Purification of Biotechnological Carboxylic Acids with an Adsorption Method Using Single-Walled Carbon Nanotubes

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Adsorption is a very important and valuable method for separation of carboxylic acids from aqueous solutions. In this study, single-walled carbon nanotubes (SWCNT) were used as an adsorbent for this purpose. Important biotechnological acids, tartaric acid and citric acid, were used. The equilibrium time and the adsorption capacity at three different temperatures (25 °C, 35 °C, and 45 °C) were investigated. Reaction kinetics and the diffusion between the acid molecules and SWCNT pores were investigated. The aim of this study was to determine the adsorption capability of SWCNT for carboxylic acids of biological importance from their fermentation media.

Introduction

Carbon nanotubes (CNTs) have porous-rich structures. That means they have very high adsorption capabilities, and CNTs can be used for removing many kinds of organic and inorganic pollutants.[1,2] Carbon nanotubes are hexagonal carbon networks that are capped by half fullerene molecules. There are two main types of carbon nanotubes: single-walled and multiwalled carbon nanotubes. Multiwalled carbon nanotubes (MWCNTs) were discovered by Iijima in 1991 and the related single-walled carbon nanotubes (SWCNTs) in 1993.[3,4] CNTs have excellent versatility and wide application fields.[5] Single-walled carbon nanotubes have become one of the most widely studied nanomaterials, primarily because of their unique physicochemical properties and wide-ranging applications in solid-state nanoelectronics, nanocomposites, nanolithography, sensing, and high-resolution imaging.[6]

The rich-porous structure is the most important characteristic of an adsorbent that is used in carboxylic acid adsorption. SWCNTs were chosen in this study for their characteristic porosity.

Carboxylic acids have a wide range of application fields, such as in the pharmaceutical, polymer, food industries, etc. Because of this, recovery of carboxylic acids is an important process in chemical engineering. In this study, a dicarboxylic acid (tartaric acid) and a tricarboxylic acid (citric acid) were adsorbed from their aqueous solutions by SWCNTs.[7−9]

Citric acid is an important product in many industrial fields. The food industry is the largest consumer of citric acid. The amount of citric acid produced is more than one million tons per year.[10,11]

Tartaric acid is used in the food and pharmaceutical industries. Wastewater from the winery industry contains tartaric acid.[12] It can be recovered from this wastewater.

All these acids are produced by the fermentation method. Purification of the carboxylic acids from fermentation broth is a very challenging process. Adsorbents must have selectivity for these acids. In this study, the adsorption experiments were carried out from aqueous solutions of the carboxylic acids. The aim is to test the adsorption capability of SWCNTs.

Numerous researchers have investigated the adsorption of carboxylic acids from aqueous solutions by using different adsorbents. Kawabata et al. separated carboxylic acid using a polymer sorbent with a pyridine skeletal structure and a cross-linked structure. The polymer sorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts.[8,13] SWCNTs are generally used for metal and protein adsorptions. For example, Lu et al. adsorbed Ni^{2+} from aqueous solution using SWCNTs.[14] Karajanagi et al. adsorbed enzymes onto SWCNTs and investigated the structure and function of the adsorbed enzymes.[6] However, there is not enough information about carboxylic acid adsorption onto CNTs in the literature.

The aim of this study is to define the sorption capability of SWCNTs, when used for the adsorption of carboxylic acids from aqueous solutions.

Material and Methods

Material. Tartaric acid and citric acid were obtained from Merck. SWCNTs were obtained from Sigma-Aldrich. SWCNTs are (40 to 60) % (by mass) carbon basis, and diameter × length is (2 to 10) nm × (1 to 5) μm and used without purification and activation. Acid solutions were prepared approximately (3, 6, 9, 12, and 15) %.

