Investigation of Breakthrough Curves of Citric Acid Adsorption

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Abstract

In this paper, experimental breakthrough curves for citric acid adsorption from aqueous solution onto ion-exchange resin at 20, 35, 55 °C have been obtained by some weak and strong basic anionic resins such as, IRA-92, IRA-93, IRA-420 and IRA-458. The results show that amberlite IRA-93 has good performance and is one of the best resins in recovery process of citric acid from aqueous solution. Also, temperature effect study show that an increase in temperature causes an increase in diffusion coefficient of particles, but the saturation capacity of resin decreases. To achieve appropriate model, three mathematical models have been analyzed to predict system properties based on statistical tests and finally, appropriate model have been determined. To examine model capability, mathematical equations have been implemented in various breakthrough curve data obtained by other investigators and the results show appropriate conformity.

Key words: Adsorption, Breakthrough Curves, Modeling, Citric Acid.

1. INTRODUCTION

Citric acid is the most widely used organic acid in the field of foods and beverages as an acidulant as well as in pharmaceutical and chemical products. It is generally produced by surface or submerged fungal fermentation mainly with aspergillus niger. However, the highest citric acid production has been obtained with the submerged fermentation method\(^1\)-\(^2\). Citric acid is typically purified by a firmly established process known as the method of
calcium salt precipitation. Citric acid can be separated from fermentation broths by a series of precipitation and isolation reactions using Ca(OH)₂ and H₂SO₄⁴. However, this process contains several batch treatments, which require large amounts of chemical reagents and a considerable amount of heat. These negative factors have directed many investigators to find new techniques to separate or purify citric acid from fermentation broths such as adsorption and electro-dialysis⁵-⁶.

Electro-dialysis as an electrochemical separation process charged membranes electrically. For separation of ionic species from aqueous solutions, electrical potential difference is used. The electro-dialysis was used in citric acid recovery. However, the main problem is costs of this technique were determined to be approximately 50% more in comparison with that of current industrial citric acid recovery process. The use of electro-dialysis requires the development of new processes to decrease waste formation and enhance productivity⁷.

Purification of organic acids particularly citric acid by adsorption process has lower production costs in comparison with that of other methods. Newly using synthetic ion-exchange resins in separation and purification of organic acids has paid attention⁸-⁹. This set of adsorbent act selectively and other component of solution remain intact. After saturation of solid adsorbent at the end of a separation operation period, its recovery is done by elution with water, acid or base. Although the principle of organic acids separation by ion-exchange method has known, but there are many details that requires development and increment. Thus, it seems that Simulated Moving Bed (SMB) by using chromatography method on the base of countercurrent continuous contact between feed and adsorbent is appropriate and effective¹⁰-¹¹.

SMB is a continuous chromatographic method which requires determined parameters like ion-exchange resins properties, adsorption equilibrium data and operation characteristics of bed. One of the best methods to specify and optimize operating parameter is preparing fitting
mathematical model from actual processes. Generally in such models, mass transfer in liquid layer outside the resin particles is negligible. The general ion-exchange reaction of resin is presented in equation 1 12-14.

\[ R-N + CH_n \leftrightarrow R-NH^{+}CH_{n+1} \]  \hspace{1cm} (1)

For acids with more than one carboxyl group and also for R-N in the equation 1 base resins are appropriate 15.

Estimation of breakthrough curves is required for successful design of an adsorption column. For a fixed-bed randomly packed adsorption column in which is fed from the top of the bed at a constant flow rate by an aqueous solution containing an organic pollutant, the mass transfer balance equation for predicting fixed-bed dynamics is 16-19:

\[ \varepsilon \frac{\partial C}{\partial t} + U_0 \left( \frac{\partial C}{\partial Z} \right) + (1 - \varepsilon) \left( \frac{\partial q}{\partial t} \right) = D_p \left( \frac{\partial^2 C}{\partial Z^2} \right) \]  \hspace{1cm} (2)

where \( \varepsilon \) is the void fraction in the column, \( C \) is the concentration, \( t \) is the time, \( U_0 \) is the superficial velocity, \( Z \) is the column depth, \( q \) is the concentration in the stationary phase, \( D_p \) is the diffusivity.

