

Calculation of Separation Processes used for the Extraction of Active Principles from Fruits of *Coreopsis tinctoria* Nutt

CLAUDIA CORINA CRISAN¹, IOAN CALINESCU¹, TANASE DOBRE^{1*}, CHRISTINA ZALARU²

¹University Politehnica of Bucharest, Department of Bioresources and Polymer Science, Department of Chemical Engineering, 149 Calea Victoriei, 010072, Bucharest, Romania

²University of Bucharest, Department of Organic Chemistry, Biochemistry and Catalysis, 90-92 Panduri Road, 050663, Bucharest, Romania

This paper presents the equilibrium data, together with their use for calculation of three separation cases, when the active principles from fruits of Coreopsis tinctoria Nutt. are extracted with n-hexane. Simple single contact extraction, simple extraction with multiple contact and countercurrent extraction stages were operating procedures that were custom equilibrium data. For simple extraction of single contact and multiple contact extraction is considered the analytical calculation, while for stage countercurrent extraction is completed by the calculating graph.

Keywords: single contact extraction, simple extraction with multiple contact, countercurrent extraction

Coreopsis tinctoria Nutt. (Asteraceae) is native from North America, in Romania being commonly cultivated for ornament in gardens. The plant is used to treat several disorders including diarrhoea, internal pains, bleeding, to strengthen blood and as an emetic [1]. The infusion of *Coreopsis tinctoria* flowering tops has been used in Portugal to control diabetes. The flowers extracts from *Coreopsis tinctoria* may contain the following compounds: marein, okanin, coreopsin, 3,4',5,6,7-pentahydroxyflavanone-*O*-hexoside, 3',5,5',7-tetrahydroxyflavanone-*O*-hexoside, 3,3',5,5',7-pentahydroxyflavanone-*O*-hexoside, flavanokanin, 3,4',5,6,7-pentahydroxyflavanone, dicaffeoylquinic acid, 3',5,5',7-tetrahydroxy flavanone, maritomein, flavanomarein, luteolin, quercetin, butein, chlorogenic acid, caffeic acid, quercetagitin-7-*O*-glucoside, myristic acid, α -pinene, camphene, limonene, α -thujone, β -linalool, β -terpineol, verbenone, borneol, myrtenal, *cis*-carveol, *trans*-carveol, carvone, bornyl acetate, β -caryophyllene, β -caryophyllene epoxide [2-13].

For elevation of this study we used the fruits of *Coreopsis tinctoria* Nutt., in order to extract the active principles, considering the processes of interest simple single contact extraction, simple extraction of multiple contact and countercurrent extraction stage, given that, n-hexane was the solvent used. The operating temperature is considered at 25°C. In development of this work, we considered that between the components of dry extract from the fruits of *Coreopsis tinctoria* Nutt. was no big difference in physico-chemical behaviour, so they are considered species have a uniform behaviour, generically called specific extract. Also we show that the specific extract is an oil remembering that this plant is from sunflower family (Asteraceae). To determine the interphase equilibrium, characterizing the

distribution of specific extract from plant material and solvent we proceeded to lift the curves N_x vs. x and N_y vs. y [14-16].

In addition to raising equilibrium curves N_x vs. x and N_y vs. y , this paper presents the equilibrium separation analysis of specific extract by simple extraction with single contact, simple extraction with multiple contact and countercurrent extraction stage.

Experimental part

Materials and methods

n-Hexane of high purity produced by Merck was used for solvent extraction of specific extract from *Coreopsis tinctoria* Nutt. fruits as plant material.

The working method for raising the equilibrium isotherm expression N_x vs. x and N_y vs. y found in experiments in which a given amount of plant material was subject to prolonged contacting with variable amounts of solvent. Maceration at 25°C for 8 days was performed. The marc was determined separately for wet and dry mass weight of it. The miscella was turbidimetry analyzed to determine if it contains plant material for distribution. The miscella sample was evaporated, when from the removal of the solvent we obtained its specific extract content.

