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Removal of Some Carboxylic Acids from Aqueous Solutions by Hydrogels

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Carboxylic acids are biotechnological substances that are used extensively in many industries, thus production and separation of carboxylic acids from product mixtures are important scientific and economic problems. The aim of this work was to investigate the removal of acetic, citric, lactic, and tartaric acids from aqueous solutions. With this aim, first the effects of time, temperature, and mixing on separation of the carboxylic acids from aqueous solutions were investigated by experimental work. After the experimental conditions were determined, separation was undertaken for different initial acid concentrations at constant hydrogel concentration. The effect of different gel−acid mass ratios on adsorption at constant initial acid concentrations was determined. The removal of acetic acid was 59.74 %, of lactic acid was 55.45 %, of citric acid was 54.22 %, and of tartaric acid was 56.85 % with a 1.5 hydrogel/acid mass ratio at the lowest concentration of each acid. Results obtained from the experimental work have been used with the Freundlich isotherm.

Introduction

Organic acids have found extensive use in many important fields ranging from pharmaceutical, food, and textile to petrochemical industries. Carboxylic acids, including acetic, citric, lactic, and tartaric acids are among the most used organic chemicals.[1,23]

It is well-known that the ideal way to produce carboxylic acids, and also other compounds having sufficient acidic properties, is the fermentation processes that already have proved to be environmentally friendly and use renewable resources. One of the most common problems of fermentation in the production of these carboxylic acids is their low concentration. For separation of organic acids from fermentation broth, a lot of methods have been investigated. Solvent extraction has been used for purification of carboxylic acids. However, the toxicity of these solvents always is a problem. Electrodialysis has been used as a technique for the isolation and purification of carboxylic acids from fermentation media. Since other anions also go with the acid, other broth components end up in the product stream by diffusion, and further processing is necessary to remove these impurities. The sorption of carboxylic acids on ion exchange resins has also been studied. This method requires additional chemicals to recover the acid from the resin. An alternative method of recovery of carboxylic acids from fermentation broth is based on sorption.[4,5]

Hydrophilic gels are called hydrogels. The hydrophilicity is due to the presence of hydrophilic groups, such as hydroxyl, carboxyl, amide, and sulfonic groups along the polymer chain. *Hydrogels* are three-dimensional polymer networks that are capable of absorbing large amounts of water. They are cross-linked polymers which consist of hydrophilic monomers. Cross-linkage can be caused by entanglement (“physical” cross-linking) or by chemical reactions (“chemical” cross-linking). A hydrogel with (sufficient but not too) high density of cross-linking positions changes its volume when it comes into contact with an aqueous solution. This variation of volume is called “swelling” or “shrinking”.[6,78]

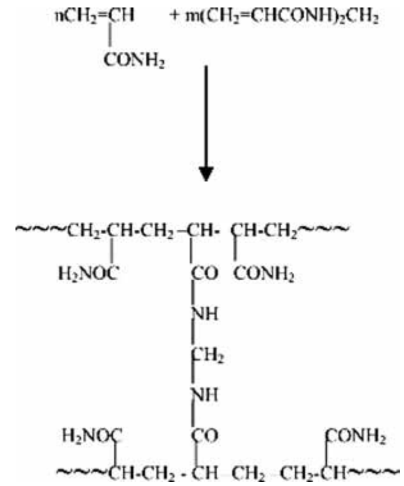

Figure 1. Schematic of preparation of cross-linked polyacrylamide.

The increasing importance of hydrogels in areas like, for example, pharmaceutical, food chemistry, medicine, and biotechnology, in some separation and concentration processes, has stimulated theoretical and experimental work on the thermodynamic properties of hydrogels in aqueous solutions. In the literature, there is some work dedicated to various aspects, such as removal of some materials in aqueous solutions using hydrogels and removal of carboxylic acids with different methods.

