



# Ceramic Nanofiltration Membrane Fouling: Application of Mathematical Modelling to the Use of Excitation Emission Matrix Spectroscopy

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**Abstract:** This paper presents a mathematical modeling for a series of experiments in which humic acid (HA) and calcium chloride ( $\text{CaCl}_2$ ) were used, in order to visualize the amount of contaminant before and after the nanofiltration (NF) process, using Excitation Emission Matrix Spectroscopy (EEMS). It allows to a better understanding of membrane fouling. The membrane used for these experiments was a NF ceramic membrane made of titanium dioxide ( $\text{TiO}_2$ ). For the experimental determinations, a constant amount of 10 mg/L HA and different amounts of  $\text{CaCl}_2$ , respectively 1, 2, 3 and 4 mmol/L were used, considering the working methodology presented in this article. The presence of the amount of contaminant in water was determined using the EEMS method using the FP-8300 Spectrophotometer, after which a spectral analysis was performed. TableCurve 3D software was used to make the mathematical models in order to ensure that the equations obtained had the same shape. The values of the correlation coefficients, corresponding to the generated equations, have values ranging from 0.91 to 0.93. In order to verify the mathematical models thus obtained, graphs of the difference between the surface obtained with the help of the mathematical models and the surface obtained by means of real data were drawn. In conclusion, it turns out that, the largest difference was obtained in the case of samples taken from the feed, with a maximum difference of 31 fluorescence intensity arbitrary units (a.u.), and for the samples taken from the permeate the difference is 14 fluorescence intensity a.u.

**Keywords:** mathematical modeling, nanofiltration (NF), humic acid (HA), calcium chloride ( $\text{CaCl}_2$ ), spectroscopy, emission excitation matrix (EEM).

## 1. Introduction

Drinking water from different sources, usually, do not correspond in terms of quality parameters (according to the legislation in force) and so they must be subjected to treatments by applying increasingly treatment methods and modern techniques. Water sources requirement imposes quality indicators that can be influenced in principal by human activities as wastewater, agriculture, hydrotechnical management etc. [1-15].

The study on the specialized references indicates that the filtration process is being increasingly used in order to produce water for different requirements [16-22].

Nano filtration (NF) is one of the most used water filtration technologies. By applying this process, the heterogeneous mixture of solution subjected to filtration, is separated into two phases/components, respectively a concentrated (brine) residual flow and a permeate (filtered) flow, which passes through

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the membrane [1, 23, 24]. Therefore, NF has attracted increasing interest for many applications, such as desalination, wastewater treatment and drinking water applications [24-26].

In order to study ceramic NF membrane fouling, several tests have been developed using humic acid (HA) and calcium chloride ( $\text{CaCl}_2$ ) as foulant models typically found in natural waters. Humic acid (HA) is a natural, completely organic product, chelating agent of dead organic matter, rich in essential minerals, trace elements and amino acids. It is made from organic soil (humus) after microbial decomposition of vegetation [1, 27-29]. Because humic substances (HS) are naturally occurring compounds, with the highest chemical activity, they simulate organic matter from flowing waters, lakes and ocean waters, which led to the choice of this contaminant for experiments as foulant models [1, 30-32].

Calcium chloride ( $\text{CaCl}_2$ ) is an inorganic, solid, crystalline compound, colorless at room temperature, very soluble in water, used to increase water hardness, dissolves in water producing chlorine and has a very large change in enthalpy, indicated by a considerable increase in temperature accompanying the dissolution of anhydrous salt in water. This property is the basis for its largest application [1].

