LIQUID-LIQUID EXTRACTION BY CONTINUOUS SOLVENT RECYCLING FOR ACETIC ACID SEPARATION

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Lucrarea abordează cercetarea experimentală şi modelarea matematică a proceselor de extracţie a acidului acetic din solutii apoase şi de re-extractie cu recircularea solventului. Cercetarea experimentală a fost realizată într-o instalaţie cu coloane separate pentru extractie şi re-extracţie. Solvenţii de extracţie utilizaţi au fost acetatul de etil şi eterul etilic. Experimental, s-a lucrat la două valori ale debitului de solvent vehiculat prin instalaţie.

Modelul matematic dezvoltat pentru caracterizarea procesului se bazează pe ipoteza că transferul de masă în coloana de extracţie se desfaşoară, la nivel de picatură, prin transport difuziv, iar în coloana de re-extractie este completat de o reactie chimică la interfată. Între rezultatele experimentale şi cele obţinute cu ajutorul modelului există o bună concordantă.

Extraction of acetic acid from aqueous solutions, with re-extraction with solvent recycling was studied by experimental investigation and mathematical modeling in view of acetic acid recovery. The experiments were carried out in a device with two separate columns for extraction and re-extraction. Ethyl acetate and ethylic ether were used as extraction solvents. Extractions were performed at two different solvent flow-rates.

The mathematical model of the process is based on the assumption that mass transfer in the extraction column, at drop's level, occurs by pure diffusion, while in the second column it is accompanied by a chemical reaction at the interface. A good agreement between the experimental data and the model was obtained.

Keywords*:* liquid-liquid extraction, acetic acid recovery, fermentation media, solvent recycling, mathematical modeling, simulation

Introduction

Acetic acid is one of the most widely used carboxylic acids. It is used in many reactions, for example in synthesis of acetic esters, or it can be used as a solvent, for example in the manufacture of cellulose acetate or pharmaceutical products. Acetic acid biosynthesis produces important quantities of aqueous solutions from which acetic acid should be economically recovered [1-3]. The separation of acetic acid from aqueous solutions by simple rectification is

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difficult, requiring a column with many stages and a high reflux ratio, the whole process being very expensive [4]. Other processes may be used, depending of the acetic acid concentration in the solution. For example, extractive distillation [5] is used for acid concentrations between 50 and 70 % w/w. By adding a third component water volatility is increased and the process may be carried out with low energy consumption. For acetic acid concentrations lower than 40 % w/w the liquid- liquid extraction can be an appropriate process [6-10]. This process is also useful when other components interfere with direct distillation.

In this paper an experimental study of acetic acid liquid - liquid extraction with back extraction and solvent recycling is presented. Ethyl acetate and ethyl ether were used as extraction solvents because of the good solubility of acetic acid into them; the rapid separation of the acid from the extract is another criterion that sustains these solvents' selection. The influence of process parameters on the separation efficiency was studied by experimental analysis and mathematical modeling.

Experimental

The experimental device is presented in Fig. 1. A piston pump transports the extraction solvent, as a dispersed phase, by injection from the vessel 3 into the extraction column (1).