A lot of studies have been done with respect to the recovery of carboxylic acids from aqueous solutions. Aljundi et al. have examined the silicalite molecular sieve for adsorption of lactic acid.[9] Inci has investigated the adsorption of many carboxylic acids with activated carbon.[10] Uslu has extracted tartaric acid with alamine 336.[11] Ince has extracted acetic acid with different dibasic esters.[12] On the other hand, hydrogels have also been used in many different applications such as removal of the Cu(II) ion and heavy metals.[13,14] Yi and Zhang have used hybrid hydrogels for extraction of methylene blue dye from aqueous solution.[15] Gündüz and Tolga have studied bovine serum albumin sorption and recovery by hydrogels.[16] Gonzalez-Saiz

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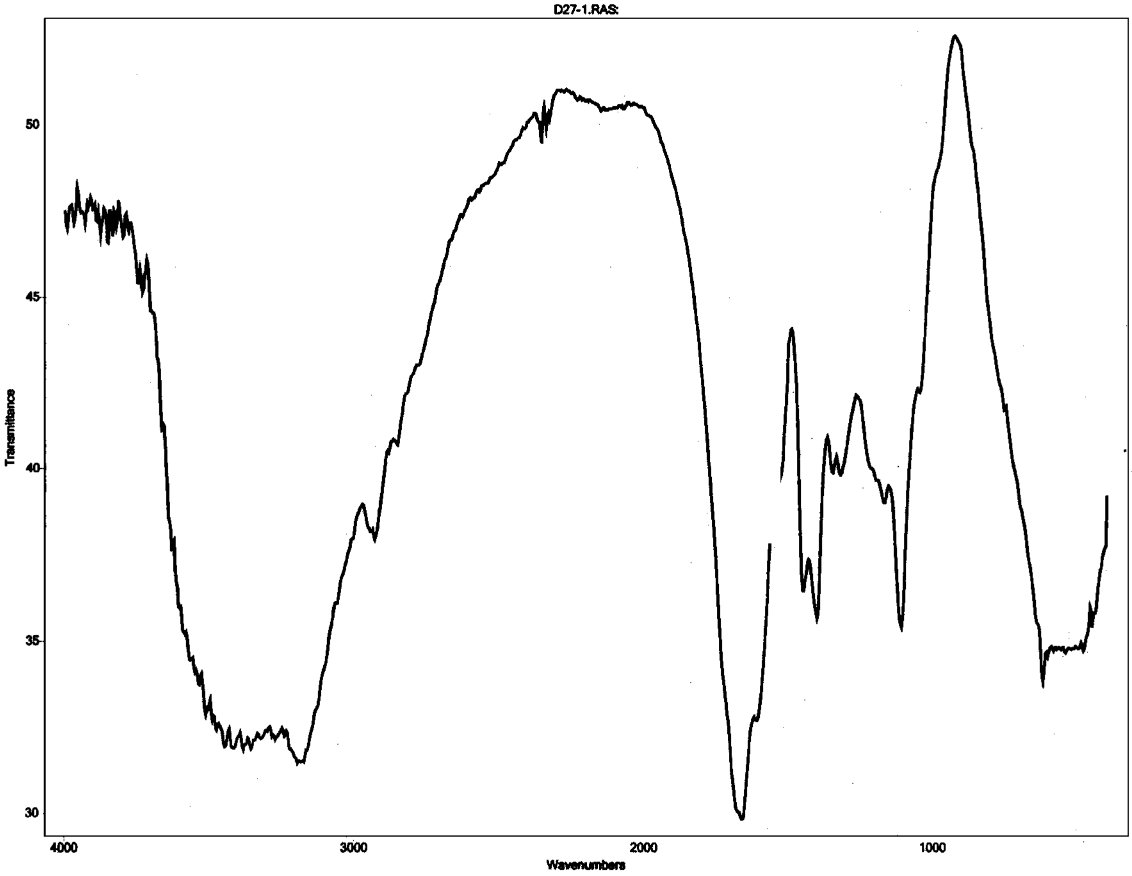

Figure 2. FT-IR spectra of the hydrogel sample.

