# Adsorption/Desorption of Organic Acids onto Different Adsorbents for Their Recovery from Fermentation Broths

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ABSTRACT: Activated carbon and a weak base resin were used as adsorbents for organic acids of relevance in green chemistry. Equilibrium adsorption studies in single and binary systems of acetic, propionic and butyric acids were carried out using various solvents (water, ethanol, and *n*-propanol) and equilibrium isotherm models were tested. The resin had a higher adsorption capacity than the activated carbon (about 35 %). Data on adsorption of binary systems suggested competition between the acids and a chain size dependence. In the studies using organic solvents, the resin showed a higher adsorption capacity than the activated carbons. This work showed the importance of conducting a complete and integrated study of an adsorption process including both adsorption and desorption steps. The use of resin with *n*-propanol as eluent achieved the best recovery in the simulated purification of propionic acid.
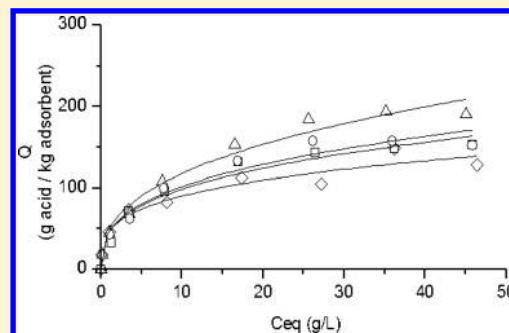
INTRODUCTION

Carboxylic acids are important synthesis compounds in dye and pharmaceutical chemistry and are also applied in preservation and disinfection in the food and tanning industries. The low molecular mass carboxylic acids are also pollutants as they are the result of degradation of larger molecules by oxidation.[1]

Production of organic acids by fermentation has gained importance in green chemistry due to a future oil scarcity (the basis for the production of these acids) and concern with the protection of the environment. Therefore, the study of downstream process (DSP) of these acids has become relevant in order to increase the technical and economic feasibility of their production by fermentation.

Adsorption, a widely used unit operation in chemical and biotechnological industries, is robust and relatively easy to operate, so it is an attractive option for the large-scale DSP of organic acids. The efficient design and operation of adsorption processes (including the desorption step) require equilibrium adsorption data for use in the kinetic and mass transfer models. These models can then be used to predict the performance of the adsorption/desorption contact processes under a range of operating conditions.[2,3] The adsorption isotherm curve is informative, since it sheds light on the phenomenona governing the interaction between adsorbate and adsorbent.[4] A variety of models have been developed to describe the adsorption process, making it easier to predict and understand the mechanisms of adsorption.

Nevertheless, recent studies on adsorption of organic acids are incomplete. Adsorption studies are usually conducted with one or two acids separately and there are no reported studies on the desorption step. Therefore, the aim of this work was to conduct a complete adsorption/desorption study of organic acids, since their DSP requires their removal from the fermentation broth and provides a means of generating a relatively high purity product.

The adsorption of three different acids of different chain lengths (acetic, propionic and butyric acids) was studied using two types of solid adsorbents, activated carbon and ion-exchange resin (the most used adsorbents cited in literature to capture organic acids) and two eluents (*n*-propanol and ethanol). Thermodynamic parameters were also evaluated to gain an understanding of the mechanisms involved. Considering that in a real system, as in a fermentation broth, more then one of these acids can be found as byproducts, multicomponent adsorption experiments were carried out to evaluate the competition between them for the adsorbents. Finally, the data obtained were used to calculate the recovery and yield of the integrated process (adsorption and desorption).

MATERIALS AND METHODS

Materials. The butyric and acetic acids used in this study were produced by Merck (Brazil); the propionic acid was produced by Across Organics (Brazil). The sodium hydroxide was also from Merck (Brazil) and the potassium biphthalate was from Synth (Brazil).

The weak base resin (anion exchanger) was donated by Purolite (Brazil) and the activated carbon, by Carbomafra (Brazil). The activated carbon (Carbomafra 119) is a granular adsorbent (mean particle size of 1.9 mm) derived from coconut shell and activated by a physical process (high temperature). The resin (Purolite A133S) is a macroporous spherical polymer

(polystyrene cross-linked with divinylbenzene matrix) with a weak anion exchange group (tertiary amine).

Ultrapure water was obtained using Milli-Q equipment from Millipore (USA). All other reagents were of analytical grade.

Experimental Methods. *Single-Component Adsorption: Adsorption Isotherms for Aqueous and Alcoholic Solutions.* The batch experiments were carried out in 100 mL flasks with 0.500 g of dry adsorbent added to 25.0 mL of the aqueous solution at different organic acid concentrations between (0.5 and 50.0) $g \cdot L^{-1}$. The flasks were shaken in an incubator at temperatures of (20, 30, 40, and 50) °C for aqueous solutions and (10 and 50) °C for alcoholic solutions at 200 rpm until equilibrium (about 14 h). Then each system was quickly filtered and the propionic acid concentration (Ceq) was quantified by titration.

Multicomponent Adsorption: Binary Isotherms for Aqueous Solutions. The protocol used for single-component isotherms was also used for multicomponent adsorption at 30 °C with the exception that there were two organic acids in each aqueous solution, each one at the same concentrations as those used in the single-component isotherm experiments. The organic acid in equilibrium concentration was determined using HPLC.

Analytical Methods. *Quantification of Organic Acids by Titration.* Volumes between 0.5 and 20.0 mL (according to concentration) of acid were titrated with a 0.01 $mol \cdot L^{-1}$ NaOH solution, using phenolphthalein as indicator. NaOH solution concentration was corrected with about 0.050 g of potassium biphthalate as a primary standard in triplicate using phenolphthalein as indicator.

Quantification of Organic Acids by High-Performance Liquid Chromatography (HPLC). The concentration of organic acids in the binary systems was evaluated using the Breeze chromatographic system (Waters, USA) equipped with a dual UV detector. A 7.8 × 300 mm Aminex HPX87H column (BioRad, USA) was used to separate the organic acids. A degassed mobile phase of 4.5 $mmol \cdot L^{-1}$ sulfuric acid filtered at 0.45 μm was used in isocratic mode at 0.6 $mL \cdot min^{-1}$. The injection volume was 20 μL and the samples had been previously filtered at 0.45 μm. Duration of the run was 20 min, the column temperature was 35 °C, and the detection was at 210 nm.

