MIND TECH

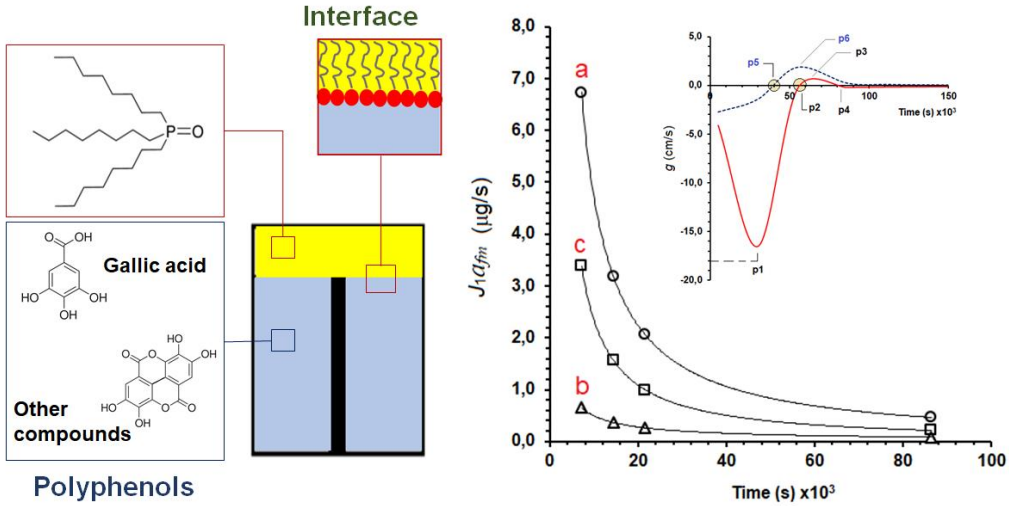
Journal of Science with Technological Applications
Research Article

Manuel Palencia[a*], **Mayra Mora**[a,b], **Tulio Lerma**[a,b]

[a] *Department of Chemistry, Faculty of Exact and Natural Sciences, Universidad del Valle, Cali-Colombia*
[b] *Mindtech Research Group (Mindtech-RG), Mindtech s.a.s., Cali – Colombia*

Corresponding author: manuel.palencia@correounivalle.edu.co

Graphical abstract



Study of time-dependent diffusion coefficient into liquid membrane systems and its application to polyphenol extractions from sugarcane bagasse

Abstract

It is widely recognized that the mathematical modeling of mass transfer in membrane processes is an essential component not only for understanding the underlying mechanisms associated with the transport, but also that is a powerful tool for design, cost estimation, control and scale-up of extraction processes. Here, a simple methodological approach for the study and description of diffusional changes during the extraction and transport processes in liquid membrane systems is developed and evaluated in the extraction and transport of gallic acid from aqueous solutions. It is concluded that, in comparison with the use of flux and distribution coefficient in function on time, a more sensitive description of diffusion coefficient can be performed using mass-transport coefficient in function on the time. In addition, it is concluded that, during the polyphenol extraction by liquid membrane based on castor oil and Cyanex 921, transportation can be affected by dissolution of membrane phase in the feed phase, and evidenced by a negative value of *g* in function of time.

Keywords
Diffusion coefficient
Liquid membrane
Mass-transport coefficient
Coupled transport

Estudio del coeficiente de difusión dependiente del tiempo en sistemas de membrana líquida y su aplicación a extracciones de polifenoles del bagazo de caña de azúcar

Resumen

Es ampliamente reconocido que el modelo matemático de la transferencia de masa en los procesos de membrana es un componente esencial no solo para comprender los mecanismos subyacentes asociados con el transporte, sino que también es una herramienta poderosa para el diseño, la estimación de costos, el control y la ampliación de la extracción de procesos. Aquí, se desarrolla y evalúa un enfoque metodológico simple para el estudio y la descripción de los cambios de difusión durante los procesos de extracción y transporte en sistemas de membrana líquida en la extracción y transporte de ácido gálico a partir de soluciones acuosas. Se concluye que, en comparación con el uso del flujo y el coeficiente de distribución en función del tiempo, se puede realizar una descripción más sensible del coeficiente de difusión utilizando el coeficiente de transporte de masa en función del tiempo. Además, se concluye que, durante la extracción de polifenoles por membrana líquida a base de aceite de ricino y Cyanex 921, el transporte puede verse afectado por la disolución de la fase de membrana en la fase de alimentación, y se evidencia por un valor negativo de *g* en función del tiempo.

Keywords

Coeficiente de difusión
Membrana líquida
Coeficiente de transporte de masa
Transporte acoplado

Recived: 02-02-2019
Accepted: 03-03-2019
Publishing date: 15 – May - 2019
Revision Code: 20160908-AAAA [Pag. 40 - 52]
Corresponding author:
manuel.palencia@correounivalle.edu.co

MIND TECH

Journal of Science with Technological Applications
Research Article

Study of time-dependent diffusion coefficient into liquid membrane systems and its application to polyphenol extractions from sugarcane bagasse

Manuel Palencia[a*], **Mayra Mora**[a,b], **Tulio Lerma**[a,b]

[a] *Department of Chemistry, Faculty of Exact and Natural Sciences, Universidad del Valle, Cali-Colombia*
[b] *Mindtech Research Group (Mindtech-RG), Mindtech s.a.s., Cali – Colombia*

Corresponding author: manuel.palencia@correounivalle.edu.co

Abstract
It is widely recognized that the mathematical modeling of mass transfer in membrane processes is an essential component not only for understanding the underlying mechanisms associated with the transport, but also that is a powerful tool for design, cost estimation, control and scale-up of extraction processes. Here, a simple methodological approach for the study and description of diffusional changes during the extraction and transport processes in liquid membrane systems is developed and evaluated in the extraction and transport of gallic acid from aqueous solutions. It is concluded that, in comparison with the use of flux and distribution coefficient in function on time, a more sensitive description of diffusion coefficient can be performed using mass-transport coefficient in function on the time. In addition, it is concluded that, during the polyphenol extraction by liquid membrane based on castor oil and Cyanex 921, transportation can be affected by dissolution of membrane phase in the feed phase, and evidenced by a negative value of g in function of time.