The overall mass balance on the adsorbed solute is:

\[ (1 - \varepsilon) \left( \frac{\partial q}{\partial t} \right) = p \]  \hspace{1cm} (3)

where \( p \) is the adsorption rate.

The initial and boundary conditions for the equation 2 are:

\[ C = C_0 \hspace{1cm} t = 0, \ Z = 0 \]  \hspace{1cm} (4)

\[ D_L \frac{\partial C}{\partial Z} = -U_0 (C_0 - C) \hspace{1cm} t > 0, Z = 0 \]  \hspace{1cm} (5)

\[ \left( \frac{\partial C}{\partial Z} \right) = 0 \hspace{1cm} t > 0, Z = L \]  \hspace{1cm} (6)

where \( C_0 \) is the initial concentration and \( D_L \) is the axial dispersion coefficient.
The following assumptions associated with the equation 2:

- No chemical reactions take place in the column.
- Radial and axial dispersions are negligible.
- The flow pattern is the ideal plug flow.
- The temperature in the column is constant with time.
- The column flow rate is constant and unchanged with the column position\(^{16-19}\).

In present study, experimental breakthrough curves for citric acid adsorption from aqueous solution onto ion-exchange resin at different temperatures have been obtained. Then, several mathematical models have been developed and analyzed to predict system properties based on experimental data.

2. BREAKTHROUGH CURVES

Equations that heretofore offered for describing breakthrough curves are kind of complicated expressions that just can describe ideal, symmetrical breakthrough curves and for other possible shapes of these curves are unable to generate acceptable results. These equations in some cases were obtained from mass balances along with simplification assumptions\(^{20-21}\) that often were offered for gas breakthrough curves, or are including additional fitting parameters to better describe asymmetric (skewed) breakthrough curves like Wood equation and other are only mathematical equations that generate “S” shape curves\(^{22-23}\).

In this research work, it was tried to derive mathematical equations that not only can predict symmetrical “S” shape breakthrough curves but also can describe other curves that deviate from. Furthermore, several models in different forms such as fractional, polynomial and exponential are developed and statistically analyzed. Finally, three new mathematical fitting models, two implicit and one explicit, in following forms are developed for prediction breakthrough curves.
2.1. Implicit models

Developed implicit models are shown in equations 7 and 8. These equations can be divided to two categories including two and three parameter models. Parameters A, B, J, n, and r are fitting constant parameters that must be determined by regression of the experimental data.

\[
\frac{C}{C_0} = \frac{A t}{B + \left(\frac{C}{C_0}\right)^n} \tag{7}
\]

\[
\frac{C}{C_0} = \frac{J \ln(1+t)}{1 + \left(\frac{C}{C_0}\right)^r} \tag{8}
\]

where A, B, J, n and r are constants.

2.2. Explicit model

Using explicit equations because of their simple usage has preference, but often it seems difficult to develop explicit equations with a suitable simplicity that possesses enough generality. Implicit models usually have better performance for describing different experimental data curves in comparison with that of explicit models. But, implicit models require trial and error calculations in order to solve them. In this section, implicit equations were transformed to their analog explicit equations. Afterwards, an explicit equation was determined by replacing \(C/C_0\) with \(t/t_F\) in equation 8.

\[
\frac{C}{C_0} = \frac{D' \ln(1+t)}{E' + \left(\frac{t}{t_F}\right)^m} \tag{9}
\]

where \(t_F\) is the time that \(C/C_0\) reaches to 0.999 and \(D', E'\) and \(m'\) are constants.

