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Research Article

Modeling Breakthrough Curves of Citric Acid Adsorption onto Anionic Resins in an Aqueous Solution

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Breakthrough curves for citric acid adsorption from aqueous solution onto ion-exchange resin at 20, 35, and 55°C have been investigated. To predict breakthrough curves, three mathematical models have been analyzed based on the values of the least square method parameters, Durbin-Watson test, and mean relative percent error and, finally, appropriate models have been achieved. Models are in good agreement with experimental data based on the results. To examine models reliabilities and accuracy, models have been compared by various breakthrough curve data obtained by other investigators. The results show appropriate agreement and in some cases regression errors have been reduced to less than 1.0 percent.

1. Introduction

Organic compounds have been excessively released into the environment because of the rapid industrialization and have caused a major global concern [1, 2]. One of the most widely used organic acids in the field of foods and beverages as an acidulant as well as in pharmaceutical and chemical products is citric acid. *Aspergillus niger* was mainly used to produce citric acid by surface or submerged fungal fermentation. However, citric acid was produced with the submerged fermentation method [3, 4].

Citric acid is the most important produced organic acid and there is a great worldwide demand for citric acid consumption because of its low toxicity compared with other acidulants used in the pharmaceutical and food industries [5]. Therefore, waste from food and pharmaceutical industries contains citric acid. In natural water systems, organic acids can stick heavy metal ions on solid surfaces by forming complexes. This process prevents the preservation of heavy metals by sediments [2]. Citric acid and acetic acid are known as organic ligands involved in the adsorption process in the soil chemistry [2].

Conventional methods for separating organic compounds are chemical precipitation, electrolysis, membrane separation, ion exchange, and absorption by activated carbon [6–9]. High capital or high operational cost or disposal of resulting sludge are disadvantages of most of these methods. In recent years, more and more attention has been paid for the investigation of low-cost materials such as agricultural by products, industrial wastes, and biological materials as adsorbents [10, 11]. Recently, modified cellulose beads and resins were utilized to adsorb some heavy metallic ions [12, 13]. Adsorption process has lower production costs for purification of organic acids particularly citric acid in comparison with that of other methods [14, 15].

Resin adsorption chromatography using different synthetic resins has been utilized to isolate and separate organic compounds with varying degrees of success. This chromatographic separation method concentrates and isolates organic compounds into operationally defined fractions depending on their relation to different resins and their back elution efficiencies [16–18]. Although the principle of organic acids separation by ion-exchange method has been known, there are many details that require development and determination. Thus, it seems that simulated moving bed (SMB) is suitable and effective by using chromatography method on the base of countercurrent continuous contact between feed and adsorbent [19, 20].

One of the continuous chromatographic methods is SMB. Parameters such as ion-exchange resins properties, adsorption equilibrium data, and operation characteristics of bed are necessary to be determined for SMB method. One of the best methods to determine and optimize operating parameters 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 [22–24]

$$\text{R–N} + \text{CH}_n \longleftrightarrow \text{R–NH}^{+}\text{CH}_{n-1}{}^{-}. \quad (1)$$

For acids with more than one carboxyl group and also for R–N in (1) base resins are appropriate [25].

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

2. Breakthrough Curves

Equations already proposed for describing breakthrough curves are complicated expressions that are just valid for ideal, symmetrical breakthrough curves and for other possible shapes of breakthrough curves and they are unable to generate agreeable results. These equations in some cases were determined from mass balance equations along with some simplification assumptions [26, 27] that often were introduced for gas breakthrough curves or include additional fitting constants to obtain better explanation of asymmetric (skewed) breakthrough curves like Wood equation and others are only mathematical equations that produce "S" shape curves [28, 29].

In this research work, it was tried to derive mathematical equations that not only can predict symmetrical "S" shape breakthrough curves but also can explain other curves that deviate from. In addition, we derived and statistically investigated different forms of several models such as fractional, polynomial, and exponential. Finally, three new implicit mathematical fitting models in following forms were derived for determination of breakthrough curves. Derived implicit models are shown in (2) through (4). Parameters D, E, F, G, H, I, m, p, and q are fitting constant parameters that must be obtained by regression of the experimental data:

$$\frac{C}{C_0} = \frac{D\ln(1+t)}{E + (C/C_0)^m} \quad (2)$$

$$\frac{C}{C_0} = \frac{Ft + G}{1 + (C/C_0)^p} \quad (3)$$

$$\frac{C}{C_0} = \frac{H\ln(1+t) + I}{1 + (C/C_0)^q}. \quad (4)$$

3. Experimental

All of the experimental data which was used in the current study was determined from our previous study [21]. The experimental apparatus includes a glass column (ID = 1 cm, height = 20 cm) and a bed (volume = 15 cm^3). Figure 1 shows a schematic diagram of the used apparatus in our experiments. The volumetric flow rate of acid in adsorption and desorption was constant and was equal to 1.5 mL/min. Furthermore, the experiments were done at three different temperatures (20, 35, and 55°C). Approximately, 25 samples were analyzed for each temperature. The concentration of citric acid in the influent solution was %2 wt and elution process is carried out by 0.2 molar sulfuric acid solution. In addition, the concentration of citric acid was obtained by a spectrophotometer UV-VIS (model: Cary 1E/Cary 3E, purchased from Varian Co.). All of experiments were performed three times to examine reproducibility and repeatability of the experiments.

Table 1: Diffusivities and resin saturation capacity at different temperatures [21].

T (°C)	$D_p \times 10^{10}$ (m^2/s)	C_m (g/L)
20	3.1	302.2
35	4.3	265.1
55	6.1	190.4

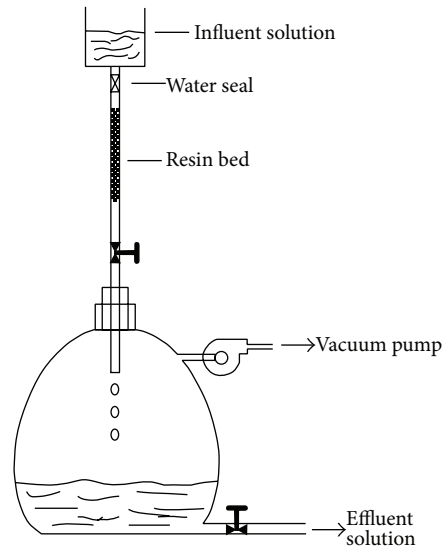

Figure 1: Schematic diagram of experimental apparatus [21].

4. Results and Discussion

In this study, the breakthrough curves have been studied at three different temperatures 20, 35, and 55°C [21]. It has been observed that weak basic resins have a better performance in citric acid recovery in water solution. Also, the diffusivity of citric acid and resin saturation capacity have been obtained. These results have been shown in Table 1 for different temperatures [21].

The constant values of all models have been obtained by "EViews software" version 3.1 [30]. It should be mentioned that number 1 has been added to the logarithmic terms because of having the value of function at point (1,1). Least

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 (2)	99.96	0.650	5.40	99.97	0.543	3.88	99.99	1.11	1.75	3.68
Equation (3)	99.88	0.491	13.60	99.88	0.529	11.26	99.93	0.848	13.33	12.73
Equation (4)	99.92	0.576	11.76	99.90	0.560	10.54	99.93	0.807	14.68	12.33

Table 3: Calculation results of the coefficients of (2) at temperatures 20, 35, and 55°C.

Models	Equation parameters	20°C	35°C	55°C
Equation (2)	D	0.177	0.163	0.135
	E	0.485	0.357	0.112
	M	−1.108	−1.086	−1.014

square method has been used for curve fitting and required statistical tests have been done on the results. R-squared and Durbin-Watson test values have been considered in function analyzing.

The R-squared (R^2) statistic is measuring the capability of developed mathematical models in predicting the coefficient values in the function. This value will be equal to one (or %100) for a perfect curve fitting.

Durbin-Watson test (D.W.) is useful to analyze the residual values which are the difference between the experimental results and model amount in each point. If there are harmonic changes in residual values, it might need to add another variable in the function to cover the variable amounts.

Another analyzed factor in this modeling is mean relative percent error, MRPE. It has been done to analyze the results of different developed function. The lower MRPE, the more efficient mathematical function in modeling. Equation (5) has been used to calculate the MRPE:

$$\mathrm{MRPE} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(C_t/C_0)_{\mathrm{Exp}} - (C_t/C_0)_{\mathrm{Equ}}}{(C_t/C_0)_{\mathrm{Exp}}}\right| \times 100. \quad (5)$$

Modeling fitting results for citric acid data have been shown in Table 2. The values of R^2 are in an appropriate level very close to 1. The results show that (2) well described the adsorption of citric acid on the IRA-93 resin.

Statistical tests show that the effectiveness of all developed equations is in an appropriate level, but (2) has better fitting results in comparison with other developed mathematical functions, especially with consideration of MRPE.

Equation (2) has been analyzed more and related constants have been estimated at 20, 35, and 55°C. The results have been presented in Table 3. Also (2) for different temperatures has been plotted in Figure 2.