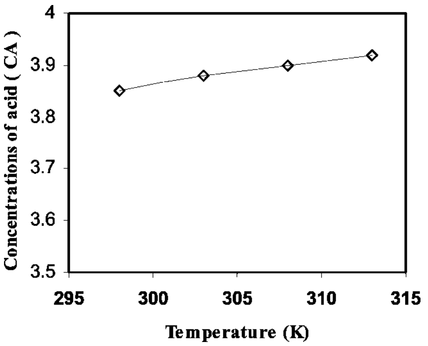

Figure 3. Temperature effect on the equilibrium acid concentration.

Table 1. Experimental Results of the Temperature Effect on the Sorption of 10.60 % Acetic Acid

temperature (K)	acid concentration (C_A) % w/w
298.15	3.85
303.15	3.88
308.15	3.90
313.15	3.92

et al. have investigated removal of citric acid using weakly basic copolymer polyacrylamide (acrylamide-co-*n*,*n'*-dimethylaminoethyl methacrylate) gels.[17] However, there are not adequate data in the literature about the removal of carboxylic acids from aqueous solutions by hydrogels.

In this study, we have investigated removal of different carboxylic acids (acetic acid, citric acid, lactic acid, and tartaric acid) from aqueous solution using hydrogels.

Table 2. Effect of Shaking on the Sorption of 10.80 % Lactic Acid at (10, 15, 30, 45, and 60) min

time (min)	(C_{Ar}) % w/w	(C_{As}) % w/w
10	10.15	10.13
15	8.15	8.16
30	5.40	5.39
45	5.30	5.29
60	4.90	4.91

Theoretical

The most important contribution to the elucidation of the swelling mechanism of ionic gels was made by Flory,[18] and a theoretical investigation was further developed by Tanaka.[19] They identified three forces acting on the ionic gel: rubber elasticity, the interaction force between polymer strands and solvent, and the dissociated ion pressure. The last force has been recognized as the determining factor in the degree of swelling of an ionic gel.

Tanaka termed the sum of these forces the osmotic pressure of the gel and concluded that whenever possible the gel adjusts its volume so that the osmotic pressure becomes zero. According to the interpretation of the swelling mechanism, the decrease of water absorbency in electrolytic solutions is due to the decrease in the osmotic pressure difference between the inside and the outside of the gel.[19]

To optimize the design of the sorption system, it is important to establish the most appropriate correlation for the equilibrium curves. The sorption of acids from aqueous solution has been well described by using the Langmuir and Freundlich isotherms. A lot of studies use these isotherms for sorption systems.[20] Karthikeyan et al. have used the Freundlich and Langmuir

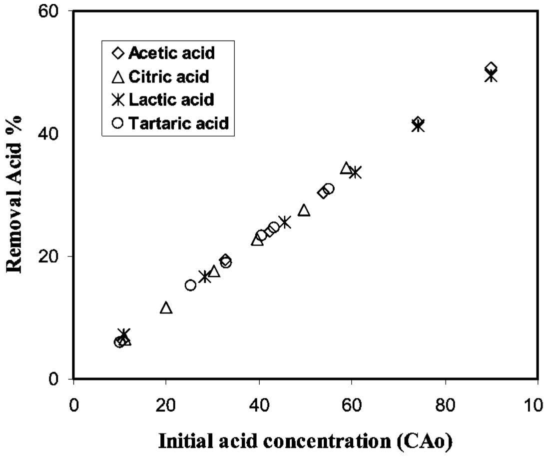

Figure 4. Effect of initial acid concentration on removal acid % (w/w) in 10 mL of hydrogel−acid mixture at 25 °C.