3. EXPERIMENTAL

In preliminary experiments, several types of weak and strong basic anionic resins such as, IRA-92, IRA-93, IRA-420 and IRA-458 were examined and finally amberlite IRA-93 was selected because of its high performance and compatibility in acid adsorption. Then,
experiments were planned to investigate temperature effect on IRA-93 adsorption capacity. The experimental apparatus consists of a glass column (ID=1 cm, height=20 cm) and a bed (volume=15 cm$^3$). A schematic diagram of used apparatus is depicted in figure 1. The volumetric flow rate of acid in adsorption and desorption is constant and is equal to 1.5 ml/min. Moreover, the experiments were carried out at three temperatures (20, 35, and 55ºC) in which about 25 samples were analyzed for each temperature. The influent solution contains %20wt of citric acid and elution process is performed by 0.2 molar sulfuric acid solution. Furthermore, the concentration of citric acid is determined by a spectrophotometer UV-VIS (Model: Cary 1E/ Cary 3E, Purchased from Varian Co.). For determination of the breakthrough curves, dynamic experiments have been developed. In addition, the concentration of citric acid was determined only at the bottom of the column and axial distribution was not considered.

![Figure 1.](image)

**4. RESULTS AND DISCUSSION**

The breakthrough curves were measured at 20, 35, and 55ºC. The results show that weak basic resins are suitable for citric acid recovery in water solutions. In addition, citric acid diffusivity and resin saturation capacity have been obtained at different temperatures and the results have been shown in table 1. Diffusivities were determined using Perry’s Chemical Engineering Handbook $^{24}$. Moreover, parameter A which is multiplied by t couldn’t properly follow up the amounts of concentration, therefore, equation 8 correlation is developed and the results improved clearly.

| T (°C) | D_p × 10^{10} (m²/s) | C_m (g/L) |
|--------|-----------------------|-----------|
|        |                       |           |

Table 1. Diffusivities and resin saturation capacity at different temperatures $^{24}$. 
In this way, number 1 is added to logarithmic term which makes that available at evident point \((0, 0)\). The constants of all models were obtained by ordinary least square method using the “Eviews software” version 3.1 \(^{25}\). In Eviews software, several examinations are performed for analyzing and fitting of data that are described as follows:

1. R-squared: The R-squared \((R^2)\) statistic measures the success of the regression in predicting the values of the dependent variable within the sample. The statistic will equal one if the regression fits perfectly.

2. Durbin-Watson Test: D.W. is another parameter considering the difference between real and model amount in every point knowing as residual. In fact, this parameter determines the relation between residual data.

| Table 2. Models fitting results for citric acid data. |
|----------------------------------------------------|
| Models | \(T=20^\circ C\) | \(T=35^\circ C\) | \(T=55^\circ C\) | Average MRPE |
|        | \(R^2\) | D.W. | MRPE | \(R^2\) | D.W. | MRPE | \(R^2\) | D.W. | MRPE |            |
| Equation 7 | 92.42 | 0.426 | 35.44 | 96.38 | 0.342 | 23.70 | 99.74 | 1.04 | 16.25 | 25.13 |
| Equation 8 | 99.91 | 0.471 | 13.01 | 99.88 | 0.460 | 12.19 | 99.83 | 0.266 | 20.62 | 15.27 |
| Equation 9 | 99.60 | 1.56  | 7.06  | 99.30 | 1.49  | 12.32 | 98.65 | 1.43 | 28.80 | 16.06 |

In addition to \(R^2\) and D.W., the mean relative percent error, MRPE, was utilized in order to choose the best fitting model. Furthermore, MRPE was used to compare the predicted results with the experimental data. MRPE was calculated from the following formula.
\[
MRPE = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{\left(\frac{C}{C_0}\right)_{\text{Exp}} - \left(\frac{C}{C_0}\right)_{\text{Equ}}}{\left(\frac{C}{C_0}\right)_{\text{Exp}}} \right| \times 100
\]

where MRPE is the mean absolute percent error, \(N\) is the number of data points, \((C/C_0)_{\text{Exp}}\) is the experimentally measured relative concentration, and \((C/C_0)_{\text{Equ}}\) is the relative concentration determined using equations.