Validation of results have been done based on comparing the results with other investigation including Lu et al. (adsorption of Pb^{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 [31–36]. In this case, 18 breakthrough curves were utilized in order to determine reliability of models. From this, (2), (3), and (4) were fitted to these breakthrough curves and the results are shown in Table 4.

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

Models	Equation (2)	Equation (3)	Equation (4)
Averaged MRPE	3.57	7.82	7.51

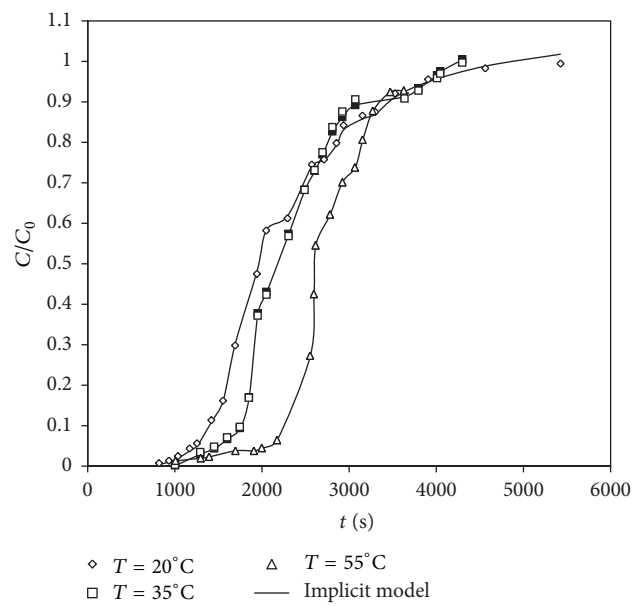

Figure 2: Citric acid adsorption breakthrough curves data points fitted by (2) at 20, 35, and 55°C [21].

The values of MRPE in Table 4 are in good agreement with experimental breakthrough curves. In addition, the amounts of R^2 are more than 0.99 for all of adsorbates. Similar to our breakthrough curves, (2) best fitted with experimental data and the average MRPE is 3.57. In addition, the results were plotted on Figures 3 through 8 for (2). Moreover, the calculation results for constants of (2) are presented in Table 5.

As mentioned above, (2) has the best conformity with experimental data and properly fitted based on R^2 values close to 1.0 and low values of averaged MRPE over breakthrough curves of citric acid which is 3.68%. Furthermore,

Table 5: Fitting different breakthrough curves based on (2), related statistical tests, and MRPE.

Breakthrough curve	Case		D	E	m	R^2%	D.W.	MRPE
Adsorption of Pb^{2+} onto ETS-10 adsorbent	u_s (m/s)	$4.67E-04$	0.107	0.074	−1.004	99.99	0.170	0.45
		$7.0E-04$	0.115	0.125	−1.021	99.99	0.310	0.92
Adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*	Particle size (mm)	0.15–0.25	0.198	0.499	−1.074	99.99	0.979	2.46
		0.25–0.50	0.203	0.505	−1.054	99.99	0.819	2.81
		0.50–1.00	0.211	0.546	−1.023	99.93	0.467	2.34
Adsorption of propylene onto zeolite 4A	Q (cm^3/min)	32.0	0.186	0.474	−1.010	99.99	0.218	1.38
		46.2	0.325	1.473	−1.144	99.90	0.337	8.54
		62.5	0.291	1.300	−1.174	99.85	0.220	5.75
Adsorption of phenols from wastewater	Adsorbent	Activated carbon	0.385	0.396	−1.029	99.94	0.899	5.59
		RCP	0.339	0.189	−0.908	99.94	2.00	3.58
		Residual coal	0.453	0.564	−0.901	99.59	0.544	3.61
Adsorption of phenol onto resin NDA-100	C_0 (mmol/L)	0.532	0.290	0.323	−1.070	99.98	0.346	4.79
		2.032	0.356	0.366	−1.079	99.98	0.320	3.39
		5.319	0.653	1.234	−1.308	99.32	0.100	10.44
Adsorption of Cr(III) onto *Agave lechuguilla* biomass	Bed length (dm)	0.5	0.257	0.250	−0.999	99.99	1.93	0.90
		1.0	0.247	0.263	0.454	99.99	0.454	2.49
		1.5	0.224	0.203	−1.300	99.99	0.394	1.17