RESULTS AND DISCUSSION

Adsorption Studies: Monocomponent Adsorption. *Activated Carbon Adsorption Isotherms.* The adsorption isotherms for acetic, propionic and butyric acids from aqueous solutions are shown in Figure 1 and adsorption data in Table 1. Three adsorption isotherm models were used to fit the experimental data: the Langmuir, the Freundlich and the Sips models. The Sips model resulted in a very bad fit and was discarded. Of the remaining two, the Freundlich model provided the better fit to the experimental points (data not shown) and was used to analyze the results. This isotherm model assumes neither homogeneous site energies nor limited levels of sorption. It is the earliest known empirical equation and is shown to be consistent with exponential distribution of active adsorption centers, characteristic of heterogeneous surfaces.[5] It is expressed as follows:

$$Q = FC_{eq}{}^{n} \tag{1}$$
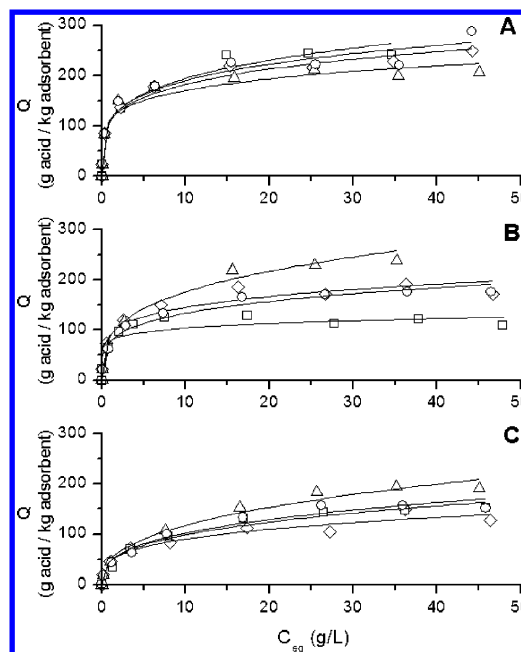
Figure 1. Adsorption isotherms of acetic (A), propionic (B), and butyric (C) acids in activated carbon at 20 °C ($\Diamond$), 30 °C ($\Box$), 40 °C (Δ), and 50 °C ($\bigcirc$). Lines refer to the fitting of Freundlich model to the data. Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in the aqueous phase at equilibrium.

where F and n are the Freundlich constants characteristic of the system, Q is the adsorption capacity (g acid/kg adsorbent), and C_{eq} is the acid's equilibrium concentration ($g \cdot L^{-1}$).

Parameter n, the heterogeneity factor, is related to the distribution of adsorption energies of the active sites on the adsorbent surface. Thus, the closer to the unit, the more homogeneous is the surface of the adsorbent; an n value of 1.0 (homogeneous surface) is the ideal Langmuir model.[6] Parameter F can be taken as a measure of adsorption capacity of a narrow subregion with sites having the same distribution energy for adsorption.[7]

The model parameters obtained for the Freundlich isotherms on activated carbon as a function of temperature are shown in Table 2. Since the experiments were performed in the same concentration range, it was possible to compare the values of F. The adsorption capacity (represented by F) is normally influenced by temperature because this parameter is dependent on the equilibrium adsorption constant, which changes with temperature;[7] however, in the temperature range studied it did not show a significant change. In comparing the adsorption of the three acids studied, it can be observed that adsorption capacity increases with aliphatic chain length, thereby confirming Traube's rule.[6] Traube found that the regularities that are seen in the physical properties of homologous series of organic molecules could be extended to their behavior on surfaces. Thus, the organic acids would be adsorbed with their carbon chain parallel to the surface of the activated carbon, where each CH_2 group contributes the same adsorption energy to the molecule. Therefore, the longer the aliphatic chain of the acid, the higher the F value since it is related to adsorption capacity, as mentioned above.

According to Kumar et al.,[8] n depends on the nature and strength of the adsorption process and the higher the value, the greater the affinity between adsorbate and adsorbent. This parameter is also dependent on temperature, but there were no

Table 1. Adsorption Data of Acetic, Propionic, and Butyric Acids in Activated Carbon at Different Temperatures[a]

	acetic acid		propionic acid		butyric acid	
$T/°C$	$C_{eq}/g \cdot L^{-1}$	$Q/g \cdot kg^{-1}$	$C_{eq}/g \cdot L^{-1}$	$Q/g \cdot kg^{-1}$	$C_{eq}/g \cdot L^{-1}$	$Q/g \cdot kg^{-1}$
20	0.11	18.63	0.03	22.77	0.02	23.86
	1.02	46.19	0.53	73.69	0.30	85.47
	3.44	72.98	2.61	120.26	2.21	136.92
	8.15	82.51	7.03	149.83	6.20	178.16
	17.32	112.49	16.32	186.52	15.30	219.43
	27.25	105.14	26.64	171.33	25.19	215.03
	36.16	148.34	36.3	191.16	34.83	228.89
	46.34	128.22	46.69	172.36	44.27	248.80
30	1.29	32.79	0.03	23.03	0.02	23.85
	3.46	70.94	0.73	65.73	0.32	81.98
	7.89	95.98	3.75	111.84	2.23	135.28
	16.93	131.85	7.50	125.00	6.28	177.76
	26.48	143.14	17.41	128.50	14.86	241.37
	36.16	147.87	27.73	113.81	24.68	244.10
	45.84	152.48	37.84	122.85	34.56	240.81
			47.88	109.05	45.24	198.48
40	0.12	18.54	0.04	22.86	0.02	23.53
	1.05	44.97	0.64	67.35	0.29	83.03
	3.51	68.38	2.67	116.85	1.93	151.28
	7.58	108.13	6.54	172.75	6.27	177.73
	16.50	152.70	15.59	219.72	15.80	194.89
	25.62	183.92	25.40	230.16	25.31	210.86
	35.15	194.44	35.22	238.07	35.37	199.05
	45.08	190.43	45.22	239.29	45.06	206.25
50	0.14	17.37	0.05	22.41	0.02	24.17
	1.10	42.82	0.74	63.19	0.30	84.80
	3.62	62.26	2.85	108.97	2.01	148.23
	7.78	100.02	7.33	133.68	6.37	179.70
	16.90	133.09	16.72	166.47	15.44	226.20
	26.16	157.28	26.61	170.56	25.49	222.25
	35.95	157.58	36.46	177.08	35.54	219.67
	45.84	152.49	46.49	175.83	44.16	288.10

[a]Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in aqueous phase at equilibrium.

significant changes in the temperature range studied. The carbonic chain did not show a definite influence on this parameter either.

