AN INTERPRETATION OF SOLID-LIQUID EXTRACTION USING THE GENERAL DIMENSIONAL METHOD

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ABSTRACT. The solid-liquid extraction is a very common method for recovery of bioactive compounds in both laboratory and large scale. Determining the conditions of operation is based for the most part on a researcher's practical experience. For scaling up to industrial conditions mathematical models or criteria equations are necessary. The paper presents the application of a general dimensional method to determine the parameters which influence the process and their respective degrees of impact. The parameters considered are: time, the equivalent diameter, the diffusion coefficient, density, dynamic viscosity, Earth's gravity, the interfacial force, the power dissipated into the process and linear velocity. The mathematical relation between the parameters in different conditions and the interpretation of this result is presented.

Keywords: solid-liquid extraction, general dimensional method, mathematical model of solid-liquid extraction, criteria equation of solid-liquid extraction.

INTRODUCTION

The solid-liquid extraction is a very common method for recovery of bioactive compounds both in the laboratory and in large scale industrial processes. The determination of laboratory conditions of operation is work based in major part on a researcher's practical experience and on empirical study. For scaling up to industrial conditions, mathematical models obtained through theoretical calculus, criteria equations and experimental data are all necessary and must be compared and adjusted for specific conditions. In this work we propose a way to present the specific influence of any parameters which can determine solid-liquid extraction by means of the general dimensional analysis method.

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For varied complex processes which offer complicate solutions, dimensional analysis is a most common way to initialise the research. In the study of a process, it can start from the differential equations which describe it, [1,2,3], or from the phenomenon theory, [4,5,6]. Knowledge of phenomenology may suggest the introduction of some variables in the list, size where is it not usually included in the differential equations. In this way, the number of variables can increase so much that the determination of the groups of similitude and the numerical constants can be a laborious task from the experimental point of view, pursued at great expense of time, materials and human energy. The classical method of the determinant criterion and the incompatibility of the groups offer a global image over the fact that for every process variables exist which are sometimes important, but at other times become secondary. The relative importance of the variables can evaluated after the identification of the numerical values of the exponents of the dimensionless groups from the π relation.

RESULTS AND DISCUSSION

The general dimensional analysis method, (GDAM), [3], through the algorithm of development, allows the reduction of the number of numerical constants belonging to the criteria relation to one single value, giving thus an important advantage over the classical method. The mathematical base, regarding the reduction of the number of numerical constants, is represented by the possibility of writing the π equation which describes a physical phenomenon:

$$\pi_1 = C_1 \cdot \pi_2 \cdot \pi_3 \cdot \pi_4 \cdot \cdots$$
, or: $(B \cdot J/E \cdot F) = C_1 \cdot (H \cdot I/N)^x \cdot (O \cdot P/R)^y \cdot \cdots$. (1),

in the form of a relation of monomial type:

$$B = k \cdot (E \cdot F \cdot H^{x} \cdot I^{x} \cdot O^{y} \cdot P^{y} \cdot \dots / J \cdot N^{x} \cdot R^{y} \cdot \dots), \qquad (2).$$

In order to treat a phenomenon using the general dimensional analysis, (GDA), this study contains three stages, [3]:

1. The first stage includes the presentation of the physical phenomenon, the assessment of the variables which interfere in its development and the separation of those which have a direct or reverse proportional action upon the variable which is considered to be most important (the independent variable). This stage can be performed by either studying the theory of the phenomenon, or can be done experimentally, and it leads to the elaboration of the matrix line of variables which describe the discussed process [1-5]. The separation of the variables is based on the mathematical evidence of the fact that a certain function, (1), or (2):

$$f_1 (B^{-1}, E, F, H^x, I^x, O^y, P^y, ... J^{-1}, N^{-x}, R^{-y},),$$
 (3),

can be rewritten under the following form:

$$f_2(E,F,H^x,I^x,O^y,P^y,...) = f_3(B,J,N,R,....)$$
 (4).

If the exponents of the dimensional equations f_2 and f_3 are only **positive** values, the solution of the non determined system of equations belonging to the exponential indexes will have only positive values.

The exponent index 0, (zero), **is not possible** because the mathematical evidence:

$$H^0 = 1 \tag{5},$$

leads to a numerical constant and the phenomenological analysis leads to a variable without importance to the process [1, 7].