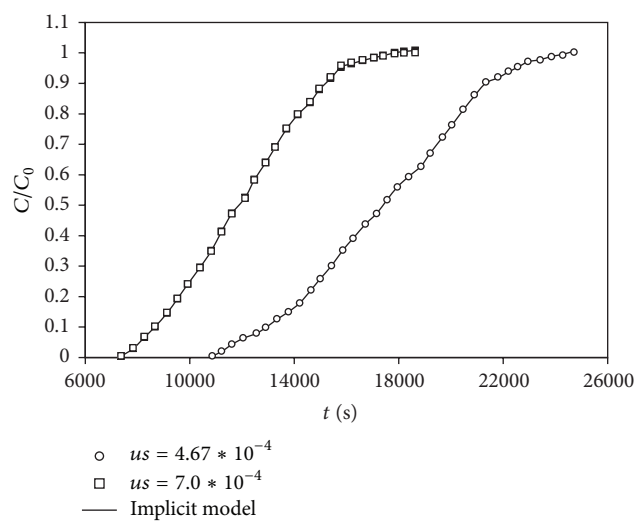

Figure 3: Breakthrough curves of Pb^{2+} adsorption onto ETS-10 at different superficial velocity fitted with (2) [31].

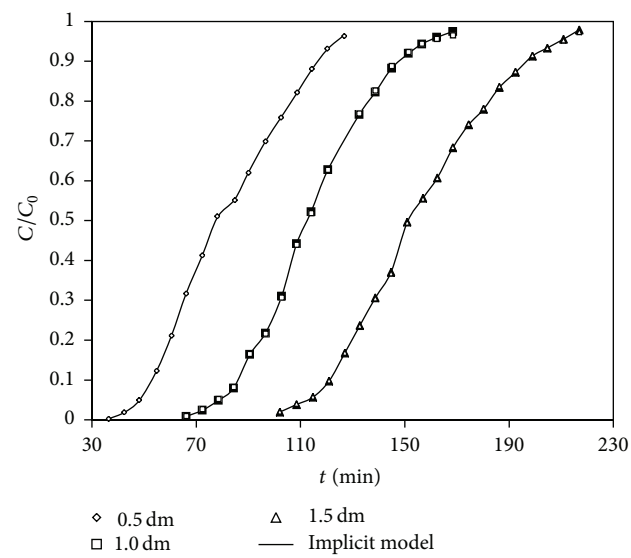

Figure 4: Breakthrough curves of Cr(III) adsorption onto *Agave lechuguilla* biomass at different bed lengths fitted with (2) [32].

the MRPE for the selected breakthrough curves from various chemical systems is 3.57%.

5. Conclusions

A statistical investigation was performed to obtain the adsorption breakthrough curves for citric acid at 20, 35, and 55°C. Furthermore, implicit models were utilized in order to correlate breakthrough curves. The results were then analyzed and summarized as follows.

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. As a result, logarithmic models show better conformity with experimental data in comparison with that of nonlogarithmic corresponding models. Since the numerical values of time are much greater than concentration ratio, taking logarithm of time reduces its amount and arises

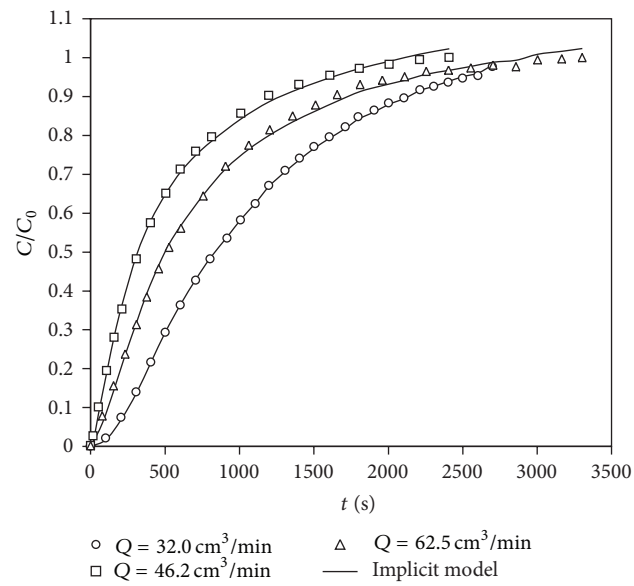

Figure 5: Breakthrough curves of propylene adsorption in zeolite 4A and different flow rate fitted with (2) [33].