Determination of the Thermodynamic Parameters for Adsorption onto Activated Carbon. The values of the thermodynamic parameters enthalpy change (ΔH_{ads}) and entropy change (ΔS_{ads}) were calculated from the plotted curve formed by the Neperian logarithm of the distribution coefficient (K_{ad}) as a function of the inverse temperature (T) using the van't Hoff equation:

$$\ln(K_{ad}) = \frac{-\Delta H_{ads}}{RT} + \frac{-\Delta S_{ads}}{R} \tag{2}$$

where R is the universal gas constant and K_{ad} is the equilibrium thermodynamic constant of the adsorption process or distribution coefficient,[1] defined as

$$K_{ad} = \frac{Q/Q^0}{C_{eq}/C_{eq}^0} \tag{3}$$

where Q^0 is 1 g·kg^{-1} and C_{eq}^0 is 1 g·L^{-1} (values small enough to be considered ideal conditions).

The value of ΔG_{ads} (free energy change) was calculated using the classic thermodynamic relation:

$$\Delta G_{ads} = -RT \ln(K_{ad}) \tag{4}$$

The change in enthalpy of adsorption was positive for propionic and butyric acids and negative for acetic acid (Table 3). There was a trend: the enthalpy increased as the chain size increased. For entropy changes negative values would also be expected because adsorbed molecules have a lower dregree of freedom than while in solution. The negative free energy shows the spontaneity of the adsorption process, and the low energy involved in the phenomenon indicates that in this case adsorption should occur by physisorption.[6]

Resin Adsorption Isotherms. As observed for the activated carbon, the Sips model was discarded due to its very bad fit to the data and the Freundlich model had a better fit than the Langmuir model for adsorption onto the resin (data not shown). Figure 2 and Table 4 contain the adsorption isotherms and data, respectively, for all three acids onto the weak base resin at four temperatures. The adsorption capacities (Table 5) were higher for the resin than for the activated carbon (from 300 to 520 g·kg^{-1} for the former and from 130 to 240 g·kg^{-1} for the latter). Adsorption of acetic acid was lower than adsorption of the other acids. The temperature range studied did not allow any change in the adsorption isotherms. Adsorption processes are generally an exothermic phenomenon and are thus spontaneous processes, accompanied by a decrease in the free energy of the system. Molecules adsorbed on solids have a lower degree of freedom than molecules in solution, which causes a decrease in entropy during adsorption, as already stated. According to the thermodynamic relation

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{5}$$

ΔH_{ads}, the enthalpy of adsorption, has to be negative for a spontaneous process, indicating that the adsorption is always exothermic. For an exothermic process, lower temperatures increase the yield of the process, which explains the decrease in F with increasing temperature. Gluszcz et al.[9] also obtained this behavior when they studied the adsorption of lactic and citric acids on weak base resins, verifying a decrease in adsorption capacity with increasing temperature. In our study the

Table 2. Freundlich Model Parameters n and F for the Data of Adsorption Isotherms for Acetic, Propionic, and Butyric Acids on Resin at Different Temperatures

	acetic acid		propionic acid		butyric acid	
$T/°C$	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n
20.0	46.98 ± 5.92	0.28 ± 0.04	92.7 ± 10.40	0.20 ± 0.04	110.98 ± 6.46	0.22 ± 0.02
30.0	46.06 ± 6.31	0.33 ± 0.04	79.0 ± 8.40	0.12 ± 0.03	110.60 ± 9.21	0.24 ± 0.03
40.0	49.00 ± 5.64	0.38 ± 0.03	87.9 ± 8.81	0.30 ± 0.03	113.41 ± 10.44	0.18 ± 0.03
50.0	46.69 ± 6.00	0.34 ± 0.04	78.1 ± 6.71	0.23 ± 0.03	113.44 ± 10.91	0.22 ± 0.03

Table 3. Thermodynamic Parameters of Adsorption of Acetic, Propionic, and Butyric Acids onto Activated Carbon

	acetic acid			propionic acid			butyric acid		
$T/°C$	$\Delta G/\text{kJ·mol}^{-1}$	$\Delta H/\text{kJ·mol}^{-1}$	$\Delta S/\text{kJ·mol}^{-1}\text{·K}^{-1}$	$\Delta G/\text{kJ·mol}^{-1}$	$\Delta H/\text{kJ·mol}^{-1}$	$\Delta S/\text{kJ·mol}^{-1}\text{·K}^{-1}$	$\Delta G/\text{kJ·mol}^{-1}$	$\Delta H/\text{kJ·mol}^{-1}$	$\Delta S/\text{kJ·mol}^{-1}\text{·K}^{-1}$
20.0	−11.6	−13.9	−0.01	−8.7	0.4	0.03	−13.7	0.9	0.05
30.0	−13.6			−9.0			−14.2		
40.0	−13.6			−9.3			−14.7		
50.0	−13.5			−9.6			−15.2		

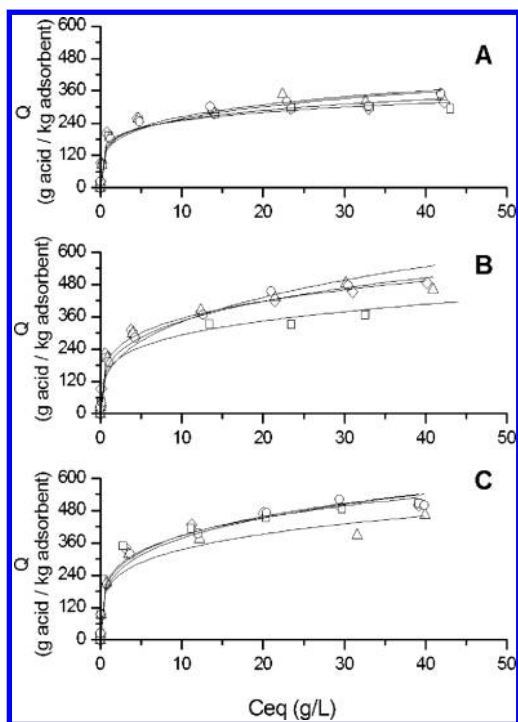**Figure 2.** Adsorption isotherms of acetic (A), propionic (B), and butyric (C) acids in resin at 20 °C (◊), 30 °C (□), 40 °C (△), and 50 °C (○). Lines refer to the fitting of Freundlich model to the data. Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in aqueous phase at equilibrium.