Table 3. Experimental Results of Equilibrium Acid Concentrations and Removal Acid % with Different Hydrogel−Acid Mass Ratios at Room Temperature

acids	hydrogel−acid mass ratio	equilibrium acid concentrations (C_A) % w/w	removal acid %
acetic acid	0.75	6.05	42.92
	1.24	4.59	56.70
	1.42	4.15	60.85
	1.836	3.25	69.34
	2.62	2.65	75.00
lactic acid	0.48	7.91	28.87
	0.98	5.91	46.85
	1.44	4.55	59.08
	1.92	3.81	65.74
	2.39	3.28	70.50
citric acid	0.48	7.39	31.57
	0.72	6.53	39.54
	1.44	4.43	58.98
	1.94	3.61	66.57
	2.92	2.76	74.44
tartaric acid	0.50	6.89	31.92
	1.10	4.98	50.75
	1.59	3.73	63.15
	1.94	3.27	67.60
	2.37	2.95	70.84

isotherms for sorption of phosphorus.[21] Weber et al. have also used these isotherms for different species.[22]

When a physical process is carried out at a constant temperature, the amount adsorbed, Q, can be quantitatively described by the Langmuir equation. It is represented by the following equation

$$(C/Q) = (K_1/Q_0) + (C/Q_0) \tag{1}$$

where C is the equilibrium concentration ($\mathrm{mol \cdot L^{-1}}$); Q is the amount sorbed at equilibrium ($\mathrm{mol \cdot g^{-1}}$); K_1 is the inverse of the Langmuir constant (K_L); and Q_0 is the sorption maxima. The plot of C/Q vs C gives a straight line showing the applicability of the isotherm. The values of Q_0 and K_1 at different concentrations can be determined from the slope and intercept of the plot. The Langmuir parameters are very useful in predicting sorption capacities and for incorporating a mass transfer relationship.

The Freundlich equation is used for heterogeneous surface energies in which the energy term in the Langmuir equation varies as a function of the surface coverage strictly due to variation in the heat of sorption. The Freundlich equation has the general form

$$Q = K_f C^{1/n} \tag{2}$$

A logarithmic plot linearizes the equation enabling the exponent n and the constant K_f to be determined.[23,24]

$$\ln Q = \ln K_f + (1/n) \ln C \tag{3}$$

The values of K_f and $1/n$ at different concentrations can be determined from the slope and intercept of linear plots of ln Q vs ln C.[10,24]

Experimental

L-(+)-Tartaric acid (> 99%), citric acid (> 99 %), lactic acid (90 %), acetic acid (> 99 %), and sodium hydroxide were purchased from Merck Co. They were used without further

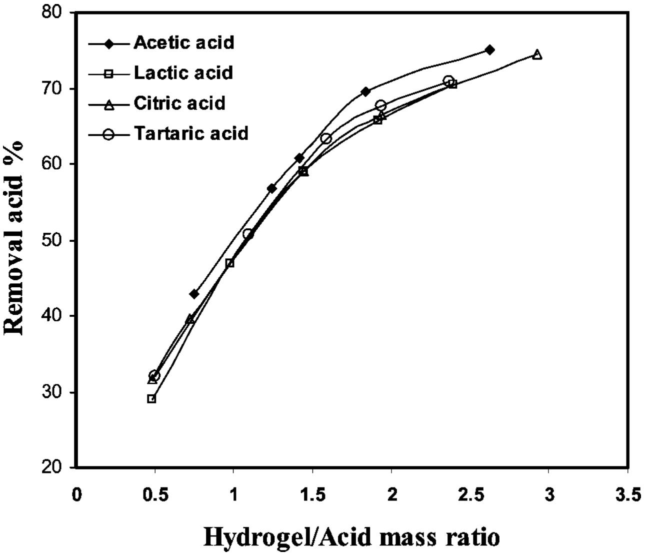

Figure 5. Effect of hydrogel−acid mass ratio on acid removal % (w/w) in a mixture of carboxylic acid−hydrogel at 25 °C.