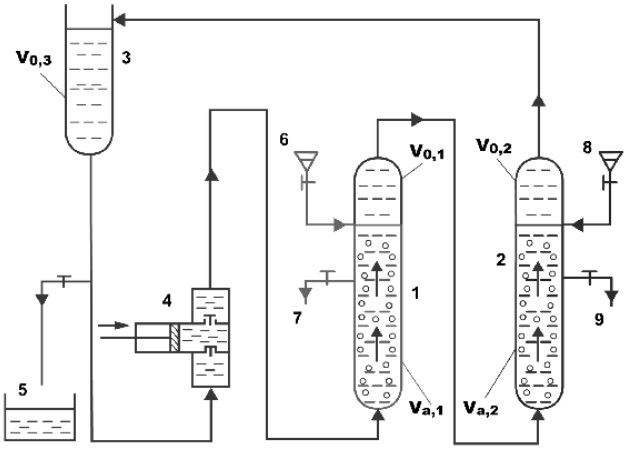

Fig. 1. Experimental setup used for acetic acid extraction: 1. extraction column containing aqueous acid solution (d=0.04 m, V_u=0.5 l); 2. re-extraction column containing NaOH stripping solution (d=0.04 m, $V_{a,1}$=0.5 l) ; 3. storage vessel with organic solvent ($V_{a,2}$=0.08 l); 4. piston pump for solvent recycling; 5. collecting vessel; 6. acetic acid solution feed; 7, 9 sampling points; 8. NaOH solution feed; V_o– volume of the organic phase accumulated above the aqueous phase; V_a– volume of the aqueous solution in the column.

This column is prevailed with a sieve, near the feeding point; the sieve helps the drops' forming. Due to the phases' different densities the drops of organic phase rise trough the column and accumulate in the free space above the aqueous solution. When the column (1) is filled, the solvent containing the extracted acetic acid goes in the re-extraction column (2). This contains a NaOH solution that strips the acid from the organic solvent – acetic acid mixture; thus the organic solvent is regenerated.

The solvent accumulates at the top of the column and is recycled with the piston pump in the process. From time to time, samples were prevailed and analyzed from both columns, in order to determine the acid and hydroxide content, by titration in presence of phenolphthalein as indicator.

The mathematical model of the whole process occurring in the above-described experimental plant is based on the following assumptions [11, 12]:

♦ In the first transfer zone the transported species has a momentary concentration C_{a1} .

♦ The initial concentration of the stripping component in the second column is chosen
so that the mass transfer to be directed from the disperse phase to the continuous phase.

♦ The volumes $V_{a1}, V_{a2}, V_{o1}, V_{o2}, V_{o3}$, are constant and perfectly mixed;

♦ The contact between the two phases is determined by the drop's rising time;

♦ At rising drops' level, in the first column, the mass transfer is a diffusion process;

♦ The mass transfer in the second column is accompanied by an irreversible chemical reaction; when the stripping agent is in excess, the chemical reaction occurs with high rate at the drop's surface.

According to the above-mentioned assumptions and considering the basic equations for each component of the experimental device, the mathematical model of the process is expressed by:

a)- Equation (1) for the disperse phase flow rate:

$$G_v = \begin{cases} G_{VM} \cdot \sin(2\pi n \tau) \text{ for} & \sin(2\pi n \tau) > 0 \\ 0 \text{ for } \sin(2\pi n \tau) < 0 \end{cases} \quad (1)$$

b)- Balance equation (2) for the transported component in the first column:

$$-V_{a1} \frac{dC_{a1}}{d\tau} = G_V \left(C_{03} - \overline{\overline{C_{01}}} \right) \quad (2)$$

c)- Initial conditions (3) concerning the concentration of the transported species in the first column and in the solvent accumulations:

$$\tau = 0, C_{a1} = C_{a10}, C_{03} = 0, \ \overline{C}_{o1} = 0 \tag{3}$$

d)- The diffusion equation (4) of the extracted component in the spherical particle rising as a drop inside the extraction column:

$$\frac{\partial C_d}{\partial \tau} = D_o^1 \left(\frac{\partial^2 C_d}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C_d}{\partial r} \right) \tag{4}$$

e)- Initial and boundary conditions (5) associated with the above diffusion equation:

$$\begin{aligned} &\tau = 0 \,; 0 < r < R; C_d = C_{o3} \\ &0 < \tau < \tau_{as1}; r = 0; \frac{\partial C_d}{\partial r} = 0 \\ &0 < \tau < \tau_{as1}; \qquad r = R; D_{oi} \frac{dC_d}{dr} = K_1 \left(C_{a1} - \frac{C_d}{K_{d1}} \right) \end{aligned} \tag{5}$$

f) - The relation (6) that describes the thermodynamic distribution of the extracted component between the contacted phases in the extraction column:

$$C_d^* = K_{d1} C_{a1} \tag{6}$$

g)- The average concentration given by (7) the extracted component for all drops entering in the first accumulation zone;

$$\overline{C}_{o1} = \frac{1}{R_{\max} - R_{\min}} \cdot \int_{R_{\min}}^{R_{Max}} \left(\frac{1}{R} \int_0^R C_{d1}(r, \tau_{as}) dr \right) dz \tag{7}$$

h)- Balance equation (8) for the extracted component in the first accumulation zone:

$$V_{o1}\frac{dC_{01}}{d\tau}=G_V\left(\overline{C}_{o1}-C_{o1}\right) \tag{8}$$

k) - The following considerations for the stripping section are accepted:
- the active component from the drops (A) reacts at the interface with the re-extraction agent (B); the stripping process occurs in three stages (9):

$$\begin{aligned} &A_{org}\rightarrow A_{org/\text{int}erface}\\ &A_{org/\text{int}erface}+bB_{1/\text{int}erface}\rightarrow C_{1/\text{int}erface}\\ &C_{1/\text{int}erface}\rightarrow C_1 \end{aligned} \tag{9}$$

- the chemical reaction, irreversible and very fast, occurs in a reaction front positioned by the values of reactant B concentration in the stripping liquid; using the relation (10) for the flux of A component, it results the critical concentration of the stripping reactant according to relations (11) and (12); this concentration decreases in time, because the component B is consumed in the chemical reaction.

$$N_{A_T}=k_d\cdot(\overline{C}_{Aorg}-C_{Ai})=K_2\cdot(C_{Ai}+\frac{1}{b}\cdot\frac{D_B}{D_A}\cdot C_{B1}) \tag{10}$$

$$C_{Ai}\cdot\left(k_d+K_2\right)=k_d\cdot\overline{C}_{Aorg}-K_2\cdot\frac{1}{b}\cdot\frac{D_B}{D_A}\cdot C_{B1} \tag{11}$$

$$\mathrm{C_{Bcr}}=b\frac{k_d}{K_2}\frac{D_o}{D_B}\overline{C}_{o2} \tag{12}$$

- when the concentration of reactant B is higher than the critical concentration ($c_B>c_{Bcr}$) the model of the stripping column shows that the process is controlled by diffusion of the active component A from the rising organic drops in the stripping solution, as it shown in the relations (13)-(16).

$$\frac{\partial C_{d,2}}{\partial\tau}=D_o^2\cdot\left(\frac{\partial^2C_{d,2}}{\partial r^2}+\frac{2}{r}\cdot\frac{\partial C_{d,2}}{\partial r}\right) \tag{13}$$

$$\tau\prec 0\,;\ 0\prec r\prec R_2\,;\ C_{d,2}=C_{0,1}\,; \tag{14}$$

$$0\prec\tau\prec\tau_{as,2}\,;\ r=0\,;\ \frac{\partial C_{d,2}}{\partial r}=0\,; \tag{15}$$

$$0 \prec \tau \prec \tau_{as,2}\,;\; r = R_2\,;\; C_{d,2} = C_{A,i}\,; \tag{16}$$

l)- The average concentration of the component in the drops at their entrance in the second accumulation zone given by (17):

$$\overline{C}_{o2} = \frac{1}{R_{\max} - R_{\min}} \cdot \int_{R_{\min}}^{R_{Max}} \left(\frac{1}{R}\int_0^R C_{d2}(r, \tau_{as})dr\right)dz \tag{17}$$

m)- Balance equations for the component A in the second accumulation zone and in the storage vessel, respectively, given by (18) and (19):

$$V_{o2}\frac{dC_{02}}{d\tau} = G_V\left(\overline{C}_{o2} - C_{o2}\right) \tag{18}$$

$$V_{o3}\frac{dC_{03}}{d\tau} = G_V\left(\overline{C}_{o3} - C_{o3}\right) \tag{19}$$

n)- The initial conditions (20) associated with the last differential relations:

$$\tau = 0\,;\; C_{o2} = C_{o3} = 0 \tag{20}$$

Results and discussions

Liquid-liquid extraction of acetic acid from synthetic solutions prepared from water and acetic acid, as well as from fermentation solutions were performed. The extractions from prepared solutions were realized in order to achieve preliminary results. Based on these results, we could see how the other components of fermentation solutions influence the whole extraction - re-extraction process. The experiments were carried out at two different flow-rates of the extraction solvent: 40 ml/min and 80 ml/min, respectively. When the synthetic solutions were used, the initial concentrations were 40 g/l acetic acid in the first column and at 70 g/l NaOH for the stripping agent. The experimental results are shown in Figs. 2-9.

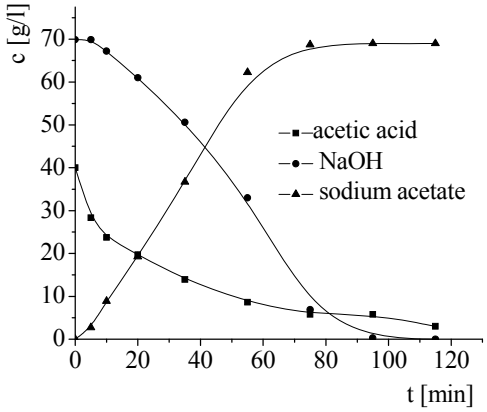

Fig. 2. Concentration profiles when acetic acid was extracted
from synthetic solution; extraction solvent: ethyl acetate, solvent flow rate: Gv=40 ml/min

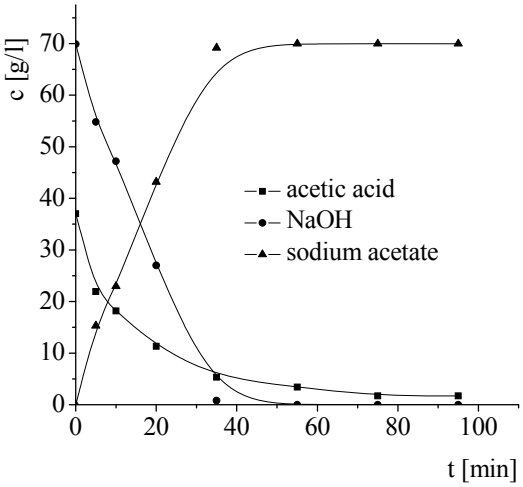

Fig. 3. Concentration profiles when acetic acid was extracted from
synthetic solution; extraction solvent: ethyl acetate; solvent flow-rate: Gv=80 ml/*min*

Fig. 2 presents the concentration profiles for the transported component, stripping agent and reaction product when acetic acid was extracted from the synthetic solutions using ethyl acetate as extraction solvent at a flow-rate of 40 ml/min.

Fig. 3 shows that increasing the extraction solvent flow-rate has a positive effect on extraction. The graphs 4 and 5 present the experimental results obtained

when acetic acid was extracted from fermentation solutions having an initial acetic acid concentration of about 20 g/l.

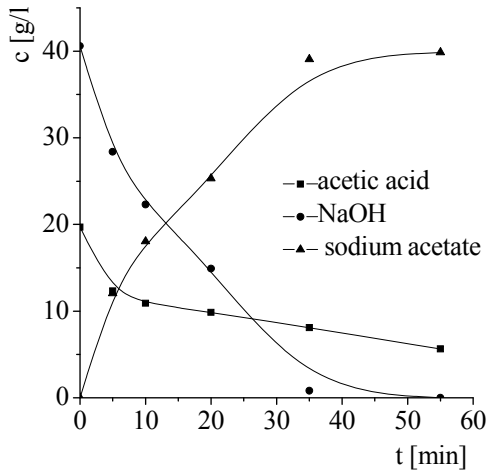

Fig.4. Concentration profiles when acetic acid was extracted from fermentation media; extraction solvent: ethyl acetate; solvent flow-rate: Gv=40 ml/min