Table 4. Adsorption Data of Acetic, Propionic and Butyric Acids in Resin at Different Temperatures[a]

	acetic acid		propionic acid		butyric acid	
$T/°C$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$
20	0.03	23.26	0	0	0.02	22.37
	0.11	91.59	0.02	23.66	0.08	92.76
	0.81	203.79	0.1	92.98	0.47	223.11
	4.55	257.52	0.6	222.93	2.79	349.07
	14.01	278.17	3.81	311.1	11.17	414.40
	23.43	294.21	12.37	379.46	20.37	453.40
	32.98	294.36	21.47	419.53	29.71	485.48
	42.27	317.57	31.03	452.73	39.16	505.30
30	0.21	88.62	0.20	15.03	0.02	23.59
	1.03	191.34	0.42	28.25	0.08	94.64
	4.79	249.95	3.29	83.45	0.78	205.45
	14.13	274.87	8.06	97.61	3.05	342.02
	23.43	295.92	17.27	138.51	11.22	426.63
	33.10	300.18	27.17	143.14	20.07	471.21
	43.03	292.54	36.51	175.61	29.37	497.71
			46.48	177.46	39.16	500.16
40	0.03	22.55	0.22	14.21	0.03	23.15
	0.18	85.92	1.13	43.86	0.10	92.96
	1.18	186.44	3.32	85.20	0.70	210.95
	4.69	255.66	7.62	118.63	3.46	317.60
	13.75	290.35	16.67	166.41	12.21	373.70
	22.41	346.59	26.02	196.34	23.70	292.04
	32.59	321.25	35.57	223.43	31.60	388.76
	42.02	338.82	44.86	250.60	39.94	463.46
50	0.02	22.76	0.24	13.03	0.01	24.44
	0.28	82.46	0.84	58.25	0.13	93.62
	1.31	180.34	3.37	80.75	0.79	208.04
	4.83	244.34	8.25	86.81	3.66	318.50
	13.48	302.03	17.68	118.13	12.03	394.45
	22.94	320.36	27.28	139.10	20.47	471.11
	33.00	304.01	37.39	131.49	29.44	521.49
	41.86	349.97			39.85	500.06

[a] Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in aqueous phase at equilibrium.

temperature range was not sufficient to give a significant change in adsorption capacity.

Parameter F had higher values for the acids with longer carbonic chains. Kanazawa et al.[10] also found that a weak base resin has a higher selectivity for butyric acid than for propionic acid, concluding that hydrophobicity influences adsorption onto this type of resin. Although resin adsorption occurs mainly by electrostatic interactions (salt formed by the acid−base reaction), as the carbonic chain increases, interaction between the carbonic chains of adsorbed and free acids are favored leading to a multilayer structure, increasing adsorption capacity through cooperativity.

Hydrophobic interaction is favored with an increase in temperature, and an adsorbed molecule can adsorb other molecules through the interaction of their carbonic chains. However, in this study parameter n showed no significant increase at higher temperatures.

Determination of Thermodynamic Parameters for Adsorption onto the Resin. In determining the thermodynamic parameters (Table 6), it could be observed that the behavior of the resins was similar to that of the activated carbon: a negative change in free energy confirming the spontaneity of the adsorption process and a negative enthalpy, characteristic of an

exothermic adsorption. Also, as in the case of activated carbon, the adsorption process probably occurred by physisorption due to the low values of the enthalpy of adsorption.[11]

Adsorption Studies: Multicomponent Adsorption. Multicomponent adsorption studies were carried out with the two adsorbents using binary mixtures of the three acids. Several models for fitting adsorption isotherm data were evaluated and only two of them generated appropriate results, a predictive model and a correlative model. The predictive model is an extended Langmuir model[12] that assumes a homogeneous surface with respect to the energy of adsorption, no interaction between adsorbed species and that all sites are equally available to all adsorbed species. It is represented by the equation

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Table 5. Freundlich Model Parameters n and F for the Data of Adsorption Isotherms for Acetic, Propionic, and Butyric Acids on Activated Carbon at Different Temperatures

	acetic acid		propionic acid		butyric acid	
$T/°C$	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n	$F/(g \cdot kg^{-1})(L \cdot g^{-1})^n$	n
20.0	163.97 ± 17.3	0.19 ± 0.03	204.2 ± 16.2	0.24 ± 0.02	228.63 ± 20.8	0.23 ± 0.03
30.0	171.00 ± 15.0	0.16 ± 0.03	168.9 ± 25.3	0.24 ± 0.05	219.67 ± 19.3	0.24 ± 0.03
40.0	156.57 ± 15.9	0.23 ± 0.03	181.3 ± 20.6	0.28 ± 0.04	198.67 ± 22.4	0.23 ± 0.03
50.0	149.27 ± 14.8	0.23 ± 0.03	155.7 ± 6.7	0.34 ± 0.03	206.33 ± 15.1	0.26 ± 0.02

Table 6. Thermodynamic Parameters for Adsorption of Acetic, Propionic, and Butyric Acids onto Resin

	acetic acid			propionic acid			butyric acid		
$T/°C$	$\Delta G/kJ \cdot mol^{-1}$	$\Delta H/kJ \cdot mol^{-1}$	$\Delta S/kJ \cdot mol^{-1}$	$\Delta G/kJ \cdot mol^{-1}$	$\Delta H/kJ \cdot mol^{-1}$	$\Delta S/kJ \cdot mol^{-1}$	$\Delta G/kJ \cdot mol^{-1}$	$\Delta H/kJ \cdot mol^{-1}$	$\Delta S/kJ \cdot mol^{-1}$
20.0	−16.2	−22.5	−0.02	−16.3	−39.0	−0.08	−17.3	−13.4	0.01
30.0	−15.9			−15.5			−17.5		
40.0	−15.7			−14.8			−17.6		
50.0	−15.5			−14.0			−17.7		

Table 7. Relative Error and R^2 for the Fitted Extended Langmuir and P-Factor Models for the Binary Systems