To determine the total content of specific extract from plant material was used simple extraction procedure with multiple contacts (Soxhlet), resulting in the concentration of 0.06 g of specific extract / g. Table 1 presents the results of experimental measurements.

With definitions of y (mass ratio of solute in solid phase), x (mass ratio of solute in liquid phase), N_y (the solid mass ratio of the marc) and N_x (mass ratio of solid in miscella)

No. crt.	n-hexane volume (mL)	Marc wet weight (g)	Marc dry weight (g)	g solution retained / g insoluble solid	Specific extract mass (g)
1	20	1.87	0.97	0.90	0.021
2	30	1.93	0.97	0.96	0.025
3	40	2.00	0.96	1.04	0.030
4	50	2.20	0.95	1.25	0.040

Table 1
EXPERIMENTAL MEASUREMENTS OF
EQUILIBRIUM

* email: tghdobre@gmail.com

No. crt.	Mass fraction of specific extract in the solution from solid y (g specific extract / g solution)	Liquid / solid mass ratio in marc $1/Ny$ (g solution / g solid)	Solid / liquid mass ratio in marc Ny (g solid / g solution)	Solid / liquid mass ratio in miscella Nx (g solid / g solution)	Mass fraction of specific extract in the solution without solid x (g specific extract / g solution)
1	0	0.71	1.408	0	0
2	0.021	0.90	1.111	0	0.021
3	0.025	0.96	1.041	0	0.025
4	0.030	1.04	0.960	0	0.030
5	0.040	1.25	0.800	0	0.040

Table 2
EQUILIBRIUM DISTRIBUTION BETWEEN PLANT MATERIAL AND SOLVENT OF SOLUTE (SPECIFIC OIL) EXTRACTED WITH n-HEXAN FROM FRUITS OF COREOPSIS TINCTORIA NUTT. (t=25°C)

Differences divided	Value	Differences divided	Value	Differences divided	Value
$f(y_0)$	-14.1590	$f(y_0, y_1)$	-128.0833	$f(y_0, y_1, y_2)$	9.2156e+003
$f(y_1)$	-17.3611	$f(y_1, y_2)$	148.3856	$f(y_1, y_2, y_3)$	-8.2596e+003
$f(y_2)$	-16.0256	$f(y_2, y_3)$	-8.5470	$f(y_0, y_1, y_2, y_3)$	-4.3688e+005
$f(y_3)$	-16.1538				

Table 3
COMPUTATION OF DIVIDED DIFFERENCES FROM RELATION (2)

the experimentally obtained data allow the construction of table 2 which contain the equilibrium data.

Figure 1 show the graphic presentation of equilibrium diagram $N \sim x, y$ resulting from data in table 2.

Pairs of points (Ny, y) give the solid drawn curve, while pairs of points (Nx, x) give liquid extraction curve. For extraction processes computation an analytical expression involving the dependence relations of $Nx \sim x$ and $Ny \sim y$ are needed as it is shown by relation (1) the dependence $Nx \sim x$ is immediate:

$$N_x = 0; \quad 0 \leq x \leq 0.04 \quad (1)$$

To establish the dependence $Ny \sim y$ is used a polynomial split of the form (2) where the differences divided have the values shown in table 3.

$$N_y = N_{y0} + f(y_0)(y-y_0) + f(y_0, y_1)(y-y_0)(y-y_1) + f(y_0, y_1, y_2)(y-y_0)(y-y_1)(y-y_2) + f(y_0, y_1, y_2, y_3)(y-y_0)(y-y_1)(y-y_2)(y-y_3) \quad (2)$$

Concrete form of relationship (2) becomes:

$$N_y = N_{y0} - 14.1590(y-y_0) - 128.0833(y-y_0)(y-y_1) + 9215.6(y-y_0)(y-y_1)(y-y_2) - 436880(y-y_0)(y-y_1)(y-y_2)(y-y_3) \quad (3)$$