Keywords
Diffusion coefficient
Liquid membrane
Mass-transport coefficient
Coupled transport Boron

1. Introduction

Liquid membrane systems (bulk liquid membrane, emulsion liquid membrane and support liquid membranes) are promising alternatives used widely in the substance separation such as synthetic and natural organic molecules and ions. [1-7] In addition, these systems can be adapted for the study of numerous systems and for the characterization of properties of substances in dissolution, by instance, the formation of molecular complexes in the synthesis of molecular-imprinted polymers, the capacity for the transportation of substance through immiscible phases for analytical applications, biomedical simulations or the study of the interaction strength of simulated systems. [8-11] In particular, liquid membranes are seen to be adequate model-in-labs for many biological systems (e.g., biological membranes and fluids). [9,11]

The diffusion coefficient (D_i) is an important transport parameter that characterizes the ability of molecules to even out any concentration fluctuation in a system; however, measured values of D_i are not available in most cases. When a non-equilibrium system is studied, the analysis of the changes of D_i on the time is highly necessary to achieve a complete understanding of phenomena which are occurring into study systems.[12-14] Many attempts have been made in order to obtain working equations for the calculation of the time-dependent D_i of molecules penetrating nonporous

membranes. However, problem is found to be highly complex when the diffusing species are the result of chemical or physical interactions between different molecules through interfaces, being a typical situation in liquid membrane systems based on coupled-transport mechanism. [12-17]

The initial point for the study of diffusion is based on the Fick's first law linking the diffusive flux and the solute concentration; and the simpler model for the description of molecular diffusion coefficient at constant temperature, in very diluted solutions, is the well-known Stokes-Einstein equation (SEEq).[18] However, for the use of SEEq, several approximations as spherical shape of molecules, isotropic medium, low concentrations, constant viscosity of solvent, null effect of interaction with other dissolved species, among others, are usually done producing a high over-simplification of systems.[14-16] In addition, the SEEq does not include important effects as the intermolecular interactions between molecules of solute and between molecules of solvent and solute, being this an aspect that is very important in the study of diffusion through a heterogeneous system.[14-16, 18]

Several strategies based on models and simulations have being developed for the study of *Di* among which are included: simulation based on molecular dynamics into equilibrium and non-equilibrium states, simulation based on the Maxwell–Stefan approach including models as Darken-Type Models and Vignes-Type Models,[13, 19, 20] and thermodynamic methods based on to Kirkwood–Buff integrals in finite systems, scaling of small system fluctuations or Kirkwood–Buff integrals.[21, 22] It has been indicated that more than 100 different mathematical models for the description and study of mass transfer in liquid membranes have been proposed between 1980 to 1995 alone;[23] but, at the same time, several authors have recognized and criticized the excessive use of procedures based on advanced mathematics, since the physical significance of the parameters involved is not absolutely understood in many case.[24, 25] However, it is widely recognized that the mathematical modeling of mass transfer in membrane processes is essential not only for understanding the underlying mechanisms associated with the transport, but also that is a powerful tool for design, cost estimation, control and scale-up of extraction processes.[18]

By the above, it is necessary to have a simple methodology that can be easily incorporated in the study of experimental or simulated systems based on liquid membrane, and in addition, preferably without additional theoretical approximations producing oversimplification descriptions, or the excessive mathematical parametrization supported in high-complexity algorithms. Here, the use of kinetic information in conjunction with a simple correlation analysis is proposed as strategy for the description mass-transfer coefficient (g) and time-dependent D_i through liquid membranes. Thus, a simple analytical methodology can be defined for the study and adequate description of diffusional changes in extraction and transport processes in this kind of systems.

1.1 Method theory

In liquid membrane systems at least three phases are contacted by two immiscible interfaces. Therefore, typical configuration is constituted by feed, membrane and stripping phases. In addition, solute transport is understood to occur in several stages including the extraction of solute molecules from feed phase, diffusion of solute molecules or solute-carrier complexes from feed-membrane interface to membrane-stripping interface and the release of solute molecules in the stripping phase.[18]

Extraction and release of solute molecules can be described by the use of distribution coefficient (k_D) that is defined for each interface to be

$$K_{D,1} = \frac{C_m}{C_1} \quad and \quad K_{D,2} = \frac{C_2}{C_m} \qquad (1)$$

where c is the analyte concentration in the corresponding phase according to the corresponding subscript (m = membrane phase, 1 = feed membrane and 2 = stripping membrane).

Here, the following notation is introduced in order to simplify the description of system: $c_1|c_m$ and $c_m|c_2$ where in the left and right sides are indicated the property or properties that are being analyzed whereas the symbol | denotes the corresponding interface.

The approach defined by equation 1 has been widely used for the description of changes on concentration of solute in heterogenous systems, where the mass transfer into $c_1|cm$ has associated a

decrease on $k_{D,1}$ whereas, on contrary, mass transfer into cm|c_2 has associated an increase on $k_{D,2}$. However, the coupling of extraction and retro-extraction, c_1|cm|c_2, not always is completely satisfied. Several situations can be related with a non-adequate solute transport: inadequate extraction or retro-extraction stages, inefficient diffusion through membrane phase, or the combination of all of them. Though extraction or retro-extraction stages are described by equation 1, information about diffusion stage cannot be directly obtained only by distribution analysis.

On the other hand, the liquid membrane system can be understood as a system experimenting perturbations on the time, and in consequence, for different times a hypothetical steady-state diffusion can be defined. Note that, though steady-state is a hypothetical state because it implies that no changes of solute concentration on the time is occurring, the total description is completely congruent with the study system (see Figure 1).

For each hypothetical steady-state the diffusion flux (J_i) is given by

$$J_i = g(C_1 + C_2) = \frac{D_i}{h}(C_1 - C_2) \qquad (2)$$

Where J_i is the flux of solute i, D_i is the diffusion coefficient of specie i and h is the thickness of membrane. Thus, by monitoring of solute flux in function of time, empirical kinetic equations can be easily obtained for a specific set of experimental conditions, and by analysis of total behavior is possible to obtain information about the changes during transport stage through membrane in term of diffusion coefficient or mass-transfer coefficient.

2. Materials and methods

2.1 Reagents

Gallic acid (Sigma Aldrich, USA) was used as polyphenol model, as membrane phase was used castor oil (Merck, USA) due to its low vapor pressure (0.192 kPa at 299.1 ± 0.1 K) and its immiscibility with water which was used as feed and stripping phases.[26] Phosphine trioctyl oxyde (Cyanex® 921, Solvay) was used as carrier. Ionic strength was adjusted using NaCl (Merck, USA) and pH was adjusted using HCl (Merck, USA) and NaOH (Merck, USA).[27, 28]

As source of vegetal material for the obtaining of polyphenols was used sugarcane bagasse (*Saccharum officinarum*) from local crops.