- 2. The second phase refers to the assembly of the matrix of the dimensional variables, the allocation of an exponent index for each variable and the building of the undetermined system of dimensional equation through the method of the "progressive homogeneity" [1]. This is followed by the identification of the whole, positive, minimum and non-null solution and the formation of the dimensional relation of monomial type formed by the variables from the dimensional matrix having as the exponent the values from the solution of the system, [3]. The relation between variables which interfere during the development of a process or of a determined physical phenomenon is explained by taking into consideration the independent variable B. The expression of the relation is the simplest for the clear explicit dimension. The relation can be raised to a certain power index without losing the physical value, the new relation being different only in external form. Practically, these raises at a power are done in order to obtain complete, (whole), values of the exponents. To obtain such values, it is necessary that the relation be raised at a power of a common multiple of the denominators which belong to the rational exponents. In the case in which the adopted denominators have the lowest common multiple, the new values of the exponents will be the lowest, they will be at a minimum.
- 3. The third phase refers to determination of the numerical factor, (the numerical constant), of the monomial type relation. This operation is done considering experimental data and the constant value of the numerical factor is the theoretical and practical guarantee of the mathematical and phenomenological correctness of the monomial type relation which was obtained trough GDAM, [1].

I propose to introduce another working stage in the methodology, [7]. This new stage should be placed between the two first stages and is expected to lead to the establishment of a certain importance hierarchy among the variables describing the process. Thus, a real mathematical basis may result in neglecting certain variables that are empirically considered to be less important,

a situation often encountered in during practical work and experimental studies. Moreover, after establishing the monomial type relation, one may operate mathematically upon it to obtain some criteria relations describing the process. Criteria expressions show the influence that different types of forces exert on the system, presenting details about this process phenomenology that would not be relevant otherwise, being dissimulated by other aspects.

The model bellow describes the dynamic solid-liquid extraction between the raw material and a solvent. During the contact of the raw material with the solvent, the dissolution of active component into solvent is initialised. This process is driven by the concentration difference of said active component between the solid and liquid phases and stops when the difference is zero. The duration of the process (process time) is a major parameter for solid-liquid extraction.

In the 1st stage, the matrix line of the variables describing the solid-liquid extraction and their influence, direct or reverse, is formed. The list of all the possible variables is presented bellow:

// τ ; D _{1,2}; d; ρ ; η ; σ ; P; g; w; c _{in}; v; //,

where:

- τ the time of process, [s];
- D_{1,2} the mass diffusion coefficient, [m²/s];
- d the equivalent diameter, [m];
- ρ the density, [kg/m³];
- η the dynamic viscosity, [Pa·s];
- σ the interfacial tension, [kg/s²];
- P the dissipate power, [kg·m²/s³];
- g the earth's gravitation, [m/s²];
- c in the initial concentration of raw material, [kg/m³];
- w the velocity, [m/s];
- v the kinematical viscosity, [m²/s].

The 2nd stage. So that the additional proposed stage, the evaluation of the importance of functional parameters, can unfold, one starts by forming the minimum list of variables that are capable to describe the process. This can be measured from the solving condition of the system of undetermined diophantian equations imposed by GDAT: minimum, complete, positive and non-null solution.

- The combination of minimum variables, whit dimensional measure of each parameter, formed the dimensional matrix presented below:

$$/\!/ \tau^a$$
, D_{1,2}b, d c //
L 0 2 1
M 0 0 0
T 1 -1 0

- L the symbol of dimension "length";
- M the symbol of dimension "mass";
- T the symbol of dimension "time".

Its undetermined system of exponents is:

L
$$2b = c$$

M $0 = 0$
T $a - b = 0$,

and has the minimum, entire, positive and not-null solution which is accepted by GDAM:

$$\begin{array}{lll} L & & c=2, \\ M & & 0=0, \\ T & & a=1; & b=1. \end{array}$$

he monomial type relation generated by these results:

$$\tau = k_1 \cdot \frac{d^2}{D_{1,2}},\tag{6},$$

is homogenous dimensionally, [s] = [s] and can form the Fourier criteria for diffusion, Fo $_{\rm D}$;

$$Fo_D = \frac{\tau \cdot D_{1,2}}{d^2} = k_1. \tag{7},$$

The expression indicated very clear and rigorously the mass transport mechanism for solid-liquid extraction, mass diffusivity.

For verification and for finding the relative importance of all parameters, the procedure is repeated, trough the introduction into the matrix line, step by step, of the desired parameter:

Through the introduction of the initial concentration of raw material, $\mathbf{c}_{\text{ in}}$:

The following solution is obtained:

$$\begin{array}{ll} L & c=2; \\ M & n=0; \\ T & a=1; \ b=1; \end{array}$$

which is unacceptable for GDAM, given that the n exponent is null, (0).