Method. Adsorption experiments were carried out in a batch type. The aim of these experiments was to determine the effect of important variables on the adsorption, such as time, initial acid concentration, and temperature. For each experimental run, 3 mL of stock acid solution and a known amount of adsorbent were taken in a 50 mL flask. This mixture was shaken at a constant speed and temperature in a thermostatted shaker. A sample was taken out periodically, and the aqueous phase was titrated with 0.1 M NaOH solution and phenolphtalein used as an indicator. SWCNT particles remain suspended and do not settle down easily. Therefore, all the samples were separated with filter paper and then analyzed. The period of equilibration was determined as 70 min for citric acid and 80 min for tartaric acid. For determining the temperature effect on adsorption, five

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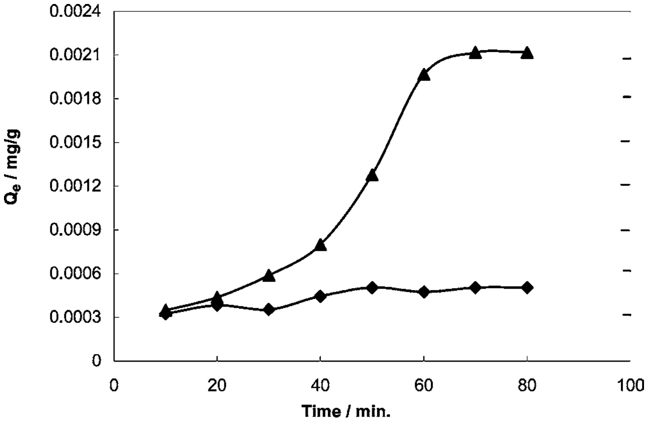

Figure 1. Equilibration time for the adsorption of acids onto SWCNT particles at 298 K: ◆, citric acid; ▲, tartaric acid.

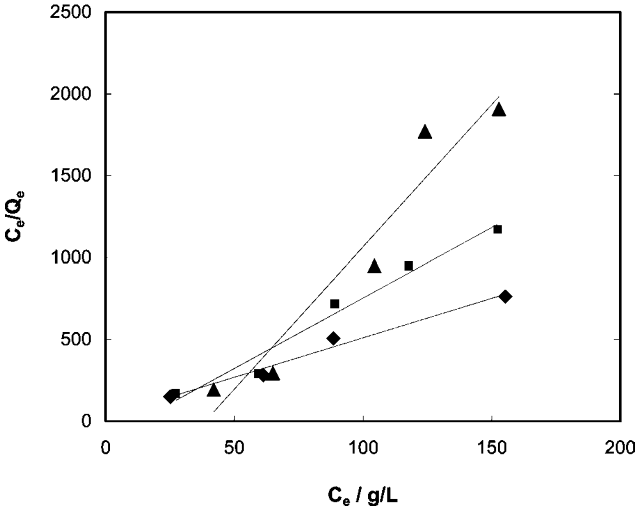

Figure 2. Langmuir isotherms of the citric acid−SWCNT adsorption at different temperatures: ◆, 298 K; ■, 308 K; ▲, 318 K.

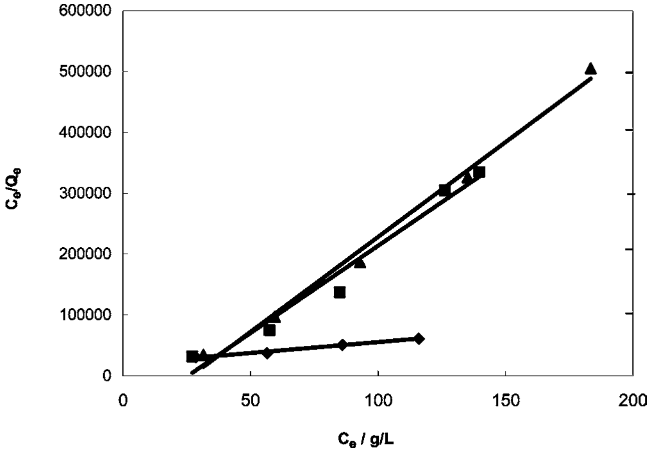

Figure 3. Langmuir isotherms of the tartaric acid−SWCNT adsorption at different temperatures: ◆, 298 K; ■, 308 K; ▲, 318 K.

different initial acid concentrations for each acid and 0.01 g of SWCNT were shaken at (298, 308, and 318) K, and then the aqueous phases were analyzed. After the equilibration, the results were used for calculation of adsorption isotherms. Langmuir and Freundlich isotherms were calculated as dependent on initial acid concentration for each temperature. The Elovich model, first order, pseudofirst-order, pseudosecond-order, and Weber−Morris intraparticle diffusion models were applied to the experimental results.

Results and Discussion

In this study, the period of achieving the equilibrium state of the adsorbent, effect of initial acid concentration, and temperature were investigated. Results of this experimental procedure were used for determining the reaction kinetics and equilibrium parameters.

