, it enhances the fruity flavours by prolonging their

release resulting in longer taste bud stimulation which is translated to the brain as a stringer

fruit flavor. Furthermore, malic acid has a longer tart sensation than citric acid which helps

to mask the unpleasant tastes of other nutrients added in a health food and beverage

products (Albion Research Notes, 2003).
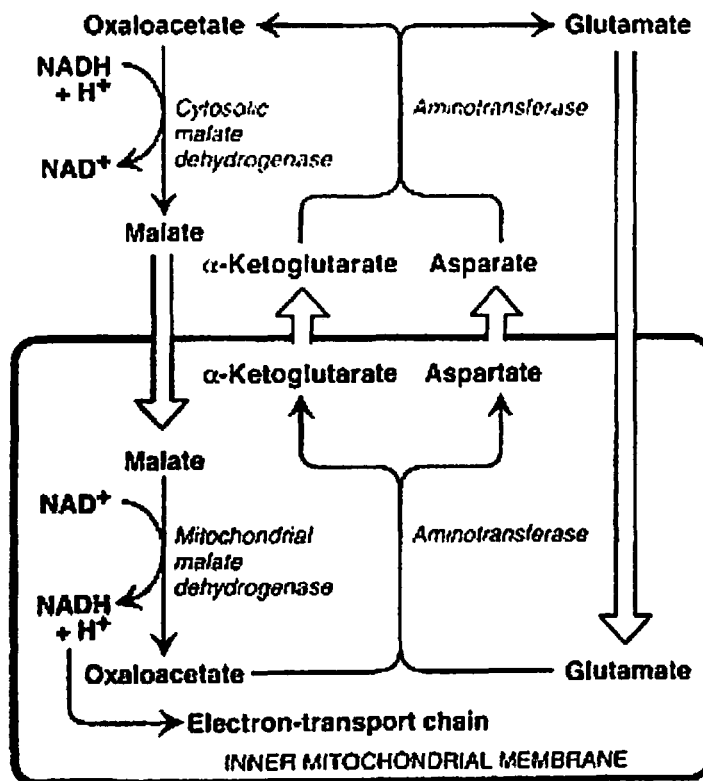
Fig. 1.2. Production of energy in the form of NADH in mitochondria