Table 4. Experimental Results of Equilibrium Acid Concentrations and Removal Acid % with Different Initial Acid Concentrations at Room Temperature

acid	initial acid concentration (C_{A0}) % w/w	equilibrium acid concentration (C_A) % w/w	removal acid %
acetic acid	90	39.25	56.38
	74.10	32.28	56.44
	53.80	23.36	56.58
	42.20	24.15	57.22
	32.70	13.25	59.49
	10.60	4.36	58.87
lactic acid	89.81	49.41	55.01
	74.30	41.30	55.58
	60.79	27.05	55.51
	45.49	20.00	56.04
	28.35	11.64	58.95
	10.80	3.66	66.12
citric acid	58.70	34.53	58.80
	49.60	27.54	55.52
	39.6	16.90	57.33
	30.1	12.56	58.28
	19.85	8.22	58.59
	11.12	4.70	57.74
tartaric acid	55.04	24.10	56.22
	43.28	18.57	57.09
	40.50	17.09	57.81
	32.85	13.93	57.59
	25.30	10.09	60.12
	10.12	4.20	58.50

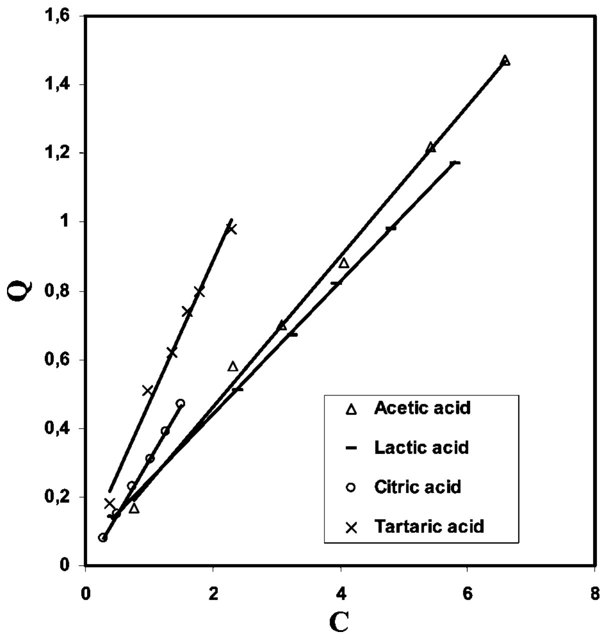

Figure 6. Linearized Freundlich isotherms for carboxylic acid sorption by hydrogel. Comparison of experimental results and model predictions.

Table 5. Freundlich Isotherm Model Constants and Coefficients of Determination for Sorption of Carboxylic Acids by Hydrogel from Aqueous Solution

	Freundlich constants						
	C	Q					
acids	(mol·L^{-1})	(mol·g^{-1})	ln C	ln Q	K_f	1/n	R^2
acetic acid	6.58	1.47	1.88	0.38	0.23	0.99	0.9953
	5.42	1.22	1.69	0.20			
	4.05	0.88	1.40	−0.13			
	3.08	0.70	1.12	−0.35			
	2.32	0.58	0.84	−0.54			
	0.77	0.17	−0.26	−1.77			
lactic acid	5.81	1.17	1.76	0.16	0.22	0.95	0.9998
	4.80	0.98	1.56	−0.02			
	3.93	0.82	1.37	−0.20			
	3.25	0.67	1.18	−0.40			
	2.38	0.51	0.87	−0.67			
	0.44	0.14	−0.82	−1.97			
citric acid	1.51	0.47	0.41	−0.75	0.31	1.05	0.9994
	1.27	0.39	0.24	−0.94			
	1.02	0.31	0.02	−1.17			
	0.75	0.23	−0.29	−1.47			
	0.49	0.15	−0.71	−1.90			
	0.28	0.08	−1.27	−2.53			
tartaric acid	2.29	0.98	0.83	−0.02	0.46	0.95	0.9901
	1.80	0.80	0.59	−0.22			
	1.61	0.74	0.48	−0.30			
	1.36	0.62	0.30	−0.48			
	0.98	0.51	−0.02	−0.67			
	0.39	0.18	−0.94	−1.71			

treatment. Stock solutions of the acids were prepared by dissolving appropriate amounts of the acids with distilled water in a flask.