The conclusion is that the newly introduced parameter, the initial concentration of raw material, c_{in} , is not important for the solid-liquid extraction.

The introduction of **kinematical viscosity**, **v**, leads to the following dimensional matrix of variables:

The non determinate system of variables exponents leads to six solutions:

Only ***** solution is acceptable under GDAT rules. The result shows that the momentum diffusivity is not important for the solid-liquid extraction. The introduction into matrix line of **solvent density**, ρ ,:

The indeterminate system of variables exponents leads to a solution unacceptable for GDAT: f = 0. Result: density of solvent is not an important parameter for solid-liquid extraction.

The introduction into matrix line of a **dynamic viscosity**, η ,:

The indeterminate system of variables exponents leads to a solution unacceptable for GDAT: f = 0. Result: dynamic viscosity of solvent is not an important parameter for solid-liquid extraction.

The introduction into matrix line simultaneously of a dynamic viscosity, η , and a solvent density, ρ ,:

leads to one accepted solution:

The monomial type relation is:

$$\tau = k_2 \cdot \frac{d^2 \cdot \eta}{D_{12}^2 \cdot \rho},\tag{8},$$

which can be re-written as:

$$\frac{\tau \cdot D_{1,2}}{d^2} = k_2 \cdot \frac{\eta}{D_{1,2} \cdot \rho}, \text{ or: } Fo_D = k_2 \cdot Sc,$$

$$\tag{9}.$$

The solution obtained trough GDAM show the following facts:

- the density and dynamic viscosity do have an impact on the solid-liquid extraction process, but only together. They have an opposite influence upon the process.
- a high density of a solvent is beneficial for the extraction. The justification of this fact is the influence of density in the case of Supercritical Fluid Extraction, (SCFE).
- lower viscosity is favours both the molecular transport mechanism and increases the diffusion coefficient. SCFE works as a good example in this case as well.

If into matrix line of variables the parameter **speed (linear velocity)**, **w**, is introduced, then:

which leads to the accepted solution:

L
$$b = 1; j = 1; c = 3;$$

T $a = 2.$

The monomial type relation is:

$$\tau^2 = k_4 \cdot \frac{d^3}{D_{1,2} \cdot w}.$$
 (10),

which can be written as:

$$\frac{\tau \cdot D_{1,2}}{d^2} \cdot \frac{\tau}{d} \cdot \frac{w}{1} = \frac{\tau \cdot D_{1,2}}{d^2} \cdot \frac{1}{\frac{d}{\tau}} \cdot \frac{w}{1} = \frac{\tau \cdot D_{1,2}}{d^2} \cdot \frac{w}{w} = k_4 ,$$
 or:
$$Fo_D \cdot Ho = k_4 , \qquad (11).$$

The result indicates two conclusions. Firstly, the newly introduced parameter, linear velocity, w, is an important one for the solid-liquid extraction. Secondly, a new non dimensional rapport appears, Homocronie (Strouhal), where the expected speed of the process is divided by the general speed of the process and characterizes non steady state processes.

The introduction into the matrix line of simultaneously **solvent** density, ρ , dynamic viscosity, η and linear velocity, w, results in:

respectively the solution:

$$\begin{array}{lll} L & c=1. \\ M & f=1; \ h=1; \\ T & a=1; \ b=1; \ j=1. \end{array}$$

Monomial type relation is:
$$\tau = k_3 \cdot \frac{d \cdot \eta}{D_{1.2} \cdot \rho \cdot w}$$
, (12),

Which can be written as:

$$\frac{\tau \cdot D_{1,2}}{d^2} = k_3 \cdot \frac{\eta}{w \cdot \rho \cdot d}, \text{ or: } Fo_D = k_3 \cdot \text{Re}^{-1}, \text{ or: } Fo_D \cdot \text{Re} = k_3, \text{ (13)}.$$

The appearance of linear velocity at dominator translates into a reverse influence to the Reynolds number, indicating that turbulence itself is less important for the process, but also that the increase of turbulence is important for the entire assembly of the process within the fluid media.

This aspect is very important to demonstrate that the principal step of the process is molecular diffusion, but that, as part of the overall process, increasing of the velocity of the fluid increases the speed of global velocity mass transfer.

For the entire generalization of momentum, heat and mass transfer of properties, an observation can be made that simultaneously with an increase in the velocity of the fluid all the coefficients for the transfer of properties increase as well.

The product between Fo_D -Re becomes constant, this fact represents the reduced the time of process, but only trough convection, not for the molecular mechanism.