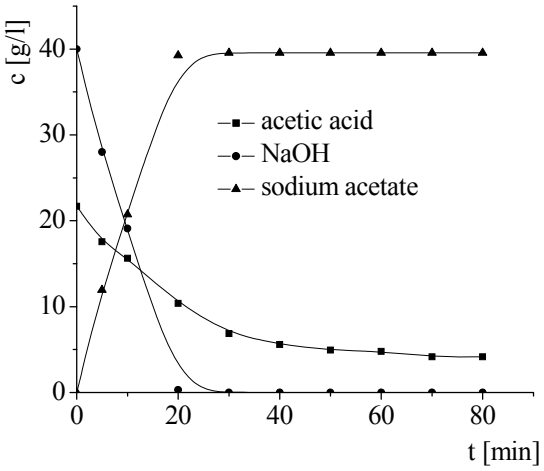

Fig. 5. Concentration profiles when acetic acid was extracted from fermentation media; extraction solvent - ethyl acetate, flow rate: Gv= 80 ml/min

The size distribution of rising drops in the extraction column, is characterized, for the reported experiments, by an identified R_{min}= 0.5 mm and R_{max}= 3.5 mm respectively. The same distribution is assigned for the rising drop in the stripping column.

Fig. 6 compares the concentration profiles of acetic acid from the synthetic solutions, for two working flow rates, using ethyl acetate as extraction solvent.

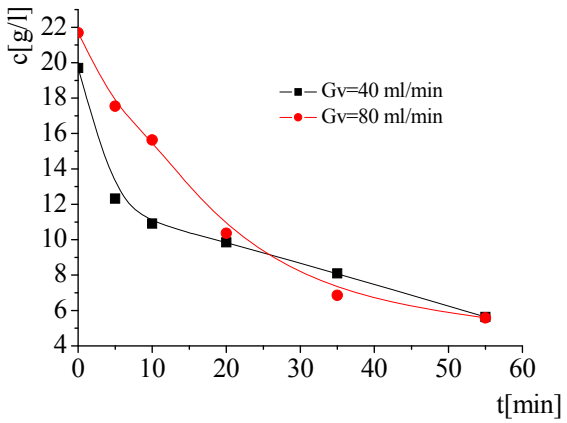

Fig. 6. Comparison between the concentration profiles for acetic acid when ethyl acetate was used as extraction solvent

As it may be seen from the above Figs., when ethyl acetate is used as organic solvent, the concentration of the stripping agent becomes zero after a period of time determined by the contacting condition. This is because the solvent also reacts with the stripping agent. Consequently, when the solvent flow rate is higher, the stripping agent is consumed faster. This combined consumption of the stripping agent makes the process insensible at the solvent flow rate change (fig. 6).

Figs. 7 and 8 present the experimental results obtained when acetic acid was extracted from fermentation solutions using ethyl ether as extracting solvent. This solvent does not react with our alkaline stripping agent and consequently, the effect of increasing the solvent the flow rate can be observed. (Fig. 9).

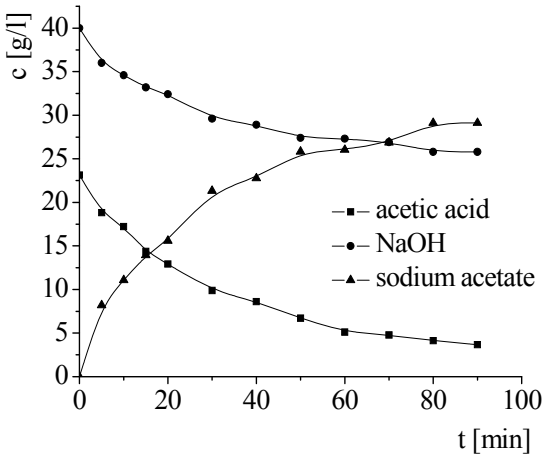

Fig. 7. Concentration profiles for acetic acid extraction from fermentation media; extraction solvent: ethyl ether, solvent flow rate Gv=40 ml/min