3-carbon Pyruvate

NADH ⌐
NAD+ ↵ → 1-carbon CO2

2-carbon Acetyl-CoA

4-carbon
Oxaloacetate

6-carbon Citrate

NAD+ ⌐
NADH ↵

6-carbon
Isocitrate

4-carbon
L-Malate

The
Citric Acid
Cycle

→ 1-carbon CO2

NAD+ ⌐
NADH ↵

5-carbon Ketoglutarate

4-carbon
Fumarate

→ 1-carbon CO2

NAD+ ⌐
NADH ↵

FAD ⌐
FADH2 ↵

4-carbon
Succinate

4-carbon
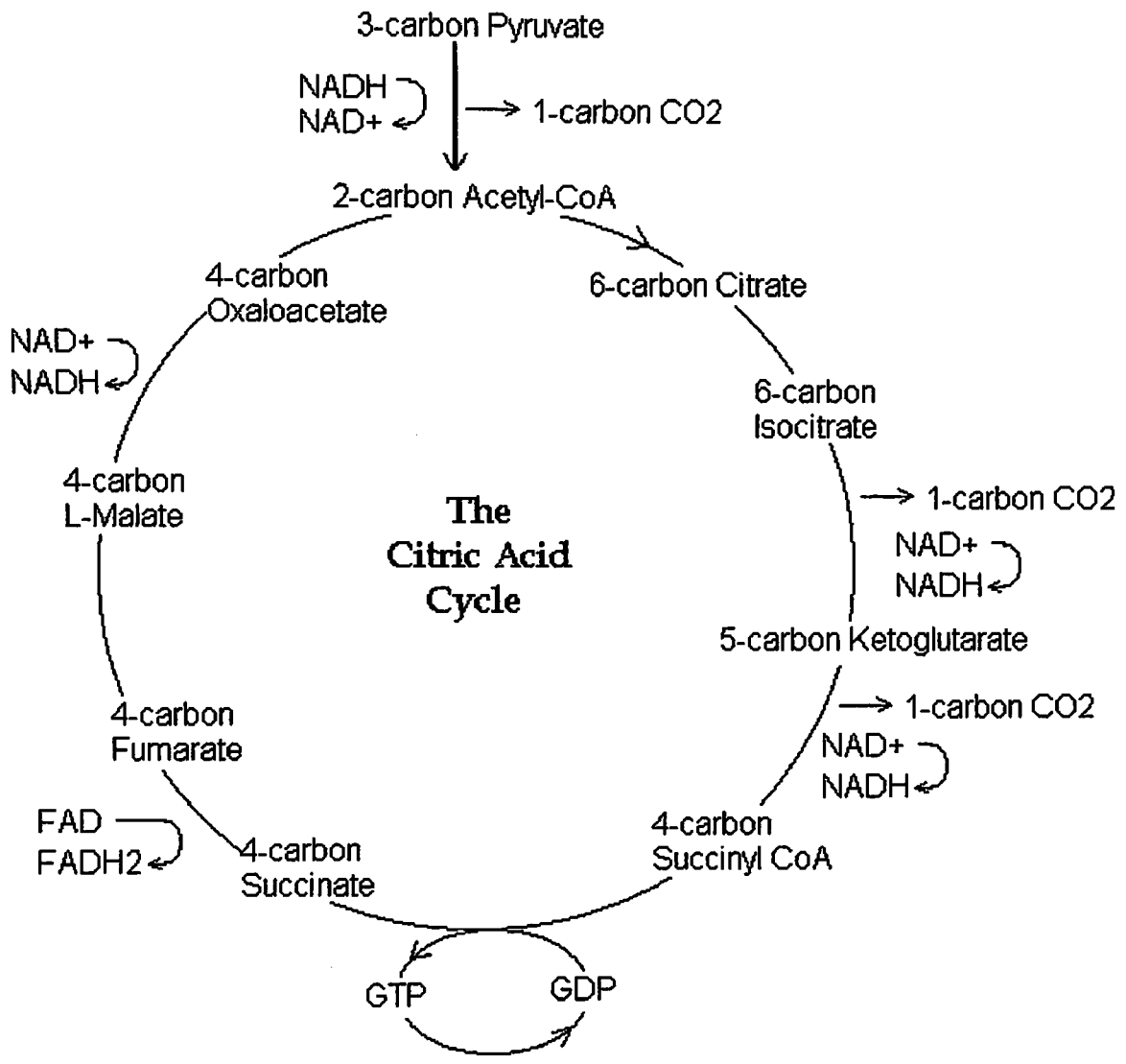Succinyl CoA

GTP   GDP

Fig.1.3. Citric Acid Cycle

LITERATURE REVIEW`

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of an adsorbent which is a solid. This action results in the formation of a thin film of atoms on the adsorbent surface called adsorbate. On the other hand, absorption occurs when a substance diffuses into a liquid or solid forming a solution.

XADs are a form of adsorbents or rather sorbents. The species that are bonded to the surface of the sorbents are called adsorbates or sorbates. These resins are categorized as synthetic porous polymeric sorbents. They are considered better than activated carbon in terms of adsorption due to their higher physicochemical properties and their capabilities of being regenerated (Xu et al., 2003). Amberlite XAD resins are manufactured by Rohm and Haas company. There have been many XADs produced like XAD-1, XAD-2, XAD-4, XAD-7, XAD-8, XAD-10, XAD-11, XAD-12, XAD-14, XAD-16, XAD-2000, XAD-2010 and many more.

The adsorption ability of the resins is attributed to their porous structures, specific surface areas and surface properties. The forces that bond the resins to adsorbates are found to be Van der Waals forces and the electron-donating ability of the functional groups on the resin surfaces particularly carboxyl and hydroxyl groups with electron accepting sorbates (Qiu & Ling, 2006). These polymeric adsorbents exhibit hydrophobic properties. It is widely used in a few countries to treat industrial effluent because of its efficient removal and can be reused (Zhang et. al., 2007).

According to the Rohm and Haas company brochure, Amberlite XAD polymeric adsorbents are very porous spherical polymers. They have high internal surfaces which can

adsorb and desorb an extensive list of compounds and species. Generally the adsorbents are divided into the hydrophobic polymers and the hydrophilic polymers. The hydrophobic polymers can adsorb soluble organic species in polar solvents like water. This behaviour is seen mostly in styrenic adsorbents. On the contrary, hydrophilic polymers adsorb species which are more polar in non-polar solvents like hydrocarbons. This is observed in acrylic and phenolic adsorbents.