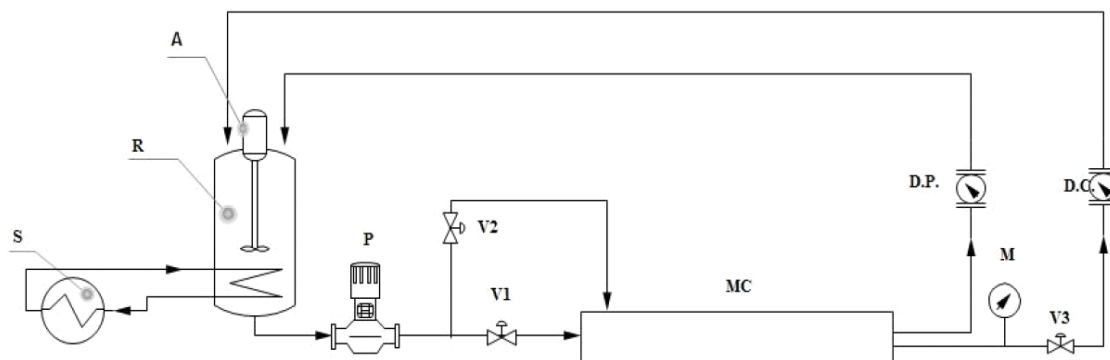
HA colloids have a negative electrical charge, as does the membrane surface. This promotes electrical repulsion between the two surfaces. However, the presence of calcium chloride reduces or even neutralizes the electrical double layer in the HA molecules present in the solution. This process is known as coagulation. This effect causes these colloids to increase their tendency to deposit on the membrane surface, because the mutual electrical repulsion is reduced, leading to the membrane to get fouled in a higher extension.

EEMS, also known as three-dimensional fluorescence (3DEEM) or fluorescence fingerprinting, is one of the most prevalent approaches due to the massive amount of data, visual maps and multidimensional information it provides [33, 34]. Fluorescence technology has been increasingly applied to the characterization of dissolved organic matter (DOM) due to its remarkable sensitivity and selectivity. Also, in the last decade, there has been an increasing interest in investigating drinking water processes using the EEM method, such as coagulation, adsorption, ultrafiltration and disinfection, thus boosting their understanding of their performance to a greater extent. It is worth mentioning that the interest for the use of fluorescent technology in order to investigate the treatment of drinking water, focusing on coagulation, adsorption, membrane filtration and disinfection is increasing [33, 34].

In this paper, the mathematical models and the correlations between the parameters that influence the NF process and the parameters followed are presented, following the results obtained for the experiments performed.

## 2. Materials and methods

The experimental set up and tests were performed at the Environmental Protection Laboratory of the Department of Environmental Technologies from University of Cadiz, Spain. The pilot plant (Figure 1) used a  $\text{TiO}_2$  NF membrane with an active surface of  $1.25 \text{ m}^2$  and with a useful/active cross section of  $0.00062 \text{ m}^2$  [1].



**Figure 1.** Flow diagram of the NF pilot plant [1]: A - mixer; R - tank with water-reagent mixture (100 L capacity); S - constant water temperature installation (heat exchanger); P - pressure pump; V1 and V3 - valves; MC - ceramic membrane; M - manometer; D.P. - flow meter for permeate; D.C. - flow meter for concentrate

The plant is provided with a tank with a mixing device R. The mixture thus obtained is directed through a pump P towards the ceramic membrane MC which performs the NF process. In order to vary the working parameters of the ceramic membrane, respectively the feed rate, a V1 valve was fitted before the filter element. By passing the mixture through MC, the two permeate and concentrated components are obtained. Their quantity is determined through the two flowmeters D.P. and D.C. In turn, the amount of precipitate can be varied through the V3 valve, which can also contribute to the variation of the pressure in the installations (parameter that can be determined through the pressure gauge M) [1].

Following the process of separating the two components, concentrated and permeate, they are introduced into the mixing recipient R [1]. Because the operation in a closed-loop circuit increases water temperature a heat exchanger, S, is used to keep a constant temperature of the mixture [1].

The mixtures colloid-coagulant salt was made directly into the tank R, using always a volume of 50 L of ultrapure water. The reagents quantities used were 10 mg/L AH (Sigma-Aldrich) to which were added different amounts of  $\text{CaCl}_2$  (Sigma-Aldrich), respectively 1, 2, 3 and 4 mmol/L [1].

