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Modeling of constant-volume continuous diafiltration by solute distribution space's perturbations through geometric series: Part I: Inert system (Washing method)

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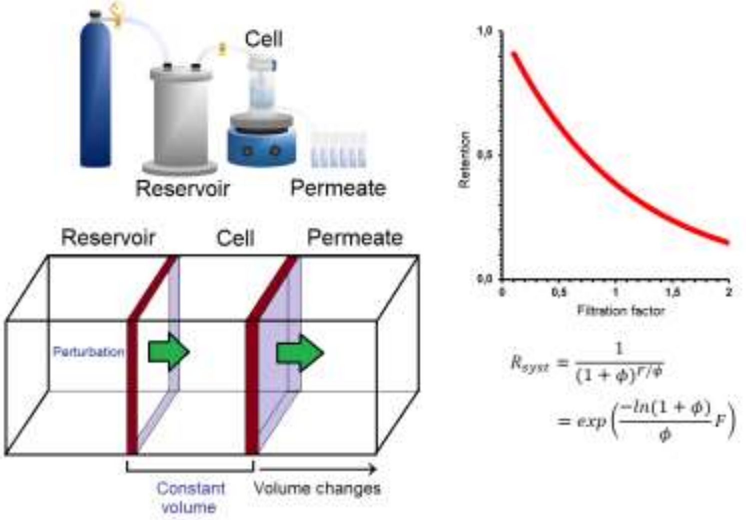
Graphical Abstract



Abstract. A new modeling of the washing method during constant-volume continuous diafiltration is described. This model is based on the analysis of small perturbations experimented by a dissolution in the inner of a diafiltration module. Thus, the analysis of small perturbations promoted during the diafiltration process permits to conclude an analytical model to describe the concentration changes in function of system parameters (e.g., filtration factor, permeate volume, time). Mathematical expression for the description of retention profile is characterized to be a geometric series with constant ratio given by $r = 1/(1+\phi)$ with a corresponding equivalent exponential equation, in addition, all parameters of model are completely defined in term of physical variables. It is concluded that retention profiles of inert system are completely defined by two volumetric parameters related with the experiment design: "collecting tube volume" and volume contained in the filtration cell. However, if the minimal permeate volume produced by the perturbation is considered, then "collecting tube volume" is equal to membrane's permeability.

Keywords: Dead-end ultrafiltration, retention profile, elution profile, washing method, analytical diafiltration.

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1. Introduction

Constant-volume by-dilution continuous diafiltration is also known as washing method. It is a membrane filtration method characterized by the continuous addition of solvent without changes in the volume. By the above, the substance in the inner of membrane module is continuously washed, and with this, the elimination or recovery of solutes able to pass though the membrane toward permeate stream is promoted (Kóvacs, 2015; Tan and Franzreb, 2019). This separation operation can be carried out in heterogeneous and homogeneous phase. In the first case, a solid-liquid biphasic system is placed in the filtration module, and usually it is used for the purification of solid by removing of small-size species or highly soluble in the washing solvent. On the other hand, when separation operation is performed in homogeneous phase, a solution is introduced in the filtration module (Lipnizki et al., 2002). Homogeneous-phase diafiltration is the basic principle of most advanced separation techniques such as polymer enhanced ultrafiltration (PEUF) or liquid-phase polymer-based retention (LPR) (Palencia, 2015; Palencia et al., 2017; Rivas et al., 2017; Huang and Feng, 2019). In this case in particular, washing method can be described as a continuous elution process in which a polymer dissolution is progressively perturbed by addition of solvent under controlled conditions (constant flux and pressure, elimination of polarization concentration layer, among others) (Palencia, 2015). As a result of perturbations, polymer-ion interaction in modified, and therefore, it has been suggested that by monitoring of changes of concentration is possible to obtain different properties of polymers, being the retention properties of ion pollutants by polymer soluble, at different conditions, the main focus of research in this way (Geckeler et al., 1986; Moreno-Villoslada and Rivas, 1998; Moreno-Villoslada et al., 2001; Moreno-Villoslada and Rivas, 2002; Moreno-Villoslada et al., 2002; Palencia et al., Muthukumar 2004; 2009; Palencia et al., 2010; Huang and Feng, 2019; Chevtaev et al., 2020). However, it also has been suggested that the adequate modeling of retention and elution profiles can be used to obtain molecular information for the characterization of polymer dissolutions. Among the different approach are the Manning theory, which is used for the theoretical description of polyelectrolyte in solution, molar-bond ratio which is used to estimate the number of available groups on polymer chain able to interact with ions in dissolution and determination of bond strong between polymers and metal ions, among others (Moreno-Villoslada et al., 2001; Tomida et al., 2001; Moreno-Villoslada and Rivas, 2002; Palencia et al., 2009; Palencia, 2015). However, at the present, available models for description of elution and retention profiles are empirical models which contain parameters that absorb the behavior of the data. These phenomenological parameters have been proposed and interpreted in different ways depending on each model (Palencia, 2015). However, although they result useful for elution and retention profile simulation, current models do not allow exploring molecular properties due to the lack of a complete physical interpretation of the respective parameters. Description of the main models can be reviewed in the literature: exponential decay model (Moreno-Villoslada and Rivas, 1998; Palencia, 2015; Rivas et al., 2017; Huang and Feng, 2019) and rational decay model (Palencia, 2015). The beginning point for the modeling of washing method is the simplest system, which is known as inert system. This system is formed by the absence of retainer elements in the filtration unit, and the single component containing the solute is the solution. Inert system is important because it is related with the inherent hydrodynamic behavior of system, and any perturbation of this behavior in more complex systems, it is attributed to the interaction of solute with one or more retainer elements (Moreno-Villoslada and Rivas, 1998; Palencia, 2015).

