

Citric acid concentration by electrodialysis: ion and water transport modelling

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Abstract

The work in this paper was aimed at the study of the ion transport behaviour of citrate ion through ion exchange membranes. A mathematical model to represent the ion and water transport behaviour of an electrodialysis (ED) process for concentrating citric acid under the influence of different current density was developed. This model is valid for any ED process with ion exchange membranes used under a similar operating condition. The value for the phenomenological coefficients is different for other types of membranes and solutes. The corresponding phenomenological coefficients have to be determined experimentally. The reliability of developed ion and water transport model was assessed through comparison with the experimental data. The results obtained showed that the developed ion and water transport model was in good agreement with the experimental data and it could be used to predict the performance of ED for citric acid concentration. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electrodialysis; Ion exchange membranes; Current density; Citric acid; Ion and water transport

1. Introduction

Citric acid is widely used in the field of pharmaceuticals, foods, cosmetics and other chemical products. As such the world market of citric acid is growing every year, and the production is estimated at 5×10^8 kg per year [1,4]. In particular, there is an increasing use of sodium citrate in washing formulations. Sodium citrate is used as builder and buffering agent in liquid detergents to replace the tetrapotassium pyrophosphates, which has become a global concern for the environment [2].

Citric acid is produced by fermentation or by chemical synthesis. The production cost in the chemical synthesis of citric acid is economically not feasible. Citric acid is recovered from the fermentation broth by a series of separation steps such as filtration, precipitation, acidification, evaporation, crystallisation and drying [3]. In the case where citrate salt is the desired product, the purified citric acid is reacted with sodium hydroxide to form a salt. According to Novalic et al. [4] and Moresi and Sappino [5], approximately 2.5 tons of calcium sulphate is produced as by-product per ton of monohydrated citric acid produced.

A number of processes for citric acid recovery from fermentation broth without precipitation have been studied, for example, the solvent extraction method [6]. The solvent extraction process reduced the processing step and waste generation. However, the solvent tend to extracts some of the impurities in the

Abbreviations: AEM, anion exchange membrane; CE, current efficiency; CS, concentrating stream; CEM, cation exchange membrane; DS, diluting stream; ED, electrodialysis

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Nomenclature

A and B	ion transport rate constant
C_c	citric acid concentration in the concentrating stream
C_d	citric acid concentration in the diluting stream
C_c^t	concentration at time $t = t$ in the concentrating stream
C_c^0	concentration at time $t = 0$ in the concentrating stream
C_d^0	concentration at time $t = 0$ in the diluting stream
dV/dt	slope of the variation of volume of concentrating stream with time
E1 and E2	electrode rinsing solution
F	Faraday constant
i	current density
I	current intensity
$n_{\text{citric}}^c(t)$	moles of citric in the concentrating stream at time $= t$
$n_{\text{citric}}^c(0)$	moles of citric in the concentrating stream at time $= 0$
Δn	amount of the salts being transferred
Q_F	amount of the electrical charges carried by the current that expressed in Faraday
S	effective area ion exchange membrane
t	time
V_c^t	concentrating stream volume at time, t
V_c^0	concentrating stream volume at time, 0
<i>Greek letters</i>	
α and β	phenomenological coefficients

fermentation broth especially in the molasses-based fermentation media. A detail review on the recovery of citric acid from the fermentation broth using classical method and solvent extraction method can be found in Pazouki and Panda [1].

Another alternative processing technique is by the use of electrodialysis (ED), which offers effective

removal of non-ionic molecules, concentrate the product and generate low by-product. Voss [9] published an article in 1986 on the deacidification of citric acid solution by ED. Since then, the ED technique has been tested using different types of ED membranes such as monopolar [7,8,10] and bipolar [11] membranes.

The objective of this paper is to present the development of a mathematical model to describe the ion and water transport behaviour in concentrating citric acid using ED with ion exchange membranes.