Table 2 shows the calculation results for selected models. As it was shown in table 2, \(R^2\) are greater than 0.99 except three cases and it is 0.999 for many cases. In addition, according to the amounts of \(R^2\), DW, and MRPE, equations 8 and 9 are well described the adsorption of citric acid on the IRA-93 resin as implicit and explicit models, respectively. Furthermore, the calculation results show that performance of equations is satisfactory except equation 7. But, equation 8 has the best fitting results in comparison with that of other models and can predict alteration of citric acid adsorption breakthrough curves with very low MRPE. In contrast, equation 9 has more %5 more MRPE in comparison with that of equation 8, but it is easy to use. On the first look, it seems that implicit equations are very difficult to use but, this kind of models are simple to determine the unknown value of the equation. Also, they are more precise than other models for breakthrough curves. Moreover, Table 3 shows the constant estimation of equation 9 for temperatures 20, 35 and 55 °C. Furthermore, the results for equation 9 are plotted in the figure 2 and this model is in conformity with the experimental data. According to figure 2, an increase in the temperature causes an increase in the adsorption of the citric acid.

In aqueous solution, weak dispersion forces dominate interactions between organic compounds and hydrophobic surfaces. Therefore, the adsorption can be considered reversible. It is proposed citric acid adsorption on IRA-93 contains four steps: diffusion through the bulk liquid, film diffusion, intra-particle diffusion, and adsorption on the solid surface. Generally, the bulk liquid diffusion and adsorption steps happen quickly and therefore, they are not rate-limiting. Intra-particle diffusion is in the pore space (i.e., pore
diffusion) or along the adsorbent surface in the pores (i.e., surface diffusion). Intra-particle diffusion studies investigating the adsorption of organic compounds showed that surface diffusion typically dominates over pore diffusion. Therefore, the citric acid adsorption by IRA-93 is also controlled by surface diffusion \textsuperscript{26-27}.

Table 3. Calculation results of the coefficients of equation 9 at temperatures 20, 35 and 55ºC.

| Models | Equation Parameters | 20ºC | 35ºC | 55ºC |
|--------|---------------------|------|------|------|
| Equation 9 | \( D' \) | 37.42 | 27.32 | 24.41 |
| | \( E' \) | 324.60 | 234.98 | 211.68 |
| | \( m' \) | -5.509 | -7.789 | -11.469 |

Figure 2.

To investigate the correlations accuracy (equations 7 through 9), the models were compared with Lu et al. (adsorption of Pb\textsuperscript{2+} in a fixed bed of ETS-10 adsorbent), Gonzalez et al. (adsorption of Cr(III) from aqueous solution onto Agave lechuguilla biomass), Grande et al. (adsorption of propylene in zeolite 4A), Ahmaruzzaman et al. (adsorption of phenol from wastewater by different adsorbents), Pan et al. (adsorption of phenol onto resin NDA-100), and Malkoc et al. (adsorption of Cr(VI) onto waste acorn of Quercus ithaburensis) breakthrough curves data \textsuperscript{28-33}.

Table 4. Models fitting results for selected breakthrough curves data.

| Models | Equation 7 | Equation 8 | Equation 9 |
|--------|------------|------------|------------|
| Averaged MRPE | 11.73 | 9.92 | 14.20 |

In detail, 18 breakthrough curves were utilized in order to determine reliability of model. From this, equations 7 through 9 were fitted to these breakthrough curves and the results are
shown in tables 4. According to table 4, MRPE (a mean value) for implicit models (equations 7 and 8) are in good agreement with experimental breakthrough curves. Furthermore, MRPE for equation 9 is acceptable, because of its explicit form. Moreover, the amounts of $R^2$ are more than 0.99 for all of adsorbates, even in the experiments with “S” shape of the curve was not ever well defined. Similar to our breakthrough curves, equation 8 best fitted with experimental data and the average MRPE is 9.92.

Breakthrough curves that were fitted based on equation 9 are shown in figures 3 to 8. Moreover, the calculation results for constants of equation 9 are presented in table 5. Though in most cases, the curve deviate from “S” shape and average MRPE in all cases is 14.20% and correlation coefficients ($R^2$) are greater than 0.984 for all cases. Consequently, though equation 9 is not adequate effective like equation 8 to fit experimental data and model deviation is considerable partly, but this equation 9 is simple to use.