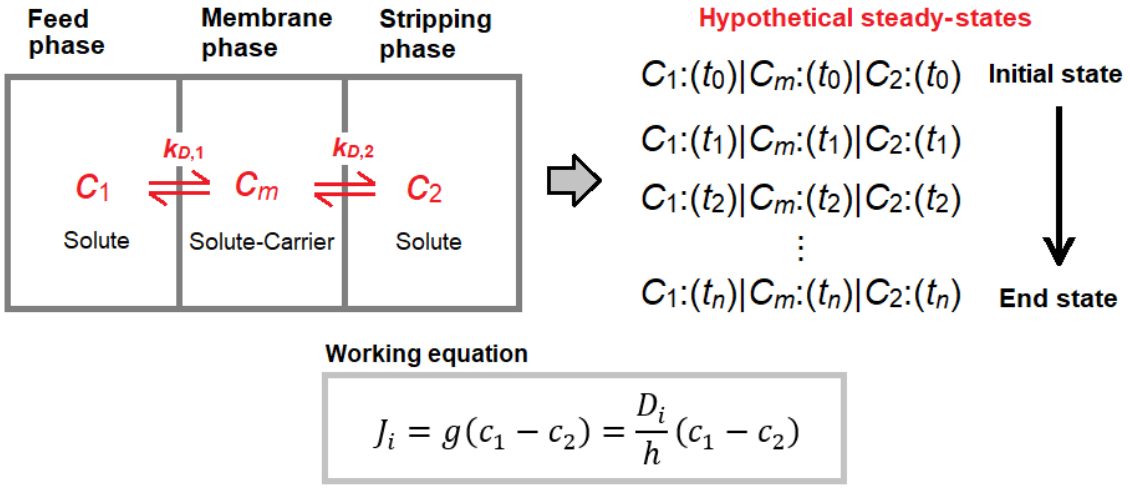


Figure 1. Ilustration of working approach: liquid membrane system (left) and hypothetical steady-state as a function on time from the initial state (t_0) to end state (tn) (right). For each t a working equation can be defined and used for different experimental conditions.

2.2 Extraction of polyphenols

Sugarcane bagasse was dried, ground and sieved through a 2 mm sieve. Later, 182 mL of ethanol-water mixture (52:48 v/v) were added to 13 g of vegetable material and sonicated using a Branson 2510 ultrasonic equipment (Marshall Scientific) at 40 kHz per 31 minutes at 62 °C.[29] Resulting mixture was washed and filtered using 468 mL of ethanol-water dissolution. The filtered was diluted using deionized water (1:5 volumetric ratio).

The polyphenol content was determined by ultraviolet-visible spectroscopy (UV-vis, Shimadzu) at 214 nm using a calibration curve between 0.5 - 30 ppm. In addition, the saccharose content was measured by polarimetry at 589 nm (P-2000 Digital Polarimeter, Jasco) using a calibration curve between 1 and 5 % saccharose.

2.3 Bulk liquid membranes

Experiments by bulk liquid membranes were made using batch-type parallel cells. These were performed without transporter and with transporter, in triplicate, using as feed phase 1.65 mL of gallic acid aqueous dissolution (30 ppm, pH 3.0), castor oil as membrane phase (0.8 mL), water at different values of pH as stripping phase (pH: 3.0, 7.0 and 9.0) and Cyanex® 921 as carrier at different molar ratio (1:1, 2:1 and 4:1).

The gallic acid concentration was measured as a function of time t (t = 2, 4, 6 and 24 h) in the feed, stripping and membrane phases. The gallic acid concentration was determined by UV-vis spectroscopy using the same method previously described. For membrane phase, liquid-liquid extraction was performed previously to the quantification using deionized water at pH 7.0 and subsequent acidification at pH 3.0.

2.4 Study of distribution and transport of gallic acid by bulk liquid membrane

Distribution constants were determined from monitoring of changes of gallic acid concentrations in the different phases and calculated by the use of equation 1. On the other hand, mass-transferring flows through the feed-membrane and membrane-stripping interfaces (J_1 and J_2, respectively) were determined by Fick's Law First, using the following equations:

$$J_1 = \frac{-V_1 C_1}{at} \quad (3)$$

$$J_2 = \frac{V_2 C_2}{at} \quad (4)$$

where V_1 and V_2 are the volumes of feed and stripping phases, respectively, whereas t and a are the time and the area of interfaces in contact, respectively; [30] in addition, Jm is defined to be $J_m = -J_1$. In addition, mass-transfer coefficient (g) was determined using the equation for diffusion in steady-state occurring across thin films described by equation 2.

2.5 Study of distribution and transport of polyphenols by bulk liquid membrane

Extraction of polyphenols by bulk liquid membranes was performed using the analogous systems than that used for gallic acid: polyphenol extract (pH 3.0) | castor oil + cyanex 921 | water (pH 7.0). Behavior of flux rate in function of time in each phase was determined from monitoring of changes of polyphenols concentrations using the total polyphenol determination by UV-vis (details were previously described in the above sections). In order to evaluate the stability of system, feed, membrane and stripping membrane were monitored by color-based digital image analysis.[31, 32]

In this case, digital image of different compartments of membrane system are recorded in digital format using a Nikon model Coolpix P530 coupled to sample holder with homogeneous luminosity (uniformity in the luminosity is achieved by white light sources around sample holder). After, images are processed and analyzed using the software Digital-Micrograph 3.7.0 (Gatan inc.).[31, 32]

In addition, sub-samples of phases were analyzed by infrared spectroscopy by attenuated total reflectance (ATR-FTIR, IR-Affinity-1) with SeZn crystal. Since feed and stripping phases are aqueous systems, with a relatively low concentration of solutes, spectra were transformed and analyzed functional-enhanced derivative spectroscopy or FEDS transform (FEDS) in order to increase the spectral resolution and achieve the identification of highly overlapped signals. [33, 34]