Here, a new model for description of inert system is shown. This is based on the changes experienced by the elution process and its developed does not introduce unknown empirical parameters. In consequence, it is an absolute model, with a complete physical interpretation, and therefore, it permits to advance toward the concept of analytical diafiltration (i.e., the use of washing method for the obtaining of molecular information of polymer systems).

2. Model development

2.1. Description of working system

The working system corresponds to dead-end ultrafiltration system (see Figure 1). It consists of a pressure unit acting as the driving force for filtration process, which is connected to a reservoir containing a washing solution, whose composition is defined in the design of the experiments. This can be characterized by characteristic pH values, ionic strength, nature and concentration of solutes, etc. In addition, reservoir is connected to stirred-cell filtration unit where an ultrafiltration membrane is located; but also, stirring is needed to avoid the effects of concentration polarization on homogeneity of dissolution in the inner of the filtration unit. Filtration unit is constituted by a cell containing the dissolution to be filtered, an internal stirring system, a membrane and a module to receive the permeate. This receiver module has a system of channels through which the permeate is collected and directed out of the system, in such a way that it is collected in sequential tubes, or if preferred in a single receiver container of greater capacity (Rivas et al., 2011; Huang and Feng, 2019).

2.1.1. Working modes

Filtration unit has been designed to operate under different working modes: (i) Diafiltration at constant volume. In these experiments a “pseudo-stationary state” or “PV-stationary state” is achieved. This is characterized because the pressure in each compartment is the same (i.e., reservoir, cell, and connecting additaments), consequently, volume is constant. However, system is not a static, since changes in the concentration are occurring as dissolution is permeated through the membrane, and therefore, system is described using the term “pseudo-stationary” or “PV-stationary” since pressure and volume are constant in the cell. (ii) Diafiltration at variable volume. In this case the reservoir is omitted and the pressure exerted produces a progressive decrease in the dissolution inside the cell. Depending on the composition of the solution contained in it, different behaviors are obtained (Palencia, 2015). By instance, when a polymer solution with a molecular weight greater

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Figure 1. Schematic representation of inert system components by dead-end ultrafiltration.

than the cut-off size of the membrane, as the solvent passes through the membrane, the polymer concentration increases, and therefore its viscosity. The above does not occur when solutions of low molecular weight species are used because these are able of crossing the membrane without significant changes in the properties of the solution, beyond the changes promoted by their interaction with the ultrafiltration membrane (Michaels et al., 1971; Rivas et al., 2003; Palencia et al., 2009).

2. 2. Independent-retainer element approximation

The diafiltration system can be divided into three regions where only one is active respect to solute retention: the membrane module. The active nature of this region is directly related with its components, which are: (i) a solution in which the solutes can be distributed, and (ii) the membrane, in the event that its interaction with the solutes is strong enough to overcome the effect of flow-mediated transport. In specific techniques, other retainer elements may be present, which usually corresponds to solutes or dispersed material of high molecular weight, which usually include water-soluble polymers (Palencia, 2015; Rivas et al., 2017; Huang and Feng, 2019), polymeric resins (Mozia et al., 2005; Tansakul et al., 2011), micelles (Filipi et al., 1999; Schwarze, 2017), and emulsions (Palencia and Rivas, 2011a; 2011b; Rivas and Palencia 2011).

Based on the above, two situations are possible: (i) that the retention of a solute by a retainer component is not affected by the presence of the other, in which case the system can be defined as a system formed by independent retainer elements, and (ii) that the retention of one or more of the retainer components of the system is influenced by the presence of the others. This last case has been little studied, and therefore few examples can be identified. One of them is polymer-assisted liquid phase retention coupled to surfactant liquid membranes (Palencia and Rivas, 2011a; 2011b; Rivas and Palencia 2011).

From independent-retainer element hypotheses is concluded that, when one or more retainer elements are in the membrane module, retention of the system (R_{syst}) can be defined as the additive contribution of individual retainer elements:

$$R_{syst} = R_1 + R_2 + R_3 + \cdots + R_n = \sum_{i=1}^{n} R_i \qquad (1)$$

where i denotes the number of retainer elements. Previous equation is consistent with the modeling of the system by distribution zone. Thus, the distribution-zone approach considers that diafiltration system is a closed system constituted by the reservoir, connection hoses, filtration cell, and permeate. Also, all retainer components are included (Palencia, 2015).