2. Experimental

The citric acid solution was concentrated using ED under the influence of electrical driving force. The ED unit comprised of 10 anion exchange membranes (AEMs) and 10 cation exchange membranes (CEMs) was supplied by Ionics Inc., USA. The effective membrane area of each cell pair was 0.0232 m². The total effective membrane area for the stack was 0.464 m². The membranes were bound to one end by an anolyte compartment and an anode, while the other end was connected to a catholyte compartment and a cathode. In the anolyte compartment, a platinised titanium anode was installed and for the cathode, stainless steel was used. The heavy cation membrane, adjacent to the anode and the heavy anion membrane, adjacent to the cathode were used to prevent water loss. The solution flowing through the cells was regulated by spacer gasket to ensure a sheet flow was obtained. The inter-membrane spacer was 1.02 mm thick. The electrode spacer was 2.04 mm thick.

The ED process involved three independent streams: diluting stream (DS), concentrating stream (CS), and electrode rinse stream. In the electrode compartments, 0.3 M sodium sulphate solution was used. Four peristaltic pumps were used to circulate the process streams and the electrode streams. Masterflex[®] pump heads 7017 and 7018 (Cole Parmer, USA) were used for the electrode streams and process streams, respectively. The ED system was operated in a batch re-circulation mode. The flow rate of the DS and of the CS was maintained at 500 ml/min. A power supply (Lineguard, USA), that serves as a regulator for the direct current (dc) source for the stack. It could supply the current in the range of 0–20 A and the voltage in the range of 0–40 V.

The effect of water transport and current density was studied during the ED of citric acid. Analytical grade citric acid solution was prepared by dissolving the citric acid crystal (J.T. Baker, USA) in deionised water. The initial concentration of citric acid for both diluting and CS were set as 0.11 M and the trials were carried out at different constant current densities (216, 345 and 432 A/m²). The citric acid concentration variation in the DS and CS was determined by titration method at every 15 min intervals. The volume variation for the DS and the CS was determined by using a graduated cylindrical tanks as mentioned by Moresi and Sappino [7].

Periodic cleaning of the ED stack was carried out to remove film or scale formed on the membrane surfaces during processing. The membranes were cleaned-in-place by recirculating a 0.05 M HCl solution for 15–30 min, followed by a 0.05 M NaOH solution and acid solution. The stack was rinsed thoroughly with deionised water after the treatment.

3. Results and discussion

3.1. Water transport model

When electricity was applied to the ED electrodes, all positively charged ions (cations) move towards the cathode (negative electrode) and all negatively charged ions (anions) move towards the anode (positive electrode). The CEMs with fixed negative charges allow the transport of cations such as proton or sodium ion to pass through them, but rejecting anions. Conversely, AEMs with fixed positive charges only allow the transport of anions such as hydroxyl or citrate ion to pass through. It was found that when the ions migrated from the DS to the CS, water molecules were also transported through the ion exchange membranes. The water molecules were transported as a result of electro-osmosis, which is due to the flow of electrical charges through the membranes and osmosis. Osmosis occurs as a result of the increase of citrate ion concentration in the CS.

In citric acid concentration process, there are two performance indicator of the process; the current efficiency (CE) of the citrate ion transport from the DS to the CS and the maximum concentration of the citric acid that could be obtained. The maximum

Table 1
Results of processing 0.11 M citric acid solution

	Trial		
	T-1	T-2	T-3
Current density (A/m ²)	216	345	432
Time (min)	90	90	90
Concentrating stream			
C_c^0 (M)	0.11	0.11	0.11
C_c^t (M)	0.18	0.20	0.21
V_c^0 (ml)	1500	1500	1500
V_c^t (ml)	1615	1657	1677
Diluting stream			
C_d^0 (M)	0.11	0.11	0.11
C_d^t (M)	0.01	0.01	0.01
V_d^0 (ml)	1500	1500	1500
V_d^t (ml)	1384	1346	1323

concentration obtained in the CS was twice of the initial concentration as shown in Table 1. These parameters especially the concentration of the citric acid in the CS is directly influenced by the present of water transport through the AEMs and CEMs.