| Breakthrough curve                      | Case          | $D'$ | $E'$ | $m'$  | $R^2\%$ | D.W. | MRPE  |
|----------------------------------------|---------------|-----|-----|-------|---------|------|-------|
| Adsorption of Pb$^{2+}$ onto ETS-10 adsorbent | $U_0$ (m/s)  | 4.67E-04 | 1.155 | 10.391 | -7.074  | 99.79 | 0.300 | 19.89 |
| Adsorption of Cr(VI) onto waste acorn of Quercus ithaburensis | Particle size (mm) | 0.15-0.25 | 6.756 | 56.061 | -4.296  | 98.52 | 0.533  | 17.89 |
| Adsorption of propylene onto zeolite 4A. | $Q$ (cm$^3$/min) | 46.2  | 3.822 | 28.073 | -1.361  | 99.87 | 0.506  | 9.39  |
| Adsorption of phenols from wastewater onto Adsorbent | Activated carbon | 5.501 | 18.613 | -5.527  | 99.24 | 1.33  | 17.63 |
| Adsorption of phenol onto resin NDA-100 | $C_0$ (mmol/L) | 0.532 | 17.640 | 80.446 | -10.763 | 99.76 | 1.68  | 15.09 |
| Adsorption of phenol onto coal | Residual coal | 5.351 | 17.116 | -2.380  | 98.41 | 0.838 | 38.74 |

Table 5. Fitting different breakthrough curves based on equation 9, related statistical tests and MRPE.
Among developed implicit equation models, equation 8 has showed the best conformity with experimental data, proper fitting indicated by $R^2$ amounts near to 1.0 (0.999) and low averaged MRPE over uneven breakthrough curves of citric acid, is 15.27. Furthermore, for the selected breakthrough curves from various chemical systems it is 9.92. The explicit model presented by equation 9 is not as effective as like implicit models to fit experimental data, but this equation is easy to use. Although in most cases, the curve deviates from “S” shape, but average MRPE over uneven breakthrough curves of citric acid is 16.06 and for selected breakthrough curves from various chemical systems is 14.20. Moreover, and correlation coefficients ($R^2$) are greater than 0.984 in all cases.

In addition, sensitivity analysis has been done for equation 9 and results have been presented on figure 9. According to Figure, Equation 9 has a good performance to a change of 20 percent of time (see slopes of the curves).

Furthermore, our data has been evaluated using other researcher’s models. Three different models derived by Adams-Bohart, Yoon-Nelson, and Chern have been chosen in order to assess our model\textsuperscript{18-19}. The results were shown on table 6. According to table 6, we improved the MRPE around 12.12% using equation 9. Moreover, equation 9 is easy to use.

Table 6. Comparison of different models and equation 9.
### Models' Name

| Model's Name | Model                                                                 | Average MRPE |
|--------------|----------------------------------------------------------------------|--------------|
| Equation 9   | \[ \frac{C}{C_0} = \frac{D' \ln(1+t)}{E' + \left( \frac{t}{I_F} \right)^m} \] | 16.06        |
| Adams-Bohart | \[ \ln \frac{C}{C_0} = k_{AB}C_0t - k_{AB}N_0 \frac{Z}{U_0} \]          | 114.52       |
| Yoon-Nelson  | \[ \ln \frac{C}{C_0 - C} = k_{YN}t - \pi k_{YN} \]                       | 90.82        |
| Chern        | \[ t = \tau + \rho N_1 \frac{dN_1}{dC_0} \ln \left( \frac{2C}{C_0} \right) + \frac{1}{1 + KC_0} \ln \left( \frac{1}{2 \left( 1 - \frac{C}{C_0} \right)} \right) \] | 18.70        |

## 5. CONCLUSION

An experimental investigation was performed to obtain the adsorption breakthrough curves for citric acid at 20, 35, and 55 °C. Amberlite IRA-93 resin was used as adsorbent. Furthermore, implicit and explicit models were utilized in order to correlate breakthrough curves. The results were then analyzed and summarized as follows.

Weak basic resins are more appropriate to adsorb citric acid onto adsorbent than strong basic resins because of their higher mechanical strength and low cost. In addition, adsorbate diffusivity in resin increases as a result of temperature increase. Then, it could be recommended that low and high temperatures are not appropriate conditions for adsorption process and middle temperature could be recommended as process design based on low diffusivity at low temperatures and resin degradation at high temperature.