2.3. Inert system

An inert diafiltration system is characterized for one single retainer element which can be understood as the place where solutes are initially distributed (i.e., solution contained in the cell). Note that, two or more substances can be present but if they do not affect the value of retention then the system is also an inert system. Effect of solution understood as a retainer element is mainly on flux in the case of promoting of fouling, changes of viscosity depending on solute concentration or solute-solvent ratio, and changes on residence time (t_r) depending on volume added to the cell. Typical inert system is formed by two components in the membrane module: the solute dissolution and an inert membrane. Thus, for a system characterized by an inert membrane respect to target solute, $R_{syst} = R_1 = 1$ at $t = 0$ or t_0 (i.e., initial time previous to beginning of filtration), but also, for an infinite elution time (t_∞), the corresponding retention is zero ($R_\infty = 0$). In this way, at t_0, system retention does not provide more information, therefore elution profiles are identified to be strategies more suitable for the description of the system. In terms of the elution profiles, at $t = 0$ there is an initial concentration (C_0) that will be restricted by the maximum solubility at working conditions. However, it is important to highlight that for inert system, t_r can be evaluated and compared under different experimental conditions by direct monitoring of changes in the permeate.

Here, R_1, R_2 and R_3 denote the retention of solution in the cell, membrane and polymer, respectively. In addition, for non-inert systems, if experiment is performed in such a way that polymer is contacted with ions or species to retain in the inner of the filtration cell, under constant stirring, then it can be assumed that all retainer elements achieved the equilibrium respect to ion concentration in dissolution. These equilibria are described by distribution constant defined to be k_{12} and k_{13}, respectively.

On the other hand, since for inert system (R_2 and $R_3 = 0$), R_1 is a function of time, and therefore,

$$R_{syst}{:}\,(t) = R_1{:}\,(t) \qquad (2)$$

or, what is the same,

$$R_{syst}{:}\,(F) = R_1{:}\,(F) \qquad (3)$$

where F is the filtration factor, defined to be the quotient between V_p and V_c. Note that, given that flux is constant, F is directly proportional to time, being the flux rate the proportional constant.

2.4. Obtaining of working equations

Here, at difference of other models, working equations are not obtained from differentiation strategies. The strategy followed was based on the generalization of one well-known equation, the dilution equation, or in order to be more exact, the generalization of mass balance respect to solute from successive perturbations during the filtration. Details are given below:

When a cell-contained dissolution volume is transferred to the permeate (V_p), an equal volume amount is transferred from the reservoir to the cell (V_N). Given that $V_p = V_N$, it is clear that volume in the inner of the cell (V_c) is constant. In addition, at t_0 is observed that $R_{syst} = 0$ and all solute molecules are in the cell, but, for $t > 0$, solute contained in the dissolution is partitioned in two zones: cell and permeate. Specifically, if $F = 1$ then C_0 is reduced at fifty percent (i.e., $C_0 = C_1/2$ where subscript denotes the corresponding value of F). Analysis for the first values of F is:

For $F = 1$

$$C_1 = \frac{C_0 V_0}{V_0 + V_1} = C_0\left(\frac{V_0}{V_0 + V_1}\right) \qquad (4)$$

For $F = 2$

$$\begin{aligned} C_2 = C_1\left(\frac{V_0}{V_0 + V_2}\right) &= C_0\left(\frac{V_0}{V_0 + V_1}\right)\left(\frac{V_0}{V_0 + V_2}\right) \\ &= C_0\left(\frac{V_0}{V_0 + V_1}\right)\left(\frac{V_0}{V_0 + V_1}\right) \qquad (5) \end{aligned}$$

therefore,

$$C_2 = C_0\left(\frac{V_0}{V_0 + V_1}\right)^2 \qquad (6)$$

For $F = 3$

$$\begin{aligned} C_3 = C_2\left(\frac{V_0}{V_0 + V_3}\right) &= C_0\left(\frac{V_0}{V_0 + V_1}\right)^2\left(\frac{V_0}{V_0 + V_3}\right) \\ &= C_0\left(\frac{V_0}{V_0 + V_1}\right)^2\left(\frac{V_0}{V_0 + V_1}\right) \qquad (7) \end{aligned}$$

therefore,

$$C_3 = C_0\left(\frac{V_0}{V_0 + V_1}\right)^3 \qquad (8)$$

In the previous equations, the terms that is associated with the perturbation as F changes are indicated in red. Thus, note that previous equations can be generalized by

$$C_c = C_0\left(\frac{V_0}{V_0 + V_t}\right)^N \quad with\ N = 0, 1, 2, 3 \ldots N \qquad (9)$$

where V_t is the permeate volume in the collecting tube, which has been defined to be constant. For this particular case, when $V_0 = V_t$ is concluded that

$$C_c = C_0\left(\frac{1}{2}\right)^N \qquad (10)$$

Consequently, $N = F$ and the equation 10 can be re-written to be

$$C_c = C_0\left(\frac{1}{2}\right)^F \qquad (11)$$

However, equation 10 is only a particular case occurring when F is an integer multiple of V_c. If the above is not true, then N is not equal to F and V_t is not equal to V_0.