The amount of the water transported was investigated and the results are plotted in Fig. 1. Graph of straight lines for different current density was obtained. This means that the amount of water transferred from the DS to CS is directly proportional to the current density applied. The slopes of the straight lines as in Fig. 1, was obtained by linear regression on the experimental data.

The transport rate data are tabulated in Table 2. The data represents the water transport rates at different current density for the DS and the CS. As expected, the algebraic sum of the water transport rate for the DS and CS is approximately equal to zero. This was an indication on the reliability of the experimental procedure used.

Based on the understanding of this water transport mechanism, a mathematical expression was developed to represent the water transport behaviour. The current density is defined as ampere (A) applied per unit square meter (m²) of the membrane surface area [12]. The water transport trend from the DS to the CS is expressed in form of Eq. (1):

$$V_c^t = V_c^0 + \Delta V_c \quad (1)$$

where V_c^t is the volume of the CS at time t , V_c^0 the initial volume of the CS and ΔV_c the volume of

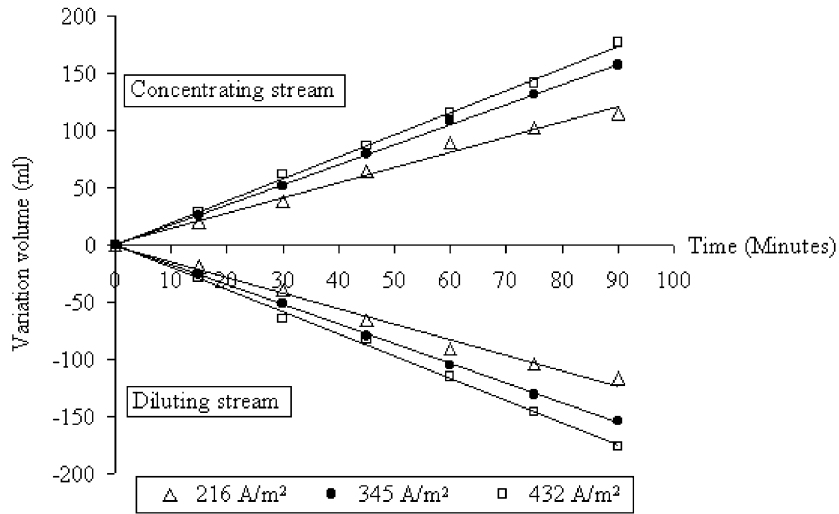


Fig. 1. Water transport profile for different current densities as a function of time.

water being transported from the DS to the CS. The final volume of the CS is the summation of initial volume and the volume transported from the DS to the CS.

In this particular case, the initial concentration was set at a constant value. The main purpose was to set a similar initial concentration for the water transport phenomenon investigation. This is important for all the lines as shown in Fig. 1 to have a similar intersect point at the y-axis. It was convenient to compare these lines under a similar initial condition. A first-order polynomial linear equation of the type $y = mx + c$ could be written as in Eq. (2).

$$V_c^t - V_c^0 = a't \quad (2)$$

The term V_c^t represents the volume in the CS, at time t . Intersect point at the y-axis indicates the initial

volume in the CS, V_c^0 and the slope of the linear line is represented by term a' . Term t represents the time.

The relationship between the water being transferred and the time is shown in Fig. 1. The rate of water transport could be evaluated from the slope (dV/dt). As was observed the amount of the water being transferred was directly proportional to the current density. A relationship between the water transport rate and the current density could be formed. This is done by plotting the water transport rates values (dV/dt) as a function of the current density as shown in Fig. 2.