If the parameter **Earth gravity**, **g**, is introduced into the equation, the following equation is obtained:

$$/\!/ \tau^a$$
, $D_{1,2}^b$, g^j , d^c , $/\!/ L$ 0 2 1 1 M 0 0 0 0 0 T 1 -1 -2 0

and leads to the accepted solution:

L
$$b = 1$$
; $j = 1$; $c = 3$; T $a = 3$.

The monomial type relation:
$$\tau^3 = k_5 \cdot \frac{d^3}{D_{1,2} \cdot g}$$
, (14),

is homogenous dimensionally, $[s^3] = [s^3]$, and can be written:

$$\frac{\tau \cdot D_{1,2}}{d^2} = k_6 \cdot \frac{d}{\tau} \cdot \frac{1}{\tau \cdot g} = k_6 \cdot \frac{w}{\tau \cdot g} = k_6 \cdot \frac{w}{\tau \cdot g} \cdot \frac{d}{\tau} \cdot \frac{1}{d} = k_6 \cdot \frac{w^2}{g \cdot d},$$
 or:
$$Fo_D = k_6 \cdot Fr, \qquad Fo_D \cdot Fr^{-1} = k_6, \qquad (15).$$

There are several conclusions that can be drawn from the above relations. Firstly, the new introduced parameter, Earth gravity, g, is an important one for the solid-liquid extraction. Secondly, the new non-dimensional rapport, Froude, appears, which describes the expected influence of action of external forces (gravity, centrifugal, magnetically, electrically, ultrasonic, microwave, etc.) upon the system. Thirdly, the possibility of solid-liquid extraction to be influenced by natural convection or of different external forces is highlighted. The overriding conclusion is that an increase of the external forces coupled with a decrease in the time of the process results in the intensification of the transport and transfer phenomena.

The introduction into the matrix line simultaneously of **dynamic** viscosity, η , solvent density, ρ , and earth gravity, g, results in:

The non determinate system of variable exponents leads to these three possible solutions:

All of these results are not accepted under GDAM. This fact shows that external forces influence only convection and not the molecular mechanism and the rate determinant step of the operation is internal diffusion or molecular transport into the boundary layer. External forces are therefore secondary parameters for solid - liquid extraction.

The introduction into the matrix line simultaneously of solvent density, ρ , dynamic viscosity, η , linear velocity, w and earth gravity, w, results in:

The non determinate system of variables exponents leads to these solutions:

Only one of the above four solutions is accepted in accordance with GDAT, indicating that the new variable, Earth gravity, g, is of secondary importance to the solid-liquid extraction process.

The monomial type relation is:
$$\tau^3 = k_7 \cdot \frac{d^2 \cdot \eta}{D_{1.2} \cdot g \cdot w \cdot \rho}$$
, (16),

is homogenous dimensionally, $[s^3] = [s^3]$, and can be expressed:

$$\frac{\tau \cdot D_{1,2}}{d^2} = k_7 \cdot \frac{\eta}{w \cdot \rho \cdot d} \cdot \frac{d}{\tau} \cdot \frac{d}{\tau \cdot g \cdot d} = k_7 \cdot \frac{\eta}{w \cdot \rho \cdot d} \cdot \frac{w^2}{g \cdot d},$$
or: $Fo_D = k_7 \cdot \text{Re}^{-1} \cdot Fr$, $Fo_D \cdot \text{Re} \cdot Fr^{-1} = k_6$, (17).

The appearance of Fr criteria at reverse power indicates clearly the secondary importance of Earth's gravity.

The introduction into the matrix line of dispersed power, P,

The indeterminate system of variables exponents leads to this solution:

a solution that is not accepted under GDAT. The result of calculus leads to the conclusion that the newly introduced variable, dispersed power, is of secondary importance or not important for solid-liquid extraction.

By formation a new matrix line, including the **dissipated power**, **P**, the density, ρ , and the dynamic viscosity, η ,:

the generated solutions are:

A single solution is accepted under GDAM, a fact which shows that the newly introduced variable, dissipated power, P, has less importance for the process.

The monomial type relation, generate from this accepted solution is:

$$\tau^2 = k_4 \cdot \frac{d^3 \cdot \eta^2}{D_{12} \cdot \rho \cdot P},\tag{18},$$

and after rearrangement becomes:

$$\left(\frac{\tau \cdot D_{1,2}}{d^2}\right)^2 = k_4 \cdot \frac{\eta}{w \cdot d \cdot \rho} \cdot \frac{w \cdot D_{1,2} \cdot \eta}{P} ,$$

or:

$$Fo_D^2 = k_4 \operatorname{Re}^{-1} \cdot K_{ND}^{-1}, \quad Fo_D^2 \cdot \operatorname{Re} \cdot K_{ND} = k_4,$$
 (19).