The relationship between N and F for any dilution factor in the inside of the filtration cell can be found as follows:

If ϕ is defined to be the fraction describing the proportion of the permeate volume in the collecting tube respect to the solution volume contained in the cell, then $\phi = V_t/V_0$. But also, the definition of ϕ can emerge intuitively by factoring V_0 from denominator from equation 9. In addition, note that if V_t is defined to be constant during the experiment, it can be identified with the magnitude of perturbation experienced by the solution. Consequently, from F definition is concluded that

$$F = \frac{V_p}{V_0} = \frac{1}{V_0}\sum V_t = \sum \frac{V_t}{V_0} \qquad (12)$$

$$F = \sum \phi = \phi N \qquad (13)$$

Therefore, N is defined by the quotient among V_p and permeate volume defined in the collecting tube. Thus, it is also concluded that N depends on flux (J_v), membrane properties as permeability, and parameter associated with the design of experiment (e.g., V_t). In this point, it is important to redefine V_t since it is clear that smaller collecting tube is given by the smaller-possible volume perturbation, which is directly related to membrane permeability under working conditions. In conclusion, from previous analysis is obtained the working equation for inert system, which is given by

$$C_c = C_0\left(\frac{1}{1+\phi}\right)^N \qquad (15)$$

For inert system, C_c depends only of C_0, F, and ϕ. On the other hand, in order to evaluate small changes on F, by using equations 13, equation 15 can be re-written to be

$$C_c = \frac{C_0}{(1+\phi)^{F/\phi}} = C_0(1+\phi)^{-F/\phi} \qquad (16)$$

Differentiating by chain rule for exponential functions

$$dC_c = \left(\frac{C_0}{(1+\phi)^{F/\phi}}\right)\left(\frac{-1}{\phi}\right) ln(1+\phi)dF \qquad (17)$$

$$dC_c = C_c\left(\frac{-1}{\phi}\right) ln(1+\phi)dF \qquad (18)$$

Reordering

$$\frac{dC_c}{C_c} = \frac{-ln(1+\phi)}{\phi}dF \qquad (19)$$

$$ln\left(\frac{C_c}{C_0}\right) = \frac{-ln(1+\phi)}{\phi}F \qquad (20)$$

Therefore,

$$C_c = C_0 exp\left(\frac{-ln(1+\phi)}{\phi}F\right) \qquad (21)$$

In this point it is important to highlight that equation 15 and 21 are completely equivalents, and therefore, as

$$R_{syst} = \frac{C_c}{C_0} \qquad (22)$$

$$R_{syst} = \frac{1}{(1+\phi)^{F/\phi}} = exp\left(\frac{-ln(1+\phi)}{\phi}F\right) \qquad (23)$$

To demonstrate the previous sentence, the simpler way is applying logarithms in the equality, thus

$$ln\left(\frac{1}{(1+\phi)^{F/\phi}}\right) = ln\left(exp\left(\frac{-ln(1+\phi)}{\phi}F\right)\right) \qquad (24)$$

Consequently, by logarithm properties

$$ln\left(\frac{1}{(1+\phi)^{F/\phi}}\right) = \frac{-ln(1+\phi)}{\phi}F \qquad (25)$$

Other important conclusion is the fact that, naturally, retention can be described by very-different mathematical expressions, being an important aspect given that previous models are described by two analogous expressions but not equivalents (see Table 1). In consequence, it is explained why previous models act as empirical equations for data fit.

Table 1. Exponential decay model and rational decay model (Moreno-Villoslada et al., 2001; Palencia, 2015).

Parameter	Working equations	
	Exponential decay model	Rational decay model
C_c	$C_c = (1 - Fe^{-jF})C_0$	$C_c = \left(1 - \frac{\alpha F}{\alpha + F}\right)C_0$
C_p	$C_p = C_0 e^{-jF}$	$C_p = \frac{\alpha}{\alpha + F}C_0$
R_{syst}	$R_{syst} = 1 - Fe^{-jF}$	$R_{syst} = 1 - \frac{\alpha F}{\alpha + F}$

3. Model analysis

3.1. Analysis of retention profile

Simulated retention profiles for different values of V_t are shown in Figure 2. It can be seen that the retention profile behavior changes depending on volume defined in the collecting tubes, and therefore, this is a parameter that should not be underestimated when establishing experiments to obtain structural or molecular information. However, in order to understand this point, it is necessary take in account the redefining of V_t; therefore, since smaller collecting tube is given by the smaller-possible volume perturbation, V_t is identified to be the volume associated with membrane permeability (L). According to Darcy law, L is defined in function of pressure (P) and flux (J_v) as