Table 2

The water transport rate at different current density for the diluting stream and the concentrating stream

Current density (A/m^2)	Water transport rate for diluting stream (m^3/h)	Water transport rate for concentrating stream (m^3/h)
216	-8.28×10^{-5}	8.04×10^{-5}
345	-10.74×10^{-5}	10.68×10^{-5}
432	-10.98×10^{-5}	10.98×10^{-5}

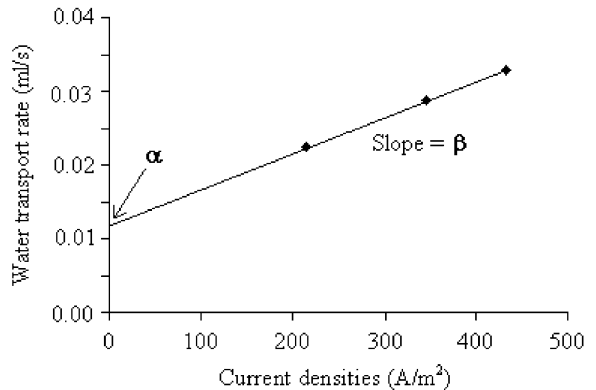


Fig. 2. The relationship between the water transport rate and the current densities.

A straight line is obtained as shown in Fig. 2. This linear line intersects at the y-axis, which indicates the water transport rate is not equal to zero when no current was applied.

$$\frac{dV}{dt} = b'i \quad (3)$$

The term b' represents the slope of the linear line as shown in Fig. 2. The term i represent the current density. Eq. (3) relates the water transport rate in term of the current density.

Rearrange and differentiate Eq. (2) to obtain Eq. (4).

$$\frac{d(V_c^t - V_c^0)}{dt} = a' \quad (4)$$

The summation of Eqs. (3) and (4) yields Eq. (5).

$$\frac{d(V_c^t - V_c^0)}{dt} + \frac{dV}{dt} = a' + b'i \quad (5)$$

Let $V = V_c^t - V_c^0$, then Eq. (5) becomes Eq. (6).

$$2\frac{dV}{dt} = a' + b'i \quad (6)$$

Eq. (6) represents the properties of the lines in Fig. 1 as well as in Fig. 2. This equation integrates the volume of the CS as a function of time and current density. Setting the initial time $t = 0$ and the initial volume equal to V_c^0 . Eq. (6) is integrated to form Eqs. (7) and (8).

$$\int_{V_c^0}^{V_c^t} dV = \int_{t=0}^t \left(\frac{a'}{2} + \frac{b'}{2}i \right) dt \quad (7)$$

$$V_c^t - V_c^0 = \left(\frac{a'}{2} + \frac{b'}{2}i \right) t \quad (8)$$

Let $a'/2 = \alpha$ and $b'/2 = \beta$, then Eq. (8) become Eq. (9)

$$(V_c^t - V_c^0) = (\alpha + \beta i)t \quad (9)$$

By rearranging Eq. (9), a linear equation as Eq. (1) is obtained.

$$V_c^t = V_c^0 + (\alpha + \beta i)t \quad (10)$$

The term ΔV_c in the Eq. (1) could be replaced by the term $(\alpha + \beta i)t$. The term $(\alpha + \beta i)t$ represents the amount of the water being transferred from the DS to the CS. Both α and β terms are called phenomenological coefficients.

3.2. Ion transport model

3.2.1. Current efficiency (CE)

The CE is related to the number of moles of an electrolyte transported from the DS to the CS across the ion exchange membrane. The migration of electrolyte is caused by the passage of electrical charges. The amount of the electrical charges is expressed in Faraday [13]. The amount of the ions transferred was evaluated by measuring the changes in the concentration of citrate ions in the product stream (CS). Under constant current conditions, the CE of citric acid ED could be defined by the Eq. (11).

$$CE = \frac{\Delta n}{Q_F} \quad (11)$$

The term Q_F is the amount of the electrical charges carried by the current expressed in Faraday. Its relationship is defined as in Eq. (12).

$$Q_F = \frac{It}{F} \quad (12)$$

The term I is the current intensity. It is defined as the current density (i) multiply with the effective membrane area (S). The effective membrane area of the ED system used in this work was equal to 0.464 m² for 20 cell pairs. The term F stands for Faraday constant, which is 96500 C/mole. Term Δn is defined as the difference in the number of moles of citric acid in the CS at time t ($n_{\text{citric}}^c(t)$) and at the initial stage ($n_{\text{citric}}^c(0)$).