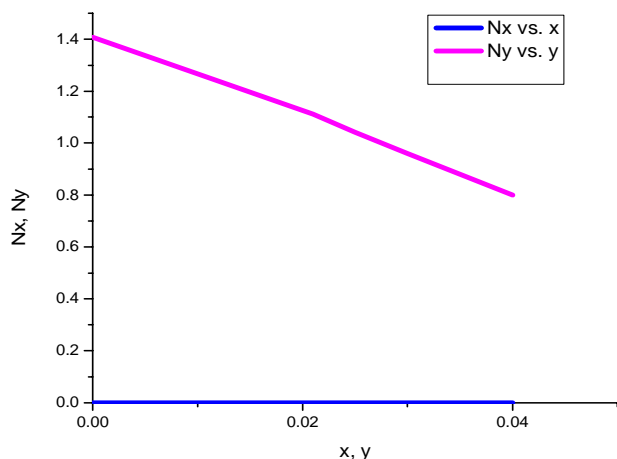


Fig. 1. Equilibrium diagram $N \sim x, y$ for extraction with hexane of specific extract

Results and discussions

First it was established that: i) separated miscella contains no solid; ii) miscella and solution from marc have the same chemical composition, since after a sufficiently long extraction time can be considered to reach equilibrium state.

Now we present the use of our experimental results for specific extract separation from fruits of *Coreopsis tinctoria* Nutt. considering the following cases:

Case A: 50 kg fruits of *Coreopsis tinctoria* Nutt. are mixed with 165 kg n-hexane in an extractor, a long time, then miscella is separated by gravity drainage from solid.

Case B: 50 kg fruits of *Coreopsis tinctoria* Nutt. are mixed with 82.5 kg n-hexane and processed as in *case A*. The resulted marc is again treated with 82.5 kg fresh n-hexane.

Case C: 50 kg fruits of *Coreopsis tinctoria* Nutt. are treated in a multiple countercurrent contacting system. For this case we have presented a graphical method for calculating the theoretical number of theoretical extraction units using the equilibrium expression by representing $N \sim x, y$ for the extraction of a 5-cell contactor.

It is required to calculate the amount of miscella and marc and their composition when working as in *Case A*, respectively in *Case B* and the yield of extraction for the three cases.

Case A - Simple single contact extraction

The schematic drawing is shown in figure 2. Extraction unit, represented by the circle is theoretical, it provides the equilibrium distribution of specific extract between phases that leave it and the phase separation is complete [16].

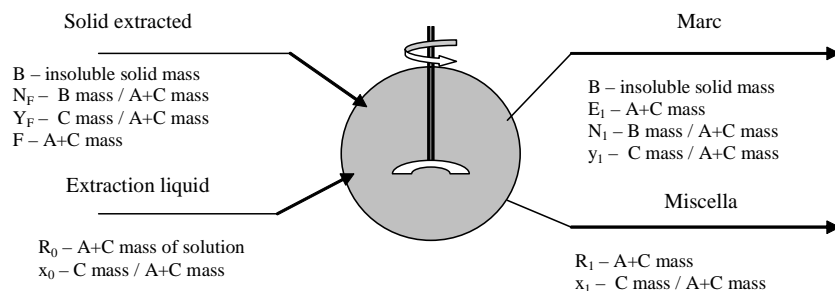


Fig. 2. Presenting simple single contact extraction [16]

The computational problem can be solved analytically, taking into account the notations given in figure 2, the defining relations of those sizes and materials balance and equilibrium custom for the contact unit [16].

Use it:

- relationship of constant mass (flow) of insoluble solid:

$$B = N_F F = E_1 N_1 \quad (4)$$

- relationship giving balance of solute:

$$F y_F + R_0 x_0 = E_1 y_1 + R_1 x_1 \quad (5)$$

- relationship giving balance of the solvent from extraction liquid:

$$F(1 - y_F) + R_0(1 - x_0) = E_1(1 - y_1) + R_1(1 - x_1) \quad (6)$$

- relationship balance of all solute - solvent:

$$F + R_0 = E_1 + R_1 = M_1 \quad (7)$$

- interphase equilibrium relationship:

$$y_1 = f(x_1) \quad (8)$$

The assembly of relations (4) - (8) allows the determination of unknowns E_1 , N_1 , y_1 , x_1 , R_1 . For numeric computation note that $F = 3$ kg specific extract, $N_F = 0.47/0.03 = 15.66$ kg solid / kg solution, $R_0 = 165$ kg initial solvent, $x_0 = 0$ kg specific extract / kg initial solvent, $y_F = 1$ kg specific extract / kg solution. The following algebraic system is obtained:

$$\begin{cases} E_1[1.408 - 14.1590y_1 - 128.0833y_1(y_1 - 0.021) + 9215.6y_1(y_1 - 0.021)(y_1 - 0.025) \\ - 436880y_1(y_1 - 0.021)(y_1 - 0.025)(y_1 - 0.03)] = 47 \\ E_1 y_1 + R_1 x_1 = 3 \\ E_1 + R_1 = 168 \\ y_1 = x_1 \end{cases} \quad (9)$$

From the first relationship of the system it is obtained:
 $E_1 = 47 / N_{y_1} = 40.2184$ kg solution in marc

Combining the last three relations system leads to:
 $x_1 = y_1 = 3 / 168 = 0.0179$ kg specific extract / g solution

It follows immediately:

$R_1 = 168 - E_1 = 127.7816$ kg solution in miscella

- amount of solid phase:

$S_1 = (50 - F) + E_1 = 87.2184$ kg

- amount of liquid phase (miscella contains no solid):

$L_1 = R_1 + R_1 N x_1 = 127.7816$ kg

The yield of extraction in this case will be:

$$\eta_{ex} = R_1 x_1 / F y_F = 0.7606$$

Case B - Simple two-stage extraction (equal quantities of fresh solvent)

The schematic drawing is shown in figure 3. The simple extraction with multiple contact is the working procedure in which the solid resulting from a simple extraction is extracted in a new stage, each time using fresh extraction liquid. [16]

For *Case B* the simple extraction methodology is applied for two units.

For the first unit where $R_0 = 82.5$ kg initial solvent and other data have values specified as in *Case A* is formed system (10):

$$\begin{cases} E_1[1.408 - 14.1590y_1 - 128.0833y_1(y_1 - 0.021) + 9215.6y_1(y_1 - 0.021)(y_1 - 0.025) \\ - 436880y_1(y_1 - 0.021)(y_1 - 0.025)(y_1 - 0.03)] = 47 \\ E_1y_1 + R_1x_1 = 3 \\ E_1 + R_1 = 85.5 \\ y_1 = x_1 \end{cases} \quad (10)$$

The system solving gives immediately:

$$\begin{aligned} E_1 &= 47 / N_{y_1} = 53.2156 \text{ kg solution in marc} \\ x_1 &= y_1 = 3 / 85.5 = 0.035 \text{ kg specific extract / kg solution} \\ R_1 &= 85.5 - E_1 = 32.2844 \text{ kg solution in miscella} \\ S_1 &= (50 - F) + E_1 = 100.2156 \text{ kg} \\ L_1 &= R_1 + R_1N_{x_1} = 32.2844 \text{ kg} \end{aligned}$$

For the second unit is written, according to the notation in figure 3, system (11):

$$\begin{cases} E_2[1.408 - 14.1590y_2 - 128.0833y_2(y_2 - 0.021) + 9215.6y_2(y_2 - 0.021)(y_2 - 0.025) \\ - 436880y_2(y_2 - 0.021)(y_2 - 0.025)(y_2 - 0.03)] = E_1N_{y_1} = FN_F = 47 \\ E_2y_2 + R_2x_2 = E_1y_1 + R_0x_0 = 1.8678 \\ E_2 + R_2 = E_1 + R_0 = 135.7156 \\ y_2 = x_2 \end{cases} \quad (11)$$

The system solving gives immediately:

$$\begin{aligned} E_2 &= 47 / N_{y_2} = 38.6697 \text{ kg solution in marc} \\ y_1 &= x_1 = 1.8678 / 135.7156 = 0.0138 \text{ kg specific} \\ &\quad \text{extract/kg solution} \\ R_2 &= 135.7156 - E_2 = 97.0459 \text{ kg solution in miscella} \\ S_2 &= (50 - F) + E_2 = 85.6697 \text{ kg} \\ L_2 &= R_2 + R_2N_{x_2} = 97.0459 \text{ kg} \end{aligned}$$

The yield of extraction in the two units will be:

$$n_{ex} = (R_1x_1 + R_2x_2) / Fy_F = 0.8227$$

Case C - Extraction stage countercurrent

The schematic drawing is shown in figure 4. Stage countercurrent extraction is the working procedure in which the extracted solid and the extraction liquid flows in countercurrent from one unit to another [16].