$$L = \frac{J_v}{P} = \frac{V_p}{A_m tP} \qquad (26)$$

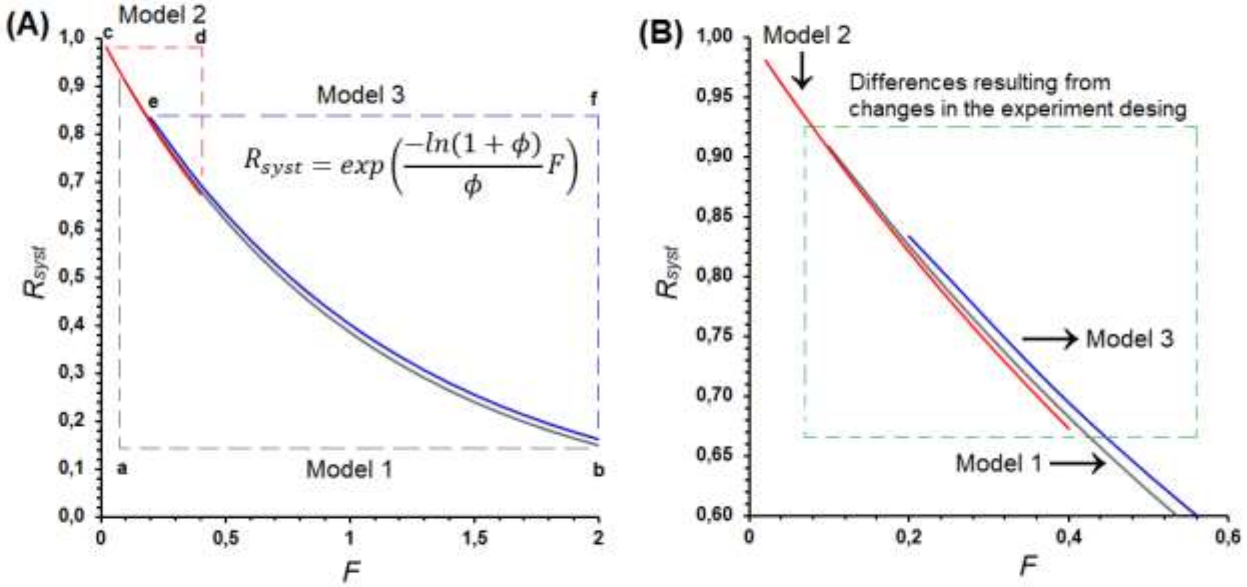

Figure 2. (A) Simulating of retention profile by Eq. 23: Model 1 (V_t = 5.0 ml, V_0 = 50.0 ml and ϕ = 0.1 for 0.1 < F < 2.0), Model 2 (V_t = 1.0 ml, V_0 = 50.0 ml and ϕ = 0.02 for 0.02 < F < 0.4), and Model 3 (V_t = 10.0 ml, V_0 = 50.0 ml and ϕ = 0.2 for 0.2 < F < 4.0); and (B) enlargement for a better visualization of the differences generated by the change of V_t in the experiments.

Table 2. Parameters of model, meaning and analysis for inert system.

Approach	Parameter	Meaning	Analysis
Retention profile	V_0	Volume in the inner of the cell	This parameter is defined by the researcher. However, for a non-inert system this parameter is defined by fraction no influenced by retainer element.
	V_p	Accumulated permeate volume	This parameter is directly related with the permeability and the filtration time. For a constant permeability only depend on filtration time. It corresponds to the sum of permeate fraction collected during the experiment.
	V_t or q	Collecting volume in the permeate or perturbation volume	This parameter is related with the minimum fraction of solution which can be transferred to the permeate. By time unit, it is the flux rate and is related with the permeability. This parameter can be divides among permeation time and membrane area to obtain the flux, but also, divided between permeation time, membrane area and applied pressure to obtain the membrane permeability. In addition, if it is divided between the membrane area then surface porosity can be calculated. Thus, in conjunction with Hagen-Poiseuille model, pore size can be stimated.
	F	Filtration factor (V_p/V_0)	It is the comparison of V_p respect to V_0. It is related directly with the time and evolution of the process respect to V_0.
	ϕ	Perturbation factor (V_t/V_0)	It is the comparison of V_t respect to V_0. It is related with the permeability. Determine the magnitude of perturbation experienced by the solution.
Elution profile	C_0	Initial concentration in the cell	It is a parameter defined by the researcher in the case of inert system. However, for a non-inert system, this parameter depends on interaction with the retainer element, and therefore, it is different as that initially placed in contacted with the retainer element.
	V_0, V_p, V_t, F, and ϕ	Previously defined	Their interpretation and analysis are the same as that given for the filtration profile

where A_m and t are membrane area and time, respectively. From equation 13 is easily concluded that $V_p = NV_t$ and therefore, in conjunction with equation 26 a relationship among V_t and L can be obtained. This is an aspect of great interest given that in previous models the influence of this parameter went unnoticed.

The influence of V_t on retention profile is understood by the analysis of experimental stages. In this case, the experiment is a dilution a constant volume which is continuously performed, and therefore, V_t determines the perturbation grade experimenting by the dissolution contained in the cell. However, it must be noted that V_t defines the first value of F, and consequently, limits the experiment in the practice. For example, it can be observed in Figure 2 that for model 1, from **a** to **b** values of F are such that $0.1 < F < 2.0$ (V_p = 100 mL or $2V_0$) whereas for model 2 and 3, from **c** to **d** and from **e** to **f**, values of F are $0.02 < F < 0.4$ (V_p = 20 mL or $0.4V_0$) and $0.2 < F < 4.0$ (V_p = 200 mL or $4V_0$). In all cases, V_0 = 50.0 ml and therefore, it is clear that V_c is other important parameter in this type of experiment. Thus, it can be concluded that $\phi = V_t/V_0$ determines: (a) the resolution (separation among two consecutive points) in the retention or elution discontinuous profile experimentally obtained,

(b) the perturbation magnitude or dilution magnitude, and (c) the path or line described by the retention profile, i.e., two experiments with the same ϕ values will have the same retention profiles (see Table 2).