According to the company, there are a few guidelines in choosing the right polymeric adsorbent for a study or application. Firstly, it depends on the nature of the solvent as mentioned before. The next guideline is the functionality of solute which can be divided into class I and class II. Class I consists of solutes with aromatic rings while class II consists of solutes whose structure is saturated with C-C bonds like proteins and peptides. The next factor is polarization where the ease of the solute to be polarized must be determined. Lastly the size of the species desired to be adsorbed must be of a suitable size. In this context, small species are of the size of <1000 D while big species must have the molecular weight of >10000 D.

There are generally two types of adsorbents: bioadsorbents produced from natural resources and synthetic adsorbents. The Amberlite XAD resins are synthetic polymeric adsorbents. Many plants, bacteria and wastes haves been used to design bioadsorbance. Naturally, the bioadsorbents are much preferred due to their low cost production and environmentally friendly nature. However, not all biosorbents are as effective as the manufactured synthetic adsorbents.

Examples of biosorbent produce by researchers all around the world include olive pomace wastes are the residues left after olives have been used in the food industry which are especially abundant in the Mediterranean. This biosorbent has been demonstrated to successfully adsorb copper from metal contaminated water (Francesca *et al.*, 2008). Another example of biosorbent is one made from durian rind pectin which was produced by scientists from Malaysia using durian wastes which are abundant during the durian season. This biosorbent has also been excellent in adsorbing heavy metals from water (Wong *et al.*, 2008). Another common fruit in Malaysia is Tamarind that was also used to produce a biosorbent capable of adsorbing heavy metals from water. Here tamarind fruit shells were utilized to adsorb hexavalent chromium from water (Popuri *et al.*, 2007). Another example of plant material used for bioadsorbent is the use of soy meal hull for the removal of acid dyes from water (Arami *et al.*, 2006). For the removal of yet another type of acid dye which is the Acid Violet 17 dye, a biosorbent was prepared from sunflower seed hull (Thinakaran *et al.*, 2008).

Other than plant materials, bacteria have also been manipulated to be made into biosorbents. *Streptococcus equisimilis, Bacillus coagulans and Escherichia colli* to adsorb chromium has been reported by Quintelas *et al.* Another study was conducted producing biosorbent from marine microalgae to adsorb heavy metals and other wastes from water due to its function in seawater (Kaewsarn, 2002; Wang *et al.*, 2008; Ncibi *et al.*, 2008).

There have not been many literature and research on the use of Amberlite XAD resins to adsorb organic acid. However, a study conducted on Chile mountain papaya has utilized XAD-7 to adsorb organic acid from its pulp. After elution with MeOH, the eluent was

11

analyzed using HPLC and found to contain about 20 organic acids including polyphenols, flavanoids and carotenoids (Simirgiotis *et al.*, 2009).

Amberlite XADs have been used to adsorb a variety of organic materials including trace metals. XAD-2000 have been used to adsorb cobalt, copper, nickel and cadmium (Duran *et al.*, 2009). XAD-2 has demonstrated capability of adsorbing various atmospheric pollutants like poly aromatic hydrocarbons (PAHs) which is present in the environment due to thermal smelting of recyclable aluminum cans (Wei, 1995) and also organophosphorus compounds (OCPs) (Nerin *et al.*, 1995), nitrogen oxides from fossil fuel combustion (Hanson et. al, 2009) and many more. XAD-16 was also used to adsorb trace metals like lead, cobalt, copper chromium and in water samples (Wuilloud, 2002; Tokalioglu, 2002).

XAD-4 has been reported to have better adsorbent properties compared to other XADs like XAD-7 and XAD-16 when adsorbing phenols from water (Kujawski *et al.*, 2003). XAD-4 has been reported to be a useful adsorbent to a wide range of aromatic compounds (Zhang *et a.l*, 2007).Trace heavy metals like cadmium, cobalt, mangan, nickel, lead and nickel in environmental samples (Kara et. al, 2005: Baytak & Turker, 2003), anionic dyes (Qiu & Ling, 2006), polyaromatic hydrocarbons in water (Fernandez-Sanchez, 2003), 4-chlorophenol (Bilgili, 2006), the removal of lanthanum and gadolinium from nitrate medium (El-Sofany, 2008) and many more.