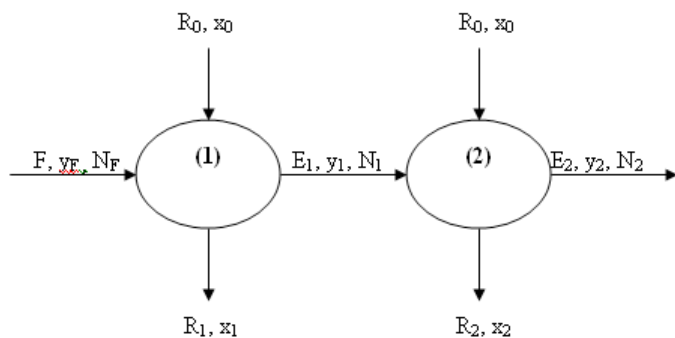


Fig. 3. Presentation of simple two-stage extraction [16]

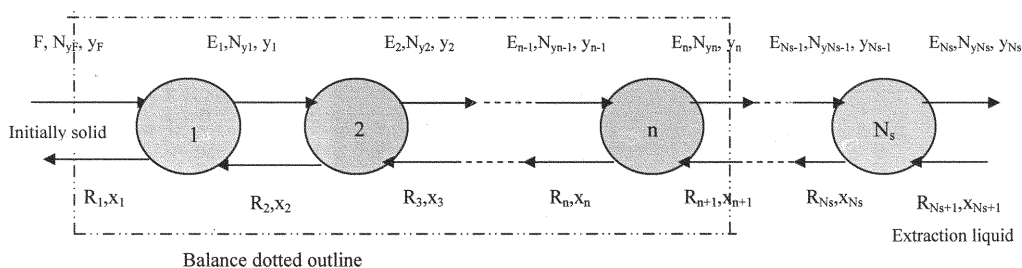


Fig. 4. Presentation scheme for stage countercurrent extraction [16]

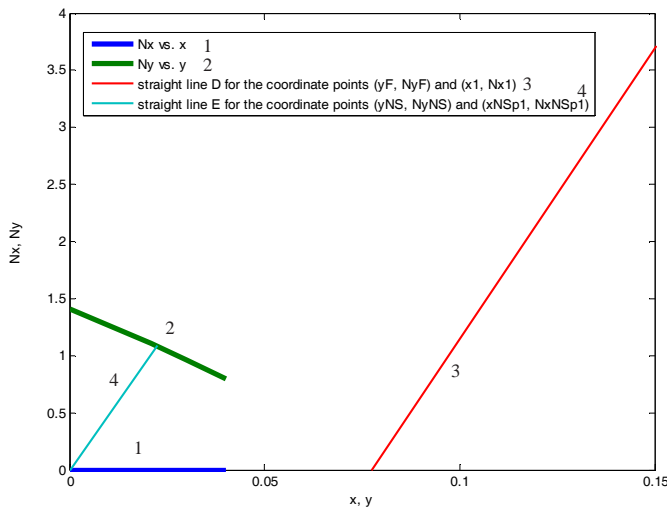


Fig. 5. Graphical calculation of the number of theoretical extraction units for $y_{NS} = 0.02249$ and $s = 3$