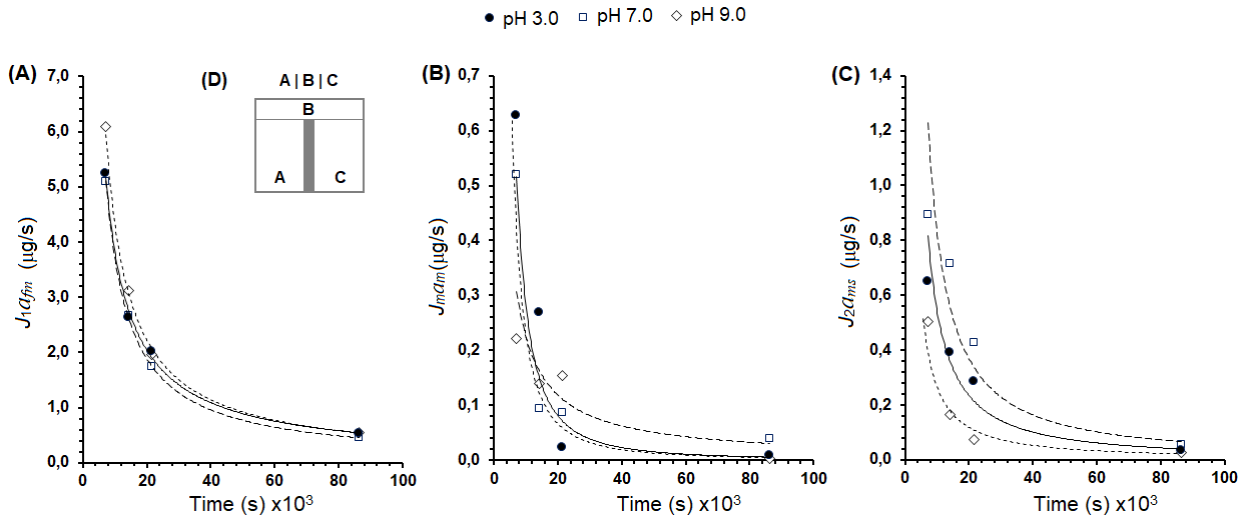


Figure 2. Rates of flux for gallic acid in the feed phase, J_1 (A), membrane phase, J_m (B) and stripping phase, J_2 (C). Feed phase at pH 3.0 and stripping phase at pH 3.0, 7.0 and 9.0 for bulk liquid membrane A|B|C being in the respective order the feed, membrane and stripping phases (or A|C when membrane phase is omitted).

Table 1. Fitting parameters for empirical model described by $Ja = r_1 t^{-r_0}$ rate of flux of gallic acid at pH 3.0, 7.0 and 9.0 in the stripping phase of bulk liquid membrane, where *a* is the area of the interfaces in contact. R^2 is the coefficient of correlation.

pH	Feed phase			Membrane phase			Stripping phase		
	r_1	r_0	R^2	r_1	r_0	R^2	r_1	r_0	R^2
3.0	35.24	0.977	0.9999	18.31	1.808	0.8651	9.06	1.219	0.9991
7.0	31.04	0.908	0.9977	14.09	1.785	0.8704	12.52	1.176	0.9909
9.0	39.81	0.963	0.9987	1.91	0.927	0.8024	3.97	1.173	0.9516

3. Results and Discussion

3.1 Development of model and analysis of extraction of gallic acid

The behavior of flux rate, at pH 3.0 in the feed and pHs 3.0, 7.0 and 9.0 in the stripping phase, for extraction of gallic acid in aqueous solution using castor oil as membrane phase, is shown in the Figure 2. It can be seen that, in the feed phase, a significant effect of stripping pH on gallic acid flux was not observed; on contrary, changes in the concentration of gallic acid in the membrane and stripping phases were observed. However, in all cases the tendency was a progressive decrease of flux rate with the time providing very little information that allows a clear understanding of the transportation process. For all cases, plots were fitted by an equation type:

$$Ja = r_1 t^{-r_0} \quad (5)$$

where r_1 and r_0 rare empirical constants (in ng/s or $\mu g x 10^{-3}$/s). Fitting parameters obtained for kinetic models are summarized in the Table 1.

The fitting of kinetic models was assumed to be satisfactory when R^2 = 0.99 since the experimental error in the quantification can be significant due to that measurements were performed from several experimental systems that were assumed to be exact replicates of one same experiment Thus, by comparison of equations 3 and 4 with the respective kinetic models is concluded that r_1 corresponds to the factor $v_1 c_1$ (i.e., r_1 is the amount of matter fluxing through $1|m$ and $m|2$). In addition, r_0 = 1.0 for the diffusion in steady-state and different to 1.0 when this condition is not satisfied. In consequence, if r_0 is compared with 1 then the assumption of steady-state can be characterized. Thus, for $1|m$ all values of r_0 were lower than 1.0 whereas for $m|2$ all values of r_0 were larger than 1.0. Besides, it can be seen that correlation fitting for membrane phase was not the better; in this particular case, the values of R^2 were

lower than 0.90, but also, a strong decrease of r_1 was observed as pH was increased, whereas values of r_0 suggest that steady-state assumption is not adequate for the description of membrane phase. Finally, for each value of pH, values of r_1 decrease through the way feed-membrane-stripping.

From the fitting of generalized kinetic equations is possible to obtain equations for the description of distribution coefficients in function of the time. Thus, for the first interface defined by feed and membrane phases (1|*m*), using the equations 1-4 is easily concluded that

$$k_{D,1} = f_v \left(\frac{r_{1,m}}{r_{1,1}}\right) t^{-(r_{0,m}-r_{0,1})} \quad (6)$$

Where $f_v = V_1 V_m^{-1}$, and analogously for the second interface (*m*|2)

$$k_{D,2} = f_v \left(\frac{r_{1,2}}{r_{1,m}}\right) t^{-(r_{0,2}-r_{0,m})} \quad (7)$$

Where $f_v = V_m V_2^{-1}$

In the Figure 3 is shown the modeling of distribution constant based on equations 6 and 7. It is observed that $k_{D,1}$ decreases markedly at short times for pH 3.0 and 7.0 in the stripping phase (approximately 1 hour). The decrease of $k_{D,1}$ is explained due to transfer of analyte from feed phase to membrane phase, and later, from membrane phase to stripping phase evidencing a coupling of extraction and retro-extraction stages.

Note that, if analyte is not transferred to the stripping phase then an increasing in the distribution is expected because analyte concentration in the feed is decreased and in the membrane is increased. But, as it is seen from figure 3B, at pH 3.0 and pH 7.0, the increase of $k_{D,2}$ shows that retro-extraction is completed, and inconsequence, the analyte concentration in the membrane phase is decreased, and in concordance with this, $k_{D,1}$ is also decreased. On contrary, when stripping solution at pH 9.0 was used a weak retro-extraction was observed. From a chemical point of view, these results are congruent with expected chemical behavior for gallic acid in function on pH. Thus, at pH 3.0, both phenolic groups as carboxylic acid group on gallic acid structure are completely protonated favoring his interaction with the carrier molecules by hydrogen bonds. Given that, c1 is decreased and cm is increased, it is expected that $k_{D,1}$ is increased and analogously the analysis can be extrapolated for $k_{D,2}$; but, as a result of coupling of mass-transferring processes from 1|*m* and *m*|2, if $k_{D,2}$ is increased (see figure 3B) then $k_{D,1}$ is decreased (see figure 3A).

