Mathematical Model Regarding the Application of the Excitation-Emission Matrix Spectroscopy in Nanofiltration Process Using Humic Acid with a TiO_2 Ceramic Membrane

MIHAELA-ELENA DASCĂLU[1], FLORIN NEDEFF[1]*, ION SANDU[2,3], EMILIAN MOSNEGUTU[1]*, ANDREI VICTOR SANDU[3,4]*, JUAN ANTONIO LÓPEZ-RAMÍREZ[5]

[1]Vasile Alecsandri University of Bacau, Department of Environmental Engineering and Mechanical Engineering, 157 Calea Marasesti Str., 600115 Bacau, Romania

[2]Alexandru Ioan Cuza University of Iasi, Arheoinvest Interdisciplinary Platform, Scientific Investigation Laboratory, 11 Carol I Blvd., 700506 Iasi, Romania

[3]Romanian Inventors Forum, 3 Sf. Petru Movila Str., Bloc L11, III/3, 700089 Iasi, Romania

[4]Gheorghe Asachi Technical University of Iasi, Materials Science and Engineering Faculty, 53A D. Mangeron Blvd., 700050 Iasi, Romania

[5]Universidad de Cadiz, Departamento de Tecnologías del Medio Ambiente, CASEM - Polig. Rio San Pedro, s/n. 11510 Puerto Real, Cadiz, Spain

A mathematical model regarding water filtration with a nanofiltration (NF) titanium dioxide ceramic membrane is presented. The experiments aimed to use the excitation-emission matrix (EEM) spectroscopy method to highlight the existence of humic acid (HA) in water, before and after the NF process. Following the established operating conditions, experiments were performed for each quantity of AH separately, leaving the installation to work at the appropriate parameters for 15 minutes. for each quantity of AH. The analyzes for EEM fluorescence were performed using the FP-8300 spectrofluorimeter. The collected samples were analyzed with Spectra Manager II software on fluorescence intensity (au - arbitrary units), with an emission wavelength (nm) between 460 and 640 nm and with an excitation wavelength (nm) between 350 and 600 nm. Following the experiments carried out, mathematical correlations were established between the parameters that influence the filtering process and the studied parameters. It is worth mentioning that as a result of the experiments carried out, a number of 20,450 values were obtained, which were used for the elaboration of mathematical models. These models, for 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. In order to validate the generated equations, they were subjected to checks, the difference being obtained between the value obtained by experimental means and the value obtained within the mathematical model. And the value of the resulting relative error, gives information on the accuracy (truth) of the mathematical model, so that it can be extended to other experiences. It turns out that this method cannot quantitatively determine the value of a parameter, but it can highlight the presence and differences between two samples.

Keywords: nanofiltration, humic acid, fluorescence, Excitation-Emission Matrix spectroscopy, mathematical model

In many countries, water scarcity can pose a significant threat to national security and can lead to conflicts in already unstable and fragile regions. Global Programme Water Strategic Framework 2017 – 2020 is based on the successful 2013-2017 GPW strategy. Its purpose is to fulfill the vision of a safe world in drinking water [1, 2].

Water and wastewater treatment, in general, and filtration, as particular application, is a method of separating solid impurities by flow through permeable porous media, called filter media or filters [1, 3-28].

NF is a separation membrane-based technology that has been widely implemented for water treatment containing organic and inorganic contaminants. It separates successfully most organic molecules, almost all viruses, most natural organic matter and a number of salts [29, 30].

NF is mainly used for treating natural water and wastewater, with the main goal of eliminating polyvalent cations, natural organic matter (NOM) and synthetic organic matter [1, 31-34]. NF membranes have characteristics between those of reverse osmosis (RO) and ultrafiltration (UF) membranes [1, 35, 36]. On the contrary of commercial NF polymeric membranes using organic constituents, ceramic membranes are based on inorganic materials, such as oxides, nitride or carbide of aluminum, zirconium and titanium [37, 38].

**email: florin_nedeff@ub.ro; emos@ub.ro; euroinvent@yahoo.com*

The fluorescence spectroscopy is considered a suitable technique to detect and track NOM during water treatment [39]. The three-dimensional excitation-emission (EEM) matrix spectroscopy is a fast, selective and sensitive technique that has proven to be a useful technique for differentiating changes, and transformations of organic matter in natural environments [40-42].

The creation of mathematical models aims to simplify representation of processes or theories in order to facilitate the understanding, prediction and control of a system. The realization of such a mathematical model makes it possible to identify the dependencies that exist between the analyzed parameters [43, 44]. The main goal of this paper is to develop a mathematical model using HA and EEM spectroscopy to assess rejection capacities of a new ceramic NF membrane.

Experimental part

The experimental determinations were performed at laboratories of the Environmental Engineering Department (Departamento de Tecnologías del Medio Ambiente) of University of Cádiz, Spain. The pilot plant that was employed for the experiments is a device able to work with polymeric and ceramic membranes. In this paper only the NF ceramic module was used (Fig. 1) [1].