3.2. Analysis of V_t and introduction of q

From previous analysis is concluded that V_t is an important factor controlling the elution process. In order to avoid confusions, because collecting tube volume is used for the deduction of the model and it can be confused with experimental collecting tube, it is suggested change the notation of V_t by q. In the Table 2 are summarized the parameters related with the model, their interpretation and analysis. Consequently, ϕ is renamed as perturbation factor.

The importance of q and ϕ is evidenced because these are the single parameters with a double influence after to simplification of working equation. These appear in the exponent and in the denominator. Since ϕ depends on q, the analysis is directed towards q. Thus, to understand its meaning, it is important to go back to the definition of N given by the equation 13, thus

$$N = \frac{F}{\phi} = \frac{V_p}{V_t} = \frac{V_p}{q} \qquad (27)$$

Given that N is an integer (see equation 9), it is concluded that V_p is always a multiple of q, therefore, q is the minimal permeate volume, which is equal to minimal volume entering to cell, and therefore, it is the minimal perturbation experienced by the solution under working conditions. Consequently, it is an error associate $\boldsymbol{q}$ with the volume collected during the experiment performing. In order to verify the previous conclusions, simulation using experimental data were performed. Working data are summarize in the Table 3. Thus, respective flux rate obtained for each pH were 0.017, 0.050, and 0.092 for pH 3.0, 4.5 and 6.0, respectively. It can be seen that though permeabilities changes among 9.3x10^{-10} and 4.0x10^{-10}, with values of q from 0.017 mL to 0.092 mL (approximately the maximum value is 5.4 times greater in magnitude with respect to the lowest values), the retention profiles are practically the same. A comparison for one point is shown in Table 4 whereas a comparison for $0 < F < 8$ is shown in Figure 3. On the other hand, when collecting tube is assumed to be q a significant error is produced in the description of retention profile. In order to exemplify the above, typical collecting volume were used: 10 and 20 mL. Comparison with profile retention using a $q = 0.092$ is shown in Figure 4. In general, as the value of q increases, the elution curve shifts to the right, and experimental information is lost because the first point on the graph is given by the lower value of F.

Table 3. Data used for simulation shown in Figure 3 (Palencia et al., 2009).

Parameter	Symbol	Value
Volume in the cell	V_0	25 mL
Surface membrane	A_m	6.23x10^{-4} m^2
Pressure	P	300 kPa
Stirring rate	-	200 rpm
Permeate volume	V_p	200 mL
Permeability (pH 3.0)	L	9.3x10^{-11} ms^{-1}Pa^{-1}
Permeability (pH 4.5)	L	2.7x10^{-10} ms^{-1}Pa^{-1}
Permeability (pH 6.0)	L	4.9x10^{-10} ms^{-1}Pa^{-1}
Membrane	-	Polyethersulfone
Collecting tube volume	-	10 mL

Table 4. Comparison of R_{syst} in one point for three pH values.

pH	q (ml)	F	R_{syst}
3.0	0.017	0.206	0.81386
4.5	0.050	0.206	0.81400
6.0	0.092	0.206	0.81408

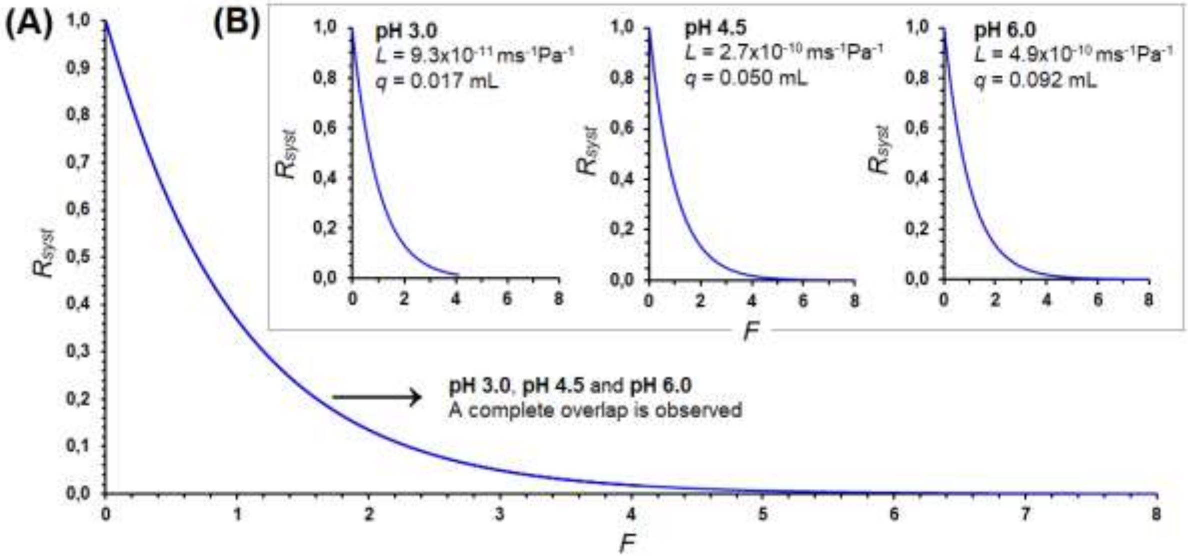

Figure 3. (A) Overlap of retention profile at different pH values and (B) individual retention profiles simulated from data in Table 3.