Effect of Process Variables. Effect of Contact Time. The carboxylic acids and SWCNT particles were in contact with each other, and the equilibration time was determined. The effect of contact time on the amount of adsorbed acid is shown in Figure 1 and Table 1. For tartaric acid, adsorbent uptake of adsorbate is fast in the initial stages of the contact period, and thereafter, it becomes slower near equilibrium. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the solute molecules on the solid and bulk phases.[15]

Effect of Initial Acid Concentration. The concentrations of initial acid concentration studied were: for citric acid (0.14, 0.33, 0.47, 0.64, and 0.82) mol·L^{-1} and for tartaric acid (0.21, 0.41, 0.61, and 1.01) mol·L^{-1}. The adsorption isotherms were applied, using the difference of initial acid concentration. It can be seen from Figures 2 and 3 and Table 2 that when C_e values increased the ratio of C_e/Q_e increased too. This means that while the initial acid concentration increased the adsorption yield decreased. This may be explained by the saturation of adsorbent surfaces.

Effect of Temperature. Three different temperatures were studied at different initial acid concentrations and a constant

Table 1. Equilibration Time for the Adsorption of Acids onto SWCNT Particles at 298 K

	initial acid conc.	initial acid conc.	amount of SWCNT	time	equilibrium conc.	amount of adsorbed acid	percentage of removal acid
	mol·L^{-1}	% w/w	g	min	C_e/g·L^{-1}	Q_e/g·mg^{-1}	%
citric acid	0.49	9.32	0.01	10	93.0	0.000324	1.14
	0.49	9.32	0.01	20	92.8	0.000384	1.36
	0.49	9.32	0.01	40	92.6	0.000444	1.57
	0.49	9.32	0.01	50	92.4	0.000504	1.78
	0.49	9.32	0.01	60	92.5	0.000474	1.67
	0.49	9.32	0.01	70	92.4	0.000504	1.78
tartaric acid	0.60	8.90	0.01	10	88.90	0.000348	1.28
	0.60	8.90	0.01	20	88.60	0.000438	1.62
	0.60	8.90	0.01	30	88.10	0.000588	2.17
	0.60	8.90	0.01	40	87.40	0.000798	2.95
	0.60	8.90	0.01	50	85.80	0.001278	4.73
	0.60	8.90	0.01	60	83.50	0.01968	7.28
	0.60	8.90	0.01	70	83.00	0.002118	7.83
	0.60	8.90	0.01	80	83.00	0.002118	7.83

Table 2. Initial Acid Concentration Changes at Three Different Temperatures

	initial acid conc.	initial acid conc.	amount of SWCNT	equilibrium conc.	amount of adsorbed acid	percentage of removal acid
	$\mathrm{mol \cdot L^{-1}}$	% w/w	g	$C_e/\mathrm{g \cdot L^{-1}}$	$Q_e/\mathrm{g \cdot mg^{-1}}$	%
citric acid						
25 °C	0.14	2.68	0.01	25.20	0.168	6.25
	0.33	6.30	0.01	61.20	0.216	3.40
	0.47	9.01	0.01	88.50	0.174	1.92
	0.64	12.20	0.01	120.70	0.218	1.77
	0.82	15.66	0.01	155.40	0.204	1.29
35 °C	0.15	2.73	0.01	27.20	0.160	5.55
	0.32	6.02	0.01	59.40	0.204	3.32
	0.47	9.00	0.01	89.00	0.124	1.37
	0.62	11.80	0.01	117.80	0.124	1.04
	0.80	15.25	0.01	152.30	0.130	0.84
45 °C	0.23	4.32	0.01	42.00	0.216	4.89
	0.35	6.70	0.01	65.00	0.22	3.27
	0.55	10.56	0.01	104.50	0.11	1.04
	0.65	12.40	0.01	124.10	0.07	0.56
	0.80	15.30	0.01	152.80	0.08	0.52
tartaric acid						
25 °C	0.21	3.02	0.01	28.50	0.302	9.58
	0.41	6.02	0.01	56.50	0.504	8.18
	0.61	9.03	0.01	86.00	0.556	6.07
	1.01	15.07	0.01	145.30	0.629	4.10
35 °C	0.20	3.00	0.01	27.20	0.282	9.39
	0.40	5.87	0.01	57.50	0.254	4.23
	0.58	8.68	0.01	85.00	0.206	2.36
	0.85	12.72	0.01	126.20	0.138	1.08
	0.94	14.01	0.01	139.70	0.139	0.98
45 °C	0.23	3.35	0.01	31.50	0.303	8.77
	0.41	6.14	0.01	59.50	0.204	3.31
	0.63	9.40	0.01	92.90	0.166	1.75
	0.91	13.59	0.01	135.20	0.138	1.01
	1.23	18.34	0.01	183.40	0.121	0.65