The designated application of XAD-4 is for the removal of aromatic hydrocarbons such as phenolsaws and pesticides from wastes. It is a hydrophobic polymer so it can adsorb

organic species in polar solvents. Since it has a high surface area and small pores it is ideal for the extraction of smaller molecules like phenols.

In packing columns where the samples are passed through glass columns of selected height and diameter followed by the elution of the column by selected solvents. A little bit of glass wool were placed at the ends of the column. The eluents were then analyzed (Kara *et al.*, 2005; Baytak & Turker, 2003). In fixed bed column where stainless steel column packed with XAD-4 was connected to a reciprocating pump. The sample is passed through the column at a certain flow rate at contact time. The effluents from the column were then quantitatively analysed (Zhang *et al.*,2007).

XAD-4 adsorb the most anionic dyes at pH 1.9 and at high pH its adsorption is reduced due to the electrical repulsion between the dyes and deprotonated or negatively charged groups on the resin surface (Qiu & Ling, 2003). In another study, XAD-4 was found to be most efficient at pH 9.0 when adsorbing samples containing cadmium ions (Shahtaheri, 2005).

In a study done by contacting dimethyl phthalate, an organic compound used as plasticizer in polyvynil chloride (PVC)- based plastics, found that an increase in contact time increases the percentage of sorption onto the XAD-4 up to 100 minutes (Zhang *et al.*, 2007).

RESEARCH OBJECTIVES

1. To study the effects of pH, shaking time, temperature, concentration of adsorbate and amount of adsorbent on the adsorption of malic acid onto XAD-4.

2. To assess the thermodynamics of the adsorption process.

3. To apply the data obtained onto two isotherm models and determining the best fit.

MATERIALS AND METHODS

Chemicals and Reagents

Spectroscopic or chromatographic grade chemicals and reagents were obtained from Merck/ Fluka (Germany) and Sigma (Germany). Malic acid with the chemical name hydroxybutanedioic acid standard was purchased from Sigma-Aldrich (Belgium). The chemicals were used as received or otherwise stated. The Amberlite XAD-4 resin was purchased from Sigma-Aldrich (Germany) and has the surface area of $725m^2/g$ and an average pore diameter of 40 Å.

Preparation of Glass ware

The glass ware was soaked in 10% nitric acid overnight and then washed thoroughly using distilled water. The glass ware was then dried in an oven at 105°C.

Purification of Amberlite XAD-4 Resin

Amberlite XAD-4 resins were washed and prepared as described previously (Bilgili, 2006). The Amberlite XAD-4 resins were transferred into a pre-cleaned and dried 500 mL capacity beaker. A Whatman 42 filter paper was folded to form a cone shape and placed inside the mouth of a pre-cleaned and dried filter funnel. An amount of XAD-4 was placed onto the filter paper inside the filter funnel's mouth. The resins were then washed with deionized water and methanol several times to remove any inorganic impurities. This was followed by washing with acetone several times and rinsing for 12 hours. Finally, the resins were allowed to dry at 60°C in an oven for 24 hours prior to use.

Preparation of Malic acid standard

Malic acid solution (100 ppm) was prepared by dissolving an accurately weighed amount of 25 mg malic acid in 250 mL double distilled water into a 500mL volumetric flask producing a 100 ppm acid solution.

UV-Visible Spectrophotometer

The UV-Visible spectrum of the 0.1M malic acid solution was measured and recorded using Varian Carry 100 UV-visible spectrophotometer. The wavelength for malic acid were found to be 212 nm. The absorbance value of malic acid was also measured before and after pH adjustments. The instrument was calibrated earlier with $KMnO_4$ solution to check its absorbance and wavelength accuracy.

Batch Adsorption Studies

Batch adsorption experiments were carried out as described previously (Bilgili, 2006; El-Sofany, 2008). The malic acid solution was adjusted to pH 2.0, 4.0, 6.0 and 8.0 with a standard pH meter where each pH contains 250mL of malic acid. Hydrochloric acid and sodium hydroxide were used to adjust the pH. The absorbance of each pH was measured using the UV-visible spectrophotometer and taken down as initial concentration, C_0.