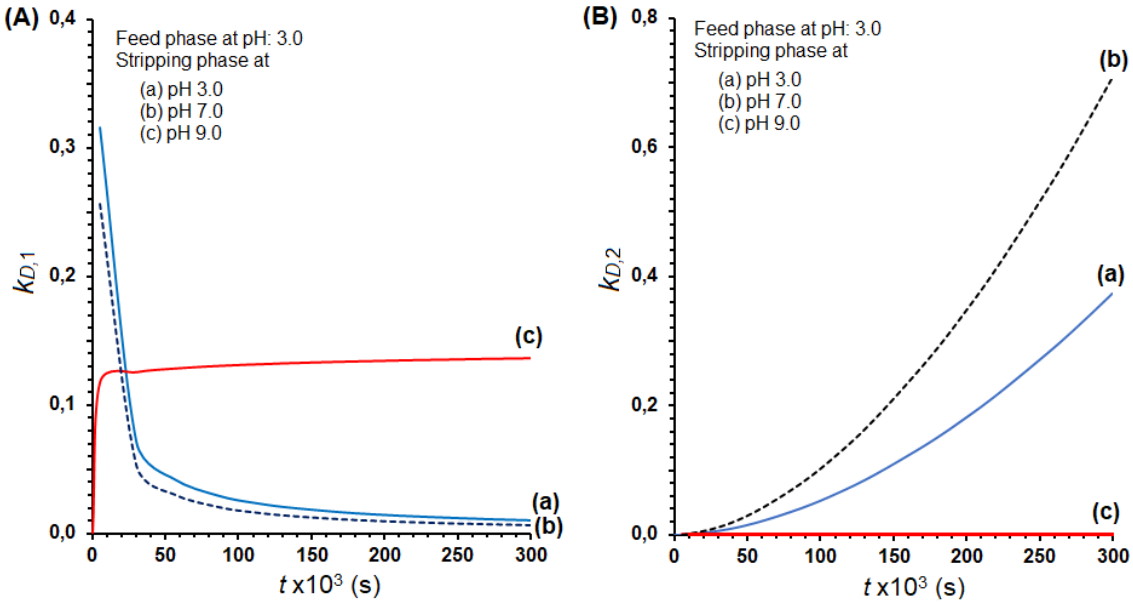


Figure 3. Modeling of changes of distribution constants on the time.

In consequence, at pH 3.0, the modeling defined by equations 6 and 7 is seen to be congruent with the expected results. However, when stripping phase at pH 9.0 is used, phenols and carboxylic acid groups on gallic acid molecules are deprotonated, decreasing the interaction with the carrier and avoiding the release of gallic acid in the stripping phase, therefore, as gallic acid molecules are extracted of feed phase, solute-carrier complex remains in the membrane phase.

On the other hand, g can be easily modeled as a function on the time at values of working pH using previous equations. Thus, a generalized expression to calculate g is given by

$$g = \frac{-r_{1,1}t^{-r_{0,1}}}{ac_1\left[1-\left(\frac{r_{1,2}}{r_{1,1}}\right)t^{-(r_{0,2}-r_{0,1})}\right]} \quad (8)$$

In the Figure 4 are shown the behaviors of mass-transfer coefficients as a function of pH for all pH gradients. For all cases, different behaviors were obtained:

When system was 3.0|9.0, g was increased from negative values to zero being zero a horizontal asymptote. In the feed the gallic acid concentration decreases (i.e., negative flux) and, when retro-extraction occurs, it is expected that in the stripping phase the gallic acid concentration is being continuously increased (i.e., positive flux), and therefore, the values of g change from negative to positive values. In consequence, horizontal asymptote is associated with a correct extraction at pH 3.0 but a poor or null retro-extraction at pH 9.0.

When system is 3.0|7.0, from analysis of g different stages can be described. First one, an extraction-diffusion stage occurs at relatively low times characterized by a variation on function on the time greater than zero ($dg/dt > 0$). In this stage, two regimes are identified, for time lower than p_1 (see Figure 4), g is controlled by dissolution reaction or distribution between membrane and feed phase, after, from p1 to p_2, g is controlled by diffusion. In this point, it can be seen that the slope between the systems is very alike. From p_2 to p_3, the transport is controlled by diffusion (it is not observed a significant change in the slope). From p_3 to p_4, the transport is controlled by stripping reaction, in this stage, g decreases being explained by a decrease in the diffusion coefficient. A small perturbation in the behavior of g suggests that some degree of perturbation of systems is produced at relatively long time (p_4 in the Figure 4B).