We must remark upon the appearance of a new non dimensional group of similitude, analogous with the Power criteria for mixing. The presence of a Reynolds and Power criteria at reverse power indicates the lower importance of dispersed power and of linear velocity of fluid media.

It is possible to analyze trough the same method the influence of the interfacial tension upon solid-liquid extraction. The minimum matrix line become:

$$^{\prime\prime}$$
 $^{\prime}$ $^{\prime}$

which doesn't have an accepted solution for GDAM:

The result of calculus leads to the conclusion that the newly introduced variable, interfacial tension, is of less importance or non important for the solid-liquid extraction.

By formation of a a new matrix line, including the interfacial tension, σ , the density, ρ , and the dynamic viscosity, η ,:

The generated solutions are:

A single solution is accepted from GDAM, a fact which shows that the newly introduced variable, interfacial tension, σ , has less importance for the process, (one solution accepted of two), but there is an increased influence of dissipated power, (one accepted solution of three), linear velocity, (one accepted solution of four) and earth gravity, (no accepted solution).

The monomial type relation, generated from this accepted solution is:

$$\tau = k_8 \cdot \frac{d^3 \cdot \eta \cdot \sigma}{D^4 \cdot \rho^2},\tag{20}$$

and after rearrangement becomes:

$$\frac{\tau \cdot D_{1,2}}{d^2} = k_8 \cdot \frac{\eta}{D_{1,2} \cdot \rho} \cdot \frac{\sigma}{w^2 \cdot \rho \cdot d} \cdot \frac{d^2 \cdot w^2}{D_{1,2}^2},$$

or:

$$Fo_D = k_8 \cdot Sc \cdot We^{-1} \cdot Pe_D^2$$
, $Fo_D = k_8 \cdot Sc^3 \cdot Re^2 \cdot We^{-1}$, (21).

The appearance of the Weber criteria at reverse power shows the secondary importance of interfacial tension.

By introduction of **all variables** which were presented initially, the matrix line becomes:

and has the solution accepted from GDAT:

This solution leads to the monomial type relation:

$$\tau^4 = k_9 \cdot \frac{d^4 \cdot \eta \cdot \sigma}{D \cdot \rho \cdot P \cdot g \cdot w},\tag{22},$$

which can be written:

$$\frac{\tau \cdot D}{d^2} = k_9 \cdot \frac{D \cdot \rho}{\eta} \cdot \frac{\eta}{w \cdot d \cdot \rho} \cdot \frac{\sigma}{w^2 \cdot \rho \cdot d} \cdot \frac{w^2}{d \cdot g} \cdot \frac{w \cdot D \cdot \eta}{P},$$

or:

$$Fo_D = k_0 \cdot Sc \cdot Re^{-1} \cdot Fr \cdot We^{-1} \cdot K_{ND}, \qquad (23).$$

The same influence of the parameters, and the formation of a criteria equation similar to the general expression, (1) is then observed.

CONCLUSIONS

GDAM method can offer the possibility to study a phenomenon from both an experimental and theoretically point of view, starting with the parameters that most likely can influence it.

The fundamental parameters for the process were highlighted during the formation of the minimum matrix line. These fundamental parameters then uncovered internal diffusion as the principal stage of the process.

GDAM can discriminate between the principal, secondary and non-important variables. These variables are selected based on a hierarchy resulting from the number of GDAM - not accepted solutions. For this purpose, interfacial tension, σ_i has lower importance in the process, (one solution accepted of two), but there is a higher influence from the dissipated power, (one accepted solution of three), linear velocity, (one accepted solution of four) and Earth's gravity, (no accepted solution). This hierarchy concludes that convection is a secondary mechanism for mass transport.

GDAM can generated a new criteria of similitude, for example: Power criteria at non steady-state mass diffusion into solid-liquid extraction,

$$K_{ND} = \frac{w \cdot D_{1,2} \cdot \eta}{P}$$
, and shows a direct relation for non steady-state operation

with time of the process via the Homocronie, (Strouhal), criteria.

The GDAM shows that the initial concentration of raw material is not an important parameter.

By introduction of all parameters the complete criteria expression is obtained, similar to relation (10).

The GDAM facilitates the experimental study of a process by making it necessary to determine a single parameter, the numerical constant k. This value is the proof for correctness of the relation.

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