Accurately measured 0.5g of Amberlite XAD-4 resin was added to eight 250mL conical flasks containing 25mL of malic acid solution each. The flasks were shaken on a Heidolph Intsrument Rotamax 120 shaker at 25 ° C and constant speed of 120rpm. Every 15 minutes one flask is taken and the contents were filtered before the supernatant was

16

measured for its absorbance value using UV-visible spectrophotometer. This is continued for every 15 minutes until 120 minutes is reached. This method was repeated for pH 2.0, 4.0, 6.0 and 8.0.

The percentage of malic acid uptake by Amberlite XAD-4 resins was calculated by the percentage difference between the initial concentration/absorbance and concentration/absorbance at every 15 minutes over the initial concentration a. A graph was plotted to better see the maximum uptake or adsorbance of malic acid by the Amberlite XAD-4 resins.

After plotting the graphs for % adsorption, the suitable pH and shaking time were observed and selected to be used as constants to investigate the effects of three other parameters affecting the adsorption properties of the malic acid. The parameters are temperature, concentration of malic acid solution and amount of adsorbents. The procedure as described above will be repeated but at the constant optimum temperature and shaking time for temperatures of 25° C, 35° C and 45° C. It will also be repeated for the amount of adsorbents of 0.5 g, 1.0 g, 1.5 g and 2.0 g and also for the concentration of malic acid solution at 100 ppm, 150 ppm and 200 ppm.

The amount of malic acid retained in the resin designated as q_e (mL/g) was calculated using the relation:

$$q_e = C_o - C_e \times \frac{V}{M}$$

C_o and C_e are the initial and equilibrium concentrations of the malic acid in the solution respectively. V is the volume of solution (mL) and M is the weight (g) of the Amberlite XAD-4 resins.

The distribution coefficient (K_d) of the malic acid ions between the aqueous phase and the resin phase was calculated from the relation:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{M}$$

The data from the results were then applied to thermodynamic formulas and two isotherm models to see the best model that will explain the adsorption process of malic acid to Amberlite XAD-4 resins.

$$\frac{initial\ absorbance, Co}{absorbance, Ce} \times 100$$

RESULTS AND DISCUSSION

The effects of shaking time, pH, and amount of XAD-4, concentration of malic acid solution as well as effect of temperature were studied. The effects of shaking time and pH were examined first with other parameters like concentration of malic acid, temperature and amount of XAD-4 taken as constants. When the optimum shaking time and pH was obtained, the values were then selected for the next parameter study. The optimum pH and shaking time was determined from the time and pH with highest % adsorption calculated from the formula.

From this the percentage adsorption, q_e or equilibrium solid phase concentration with the unit mL/g is calculated. This value indicates the amount of malic acid retained on the XAD-4 adsorbents. Other than that the distribution coefficient or K_d of malic acid between the aqueous phase and the resin phase was calculated. All calculations were also recorded on plots to observe the trends that the values follow.

Determination of Wavelength

Before running the samples in the UV-Visible spectrophotometer, the wavelength for malic acid must first be measured. This is done by running malic acid at 0.01M in the instrument at a set wavelength range of 200 nm to 400 nm. Malic acid showed the highest absorbance peak at 212 nm. The wavelength of 212 nm was chosen for this study.

Effect of Shaking Time

The values of % absorbance , K_d and Q_e were all recorded in the tables 1, 2, 3 and 4. Note that C_o is the initial concentration while C_e is the equilibrium concentration at each minute. The value of K_d and Q_e were also included in the tables.

From the plot % adsorbance versus shaking time at pH 2.0, 4.0, 6.0, and 8.0 (fig. 5.1.), the trend is an increase in % adsorbance as contact or shaking time increases. From time 0 to about 75 minutes, there is a gradual increase in % adsorbance. After 75 minutes, the % adsorbance becomes stable with only a slight increase or decrease in % adsorbance. This shows that after 75 minutes equilibrium is slowly being reached. At equilibrium, the amount of malic acid ions retained on the resins are saturated and so there is not enough space for more ions to be retained on the resins. Another reason is no more ions are left in the solution since almost all of the ions have been adsorbed onto the resin. Therefore, it can be stated that the optimum shaking or contact time of malic acid with XAD-4 at a constant temperature of 25°C, 0.5g XAD-4 and malic acid concentration of 0.1M is 75 minutes at wavelength of 212 nm.