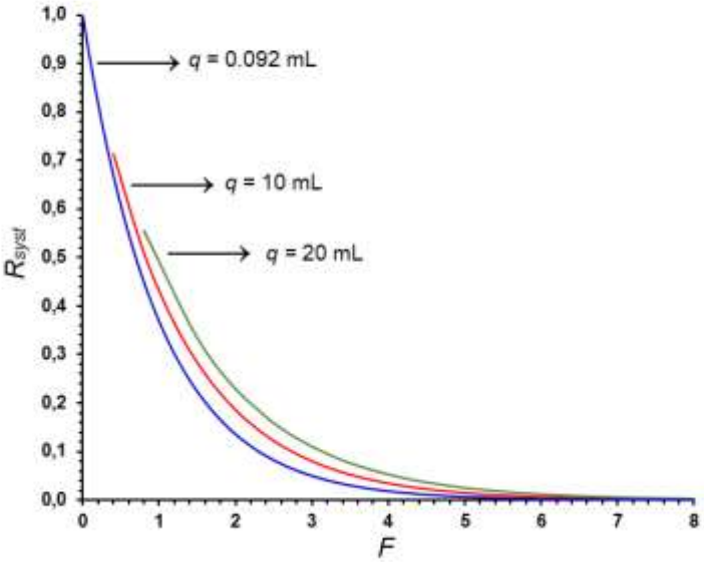

Figure 4. Comparison of retention profile for q = 0.092 mL, 10 mL and 20 mL.

3.3. Analysis of retention as function of *N*

Model is based on the distribution-zone model which has been previously proposed (Palencia et al., 2010; Palencia, 2015). In this model, for LPR, solute is distributed in different zones including solution, membrane when it acts as active component, polymer (if any), permeate and reservoir in the case of enrichment method. For inert system, it is only possible the distribution in two zones: solution contained in the cell and permeate.

When retention values obtained for R_{syst} are carefully analyzed, it is noted that these follow a typical behavior of a geometric series in function of N. Thus, if a Riemann series is described to calculate the area under the curve between two points or for all retention profile (S), a geometric series with constant ratio between successive terms to $(1+\phi)^{-N}$ (see Figure 5A).

$$S = R_{syst} \cdot N = f(N) \cdot N = \sum_{N=0}^{\infty} \frac{1}{(1+\phi)^N} \qquad (28)$$

which is developed as

$$S = 1 + \frac{1}{(1+\phi)^1} + \frac{1}{(1+\phi)^2} + \cdots + \frac{1}{(1+\phi)^N} \qquad (29)$$

The above relation can be understood considering that each perturbation is really the partition of solute's distribution space analogous to continuous partition in one- or two-dimensions, procedures which also produce typical geometric series (see Figure 6). In this case, volume partitioning is determined by the values of q. Though it is not developed, these properties must be studied because they can offer interesting information for the analysis of diafiltration problems for non-inert systems.

It is important to note that the non-retained fraction, i.e., fraction passing through the membrane, is easily calculated by subtraction of R_{syst} to unity. Thus,

$$1 - R_{syst} = 1 - \frac{1}{(1+\phi)^N} \qquad (30)$$

A comparison of retention and elution profile is shown in the Figure 5B. Basically, these curves show a complementary behavior.