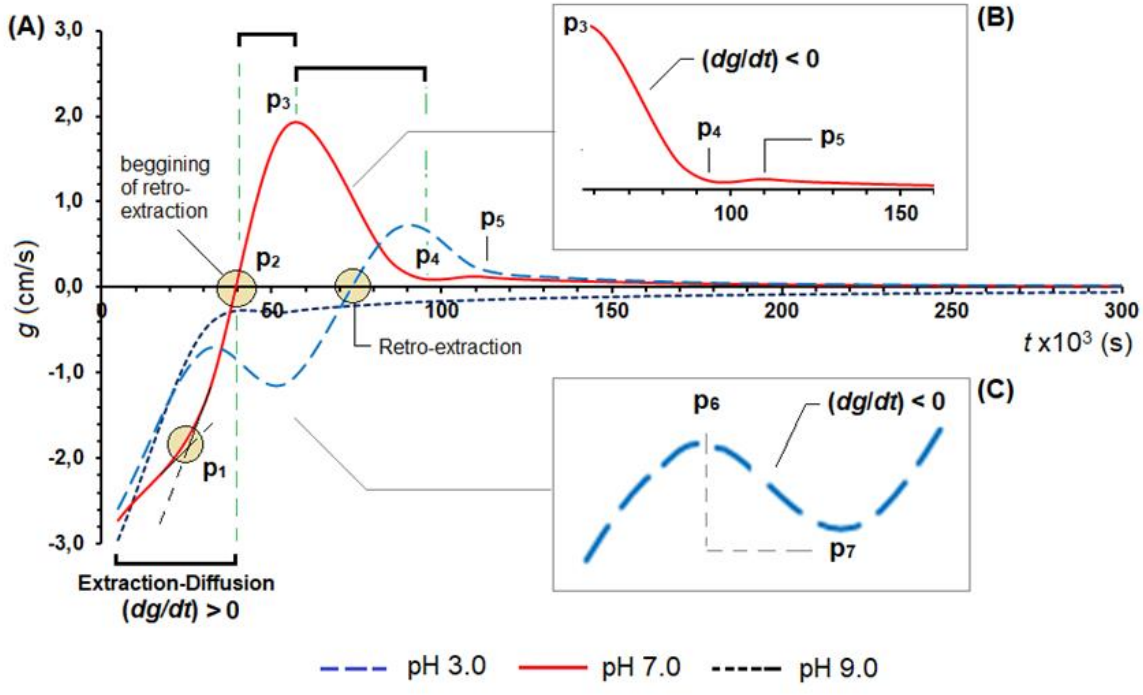


Figure 4. (A) Modelling of mass transfer coefficient (g) as a function on time for extraction of gallic acid by bulk liquid membrane at several pH in the stripping phase (3.0|3.0, 3.0|7.0 and 3.0|9.0). Expanding segments of modeling results (B and C).

This perturbation can be explained by a significant change of interface between membrane and stripping phase by dissolution of membrane phase. When system is 3.0|3.0, extraction occurs from t = 0 to p_6 being controlled by diffusion, however, a decrease is evidenced. The decrease between p6 and p_7 suggests that process of extraction and retro-extraction are not coupled being explained this behavior as a result of slow diffusion of polyphenol-carrier complex (Figure 4C). According to the equation 2, $D_i = hg$ where h is assumed to be a constant. In consequence, modeling described by equation 8 should be a proper description for diffusion coefficient. Given that g is defined from experimental data easily measured, the importance of g as working equation is that changes non-evidenced by the study of the flux and distribution coefficient in function on time.

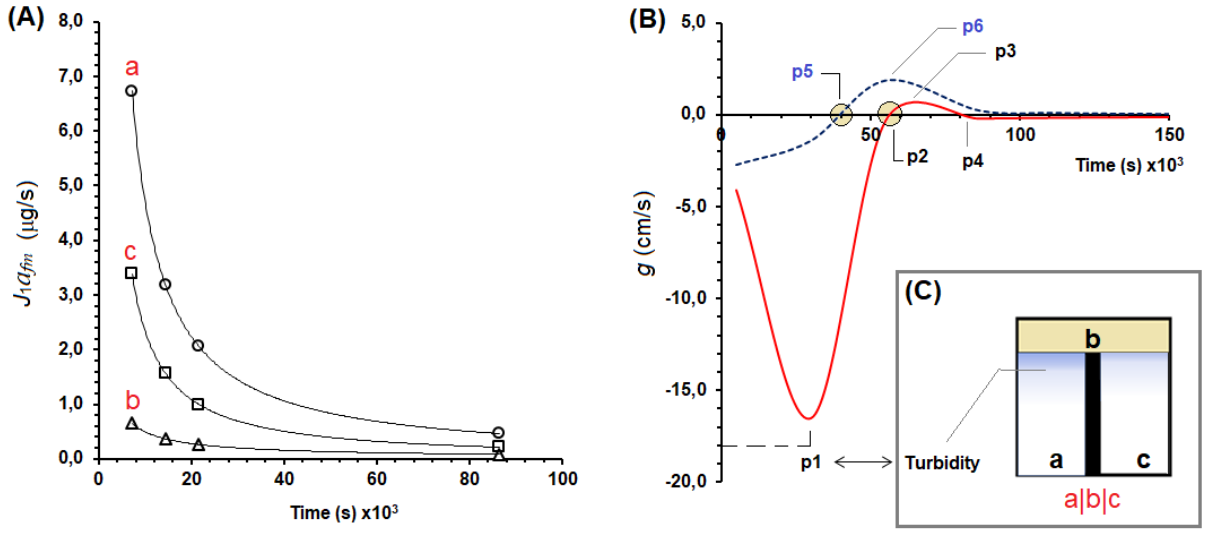


Figure 5. (A) Rates of flux for polyphenols from bio-oil by monitoring of feed phase (a), membrane phase (b) and stripping phase (c), in a a|b|c with the following composition: bio-oil (pH 3.0) | Cianex 921 + castor oil | H_2O (pH 7.0); (B) modeling of g in function of the time, and (C) schematic representation of visual changes in the feed and stripping phases.

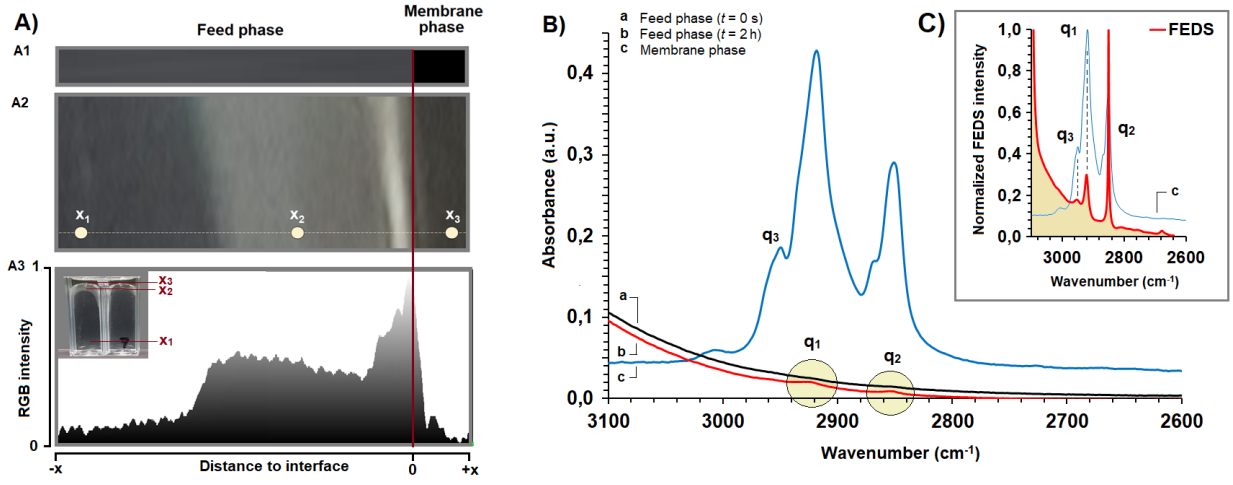


Figure 6. (A) Digital image of feed compartment: initial state (feed phase | membrane phase) (A1), digital image of feed compartment at t = 2 hours (A2) and normalized RGB intensity in function of interface (A3). (B) Infrared spectra of feed phase at t = 0 s (a), feed phase at t = 2 hours (b) and membrane phase (c). (C) FEDS transform of infrared spectrum of feed phase at t = 2 hours compared with the infrared spectrum of membrane phase