		P-factor model					
		P-factor		R^2		relative error (%)	
binary system	acid	CM119	PLA133	CM119	PLA133	CM119	PLA133
acetic and butyric	acetic	8.87 ± 1.7	1.87 ± 0.09	0.041	0.720	61.0	16.7
	butyric	1.24 ± 0.02	1.68 ± 0.17	0.982	0.947	15.4	18.2
acetic and propionic	acetic	8.87 ± 2.02	1.62 ± 0.16	0.065	0.670	81.5	18.0
	propionic	1.00 ± 0.04	2.53 ± 0.11	0.944	0.939	16.4	14.5
propionic and butyric	propionic	3.33 ± 0.8	2.86 ± 0.14	0.130	0.903	88.6	16.3
	butyric	1.60 ± 0.3	1.80 ± 0.03	0.973	0.964	16.8	15.8

		extended Langmuir model	
		relative error (%)[a]	
binary system	acid	CM119	PLA133
acetic and butyric	acetic	17.5	17.5
	butyric	34.8	41.7
acetic and propionic	acetic	66.2	7.58
	propionic	28.6	23
propionic and butyric	propionic	56.8	290.4
	butyric	58.4	56.4

[a]Relative error: average of the differences between observed and predicted values of the isotherms.

$$Q_i = \frac{Q_{m,i} K_{l,i} C_{e,i}}{1 + \sum K_{l,i} C_{e,i}} \tag{6}$$

where Q_i is the amount of solute i adsorbed by a mass of adsorbent, $C_{e,i}$ is the equilibrium concentration of solute i and $K_{l,i}$ and $Q_{m,i}$ are the parameters of the Langmuir model for the single adsorption isotherm of solute i (desorption constant and maximum adsorption capacity, respectively).

The other model having a good fit to the data was the P factor model:

$$Q_{i,\text{multi}} = \frac{1}{P_i} \frac{K_{l,i} Q_{m,i} C_{eq,i(\text{mono})}}{1 + K_{l,i} C_{eq,i(\text{multi})}} \tag{7}$$

where i is the corresponding solute in the monocomponent (mono) or multicomponent (multi) system. This correlative model has an interaction factor P, defined as the ratio of the maximum adsorption capacity of a solute in a single system to the maximum adsorption capacity in a multicomponent system. It requires the fitting parameters of single-component Langmuir isotherms and the multicomponent isotherm data.[13]

The P-factor model shows a better fit for most of the systems (Table 7). However, neither of the models provided a good fit for the shorter chain fat acid in the binary system on activated carbon due to their inability to predict the drop in adsorption capacity observed in the binary adsorption isotherm data (Figure 3 and Table 8). Moreover, the relative error of the model (the average difference between observed and predicted values) was high. This is problably due to the fact that the P-factor uses the Langmuir model, which predicts a maximum adsorption capacity, but our experimental adsorption capacity data increased continuously. Additionally, a multicomponent adsorption is a complex process that is difficult to describe with only one adjustable parameter. The P values showed that the adsorption capacity of all the acids decreased in the multicomponent system, indicating competition between these acids. Although this model provided the best fit to the data, parameter P did not provide a proper fit for all the systems tested, so no comparison can be made between them.

In all binary systems evaluated, the shorter chain carboxylic acid had a lower adsorption capacity, especially with activated carbon. A remarkable behavior observed on the activated

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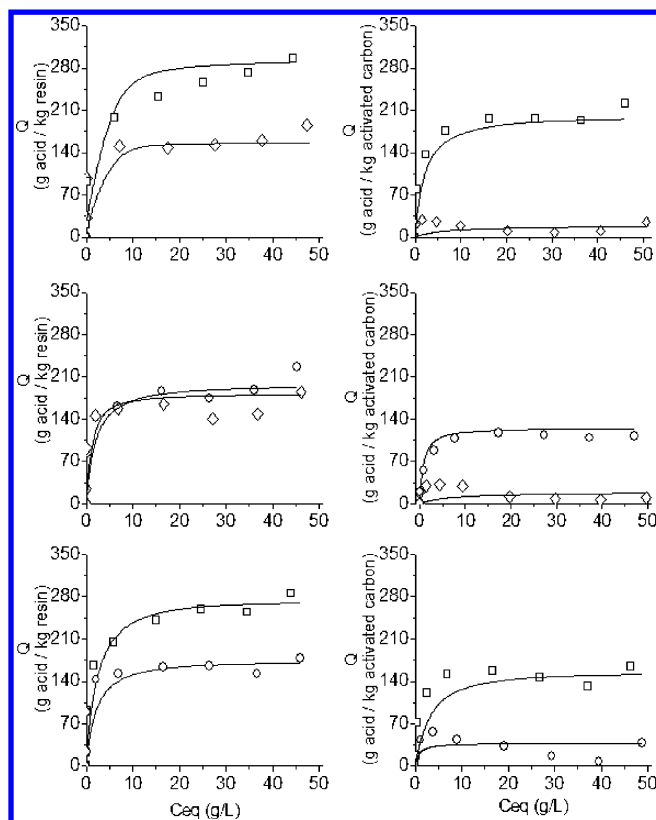
Figure 3. Adsorption isotherms of binary systems of acetic ($\Diamond$), propionic ($\bigcirc$), and butyric ($\square$) acids onto activated carbon (first column) and resin (second coumn) at 30 °C. Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in aqueous phase at equilibrium. Lines refer to the fitting of P-factor model.

carbon was an increase in the adsorption capacity of the shorter chain fat acid, followed by decay.

The adsorption mechanisms were different for the two adsorbents, but in both cases, as in the single-component studies, the longer chain fat acid had a higher affinity for the adsorbent. In the resin, the main interaction should occur between the carboxylic acid groups and the amino groups of the resin. As the acids have only one carboxyl group, the difference in adsorption capacity must be due to the lower acidity of the acids with a longer aliphatic chain. The conjugate base (R—COO⁻) of the acids with a longer molecular chain in aqueous solution has a stronger negative charge so it binds more effectively to the positive sites of the resin. As previously explained with Traube's rule, for activated carbon, the main adsorption mechanism should be a hydrophobic interaction of aliphatic chains with the surface of the activated carbon (mainly hydrophobic), which would explain the higher adsorption capacity of the longest aliphatic chain acids. In the case of activated carbons, the decrease in adsorption capacity of the shorter chan fat acid as the equilibrium concentration increases in binary systems is probably due to selectivity caused by the larger chain fat acid, which has a higher affinity for activated carbon and occupies more sites on its surface.