Under constant current conditions, the CE of citric acid is defined by Eq. (13).

$$CE = \frac{[n_{\text{citric}}^c(t) - n_{\text{citric}}^c(0)]F}{It} \quad (13)$$

At any time t , $n_{\text{citric}}^c(t)$ could be determined from the citric acid concentration profile in the CS as given in Fig. 3 by multiplying the value with the amount of water transferred under similar condition.

Expression of ($n_{\text{citric}}^c(t)$) in term of (V_c^t) and (C_c^t) is obtained as Eq. (14).

$$n_{\text{citric}}^c(t) = V_c^t C_c^t \quad (14)$$

Similarly, the initial number of moles citric acid in the CS ($n_{\text{citric}}^c(0)$) is defined as the initial volume in the CS multiplying by the initial citric acid concentration. Both initial volume as well as the initial

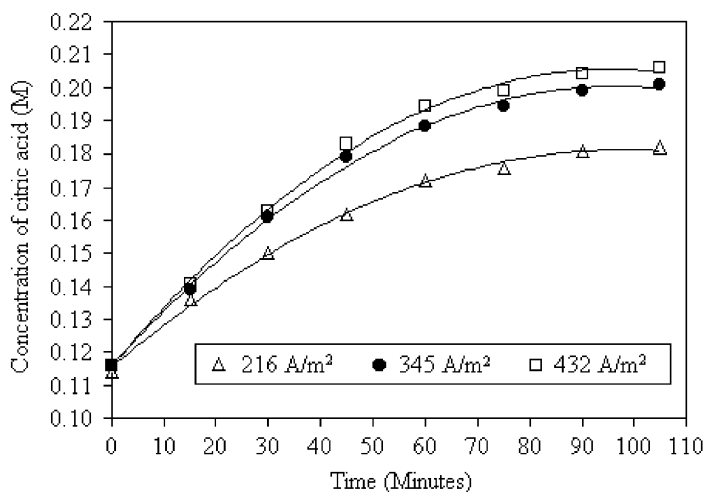


Fig. 3. Tabulated experimental data of citric acid concentration profile in the concentrating stream for various constant current densities.

concentration is obtained from Figs. 1 and 3, respectively. The relationship of $(n_{\text{citric}}^c(0))$ is expressed as in Eq. (15).

$$n_{\text{citric}}^c(0) = V_c^0 C_c^0 \quad (15)$$

The effect of water transport on the CS should be considered in CE determination. Thus, Eq. (11) was modified to include all the terms involved. A complete relationship of CE is shown as in Eq. (16). This equation is used in the CE calculation.

$$\text{CE} = \frac{[C_c^t V_c^t - C_c^0 V_c^0] F}{It} \quad (16)$$

3.2.2. Determination of current efficiency

As shown in Eq. (16), when the values of current I increases the CE decreases. This phenomenon resulted from the chemical potential difference between the diluting and CS. The electrotransport of co-ions leakage also affect the loss in CE [4].

Fig. 4 shows the result of the CE as a function of citric acid concentration difference between the CS and the DS when the initial citric acid concentrations in both streams were equal $C_c^0 = C_d^0$. From Fig. 4, it was observed that the experimental data could be plotted on a straight line. This means that the CE obeys a simple mathematical equation:

$$\text{CE} = A - B(C_c^t - C_d^0) \quad (17)$$

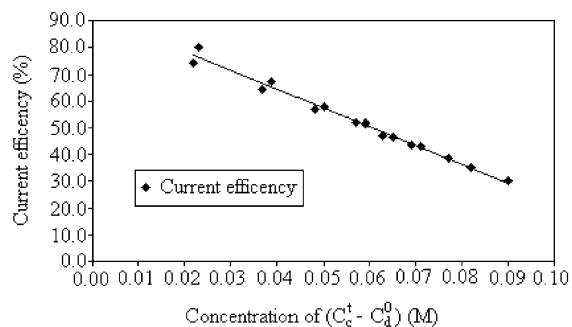


Fig. 4. Electrodiagnosis current efficiency as a function of citric acid concentration difference between the CS and the DS when the initial citric acid concentrations in both streams were equal $C_c^0 = C_d^0$.

From Eq. (17), the term A is the intersect value on the y-axis of the graph in Fig. 4. Meanwhile, term B represents the slope value of the linear line. In this study, both terms A and B are called as ion transport rate constants.

As both Eqs. (16) and (17) express the CE of the system, both equations could be solved simultaneously in order to eliminated term CE that appear in the equation. Therefore, these equations were rearranged in term of concentration of the CS at time t (C_c^t). Through this method, a new ion transport model was developed as illustrated in Eq. (18). The rate of the

Table 3

Overall phenomenological coefficient of water transport and ion transport rate constant for citric acid for different concentration of the concentrating stream

Initial citric acid concentration of the concentrating stream	Phenomenological coefficients		Ion transport rate constant	
	α ml/s	β (ml cm ²)/A s	A M/A s	B (A s) ⁻¹
Condition of $C_c^0 = 0$	0.035	0.545	0.020	0.243
Condition of $C_c^0 = C_d^0$	0.013	0.467	0.044	0.314

ion transfer was evaluated base on the concentration in the CS.

$$C_c^t = \frac{[A + BC_d^0]It + C_c^0 V_c^0 F}{V_c^t F + BIt} \quad (18)$$

From Eq. (18) V_c^t represent the volume of the CS as a function of time. It indicates the water transport behaviour through the ion exchange membranes. Eq. (18) was expended further by substituting the water transport model of Eq. (10) to obtain an equation of ion transport model as expressed in Eq. (19). The rate of ion transport was determined by evaluating the citric acid concentration in the CS at any time t .

$$C_c^t = \frac{[A + BC_d^0]It + C_c^0 V_c^0 F}{V_c^0 F + (\alpha + \beta t)tF + BIt} \quad (19)$$

Eq. (19) describes the behaviour of concentration process of citric acid by using ED. This equation is a general equation that represents the ion transport behaviour of the ED system. Different in ion exchange membrane as well as different solutes would affect the

value of constant A and B . Therefore, these constants should be determined experimentally for different ion exchange membranes and solutes used.

Based on the phenomenological coefficient as shown in Table 3, the developed ion transport rate model could be used to calculate the concentration profile of ED process for citric acid.

3.3. Water and ion transport model reliability test

In order to verify the developed water transport model which represents the actual behaviour of the ED system, the calculated values were then compared with the collected experimental data. Both calculated as well as experimental results are plotted in graph as shown in Fig. 5.

Fig. 5 compares the results of the experimental and the calculated values of water transport for different current density. The graph shows a good agreement between the experimental and calculated results. This indicates that the developed water transport model

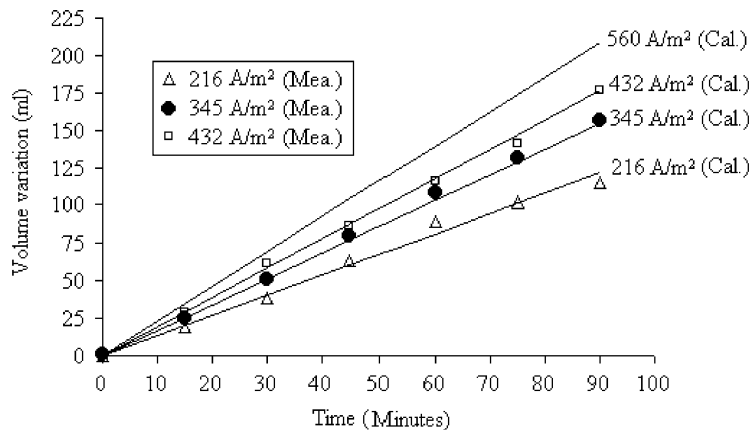


Fig. 5. Measured (Mea.) and calculated (Cal.) results of water transport for different constant current densities.