adsorbent dosage (0.01 g). The temperatures chosen for this study were (298, 308, and 318) K. As shown in Figure 3, the maximum ratio of C_e/Q_e for tartaric acid is 250 000 at 298 K, 400 000 at 308 K, and 600 000 at 318 K. These values show that the adsorption efficiency of the adsorbent decreased with increasing temperature. Also the Q_{max} values decrease with increasing temperature, as shown in Table 1. The adsorbent showed an exothermic nature of adsorption, like most adsorption reactions.

Equilibrium. Equilibrium is generally expressed in terms of the concentration of the adsorbate in the fluid and the adsorbate loading on the adsorbent. Adsorption isotherms obtained from experimental studies provide an upper limit on the adsorption of adsorbate from a given fluid mixture on a specific adsorbent for a designated set of conditions.[16] Langmuir and Freundlich isotherms were applied to the experimental data in this study.

Langmuir Isotherm. The Langmuir equation[17−19]

$$q_A = \frac{K_A Q_{max} C_e}{1 + K_A C_e} \tag{1}$$

Q_{max} denotes the maximum adsorbent uptake; q_A denotes the experimental adsorbent uptake; K_A is a coefficient; and C_e is the equilibrium concentration. It is related to the affinity between the adsorbent and adsorbate. The values of K_A and Q_{max} are determined by the following equation to which eq 1 is transformed.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \tag{2}$$

Table 3. Isotherm Parameters for Adsorption of Tartaric and Citric Acid onto SWCNTs

Langmuir Isotherm

tartaric acid				citric acid			
T/K	Q_{max}	K_L	R^2	T/K	Q_{max}	K_L	R^2
298	$2.28 \cdot 10^{-3}$	0.018	0.9817	298	0.210	0.17	0.9781
308	$3.49 \cdot 10^{-4}$	−0.039	0.9674	308	0.116	−0.08	0.9711
318	$3.21 \cdot 10^{-4}$	−0.037	0.9914	318	0.057	−0.03	0.9335

Freundlich Isotherm

tartaric acid				citric acid			
T/K	K_f	n	R^2	T/K	K_f	n	R^2
298	$1.69 \cdot 10^{-4}$	1.94	0.9483	298	9.01	−1.05	0.3603
308	$4.39 \cdot 10^{-3}$	−2.14	0.8728	308	0.34	−5.12	0.3699
318	$5.27 \cdot 10^{-3}$	−1.93	0.9943	318	0.12	9.64	0.8525

The values of K_L and Q_{max} are determined from the intercept and slope of the straight line in Figures 2 and 3. Q_e is the adsorption capacity of the adsorbent. The calculated parameters of the Langmuir equation for the three temperatures are presented in Table 3.

Freundlich Isotherm. The second isotherm used in this study was the Freundlich isotherm.[18,20]

$$Q_e = K_f C_e^{1/n} \tag{3}$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined

$$\log Q_e = \log K_f + (1/n) \log C_e \tag{4}$$

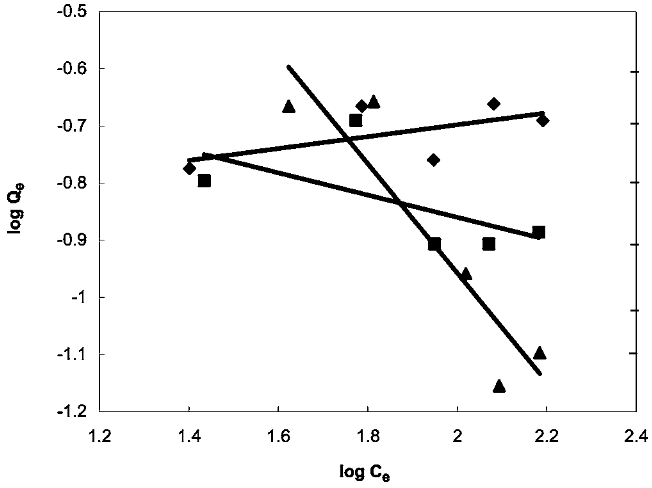

Figure 4. Freundlich isotherms of the citric acid−SWCNT adsorption at different temperatures: ♦, 298 K; ■, 308 K; ▲, 318 K.