3.2 Application of model in the transportation analysis during extraction of polyphenols from sugarcane bagasse aqueous extract

In the Figure 5A are shown the behavior of flux rates of polyphenols in function of time for all phases (feed, membrane and stripping phases). It is evidenced that the data can be fitted to the model described by equation 5, in concordance with the behavior described for gallic acid. Respective values associated with analysis of correlation are summarized in the Table 2.

On the other hand, in the Figure 5B is shown the behavior of *g* as a function of the time and compared with the result obtained for gallic acid. It can be seen that *g* decreases from $t = 0$ to p_1 being an unexpected result. This behavior suggest that mass transportation is taking place in the opposite direction, i.e., from membrane phase to feed phase (*g* is decreased in function of the time being congruent with the decrease of $k_{D,1}$). In addition, visual changes associated with the formation of a 'cloud' were identified in the feed compartment (illustration is shown in the Figure 5C and analyzed below). In the Figure 6 is shown the digital image analysis of feed compartment. The analysis by surface anisotropy (in this case, changes in color intensity defined in RGB space along a path defined from x_1 to x_3 on the image).

Thus, analysis of image shows two interesting aspects: (i) homogeneity of dissolution in the feed is perturbed being more intense the change in the vicinity of the interface and (2) changes can be explained by the instability of membrane phase that is partially dissolved in the feed phase being the reason of the appearing of 'cloud' in the feed phase. In order to acquire more evidence supporting the negative values of g, feed phase was analyzed by infrared spectroscopy at different times. It can be seen in the Figure 6C that signals associated with the C-H are increased and identified in the spectrum (note that q_1, q_2 and q_3 are highly intense into infrared spectrum of membrane phase whereas these signals are not identified in the infrared spectrum of feed phase; if transportation is occurring from x_1 to x_3 then these signals should not identified at $t = 2$ hours). Returning to the analysis of *g* as a function of time, *g* is increased from p_1 to p_2 (Figure 6B) with an analogous behavior to that observed for gallic acid (from p_2 to p_4 and times greater than p_4).

Table 2. Fitting parameters for empirical model described by $Ja = r_1 t^{-r0}$ for rate of flux of polyphenols at pH 3.0 in the feed phase and 7.0 in the stripping phase of bulk liquid membrane (*a* is the area of the interfaces in contact. R^2 is the coefficient of correlation).

pH	Feed phase			Membrane phase			Stripping phase		
	r_1	r_0	R^2	r_1	r_0	R^2	r_1	r_0	R^2
3.0	56.40	1.077	0.9810	3.33	0.826	0.7529	30.45	1.112	0.7741

4. Conclusions

A simple methodology for the study of time-dependent diffusion coefficient in liquid membrane systems is described. For that, system is described by a set of hypothetical steady-states which are defined and monitored from experimental data. From this approach a simple modeling of mass-transport coefficient using kinetic data was developed and connected with diffusion coefficient. It is concluded that, in comparison with the use of flux and distribution coefficient in function on time, a more sensitive description of diffusion coefficient can be performed using mass-transport coefficient in function on the time. On the other hand, it is concluded that, during the polyphenol extraction by liquid membrane based on castor oil and Cyanex 921, transportation can be affected by dissolution of membrane phase in the feed phase, and evidenced by a negative value of *g* in function of time.

Acknowledgements

Authors thanks to Universidad del Valle and Mindtech s.a.s.

Funding

This work was supported by the Universidad del Valle and Mindtech s.a.s.

Interest conflict

The authors declare that there are no conflicts of interest

References

[1]. Pourkhanali K., Saleh M., Khayati G. Performance Evaluation of Bulk Liquid Membrane Technique on p-Nitrophenol Removal from Aqueous Solution, Chem. Biochem. Eng. Q., 32 (2018) 83–90.
https://doi.org/10.15255/CABEQ.2016.1033

[2]. Diaconu I., Mirea C.M., Ruse E., Nechifor G., Selective recovery of phenolic derivatives through the technique of liquid membranes, Environ. Eng. Manag. J. 14 (2015) 625.
https://doi.org/10.30638/eemj.2015.069

[3]. Balasubramanian A., Venkatesan S. Removal of Phenolic Compounds from Aqueous Solutions by Emulsion Liquid Membrane Containing Ionic Liquid [BMIM]+[PF6]− in Tributyl Phosphate, Desalination 289 (2012) 27-34.
https://doi.org/10.1016/j.desal.2011.12.027

[4]. Yu P., Chang Z., Ma Y., Wang S., Cao H., Hua C., Liu H., Separation of p-nitrophenol and o-nitrophenol with three-liquid-phase extraction system, Sep. Purif. Technol. 70 (2009) 199-206.
https://doi.org/10.1016/j.seppur.2009.09.016

[5]. Wojciech Cichy, W., Schlosser, S., Szymanowski, J., Extraction and pertraction of phenol through bulk liquid membranes, J. Chem. Technol. Biotechnol. 80 (2005) 189-197.
https://doi.org/10.1002/jctb.1178

[6]. Ng YS., Jayakumar NS., Hashim MA. Performance evaluation of organic emulsion liquid membrane on phenol removal, J. Hazard. Mater. 184 (2010) 255-260.
https://doi.org/10.1016/j.jhazmat.2010.08.030

[7]. Szczepański P., Diaconu I., Transport of p-nitrophenol through an agitated bulk liquid membrane, Sep. Sci. Technol. 47 (2012) 1725-1732.
https://doi.org/10.1080/01496395.2012.659316

[8]. Clements A., Bursac D., Gatsos X., Perry AJ., Civciristov S., Celik N., Likic VA., Poggio S., Jacobs-Wagner C., Strugnell RA., Lithgow T. The reducible complexity of a mitochondrial molecular machine, PNAS 106 (2009) 15791-15795.
https://doi.org/10.1073/pnas.0908264106