Table 1: Effect of shaking time at pH 2 and $C_o = 0.0535$

Time (min)	Absorbance (C_e)	Adsorption %	C_o-C_e	$q_e= (C_o-C_e)V/M$ (mL/g)	$K_d= q_e/C_e$ (Distribution coefficient)
15	0.0376	29.72	0.0159	0.795	21.1436
30	0.0358	33.08	0.0177	0.885	24.7207
45	0.0304	43.18	0.0231	1.155	37.9934
60	0.0290	45.79	0.0245	1.225	42.2414
75	0.0277	48.22	0.0258	1.29	46.5704
90	0.0270	49.53	0.0265	1.325	49.0741
105	0.0267	50.09	0.0268	1.34	50.1873
120	0.0267	50.09	0.0268	1.34	50.1873

Table 2: Effect of shaking time at pH 4 and $C_o = 0.0355$

Time (min)	Absorbance (C_e)	Adsorption %	C_o-C_e	$q_e = (C_o-C_e)V/M$ (mL/g)	$K_d= q_e/C_e$ (Distribution Coefficient)
15	0.0238	32.96	0.0117	0.585	24.5798
30	0.0231	34.93	0.0124	0.62	26.8398
45	0.0203	42.82	0.0152	0.76	37.4384
60	0.0198	44.22	0.0157	0.785	39.6464
75	0.0195	45.07	0.0160	0.80	41.0256
90	0.0189	46.76	0.0166	0.83	43.9153
105	0.0188	47.04	0.0167	0.835	44.4149
120	0.0189	46.76	0.0166	0.83	43.9153

Table 3: Effect of shaking time at pH 6 and $C_o = 0.0412$

Time (min)	Absorbance (C_e)	Adsorption %	C_o-C_e	$q_e = (C_o-C_e)V/M$ (mL/g)	$K_d = q_e/C_e$ (Distribution coefficent)
15	0.0259	37.14	0.0153	0.765	29.5367
30	0.0233	43.45	0.0179	0.895	38.4120
45	0.0229	44.42	0.0183	0.915	39.9563
60	0.0226	45.15	0.0186	0.930	41.1504
75	0.0221	46.36	0.0191	0.955	43.2127
90	0.0222	46.12	0.019	0.95	42.7928
105	0.0215	47.82	0.0197	0.985	45.8140
120	0.0215	47.82	0.0197	0.985	45.8140