To study the performance of the NF process, samples were taken, both before and after the filtration process from the permeate. Also, the presence of  $\text{CaCl}_2$  in water was determined with the Spectrophotometer FP-8300, with the help of which a spectral analysis of the intensity of the ultraviolet light was performed in each filtered water sample. Spectral analysis of ultraviolet light measures the amount of UV light absorbed by a water sample. This measurement is made by passing a low and continuous flow of water through a glass tank illuminated by a UV beam with a wavelength of 254 nm, where the amount of light absorbed (UVA-UV absorber), respectively transmitted (UVT - ultraviolet transmission) from the incident light is measured [1].

The experimental determinations were carried out considering the working methodology presented in Figure 2.

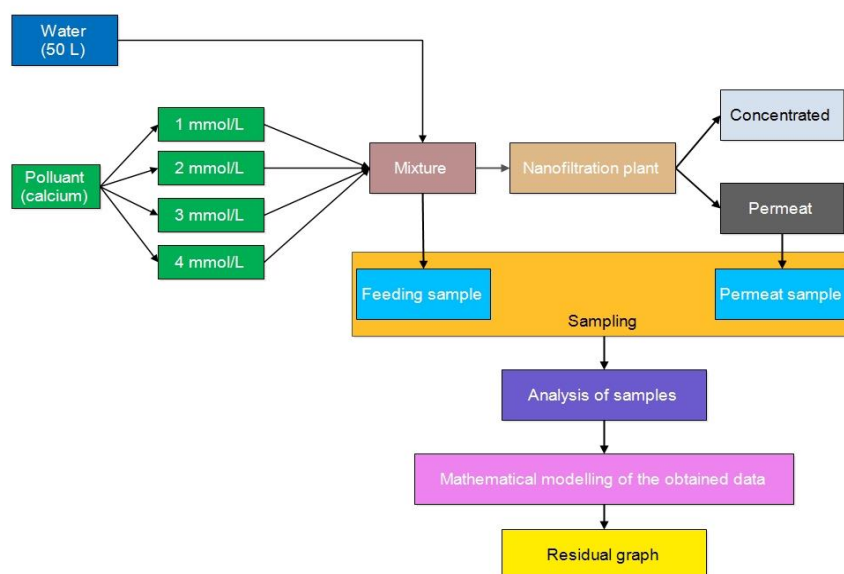


Figure 2. Working methodology

### 3. Results and discussions

#### 3.1. Mathematical model

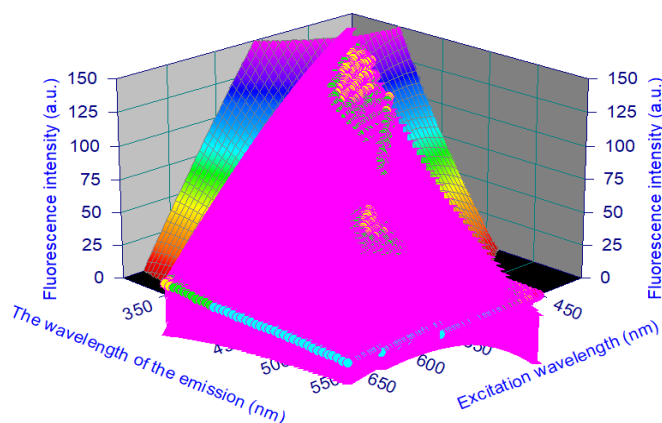
For the mathematical model of the variation of the fluorescence intensity (au) as a function of the variation of the emission wavelength (nm) and of the variation of the excitation wavelength (nm), in order to highlight the presence of Ca in ultrapure water TableCurve 3D program was used. The mathematical models were designed for the two sets of samples, both for the ones taken from the feed of the NF plant and for those obtained after the NF process, respectively from the permeate [1].

The program used to create mathematical models, TableCurve 3D, is designed to generate surfaces corresponding to a data set, using over 450 million equations [1]. It is worth mentioning that for each determination, a set of 20,450 values were obtained, which were used for the elaboration of mathematical models. Following the modeling of the experimental data, two distinct mathematical models corresponding to the two sources from which the samples were taken were obtained:

- for the feed sample the following equation was generated:

$$z = a + b \cdot \ln x + \frac{c}{y} + d \cdot (\ln x)^2 + \frac{e}{y^2} + \frac{f \cdot \ln x}{y} \quad (1)$$

which corresponds to the response surface shown in Figure 3, in which the variation of the fluorescence intensity (au) is presented as a function of the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm), for an amount of Ca of 1 mmol/L.