The FTIR spectra of dry gels were obtained by using a Digilab, Excalibur-FTS 3000 MX model instrument. The resolution of the FTIR was 4 cm^{-1}. The dry gel powder was thoroughly ground with potassium bromide (KBr) (IR grade, Merck-Germany) at a ratio of 1:200 and pressed into a pellet, and the spectrum was then recorded.

A cross-linked polyacrylamide (CPAAm) was prepared by free radical polymerization of acrylamide (AAm) and *N*,*N*-methylenebisacrylamide (NMBA) in bidistilled water. A schematic of the cross-linked polyacrylamide is shown in Figure 1. A cross-linked acrylamide hydrogel was used in this study. It was identified by FTIR analysis. The hydrogel used was swollen with distilled water until the swelling equilibrium ratio for all experiments.

The adsorption of acids from aqueous solutions was carried out at four different conditions by changing temperature, the shaking effect, acid−hydrogel ratio, and initial acid concentration.

In the first stage, the effects of temperature and shaking were investigated. A Nüve ST 402 shaking water bath was used in this step. For the temperature swing experiment, 10.60 % acetic acid solutions were prepared, and the same amount of hydrogel was added in Erlenmeyer flasks. These mixtures were kept at four different temperatures, (25, 30, 35, and 40) °C. For determination of the effect of shaking, 10.8 % lactic acid solutions were prepared, and the same amount of hydrogel was added in two Erlenmeyer flasks. One of them was shaken at room temperature, and the other mixture was kept at room temperature without shaking. In this step, samples of the solutions were taken at different times, (10, 15, 30, 45, and 60) min. The acid concentrations of the aqueous phase were determined.

In the second stage, four different initial solution concentrations of each acid were prepared by dilution of appropriate amounts of the stock acid solutions. These concentrations were 10.60 %, 32.70 %, 42.20 %, 53.80 %, 74.10 %, 90 % (w/w) for acetic acid; 10.80 %, 28.35 %, 45.49 %, 60.79 %, 74.3 %, 89.81 % (w/w) for lactic acid; 11.12 %, 19.85 %, 30.10 %, 39.60 %, 49.60 %, 58.7 % (w/w) for citric acid; and 10.12 %, 25.30 %, 32.85 %, 40.45 %, 43.28 %, 55.04 % (w/w) for tartaric acid.

Acid solutions in known concentrations were taken in a 100 mL Erlenmeyer flask. Hydrogels were added to the Erlenmeyer flask in a 2/3 mass ratio. Erlenmeyer flasks were kept for 24 h at 25 °C to reach equilibrium. The contents of the Erlenmeyer flasks were filtered, and the acid concentrations of the aqueous phase were determined by titration with 0.1 N aqueous sodium hydroxide. The aim of this investigation was to determine the optimum initial concentration of the acids.

In the third step, the same amounts of the acids at the lowest concentration for each acid (acetic acid 10.60 %, lactic acid 10.80 %, citric acid 11.12 %, and tartaric acid 10.12 %) were weighed, and mixtures with different ratios of hydrogel/acid were prepared to determine the optimal hydrogel−acid ratio to show the effect of the ratio on sorption.

All of the experiments were performed using a 100 mL Erlenmeyer flask at 25 °C, except the temperature swing experiments. The volume of the aqueous phase was 10 mL in all experiments. The contents of the Erlenmeyer flasks were then filtered, and the acid concentrations of the aqueous phase were determined by titration with 0.1 N aqueous sodium hydroxide.