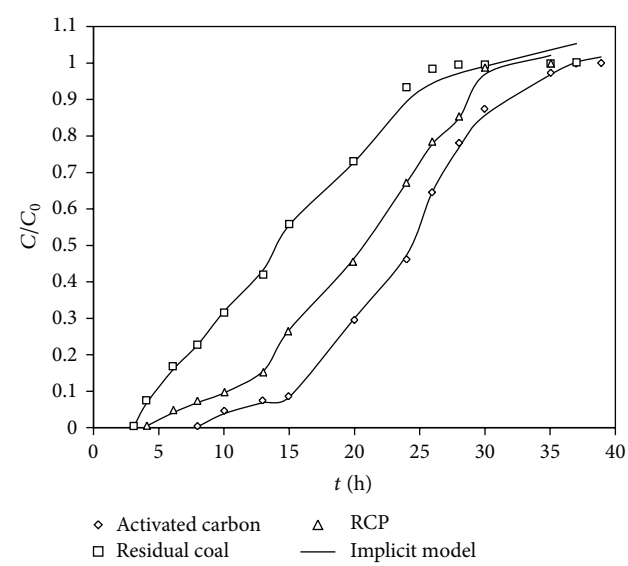

Figure 6: Breakthrough curves of phenol adsorption onto different adsorbent fitted with (2) [34].

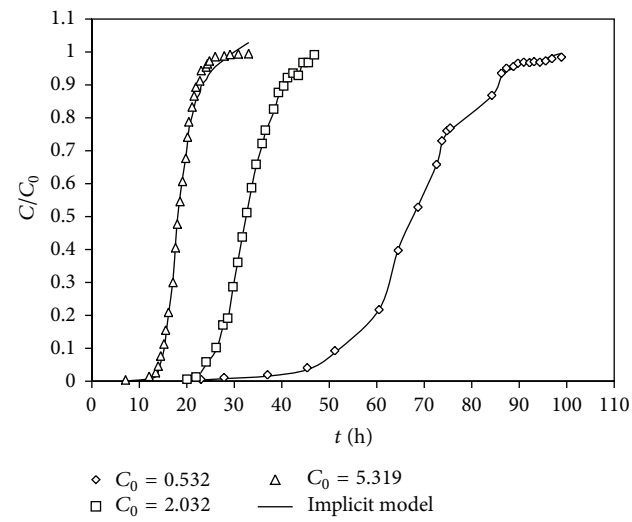

Figure 7: Breakthrough curves of phenol adsorption onto resin NDA-100 fitted with (2) [35].

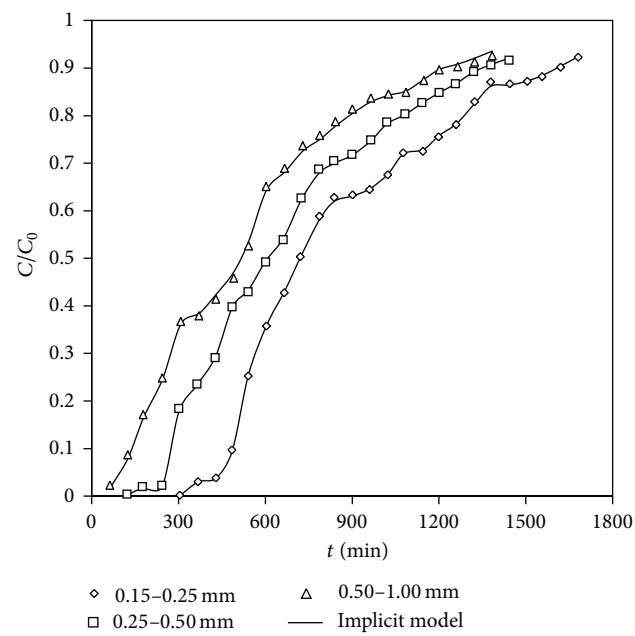

Figure 8: Breakthrough curves of Cr(VI) adsorption onto waste acorn of *Quercus ithaburensis* fitted with (2) [36].

propriety in equation and consequently logarithmic models give better results which is very obvious. Additionally, the unit of time has no effect on regression quality and just changes the value of constant parameter in models.

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.

Nomenclature

A-B: Equation constant parameters
C: Concentration, (kg/m^3)
C/C_0: Relative concentration
C_m: Saturation capacity, (kg/m^3)
D: Equation constant parameter
D': Equation constant parameter
D_P: Diffusivity, (m^2/s)
D.W.: Durbin-Watson statistic
E-J: Equation constant parameters
E': Equation constant parameter

K: Number of equation parameters
m-r: Equation constant parameters
m': Equation constant parameter
MRPE: Mean absolute percent error
N: Number of data points
R^2: Correlation coefficient
$\overline{R}^2$: Adjusted correlation coefficient
SBM: Simulating moving bed
T: Time (s, min or hr)
t_F: The time that C/C_0 reaches to 0.999
T: Temperature, (°C)
$\hat{\varepsilon}$: Absolute error of regression.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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