Because of their structure, implicit mathematical models have good flexibility to describe various breakthrough curves with different steepness and shapes even for unusual “S” shape
type and also can predict alteration of various adsorption breakthrough curves, but explicit model generates smooth “S” shape curves. As a result, logarithmic models show better conformity with experimental data in comparison with that of non-logarithmic corresponding models. Since the numerical values of time are much greater than concentration ratio, taking logarithm of time reduces its amount and arise propriety in equation and consequently logarithmic models give better results which this is very obvious.

To probe the accuracy of the models, our models were compared with other researchers’ experimental data. Totally, 18 breakthrough curves have been investigated. The results show that our models can describe breakthrough curves with a wide range of data. Furthermore, we compared our model with Adams-Borhat, Yoon-Nelson, and Chern’s models and the results were in satisfactory agreement.

**Nomenclature**

- \((C/C_0)_{\text{Equ}}\): Relative concentration determined using equations
- \((C/C_0)_{\text{Exp}}\): Experimentally measured relative concentration
- A: Equation constant parameter
- A: Mass-transfer area per unit volume of the bed, (1/m)
- B: Equation constant parameter
- C: Concentration, (kg/m\(^3\))
- \(C/C_0\): Relative concentration
- \(C_0\): Initial concentration, (kg/m\(^3\))
- \(C_m\): Saturation capacity, (kg/m\(^3\))
- D.W.: Durbin-Watson statistic
- D’: Equation constant parameter
\( D_L \)  Axial dispersion coefficient, \((m^2/s)\)

\( D_P \)  Diffusivity, \((m^2/s)\)

\( E' \)  Equation constant parameter

\( J \)  Equation constant parameter

\( K \)  Langmuir model parameter, \((m^3/mol)\)

\( k_{AB} \)  Constant in the Adams–Bohart model, \((1/kg.s)\)

\( K_L \)  Overall liquid-phase mass-transfer coefficient \((m/s)\)

\( k_{YN} \)  Constant in the Yoon and Nelson model, \((1/s)\)

\( m' \)  Equation constant parameter

\( MRPE \)  Mean Absolute Percent Error

\( N \)  Number of data points

\( N \)  Equation constant parameter

\( N_0 \)  Saturation concentration in the Adams–Bohart model, \((1/kg)\)

\( N_1 \)  Langmuir model parameter, \((m^3/mol)\)

\( P \)  Adsorption rate, \((mol/s.kg \text{ dry resin})\)

\( Q \)  Concentration in the stationary phase, \((mol/kg \text{ dry resin})\)

\( Q \)  Volumetric flow rate, \((cm^3/min)\)

\( R \)  Equation constant parameter

\( R^2 \)  Correlation coefficient

\( SBM \)  Simulating Moving Bed

\( T \)  Time \((s, \text{ min or hr})\)

\( T \)  Temperature, \((^\circ C)\)

\( t_F \)  The time that \( C/C_0 \) reaches to 0.999

\( U_0 \)  Superficial velocity, \((m/s)\)

\( Z \)  Column depth, \((m)\)

**Greek Letters**
\( \varepsilon \)  Void fraction in the column

\( P \)  Bed density, (kg/m\(^3\))

\( T \)  Half time at C/C_0=0.5, (s)

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Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. Citric acid adsorption breakthrough curves data points fitted by equation 9 at 20, 35 and 55 °C.

Fig. 3. Breakthrough curves of Pb^{2+} adsorption onto ETS-10 at different superficial velocity fitted with equation 9.

Fig. 4. The adsorption breakthrough curves of Cr(VI) onto waste acorn of Quercus ithaburensis fitted with equation 9.

Fig. 5. The adsorption breakthrough curves of phenol onto resin NDA-100 in different initial concentration fitted with equation 9.

Fig. 6. The adsorption breakthrough curves of Phenol onto different adsorbent fitted with equation 9.

Fig. 7. Breakthrough curves of phenol adsorption onto resin NDA-100 in different initial concentration fitted with equation 9.

Fig. 8. Breakthrough curves of Cr(III) adsorption onto lechuguilla biomass at different bed lengths fitted with equation 9.

Fig. 9. Sensitivity analysis for equation 9.
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