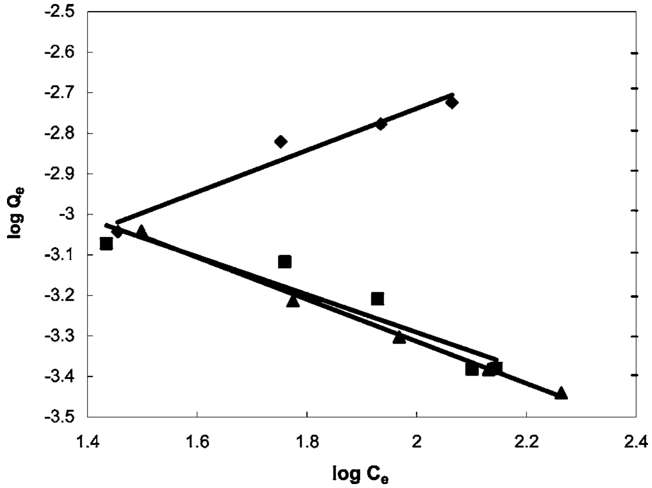

Figure 5. Freundlich isotherms of the tartaric acid−SWCNT adsorption at different temperatures: ♦, 298 K; ■, 308 K; ▲, 318 K.

The values of K_f and $1/n$ at different concentrations were determined from the slope and intercept of the linear plots of log Q_e and log C_e. Figures 4 and 5 show the plots of Freundlich equilibrium isotherms for citric acid and tartaric acid adsorption at three different temperatures. Results of the Freundlich equation are presented in Table 3.

The Langmuir isotherm when fitted to experimental results for both acids gave R^2 values of 0.9812 for tartaric acid and 0.9769 for citric acid. For this reason, the Langmuir isotherm was found to best represent the data for tartaric and citric acid adsorption onto SWCNTs.

Kinetics. Surface diffusion has an extremely important role for intraparticle diffusion in many liquid-phase adsorption systems. A number of studies on surface diffusion have been carried out to elucidate the mechanism of surface diffusion and to develop an estimation procedure of surface-diffusion coefficients. The estimation of diffusion coefficients, however, is extremely difficult because they vary to a high degree according to a combination of adsorbates, adsorbents, and solvents. A strict understanding of the surface-diffusion mechanism is essential for the establishment of the estimation of diffusion coefficients. The dependence of this coefficient, on both temperature and the amount adsorbed, q, can be investigated as a characteristic feature of surface diffusion.[21] For the estimation of the surface-diffusion coefficient, numerous diffusion models have been developed. The Weber−Morris intraparticle diffusion model is one of them.

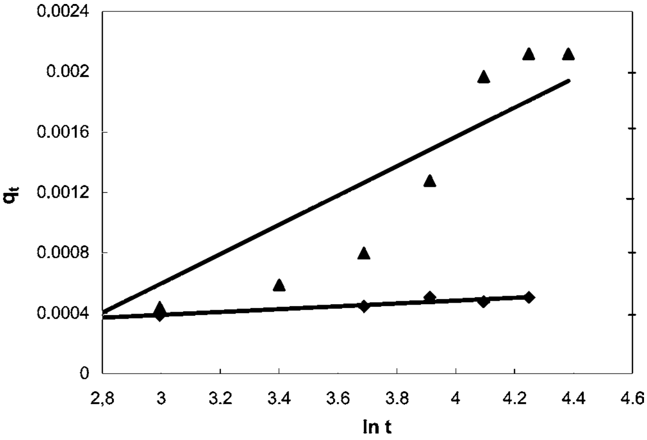

Figure 6. Elovich model of the acid−SWCNT adsorption: ♦, citric acid; ▲, tartaric acid.