Desorption Studies. Propionic acid was used as an acid model for the desorption studies through determination and analysis of adsorption isotherms. Nakano et al.[14] used ethanol to remove propionic acid adsorbed on a column packed with activated carbon. All of the acids were easily removed from the adsorbent by circulating ethanol through the column. Chen and

Ju[15] used sodium hydroxide as eluent to desorb lactic acid adsorbed onto a polyvinylpyridine resin. The lactic acid was removed, but the adsorption efficiency of the resin decreased each time the process was repeated. Desorption using bases was not examined because the subsequent generation of salts could damage the environment or increase costs by the need for their elimination. For this work we chose alcohols as eluents. Ethanol and n-propanol were tested as desorbents for both adsorbents (resin and activated carbon).

The resin had a high adsorption capacity (Figure 4 and Table 9): up to 425.5 g acid·kg⁻¹ resin in ethanol and 206 g·kg⁻¹ resin in *n*-propanol, similar to values for the aqueous systems. The activated carbon had much lower adsorption capacities than the resin for both desorbents used. Adsorption capacity was higher in *n*-propanol than in ethanol for activated carbon, and this difference was opposite for the resin. Parameter F of the fitted Freundlich model varied significantly only in the ethanol-carbon system in terms of change in temperature (Table 10), where F decreased with increasing temperature. As the analysis was done using only two alcohols, it is not possible to draw any conclusions regarding the influence of the aliphatic chains of the alcohols on the adsorption process.

The resin showed higher F values than the activated carbon for both desorbents. Alcohols are weaker acids than carboxylic acids. The acid—base reaction occurs preferentially between carboxylic acids and amino groups of the resin, so the alcohol molecules cannot efficiently displace the adsorbed carboxylic acids.

In activated carbon the hydrophobic interaction that keeps the acid adsorbed is weaker than the electrostatic interaction in the resin. The former can be broken using alcohols because they are more hydrophobic than the organic acids of the same size. They preferentially interact with the hydrophobic sites on the activated charcoal surface originally occupied by the acid.[6] Temperature did not influence parameter n in any of the adsorbents. For the resin, there was no difference for this parameter. On the other hand, for the activated carbon the values using *n*-propanol were higher than those for ethanol (Table 10). As stated for the resin, we cannot draw any conclusions on the influence that size of the alcohol has on the adsorption process studied.

Batch Desorption Simulation. A desorption process simulation was carried out in batch mode. The mass balance

$$C_0V + Q_0 = Q_eM + C_{eq}V \qquad (8)$$

where C_0 and C_{eq} are the initial and equilibrium acid concentrations in solution, Q_0 and Q_e are the initial and equilibrium acid concentrations in the adsorbent, M is the adsorbent mass, and V is the solvent volume, and the Freundlich isotherm (eq 1) were used to show how much solvent would be necessary to achieve a required acid recovery. The base case for the simulation was the following: a single batch (1 tank), a desorption temperature of 50 °C, equilibrium state, an adsorbent mass of 1 kg and a mass of 500 g adsorbed propionc acid.

The volume of ethanol required to desorb the propionic acid from the resin was larger than that of n-propanol for any recovery studied using one tank (e.g., about 168 000 L for 99 % recovery, shown in Table 11). The volumes of ethanol were relatively smaller for desorption from activated carbon (e.g., 12.8 L for a 99 % acid recovery) and were also smaller than those obtained with *n*-propanol. However, in both cases these

Table 8. Adsorption Isotherms Data of Binary Systems of Acetic, Propionic, and Butyric Acids onto Activated Carbon and Resin at 30°C[a]

activated carbon											
acetic acid				propionic acid				butyric acid			
butyric acid		propionic acid		acetic acid		butyric acid		acetic acid		propionic acid	
C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	21.3	0.1	19.4	0.1	19.8	0.2	14.6	0.1	20.8	0.1	17.9
1.5	28.7	1.4	30.2	0.9	55.3	1.1	42.6	0.4	79.2	0.6	72.2
4.6	25.8	4.3	32.0	3.2	87.4	3.8	56.9	2.3	136.7	2.5	121.7
9.9	18.7	9.4	29.3	7.7	107.5	9.0	43.8	6.6	175.5	6.9	151.5
20.3	10.3	19.7	11.5	17.4	116.8	19.2	33.1	16.3	195.2	16.7	157.6
30.5	8.1	29.7	8.5	27.3	113.8	29.4	16.6	26.4	195.1	26.9	146.6
40.7	10.4	39.7	6.7	37.2	108.7	39.5	7.7	36.5	192.9	37.1	131.6
50.7	25.2	49.6	9.9	47.1	111.3	48.8	38.1	46.0	220.9	46.4	165.0
resin											
acetic acid				propionic acid				butyric acid			
butyric acid		propionic acid		acetic acid		butyric acid		acetic acid		propionic acid	
C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹	C_{eq}/g·L⁻¹	Q/g·kg⁻¹
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.0	24.9	0.0	24.2	0.0	23.4	0.0	23.3	0.1	20.9	0.1	21.7
0.1	97.4	0.1	92.1	0.3	85.1	0.2	88.9	0.2	91.8	0.2	91.1
7.2	150.5	2.0	146.0	2.1	143.1	2.1	142.8	6.1	197.4	1.6	166.6
17.5	148.3	6.8	158.0	6.8	161.2	6.9	152.7	15.5	231.9	5.9	204.7
27.7	152.5	16.6	164.7	16.2	186.7	16.5	164.0	25.2	255.2	14.9	240.6
37.7	160.0	27.1	140.6	26.4	174.4	26.5	165.7	34.9	272.0	24.6	258.6
47.5	185.4	36.9	148.1	36.1	188.3	36.7	152.8	44.6	296.2	34.6	254.6
		46.2	184.6	45.3	226.7	46.1	178.6			43.9	285.6