Table 4: Effect of shaking time at pH 8 and $C_o = 0.0430$

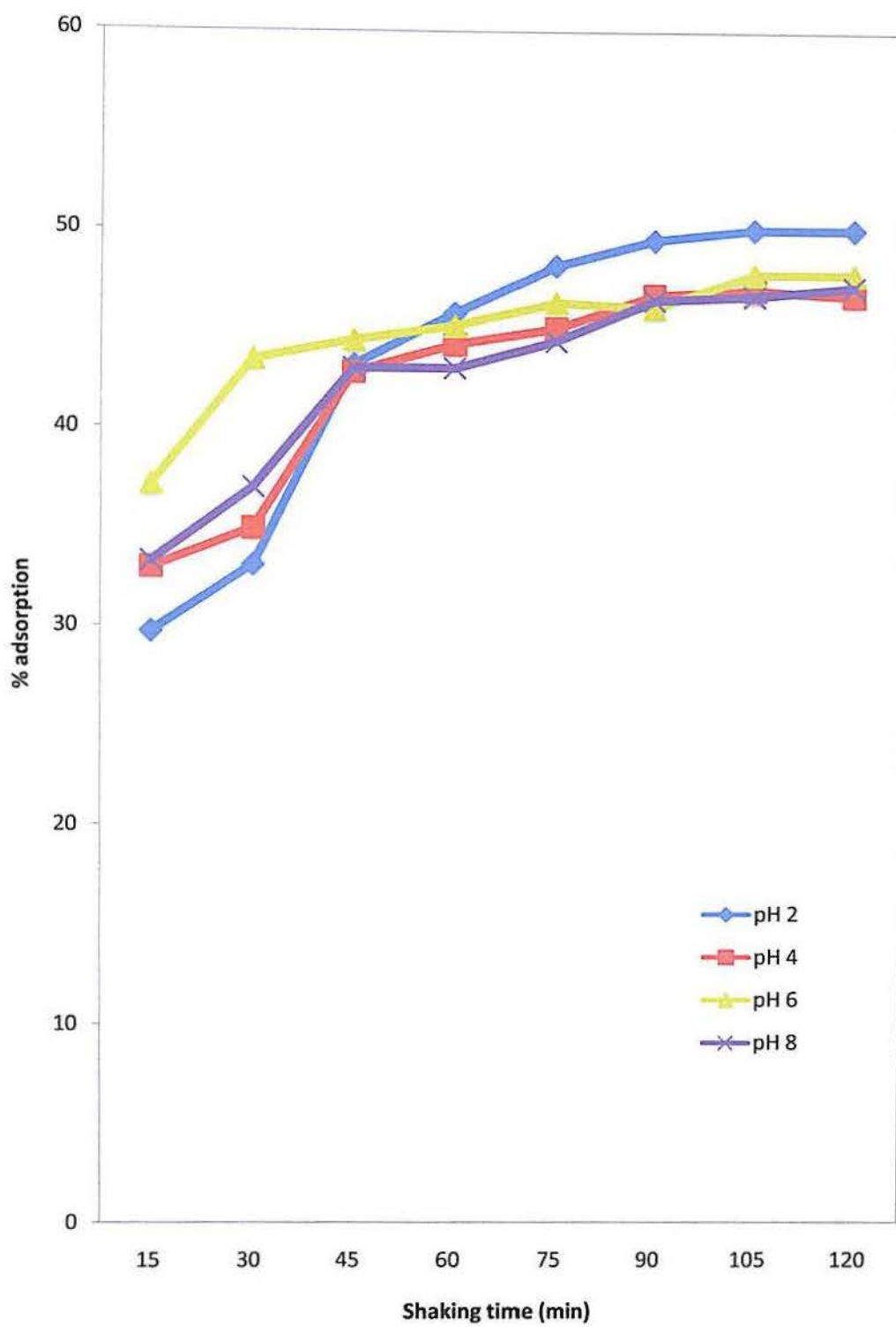| Time (min)	Absorbance (C_e)	Adsorption %	C_o-C_e	$q_e = (C_o-C_e)V/M$ (mL/g)	$K_d = q_e/C_e$ (Distribution coefficent)
15	0.0287	33.26	0.0143	0.7150	24.9129
30	0.0271	36.98	0.0159	0.7950	29.3358
45	0.0245	43.02	0.0185	0.9250	37.7551
60	0.0245	43.02	0.0185	0.9250	37.7551
75	0.0239	44.42	0.0191	0.9550	39.9582
90	0.0230	46.51	0.0200	1.0000	43.4783
105	0.0229	46.74	0.0201	1.0050	43.8865
120	0.0227	47.21	0.0203	1.0150	44.7137

Fig. 5.1. Plot of adsorption % vs shaking time (min)

The graphs of q_e and K_d as a function of time were plotted in fig. 5.2. and 5.3. respectively. As with the % adsorption, all plots displayed a trend of gradual increase up to 75 minutes followed by a decline or slight increase in q_e or K_d values. From these graphs the slight increase and decrease in % adsorption were exaggerated when the values were converted to q_e and K_d values. However, the optimum shaking of 75 minutes still remain the same in all graphs.

The values of q_e depict the amount of malic acid ions retained on the surface of XAD-4. As observed from the graphs, even though the optimum shaking time is at 75 minutes, the amount of malic acid ions retained was different at each pH. This shows that pH also plays a role in the amount adsorbed. However, this matter will be discussed in the following pages under the effects of pH.

K_d is calculated and plotted onto graphs to see the distribution coefficients of malic acid ions in the aqueous solution and the adsorbance layer. Distribution coefficient or partition coefficient can be defined as the ratio of concentration of malic acid retained on the XAD-4 adsorbents to the concentrations of malic acid ions in the aqueous solution. A high K_d value indicates that there are more malic acid ions retained on the resin surface compared to ions left in the solution. From the graphs, it is observed that with increasing time, the amount of ions on the resins are also increasing and at 75 minutes the most amount of ions are retained on the adsorbent surface. At equilibrium, the ratio becomes stable with only slight decrease or increase in the values.