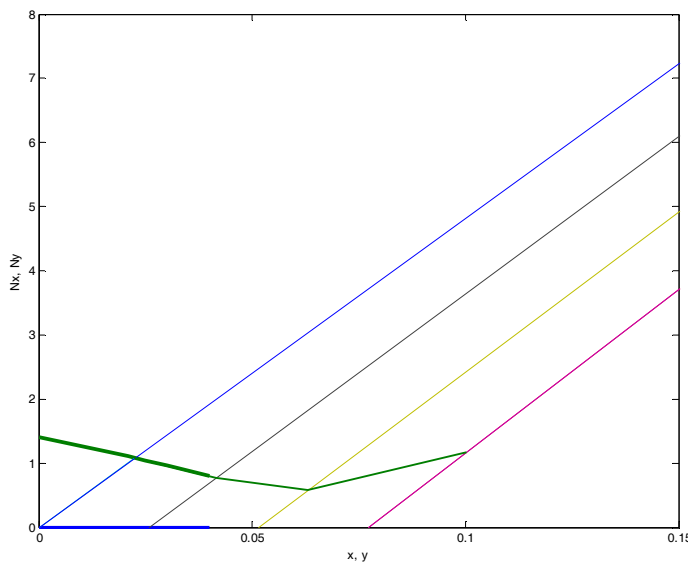


Fig. 6. Graphical calculation of the number of theoretical extraction units for $y_{NS} = 0.02249$ and $s = 3$

- relationship giving balance of the solvent from extraction liquid:

$$R_{n+1}(1 - x_{n+1}) - E_n(1 - y_n) = R_1(1 - x_1) - F(1 - y_F) \quad (14)$$

- relationship balance of all solute - solvent:

$$R_{n+1} - E_n = R_1 - F \quad (15)$$

To obtain the mathematical model of unity in a series of contact stages at the relations (12) - (15) is added the equilibrium relationship for the current unit "n":

$$y_n = f(x_n) \quad (16)$$

There is a graphical method of calculation which use the representation of equilibrium ($N \sim x, y$) and operating relationship. Here the operating relationship (line section) has the ability to pass through a fixed point called the pole of operation. Graphic locates its position in the customization of (15) for the current unit "n" and end units of the plant (17):

$$F - R_1 = E_{n-1} - R_n = E_{NS} - R_{NS+1} = \Delta_R = const. \quad (17)$$

Graphical interpretation of the relation (17) leads to the conclusion that the operating pole is at the intersection of straight lines FR_1 and $E_{NS}R_{NS+1}$, where F, R_1, E_{NS}, R_{NS+1} , is the position figurative in the representation $N \sim x, y$, the supply

of solid, the final extraction liquid, the extracted solid, respectively the initially extraction liquid.

Because it is difficult to interpolate conode in the representation $N \sim x, y$, the calculating graph of this representation is coupled with that of diagram $y \sim x$ to trace the operating curve in it.

The number of contact steps (units) results by applying in diagram $y \sim x$ operating and equilibrium relations (stepped lines) from one end of the installation. Solving the problem of calculation by computer graphics was programmed using Matlab applications.

The algorithm can be systematized, in agreement with the notation in figure 4, as follows:

- 1 - It is proposed to y_{NS} the value 0.02249;
- 2 - Calculate N_{yNS} from the relationship $N_v \sim y$ and N_{xNS+1} and knowing x_{yNS+1} (in this case $x_{NS+1} = 0$ and $N_{xNS+1} = 0$);
- 3 - For the entire plant is written the solid, the solute and the fluid balance causing values for E_{NS}, R_1, x_1 ;
- 4 - Write the equation of a straight line (D) passing through the coordinate points (y_F, N_{yF}) (point F) and (x_1, N_{x1}) and the equation of a straight line (E) passing through $E_{NS}(y_{NS}, N_{yNS})$ and $R_{NS+1}(x_{NS+1}, N_{xNS+1})$ as shown in figure 5.
- 5 - The lines intersect (D) and (E) determining the position of the operating pole $\Delta(x_\Delta, N_\Delta)$;
- 6 - The interval between x_{NS+1} and x_1 is divided into "s" equal portions, so that $x_i = x_{NS+1} + ih, i = 1, s$ as shown in figure 6.