[a] Q = adsorption capacity at equilibrium; C_{eq} = acid concentration in aqueous phase at equilibrium.
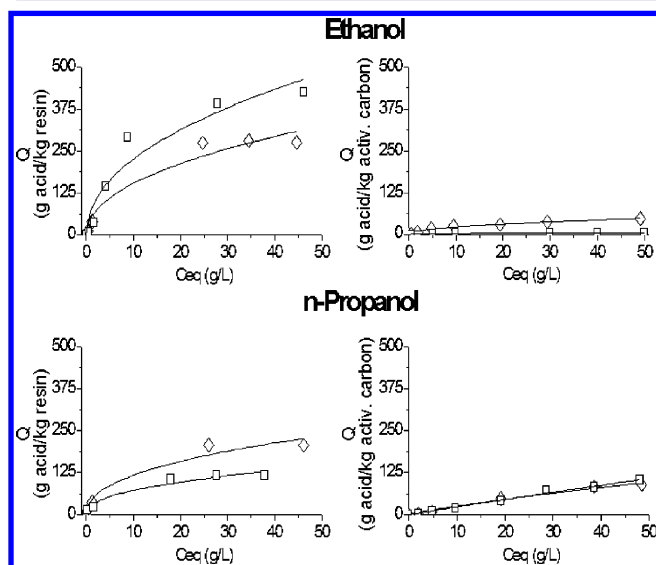

Figure 4. Adsorption isotherms of propionic acid in ethanol and n-propanol at 10 °C (◇) and 50 °C (□) using resin and activated carbon as adsorbents. Lines represent fitting to Freundlich model.

values are still definitely too high for an economically efficient process.

Simulation of a Multistage Countercurrent Desorption Process. The results for desorption in a single batch were poor so we studied the possibility of using a multidesorption process with several tanks in countercurrent mode (Figure 5 shows an example with four tanks). This process minimizes the amount of solvent and maximizes the amount of adsorbate desorbed.

The simulation was similar to that used in the single batch, but in this case system's equations were obtained for each desorption tank and solved using Excel software. The volume of eluent required for each tank to achieve (90 and 99) % recoveries of the acid using ethanol and n-propanol as eluent was evaluated for both adsorbents.

The base case for the simulation was an initial propionic acid load of 500 g·kg⁻¹ of adsorbent, an adsorbent mass of 1 kg in each tank, eluent free of propionic acid, equilibrium state in each tank and the same volume of eluent in each tank.

The countercurrent process had a higher efficiency than single batch desorption. The volume of eluent necessary per tank decreased as the number of desorption tanks increased (Table 11). Even for a recovery as high as 99 %, this process required considerably less solvent than with single batch desorption. The volume required to desorb the acid in the resin was still much higher than the values obtained for activated carbon.

The volumes of ethanol required for activated carbon were extremely small, utilizing less than 1 mL to obtain the required desorption and generating extremely high concentrations. These solutions obtained by solving the model system are mathematically correct, but not physically feasible. One possibility is that the system formed by these equations has more than one possible solution and the resolution method does not recognize the others. We modified the initial values of the variables to start the interaction, but no other solution was found.

Table 9. Adsorption Isotherms Data of Propionic Acid in Ethanol and *n*-Propanol at (10 and 50) °C Using Resin and Activated Carbon As Adsorbents

n-propanol				ethanol			
10 °C		50 °C		10 °C		50 °C	
$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$	$C_{eq}/\text{g·L}^{-1}$	$Q/\text{g·kg}^{-1}$
Activated Carbon							
1.9	3.2	1.9	3.4	0.5	1.5	0.5	0.2
4.8	9.6	4.8	10.6	1.9	6.1	5.0	2.5
19.2	48.5	9.6	20.4	4.7	18.1	9.9	3.7
38.5	83.7	19.2	42.3	9.5	25.2	29.9	5.2
48.5	90.0	28.7	72.8	19.4	30.3	40.0	5.0
		38.5	82.0	29.4	37.0	50.0	4.9
		48.1	103.0	49.2	47.2		
Resin							
0.21	13.99	0.19	15.15	0.30	10.09	0.43	7.47
1.27	37.34	1.54	22.51	1.21	40.15	1.61	35.07
26.04	206.53	17.91	104.80	24.63	275.34	4.08	144.38
46.09	206.34	27.67	116.60	34.48	281.41	8.65	291.03
		37.82	116.76	44.68	276.17	27.91	391.61
						46.07	425.51

Table 10. Freundlich Parameters Estimated with the Data on Adsorption of Propionic Acid onto Activated Carbon and Resin Using Ethanol and *n*-Propanol as Solvents

		n-propanol		ethanol	
adsorbent	$T/°\text{C}$	$F/(\text{g·kg}^{-1})(\text{L·g}^{-1})^n$	n	$F/(\text{g·kg}^{-1})(\text{L·g}^{-1})^n$	n
activated carbon	10	4.07 ± 1.41	0.81 ± 0.09	7.25 ± 1.21	0.48 ± 0.05
	50	2.74 ± 0.60	0.94 ± 0.06	1.39 ± 0.37	0.35 ± 0.08
resin	10	43.84 ± 16.10	0.42 ± 0.10	52.03 ± 20.90	0.47 ± 0.11
	50	27.52 ± 6.90	0.42 ± 0.08	77.51 ± 24.50	0.47 ± 0.09

Table 11. Volume of Eluent Required for Acid Recovery in Single and Multistage Countercurrent Desorption Process

|			eluent volume/L[a]				
adsorbent	desorbent	recovery/%	1 tank	3 tanks	4 tanks	5 tanks	6 tanks
activated carbon	n-propanol	90	20.5	3.5	2.8	2.5	2.3
		99	261.0	10.1	15.7	5.1	4.3
	ethanol	90	0.0016	0.00093	0.00064	0.00051	0.00045
		99	12.8	0.104	0.0598	0.044	0.036
resin	n-propanol	90	108.4	7.7	5.4	4.4	3.8
		99	28666.4	303.6	175.9	128.7	105.6
	ethanol	90	1143.3	91.4	65.2	53.3	46.7
		99	168743.0	2107.2	1230.2	900.5	738.0

[a]Each tank.

The final acid concentrations obtained for activated carbon were higher, reflecting the smaller volume of alcohol required (Table 12). For desorption from activated carbon with ethanol, the concentrations were relatively high, reaching values above 1000 kg·L^{-1}. Using *n*-propanol as eluent, the concentrations did not exceed 200 g·L^{-1}. Using propanol in resin with 90 % recovery, the solvent volumes and acid concentrations were close to those obtained using activated carbon and *n*-propanol with 99 % recovery.