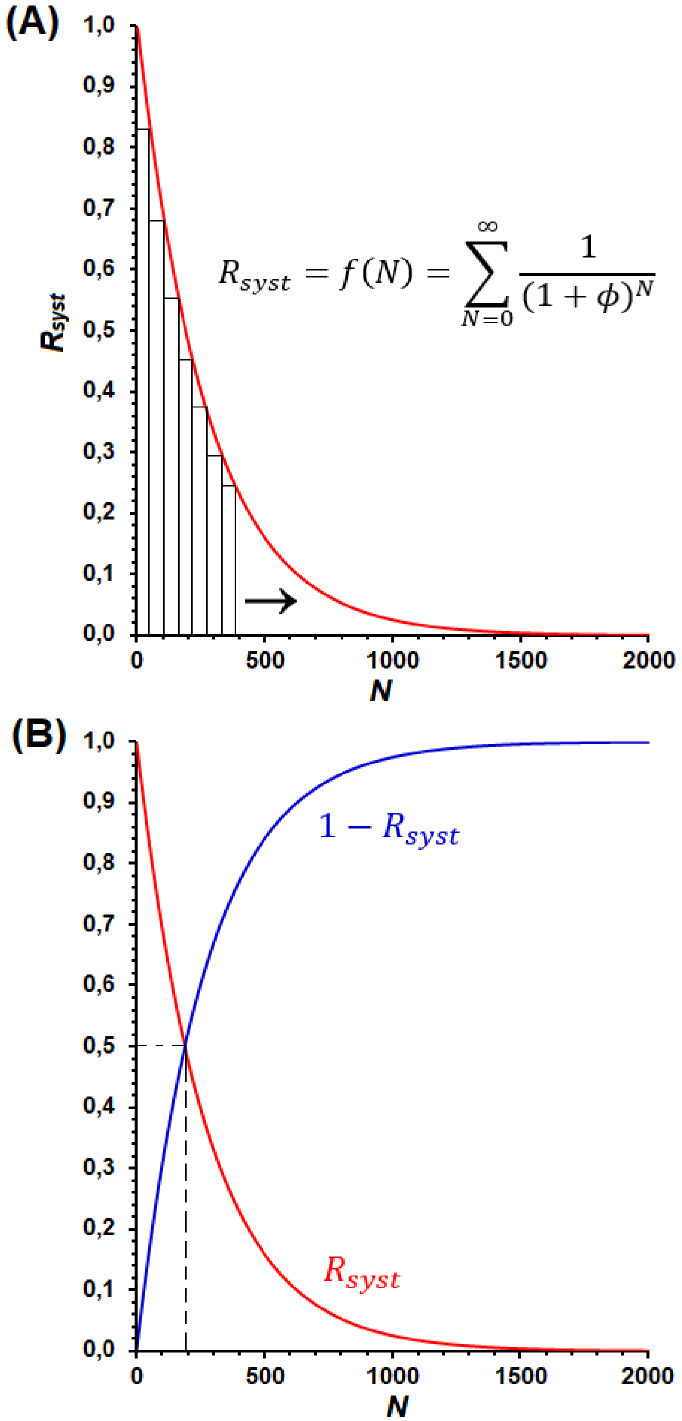

Figure 5. (A) Retention profile as function of N with q = 0.092 mL (V_c = 25 mL) and (B) comparison of retention and elution curves (R_{syst} and 1-R_{syst}, respectively).

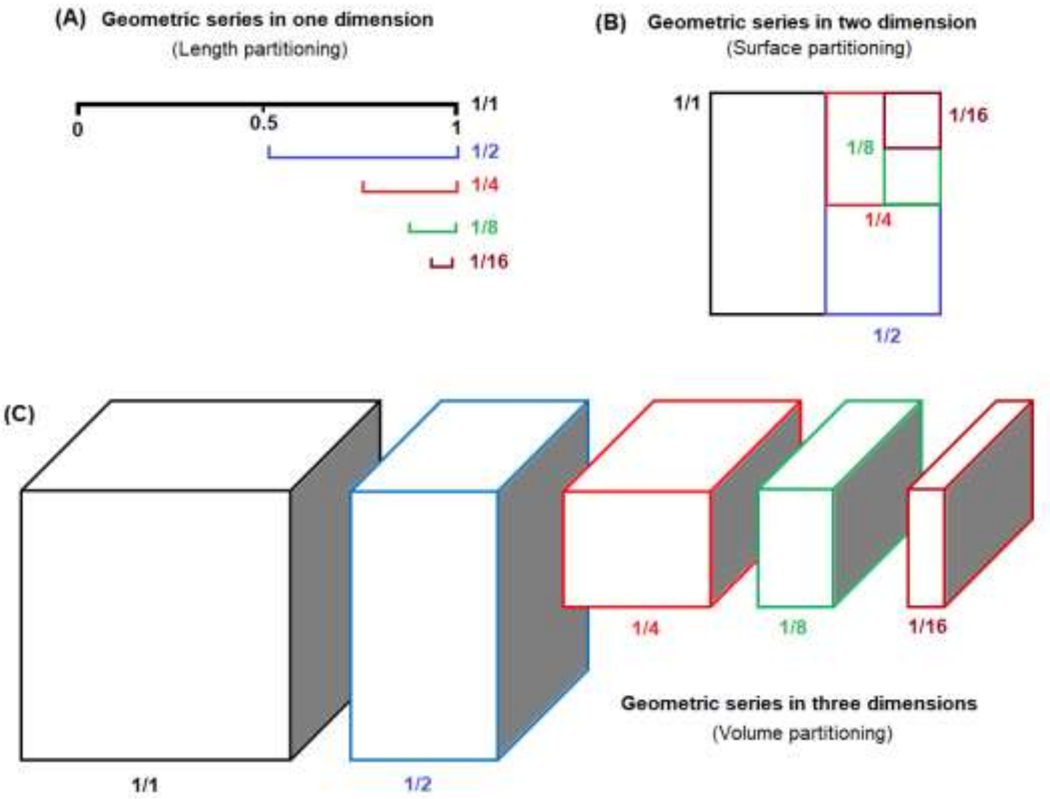

Figure 6. Illustration of recurrence of geometric series: (A) Length partitioning or 1D, (B) surface partitioning or 2D and (C) volume partitioning or 3D (in all cases have been illustrated the same geometric series to ease the comparison).

4. Conclusions

A new mathematical description for modeling of inert system during continuous diafiltration was developed. This is characterized to show two equivalent-mathematical forms which are analogous to those obtained by previous models. A main aspect of model is that all parameters appearing in it are completely identified, and fit parameters are not introduced. Thus, connection among hydrodynamic aspects, membrane properties and experimental behavior is completely achieved.

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Conflict interest. Authors declare that there is no conflict of interest.

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