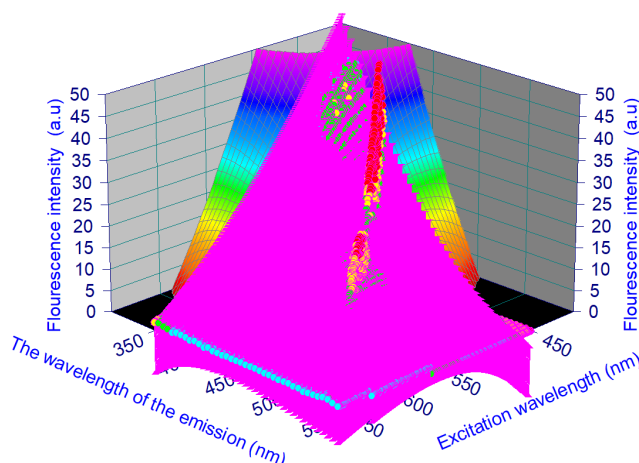
**Figure 3.** Variation of fluorescence intensity (a.u.) depending on the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm) for the feed sample

Within this graphical representation, the surface generated by the TabelCurve 3D program is represented by means of the curved surface, and the values introduced in this mathematical model are presented through pink. The following equation was generated for the permeate sample:

$$z = a + b \cdot \ln x + c \cdot \ln y + d \cdot \ln x^2 + e \cdot \ln y^2 + f \cdot \ln x \cdot \ln y + g \cdot \ln x^3 + h \cdot \ln y^3 + i \cdot \ln x \cdot \ln y^2 + j \cdot \ln x^2 \cdot \ln y \quad (2)$$

where:  $z$  represents the variation of the fluorescence intensity (a.u.);  $x$  - emission wavelength variation (nm);  $y$  - the variation of the excitation wavelength (nm);  $a, b, c, d, e, f, g, h, I$  and  $j$  is the coefficients of the equation.

As in the case of the model generated for the sample taken from the feed, and in the case of the sample from the permeate, a surface described in figure 4 was generated by means of a mathematical equation. The representations of the two components that make up the graphical representation presented in Figure 4 are the same as in Figure 3.



**Figure 4.** Variation of fluorescence intensity (a.u.) as a function of the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm) for the permeate sample

For the two mathematical models in Tables 1 and 2 are presented the values of the coefficients that compose the generated equations.

**Table 1.** The values of the coefficients of the equations corresponding to the variation of the ca content, obtained from feed sample

Parameter variation HA	The values of the constants					
	a	b	c	d	e	f
1 mmol/L	-29308.04487	8228.532894	3295840.488	-571.91179	-8452396.964	-505575.3088
2 mmol/L	-24538.12389	6812.879133	2994771.585	-466.1664619	-1003657.576	-464255.1062
3 mmol/L	-22217.5725	6116.819839	2871971.562	-413.8507783	370423.7097	-446254.1106
4 mmol/L	-19917.71924	5412.106258	2795071.46	-359.4042292	3989011.62	-436996.4642

**Table 2.** The values of the coefficients of the equations corresponding to the variation of the ca content, obtained for the permeate

Par. var. HA	The values of the constants									
	a	b	c	d	e	f	g	h	i	j
1 mmol/L	266236.3676	-58975.30638	-68123.43409	-52.9869185	984.5737614	19294.46095	257.4130209	195.5747144	-719.8876115	-806.0290982
2 mmol/L	339935.8336	-76028.68888	-86302.88998	502.7619147	1649.400988	23687.92331	278.7176346	226.2298555	-912.0702823	-963.9632016
3 mmol/L	387966.6814	-88189.50737	-97045.77845	949.4503055	1811.8501	26718.90191	291.0283198	262.3082501	-1041.042976	-1076.196483
4 mmol/L	450817.1479	-97442.11101	-118171.8552	1116.004971	3872.244009	29386.11897	303.4699606	201.4051886	-1189.255911	-1142.329081