The simulation of the overall process of adsorption and desorption in multistage countercurrent mode was also evaluated (Figure 5). The base case for this simulation was an adsorbent mass of 1000 kg, a 30 g·L^{-1} propionic acid solution for adsorption, an eluent volume of 5000 L in each desorption tank and temperatures of (30 and 50) °C for desorption and adsorption, respectively. The adsorbed mass of propionic acid was obtained from the single adsorption isotherms.

The yield of propionic acid (ratio of the propionic acid mass in the solution leaving the last desorption tank to the acid mass in the initial solution before adsorption) for a simulation of up to six tanks is shown in Table 13. Using ethanol as desorbent, there was no appreciable change in yield between one and six desorption tanks. However, there was a significant increase in yield for the two adsorbents with n-propanol as desorbent (minimum of 10 % for activated carbon and 18 % for resin). In addition, the increase in yield with more than three tanks is very small (a maximum of 1.9 % for the activated carbon and 5.5 % for the resin). Thus, the use of more than three desorption tanks is not feasible because the increase in yield will certainly not exceed the extra cost of the additional tanks.
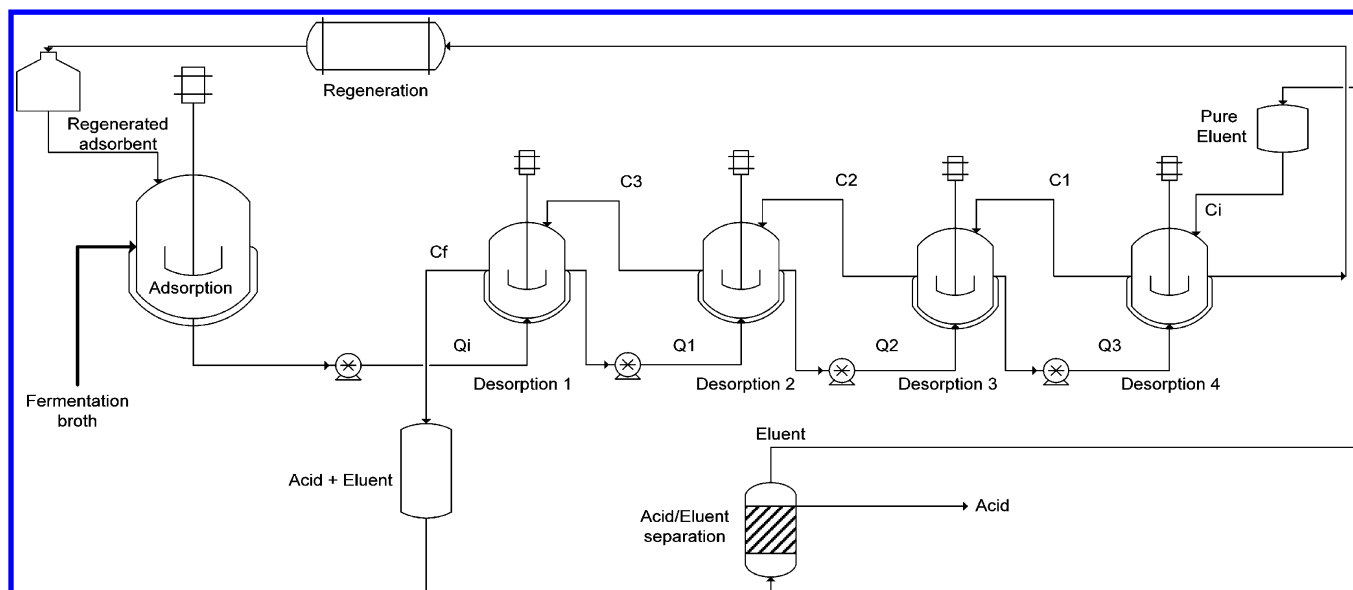
Figure 5. Adsorption and desorption process flow diagram for propionic acid using four desorption stages. The adsorption tank is loaded with the acid solution and the adsorbent. After equilibrium, all the adsorbent is transferred to the first desorption tank and the desorption eluent, from the second tank, is added. When equilibrium is reached the adsorbent is moved to the next desorbent tank and the solvent is moved to the tank in the opposite direction. The process continues until the adsorbent is moved through all the tanks. After the last desorption tank, the alcohol-propionic acid mixture is separated. The desorbent is pumped to the fourth stage desorption process. The adsorbent, after going through all stages of desorption, is regenerated and used again in the adsorption. The acid in the liquid from the first tank goes to a separation stage to generate the final product. The eluent is regenerated and recycled in the process.

Table 12. Acid Concentration Recovered in Single and Multistage Countercurrent Desorption Process

adsorbent	desorbent	recovery/%	propionic acid concentration[a]/$g \cdot L^{-1}$				
			1 tank	3 tanks	4 tanks	5 tanks	6 tanks
activated carbon	*n*-propanol	90	22.0	127.2	158.2	179.5	194.6
		99	1.9	49.2	56.4	96.4	114.0
	ethanol	90	27898.0	483701.7	702353.6	873951.2	1005764.1
		99	38.8	4752.3	8265.8	11292.4	13711.9
resin	*n*-propanol	90	4.2	58.8	83.6	103.0	118.0
		99	0.017	1.6	2.8	3.8	4.7
	ethanol	90	0.4	4.9	6.9	8.4	9.6
		99	0.003	0.2	0.4	0.5	0.7

[a]Each tank.

Table 13. Yield of Propionic Acid Adsorption and Desorption Process Using Ethanol and *n*-Propanol as Eluents

eluent	adsorbent	process yield/%				
		1 tank	3 tanks	4 tanks	5 tanks	6 tanks
ethanol	activated carbon	36.2	37.3	37.4	37.4	37.4
	resin	13.6	18.8	19.4	19.7	19.8
n-propanol	activated carbon	25.6	35.3	36.4	37.0	37.2
	resin	46.0	64.2	67.0	68.7	69.7

CONCLUSIONS

This work showed the importance of having a complete and integrated study of an adsorption process, addressing both adsorption and desorption steps. An adsorption system with a high adsorption capacity can encounter problems with desorption, thereby decreasing the overall process yield. This study of the target molecule with different adsorbents and eluents and all steps of the separation and recovery process and costs will provide a better understanding of a real design.

For the overall adsorption/desorption process, a combination of resin as adsorbent and *n*-propanol as eluent showed the best recovery of propionic acid (64 %) using a countercurrent desorption process with three tanks.

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Notes
The authors declare no competing financial interest.

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