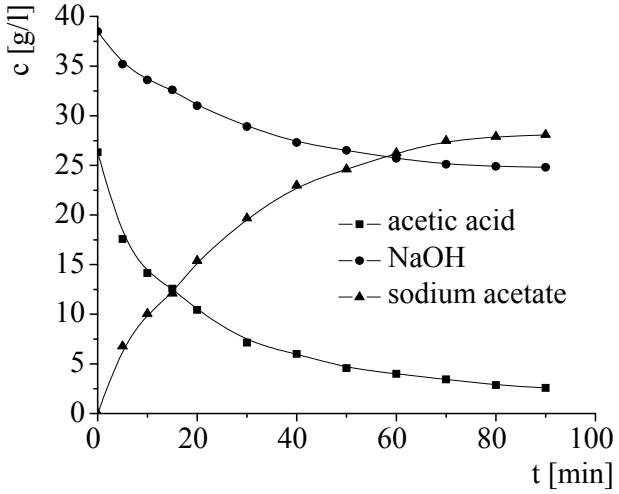

Fig 8. Concentration profiles when acetic acid is extracted from fermentation media; extraction solvent: ethyl ether; solvent flow rate: Gv=80 ml/min

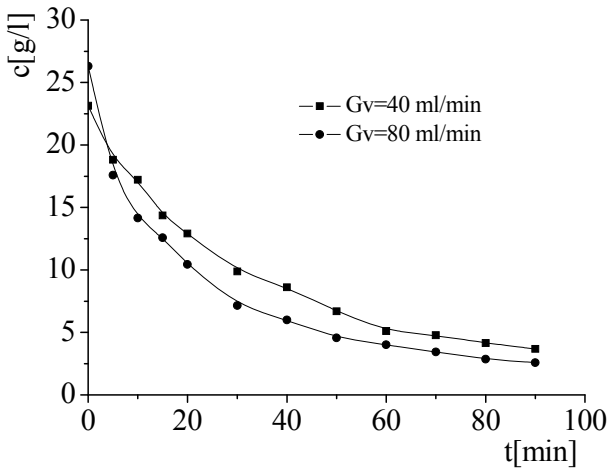

Fig. 9. Comparison between concentrations profiles for acetic acid whenethyl ether was used as extraction solvent

Process model simulation

The experiments where ethyl ether is the extraction solvent are in agreement with all previous process model considerations. For the process simulation based on the above described mathematical model, most of process parameters have been experimentally measured (R_{max}, R_{min}, τ_{asc1}, τ_{asc2}) or computed using the adequate relationships (K_1, K_2, D_O^1, D_O^2, D_A, D_B). A parameters identification procedure was used for establishing the acetic acid partition coefficients (K_{d1}), between the solvent and the extraction media corresponding to the contacted phases in the first column and the acetic acid apparent distribution coefficient for the contacted phases in the striping section (k_d).

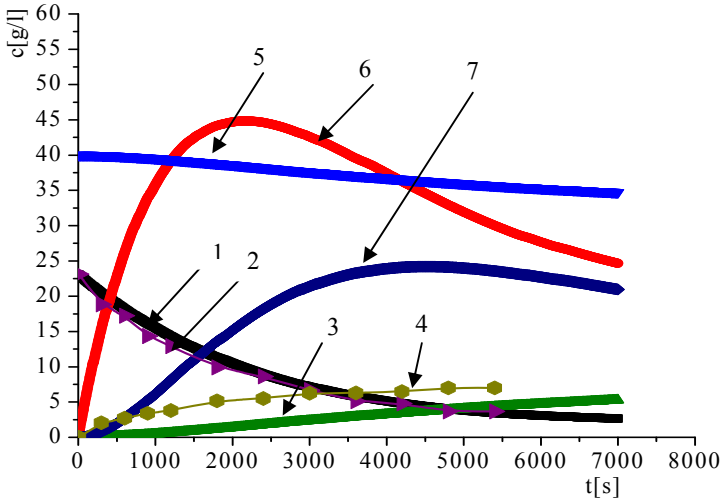

Fig. 10. Simulated and experimental curves (2,4) for major components of the experimental device when ethyl ether extraction occurs at $G_v = 40$ cm^3/min:
acetic acid in extraction column: simulated (1) and experimental (2), sodium acetate in the stripping column: simulated (3) and experimental (4), sodium hydroxide in stripping column (5), acetic acid in the first accumulation zone (6), acetic acid in the second accumulation zone(7).