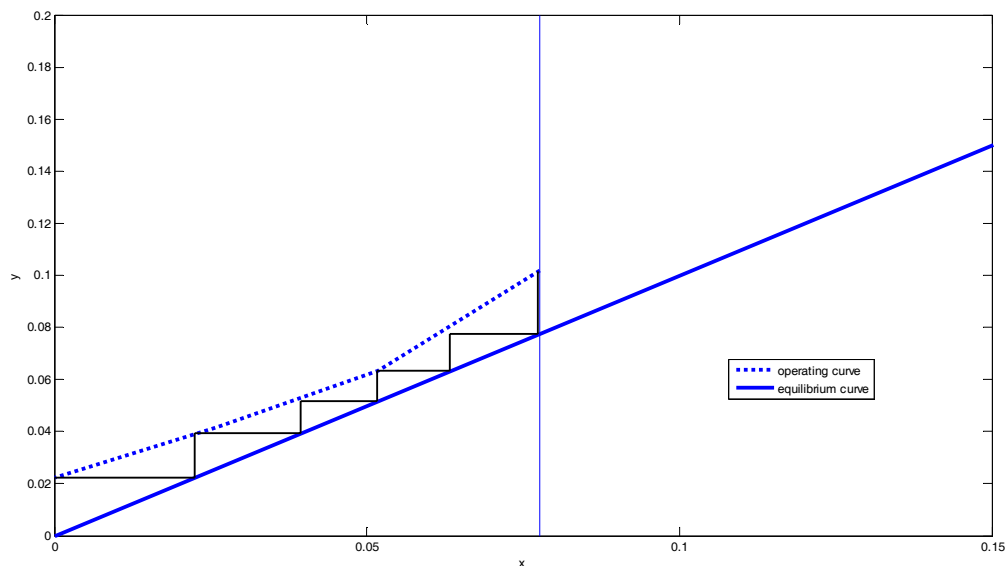


Fig. 7. Graphical calculation of the number of theoretical extraction units for $y_{NS} = 0.02249$ and $s = 3$

7 - For each point of division is calculated N_{xi} from the expression $N_x \sim x$ (in this particular case $N_{xi} = 0$) so that it has the current graphics position $R_i(x_i, N_{xi})$; $i = 1, s$;

8 - For each point R_i is determined the straight line (D_i) passing through it and the pole $\Delta_R(x_\Delta, N_\Delta)$;

9 - The straight line (D_i) intersect $N_x \sim y$ curve determining the intersection position $E_{i-1}(y_{i-1}, N_{i-1})$;

10 - Pairs of points (x_i, y_{i-1}) causes in the representation $y \sim x$ the operating curve;

11 - Determine an analytical expression of the equilibrium curve, for example by Newton polynomial;

12 - Starting from (x_{NS+1}, y_{NS}) apply classic algorithm for determining the theoretical extraction units, as shown in figure 7.

13 - If the number of units obtained by theoretical calculation is identical with the statement, the problem is solved; if it is less like the statement, it is proposed a lower value for y_{NS} and the calculation restart from 1; if it is high as in the statement, it proposes a higher value for y_{NS} and the calculation restart from 1.

For $y_{NS} = 0.02249$ the number of units obtained by theoretical calculation is identical with that of the statement.

Research goal is to obtain experimental data to characterize the extraction isotherm

Conclusions

Research goal is to obtain experimental data to characterize the extraction isotherm.

The experimental equilibrium at n-hexane extraction of specific extract (oil) from fruits of *Coreopsis tinctoria* Nutt. has been obtained as $N_x \sim x$ and $N_y \sim y$ dependencies.

The computations have found that between simple single contact extraction (*Case A*) and simple two-stage extraction (*Case B*), the two-stage is better, because at the same amount of extraction liquid (n-hexane) we obtain a better yield of extraction.

From a practical point of view must be considered the effort, however, more work for simple two-stage extraction.

A Matlab implementation of mathematical model of countercurrent multistage extraction is given and for a

system with 5 contacting units has obtained the extraction yield of specific extract near to 0.9775.

Calculation of separation processes based on the experimental results obtained in the laboratory allow implementation of processes to industrial scale or optimization of existing ones.

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