Results and Discussion

The hydrogel structure as characterized by FTIR is depicted in Figure 2 and confirms the formation of acrylamide as is evident from bands appearing at (3437 and 3383) cm^{-1} (N−H stretching) and (1659 and 1666) cm^{-1} (C═O stretching band), and asymmetrical and symmetrical stretching of C−H is found at (2937 and 2933) cm^{-1}, respectively. The spectra also show a broadband at 1454 cm^{-1}, which is due to the presence of the (−C−N) group of the cross-linking agent (*N*,*N*-methylene bisacrylamide) and acrylamide.

The sorption of acetic acid by hydrogel at (25, 30, 35, and 40) °C is shown in Figure 3 and Table 1. It can be seen that the equilibrium concentration was found to increase with an increase in temperature only slightly. The equilibrium concentration is 3.85 % (w/w) at 25.15 °C (= 298.15 K) and 3.92 % (w/w) at

40 °C (= 313.15 K). The temperature was found to have a negligible effect on the adsorption. The sorption behavior of the gel is not influenced by temperature.

In the shaking effect experiment, it can be seen that shaking is not a factor for removal of carboxylic acids by hydrogel. The sorption of lactic acid by the hydrogel is shown in Table 2. Shaking does not affect the sorption of carboxylic acids by the hydrogel.

Sorption capacities of the hydrogel are presented as a function of initial concentration of carboxylic acid within the aqueous solutions in Figure 4 and Table 4. The initial concentration was changed in the range of (10 to 90) % for the different acids. It can be seen that the equilibrium acid concentration increases with increasing initial acid concentration.

Subsequently, five samples (10 mL for every sample) of each acid at the lowest concentration were prepared. Hydrogel was then added with increasing hydrogel/acid mass ratio for the four carboxylic acids, and the mixture was allowed to reach equilibrium. In this way, the influence of the hydrogel/acid mass ratio was investigated on the sorption of the carboxylic acids. The hydrogel/acid mass ratio was changed in the range of 0.5 to 3. Figure 5 and Table 3 give the ratios, equilibrium acid concentrations, and percentage removed of each carboxylic acid. It can be seen that the sorption of the carboxylic acids increases with increasing ratio to an optimal value of 1.5 to 2. When the ratio increases more than the optimal value, small changes are observed for the acid concentration extracted.

To optimize the design of the sorption system, it is important to establish the most appropriate correlation for the equilibrium curves. The Freundlich isotherm equations have been applied in this study. The linearized Freundlich isotherms of carboxylic acids are shown in Figure 6. The Freundlich sorption constants evaluated from the isotherms with their coefficients of determination (r^2) are given in Table 5. The Freundlich model agrees well with the experimental data of the carboxylic acids considering that the obtained linear regression coefficients are greater than 0.98.

Conclusions

The aim of this study was to determine the sorption capacity of carboxylic acids on hydrogel from aqueous solutions. In this study, removal of acetic acid was 59.74 %, of lactic acid was 55.45 %, of citric acid was 54.22 %, and of tartaric acid was 56.85 % at a hydrogel/acid mass ratio of 1.5 and the lowest concentration of each acid. The values of the Freundlich isotherm coefficients have been determined and show good agreement with the experimental data.

Symbols and Abbreviations

C	equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$)
C_A	equilibrium acid concentration ($\text{mg}\cdot\text{L}^{-1}$)
C_A0	initial acid concentration ($\text{mg}\cdot\text{L}^{-1}$)
C_Ar	acid concentration of rested solution ($\text{mg}\cdot\text{L}^{-1}$)
C_As	acid concentration of shaked solution ($\text{mg}\cdot\text{L}^{-1}$)
T	temperature (K)
K_1	inverse of Langmuir constant
K_f	Freundlich constant
n	exponential constant of Freundlich equation
Q	amount sorbed ($\text{mol}\cdot\text{g}^{-1}$)
Q_0	maximum sorption ($\text{mol}\cdot\text{g}^{-1}$)
R	correlation coefficient

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