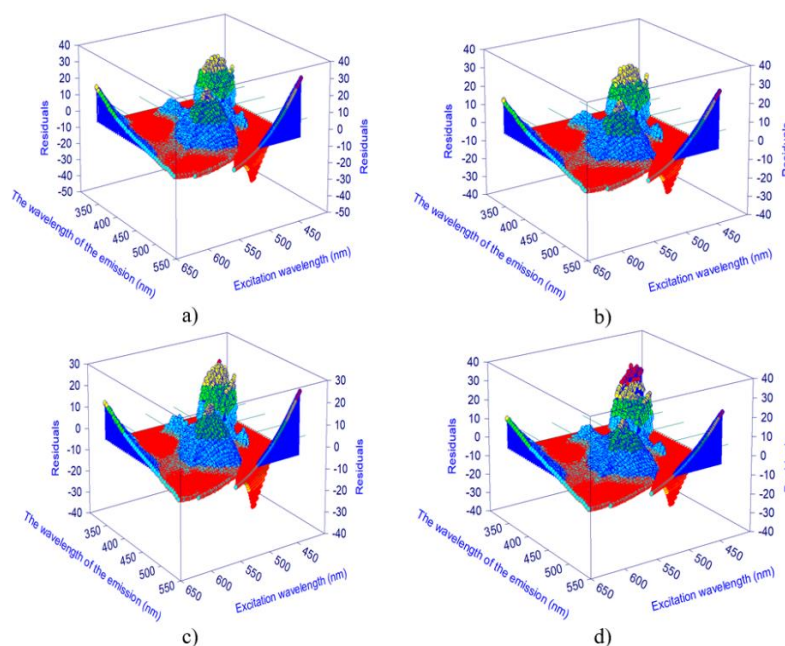
According to equations (1) and (2) we have different values of the correlation coefficient whose value is shown in Table 3.

**Table 3.** The values of the correlation coefficients corresponding to the mathematical models

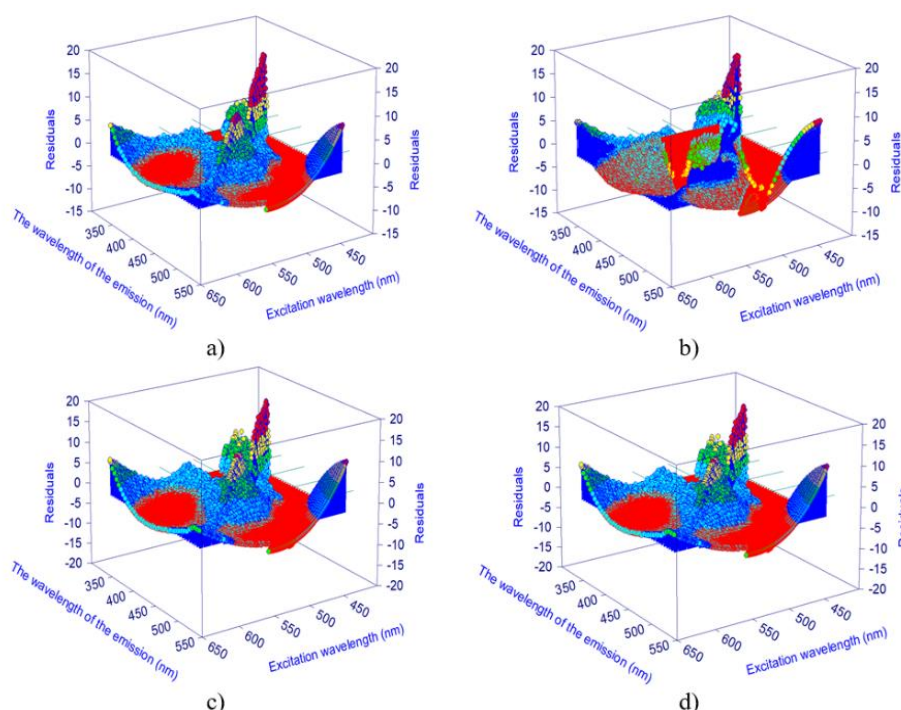
Parameter variation HA	Source of sampling	The value of the correlation coefficient $r^2$
1 mmol/L	for feed sample	0.910118567
2 mmol/L		0.913014324
3 mmol/L		0.912700785
4 mmol/L		0.911904016
1 mmol/L	for permeate	0.915493822
2 mmol/L		0.923483593
3 mmol/L		0.926886881
4 mmol/L		0.931087745