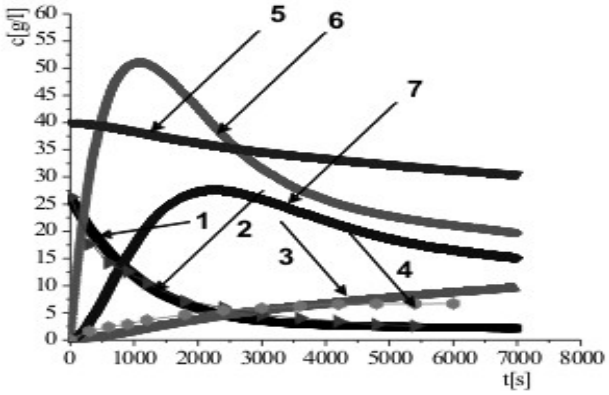

Fig. 11. The simulated evolution of major components of the experimental device when ethyl ether extraction occurs at $G_v = 80$ cm^3/min; curves 1-7 have the same significance as those in Fig. 10.

Fig. 10 presents a detailed process simulation when the solvent flow rate is 40 ml/min. The values of the model's parameters are presented in Table 1.

As it can be seen from Fig. 10, the experimental and computed data are in a good agreement. The experimental results obtained at a solvent flow – rate of 80 ml/min are also in agreement (Fig. 11). It is important to specify that in all the experiments the volume of extraction solvent was 100 cm^3 equally distributed between the accumulation zones of the experimental device and the storage solvent reservoir. Increasing or decreasing the solvent quantity and its distribution between the experimental device components affects the process evolution, according to relations (8), (18) and (19). It is important to specify that it is possible to operate with a minimal quantity of solvent; flow and efficient drops dispersion of the extraction solvent in the extraction and stripping columns allow this operating manner.

The values of operating and model parameters used for simulations are presented in Table 1.

Table 1.

Values of operating and model parameters used for simulations

	Parameter	Experiment 1	Experiment 2
1.	Disperse phase flow rate, G_v, (mL/min)	40	80
2.	Volume of the aqueous phase in the first column, V_{a1} (mL)	455	
3.	Volume of the aqueous phase in the second column, V_{a2} (mL)	315	
4.	Volume of the first accumulation zone, Vo_1 (mL)	33	
5.	Volume of the second accumulation zone, Vo_2, (mL)	33	
	Volume of the third accumulation zone Vo_3, (storage vessel) (mL)	33	
6.	Initial concentration of the stripping agent, C_B, (NaOH) (g/L)	70	
7.	Initial concentration of acetic acid in the first column, C_{a1} (g/L)	23	26
8.	Mass transfer coefficient in the first column, K_1 (m/s)	$5*10^{-6}$	$5*10^{-6}$
9.	Partition coefficient in the first column, K_{d1}	6	9
	Apparent distribution coefficient in the stripping column, k_d	0.5	
10.	Maximum radius of the drop, R_{max} (mm)	3	
11.	Minimum radius of the drop, R_{min} (mm)	0.5	
12.	Drop's rising time in the first column, τ_{as1} (s)	6	6
13.	Drop's rising time in the second column, τ_{as2} (s)	7	5
14.	Diffusion coefficient of acetic acid in the organic solvent, D_{o1} (m^2/s)	$7*10^{-10}$	
15.	Diffusion coefficient of sodium acetate (reaction product) in the organic solvent, D_{o2} (m^2/s)	$8*10^{-10}$	