Table 4. Kinetic Parameters for the Removal of Carboxylic Acids by SWCNTs

Elovich Model					
tartaric acid			citric acid		
α	β	R^2	α	β	R^2
$1 \cdot 10^{-4}$	1000	0.7940	$2.73 \cdot 10^{-4}$	11111.1	0.9501

W−M Intraparticle Diffusion Model					
tartaric acid			citric acid		
k_{id}	I		k_{id}	I	
$mg \cdot g^{-1} \cdot min^{-1/2}$	$mg \cdot g^{-1}$	R^2	$mg \cdot g^{-1} \cdot min^{-1/2}$	$mg \cdot g^{-1}$	R^2
0.0004	−0.0016	0.9584	$3 \cdot 10^{-5}$	0.0002	0.8921

	pseudofirst-order			pseudosecond-order		
	Q_o	K_1	R^2	Q_e	K_2	R^2
tartaric acid	$1.97 \cdot 10^{-3}$	$9.2 \cdot 10^{-3}$	0.9710	$-2.58 \cdot 10^{-3}$	2.54	0.6907
citric acid	$2.55 \cdot 10^{-4}$	0.03	0.6806	$5.56 \cdot 10^{-4}$	220.48	0.9925

To determine the kinetics of adsorption of citric and tartaric acid onto SWCNTs, first-order, pseudofirst-order, pseudosecond-order, Weber−Morris intraparticle diffusion, and Elovich models were applied.

Elovich Equation. The Elovich model equation is generally expressed as[22]

$$\frac{dQ}{dt} = \alpha \exp(-\beta Q) \tag{5}$$

where α is the initial adsorption rate ($mg \cdot g^{-1} \cdot min^{-1}$) and β is the desorption constant ($g \cdot mg^{-1}$) during any one experiment. To simplify the Elovich equation, $\alpha\beta t \gg t$ is assumed, and by applying the boundary conditions $Q = 0$ at $t = 0$ and $Q = Q$ at $t = t$ the equation becomes

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{6}$$

A plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$ (Figure 6). The constants are listed in Table 4.

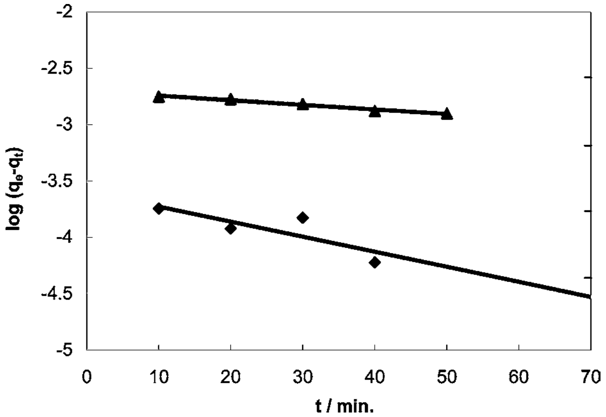

Figure 7. First-order kinetic of the acid−SWCNT adsorption: ♦, citric acid; ▲, tartaric acid.

First-Order Model. The Lagergren rate equation may have been the first rate equation used for the sorption of solid−liquid systems.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

After integration of eq 7, the equation can be linearized as eq 8

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{8}$$

In this equation, k_1 is the first-order rate coefficient (min^{-1}). In this model, the limiting phenomenon is intraparticle mass transfer resistance.[23]

Pseudosecond-Order Model.[15] The equation for the pseudo-second-order model is shown below.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

In this equation, k_2 is the pseudosecond-order rate coefficient ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$). If eq 9 is integrated, a linear equation is obtained. This equation is shown as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{10}$$

The initial sorption rate, Γ ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$), at $t \rightarrow 0$ is defined as

$$\Gamma = k_s q_e^2 \tag{11}$$

The values of k_2 and calculated q_e are obtained from the slope of the plot t/q_t versus t. Γ and k_2 are obtained from the intercept. In this model, the limiting phenomenon is the adsorption mechanism, not the transfer of mass resistance.[23] The first-order and the pseudosecond-order model parameters are shown in Table 4, and plots of both models can be seen in Figures 7 and 8.