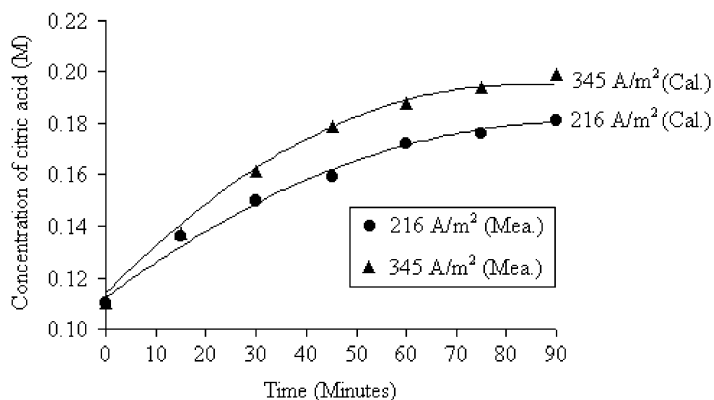


Fig. 6. Variation results between both calculated (Cal.) and measured (Mea.) data for citric acid concentration at current densities of 216 and 345 A/m² in the case of $C_c^0 = C_d^0$.

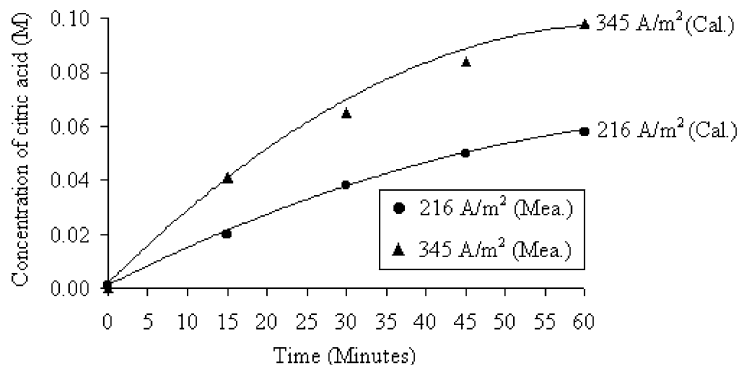


Fig. 7. Variation results between both calculated (Cal.) and measured (Mea.) data for citric acid concentration of 216 and 345 A/m² in the case of $C_c^0 = 0$.

(Eq. (10)) is reliable to describe the actual water transport behaviour for this ED system. This model could also be used for the prediction of other condition for water transport phenomena operation under similar operating condition. For example, the behaviour of the graph to predict water being transferred at current density of 560 A/m², a straight line with the higher slope was obtained.

In order to assess the reliability of the ion transport rate model, the calculated results were also compared with the measured experimental data. Both calculated and measured results for each condition are plotted in Figs. 6 and 7. From both Figs. 6 and 7, the calculated results for the amount of the ions being transferred are almost identical with the experimental results. Thus,

the developed ion transport model is reliable and it express the actual behaviour of the ED system.

4. Conclusions

The models developed for both water transports as well as ion transport were the general models for monopolar ion exchange membrane ED process. Both models valid for ion exchange membrane used under a similar operating condition. The values for the phenomenological coefficients are different for different types of membranes and solutes. The corresponding phenomenological coefficients have to be determined experimentally. The developed models were found

reliable based on the estimated results, experimental data as well as simulation results. The model developed produce estimated results that were converge with both experimental data and the simulation data. The ion transport model could further be modified for the optimisation study of the ED system.

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