From the analysis of the mathematical models generated by the TableCurve 3D program, it is found that the value of the correlation coefficient is not less than 0.9, which gives a very close approximation of the values obtained through the mathematical models to the real values used for the elaboration of these models.

In order to highlight the difference between the real values and the values obtained by means of mathematical models, a graphical representation is made which bears the name of residual graph. Within this type of graph, the difference between the surface generated by the mathematical models and the values introduced for generating the mathematical models is realized. Such graphical representations are presented in Figures 5 and 6.



**Figure 5.** Graphical representations of the residual variation obtained from the analysis of the feed samples: a) 1 mmol/L; b) 2 mmol/L; c) 3 mmol/L; d) 4 mmol/L



**Figure 6.** Graphical representations of the residual variation obtained from the analysis of the permeate samples: a) 1 mmol/L; b) 2 mmol/L; c) 3 mmol/L; d) 4 mmol/L

By analyzing the residual graphs, and considering the values introduced in the mathematical models, the following conclusions can be drawn:

- in the case of the analysis carried out for the sample taken from the feed, the maximum difference obtained between the experimental value and the mathematical value varied according to the amount of Ca used in the experimental determinations thus:



- for the quantity of Ca of 1 mmol/L a maximum difference of 31 a.u. was obtained.
- for the quantity of Ca of 2 mmol/L a maximum difference of 28 a.u. was obtained.
- for the Ca quantity of 3 mmol/L a maximum difference of 27 a.u. was obtained.
- for the Ca quantity of 4 mmol/L a maximum difference of 25 a.u. was obtained.
- for the sample taken from the permeate the maximum difference between the experimental value and the mathematical value varied as follows:
  - for the quantity of Ca of 1 mmol/L a maximum difference of 10 a.u. was obtained.
  - for the quantity of Ca of 2 mmol/L a maximum difference of 12 a.u. was obtained.
  - for the quantity of Ca of 3 mmol/L a maximum difference of 13 a.u. was obtained.
  - for the quantity of Ca of 4 mmol/L a maximum difference of 14 a.u. was obtained.

#### 4. Conclusions

The experimental researches that aimed to identify the methods of decontamination of wastewater, presented in this paper, aimed to extend as widely as possible this modern process of water filtration, respectively by using the process of filtering through nanofiltration membranes (NF) to help improve the quality of filtered water.

At the same time, the operation of the NF membrane was monitored under different working conditions, respectively within this article it was opted for HA water contamination and the use of different quantities of CaCl<sub>2</sub>, in order to study membrane fouling.

Following the analysis performed with the help of the FP-8300 Spectrophotometer, for each sample, were obtained 20450 values which subsequently used to create a mathematical model.

TableCurve 3D software was used to make the mathematical models and the equations obtained were of the same shape.

The values of the correlation coefficients, corresponding to the generated equations, have values ranging from 0.91 to 0.93.

In order to verify the mathematical models thus obtained, graphs of the difference between the surface obtained with the help of the mathematical models and the surface obtained by means of real data were drawn. The largest difference was obtained in the case of samples taken from the feed, with a maximum difference of 31 a.u., and for the samples taken from the permeate the difference is 14 a.u.

The elaborated mathematical models, for the sets of values of the order of tens of thousands, verified both from the point of view of the real values and from the point of view of the regression coefficients (coefficients close to the value 1), demonstrate the quantity and the very good quality of the experimental data, respectively of the measured and calculated sizes. This also confirms the rigorous way of designing, realizing and interpreting the experiments.

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Manuscript received: 8.04.2020