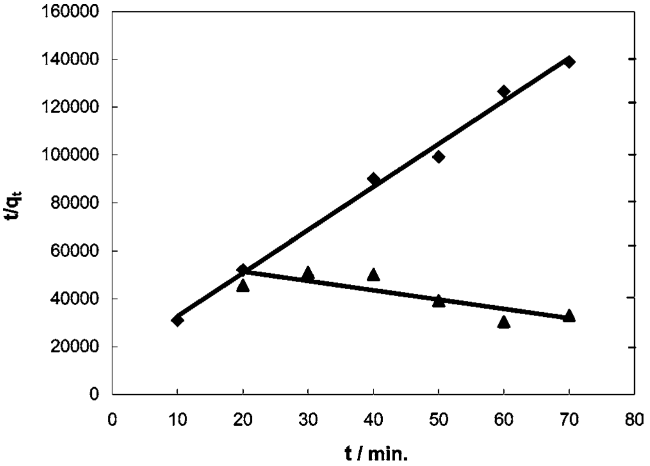

Figure 8. Pseudosecond-order kinetic of the acid−SWCNT adsorption: ♦, citric acid; ▲, tartaric acid.

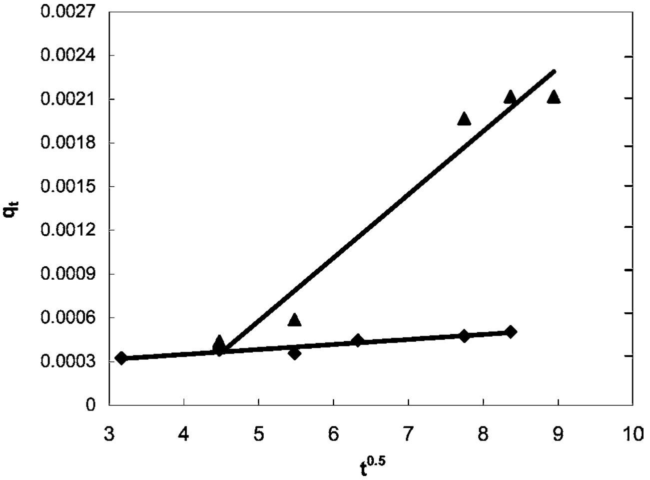

Figure 9. Weber and Morris intraparticle diffusion plot of the acid−SWCNT adsorption: ♦, citric acid; ▲, tartaric acid.

The first-order and pseudosecond-order models were investigated for both of the acids, calculated from linear regression. Tartaric acid was fitted with the first-order kinetic model, and its correlation coefficient was 0.97 as shown in Figure 7. Citric acid was fitted with the pseudosecond-order kinetic model, and its coefficient of determination was 0.99 as shown in Figure 8.

Weber and Morris Intraparticle Diffusion Model.[15] Intraparticle diffusion can be estimated using the Weber−Morris intraparticle diffusion model.

$$q_t = k_{id}t^{1/2} + \text{I} \tag{12}$$

In eq 12, k_{id} is the intraparticle diffusion rate coefficient, and I gives an idea about the thickness of the boundary layer. These values can be found by a plot, q_t versus $t^{1/2}$. The slope is k_{id}, and the intercept is I. As seen in Figure 9, the straight lines deviate from the origin. The difference between final mass transfer rate and initial mass transfer rate may cause the deviations of the straight lines. Also, this deviation can show that pore diffusion is not the only rate-controlling step.[15] I and k_{id} values are shown in Table 4.

Conclusions

The following conclusions can be presented:

(1) In this study, the adsorption of tartaric and citric acid on SWCNTs was investigated. The parameters which affect the adsorption reaction were determined. An increase of the initial acid concentration decreases adsorption, as does an increase of temperature. So, it is understood that the adsorption reaction is an exothermic reaction.

(2) The Langmuir and Freundlich isotherms were applied to the experimental data, and the equilibrium data for the adsorption of both of acids were represented by the Langmuir isotherm. This result shows that the adsorption processes progress via monolayer formation.

(3) The adsorption kinetics was found to follow a second-order rate expression for citric acid and a first-order kinetic model for tartaric acid. Citric acid was fitted with the Elovich model and tartaric acid with the Weber−Morris intraparticle diffusion model. As a result of these kinetic models, we can say that when tartaric acid adsorbs onto SWCNTs the rate-limiting phenomenon is intraparticle mass transfer resistance, but when citric acid adsorbs onto SWCNTs the rate-limiting phenomenon is the adsorption mechanism.

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