The mathematical model presented in this paper is not appropriate for ethyl acetate as extraction solvent. This is because in the stripping column the simple process of acetic acid consumption is accompanied with ethyl acetate alkaline hydrolysis; these two processes occurring at the level of solvent drop's surface cannot be characterized only by a diffusion process with irreversible reaction of acetic acid. The graphic from Fig. 12 shows the mentioned

discordance between the experimental and simulated data. The values of model parameters used for simulation were $K_1=6\cdot10^{-6}$ s/m, $k_2=10\cdot10^{-5}$ s/m, $D_0^1 = 6\cdot10^{-10}$ m^2/s, $D_0^2 = 8\cdot10^{-10}$ m^2/s, $K_{d1} = 6$, $k_d = 3.8$, $R_{max} = 0.003$ m, $R_{min} = 0.0005$ m , $\tau_{asc1} =$ 5 s, $\tau_{asc2} = 9$ s, n = 0.5, $D_A=9\cdot10^{-9}$ m^2/s and respectively $D_B=9\cdot10^{-9}$ m^2/s. The high values of the mass transfer coefficient around the drop from stripping column and of drop rising time in the same column are consequences of an active Marangoni effect that appears at its surface [13, 14]. For this case using ethyl acetate as extraction solvent, the approaching of experimental and simulated data could be obtained using a more complex model for the stripping process.

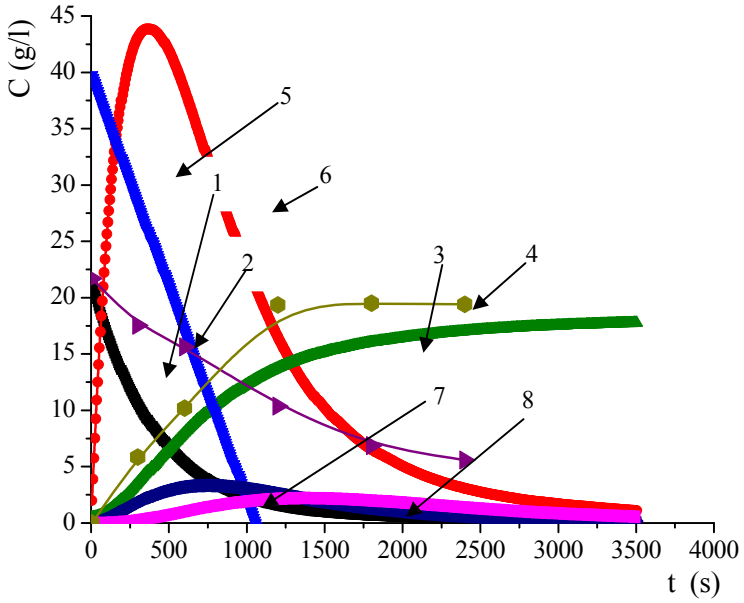

Fig. 12. The simulated evolution of concentrations for major components of the experimental device when ethyl acetate extraction occurs at $G_v = 40$ $cm^3/min.$, curves 1-7 have the significance as those in Fig. 10, 8- acetic acid concentration in the recycling vessel

Conclusions

Experimental studies concerning the extraction of acetic acid from synthetic and fermentation media, with re-extraction and solvent recovery were performed in an experimental plant having two columns as major components. The experimental results illustrate the possibility to use ethyl ether and ethyl acetate as specific solvents. Increasing the solvent flow rate for ethyl ether, has a positive influence on the extraction efficiency.

The use of ethyl acetate as extraction agent in the second column, for recovering acetic acid has been shown limited because this solvent is decomposed by alkaline hydrolysis.

The process mathematical model was obtained as an assembly of models for every experimental plant (extraction column, stripping column, pump, storage vessel).

Model computed data are in a good agreement with the experimental ones when ethyl ether is the extraction solvent. However when ethyl acetate is used the model of stripping process should be reconsidered taking into account its decomposition in alkaline media.

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