[9]. Vonck J., Schäfer E. Supramolecular organization of protein complexes in the mitochondrial inner membrane, Biochim. Biophys. Acta (BBA) - Mol. Cell Res. 1793 (2009) 117-124.
https://doi.org/10.1016/j.bbamcr.2008.05.019

[10]. Muhammad T., Nur Z., Elena V. Piletsk EV., Osmanjan Yimit O., Piletsky SA. Rational design of molecularly imprinted polymer: the choice of cross-linker, Analyst 137 (2012) 2623-2628.
https://doi.org/10.1039/C2AN35228A

[11]. de la Serna JB., Schütz GJ., Eggeling C., Cebecauer M. There Is No Simple Model of the Plasma Membrane Organization, Front. Cell Dev. Biol. 4 (2016) 106.
https://doi.org/10.3389/fcell.2016.00106

[12]. WuKeith J., Berland M. Propagators and Time-Dependent Diffusion Coefficients for Anomalous Diffusion, Byophys. J. 95 (2008) 2049-2052.
https://doi.org/10.1529/biophysj.107.121608

[13]. Liu X., Schnell SK., Simon JM., Krüger P., Bedeaux D., Kjelstrup S., Bardow A., Vlugt T. Diffusion Coefficients from Molecular Dynamics Simulations in Binary and Ternary Mixtures. Int. J. Thermophys. 34 (2013) 1169–1196.
https://doi.org/10.1007/s10765-013-1482-3

[14]. Dudek G., Borys P. A Simple Methodology to Estimate the Diffusion Coefficient in Pervaporation-Based Purification Experiments. Polymers (Basel) 11 (2019) 343-356.
https://doi.org/10.3390/polym11020343

[15]. Borys P., Grzywna Z.J. An analytical solution to the idealized batch pervaporation experiment: A way to determine the diffusion and partition coefficients. J. Membr. Sci. 476 (2015) 525–529.
https://doi.org/10.1016/j.memsci.2014.12.012

[16]. Giacomazzi E., Picchia FR., Arcidiacono N. A review of chemical diffusion: Criticism and limits of simplified methods for diffusion coefficient calculation. Combustion Theor. Modell. 12 (2008) 135-158.
https://doi.org/10.1080/13647830701550370

[17]. Alhusseini A., Ajbar A. Mass transfer in supported liquid membranes: A rigorous model. Math. Comput. Model. 32 (2000) 465-480.
https://doi.org/10.1016/S0895-7177(00)00145-X

[18]. Crank J. The mathematics of diffusion, Clarendon Press - Oxford (1975) 1-414.

[19]. Leonardi E., Angeli A. On the Maxwell-Stefan Approach to Diffusion: A General Resolution in the Transient Regime for One-Dimensional Systems. The J. Phys. Chem. B 114 (2009) 151-164.
https://doi.org/10.1021/jp900760c

[20]. Vergara A. Use of Kirkwood–Buff Integrals for Extracting Distinct Diffusion Coefficients in Macromolecule–Solvent Mixtures. Macromol. Theory and Simul. 25 (2016) 497-501.
https://doi.org/10.1002/mats.201600040

[21]. Kale GB. Thermodynamic Diffusion Coefficients. Defect and Diffusion Forum, 279 (2008) 39-52.
https://doi.org/10.4028/www.scientific.net/DDF.279.39

[22]. Kattner UR., Campbell CE. Modelling of thermodynamics and diffusion in multicomponent systems. Mat. Sci. Technol. 25 (2009) 443-459.
https://doi.org/10.1179/174328408X372001

[23]. Noble RD., Alexander Stern SA. Membrane separations technology: principles and applications, volume 2. Elsevier, 1995.

[24]. Cussler EL. Multicomponent Diffusion. Elsevier, 2013.
[25]. De Gyves J., Rodriguez, E. Metal ion separations by supported liquid membranes. Ind. Eng. Chem. Res. 38 (1999):2182–2202.
https://doi.org/10.1021/ie980374p
[26]. Ndiaye P., Tavares F., Dalmolin I., Dariva C., Oliveira D., Oliveira J. Vapor Pressure Data of Soybean Oil, Castor Oil, and Their Fatty Acid Ethyl Ester Derivatives. J. Chem. Eng. Data 50 (2015) 330-333.
https://doi.org/10.1021/je049898o
[27]. Palencia M., Rivas B. Metal ion retention by emulsion liquid membrane coupled to liquid-phase polymer-based retention. Colloid Polym. Sci. 289 (2011) 1695-1709.
https://doi.org/10.1007/s00396-011-2490-0
[28]. Palencia M., Rivas B. Metal-ion retention properties of water-soluble amphiphilic block copolymer in double emulsion systems (w/o/w) stabilized by non-ionic surfactants. J. Colloid Interf. Sci. 363 (2011) 682-689.
https://doi.org/10.1016/j.jcis.2011.05.089
[29]. Feng S., Luo Z., Zhang Y., Zhong Z., Lu B. Phytochemical contents and antioxidant capacities of different parts of two sugarcane (Saccharum officinarum L.) cultivars. Food Chemistry. 151 (2014) 452-458.
https://doi.org/10.1016/j.foodchem.2013.11.057
[30]. Cichy W., Schlosser S., Szymanowski J. Extraction and pertraction of phenol through bulk liquid membranes. J. Chem. Technol. Biotechnol. 80 (2005) 189-197.
https://doi.org/10.1002/jctb.1178
[31]. Palencia M., Lerma T., Palencia V. Description of fouling, surface changes and heterogeneity of membranes by color-based digital image analysis. J. Membr. Sci. 510 (2016) 229-237.
http://dx.doi.org/10.1016/j.memsci.2016.02.057
[32]. Cajiao N., Mora H., Palencia M. Determination of microorganism cellular concentration by digital image quantitative analysis (DIQA). J. Sci. Technol. Appl. 1 (2016) 77-86.
https://doi.org/10.34294/j.jsta.16.1.7
[33]. Palencia VJ., Martínez JM. Spectral data transformation analysis by simple mathematical functions: Fourier transform infrared spectrum. J. Sci. Technol. Appl. 3 (2017) 44-55.
https://doi.org/10.34294/j.jsta.17.3.23
[34]. Palencia M. Functional transformation of Fourier-transform mid-infrared spectrum for improving spectral specificity by simple algorithm based on wavelet-like functions. J. Adv. Res. 14 (2008) 53-62.
https://doi.org/10.1016/j.jare.2018.05.009.