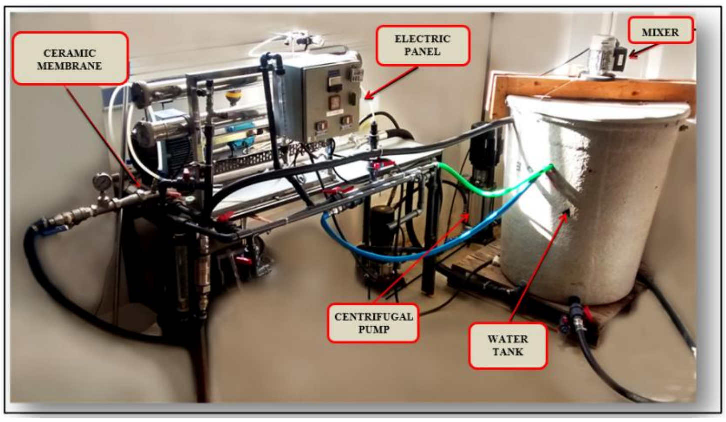

Fig. 1. Picture of the used NF pilot plant at the laboratory of University of Cádiz, Spain [1]

The honeycomb ceramic membrane is a prototype with a length of 1.2 m, 163 channels, an expanded surface of 1.25 m^2 and a nominal average pore size of 0.9 nm [1]. This membrane uses the cross flow filtration mode, which means that the permeable flow is directed perpendicular to the supply flow. Thus, the impurities are swept with the rejection out, leaving the device as a concentrated residual flow [1, 45].

The humic acid solutions used in the experiments were produced by adding increasing concentrations (10, 25, 50, 75, 100 mg/L) of this reagent (Aldrich Chemistry) to ultrapure water in a tank of 50 L capacity [1, 46]. Humic acid was chosen as a pollutant because, according to the literature, humic materials contain, in addition to fulvic acid, many phytochemical nutritional groups including natural sterols, hormones, fatty acids, polyphenols and ketones with subgroups including compounds such as: flavonoids, flavones, flavins, catechins, tannins, quinones, isoflavones, tocopherols and others [47-50], components that are also commonly found in natural and wastewater treated by the NF process.

For analyzing the humic acid content of water, the JASCO FP-8300 spectrofluorimeter was used, which is equipped with approximately 50 types of sample media to facilitate the research work. These include supports of thermostated water samples or Peltier thermostats for temperature control, micro tank holders that make it possible to measure samples on the order of milliliters and "one-drop" accessories with which fluorescence can be measured [51].

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 - ultraviolet), respectively transmitted (UVT - ultraviolet transmission) from the incident light is measured [52, 53].

To highlight the values obtained from the spectrofluorimeter analyzes, the Spectra Manager II software was used (fig. 2), software that contains the programs needed to record the spectra on the excitation and emission side, the basic kinetic measurements, the quantitative measurements and the measurements at a fixed wavelength [1, 54].

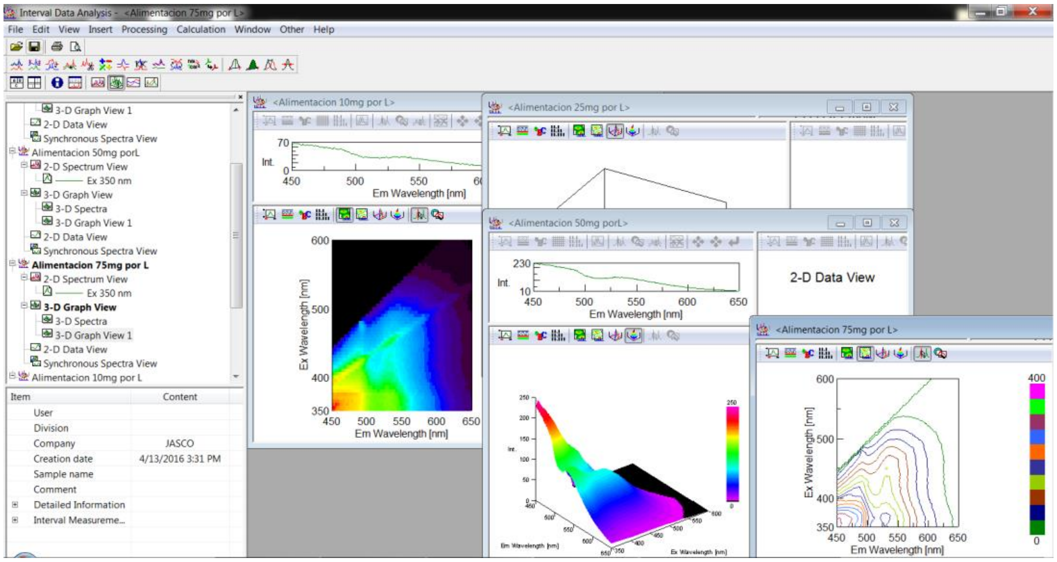

Fig. 2. The image of a window in Spectra Manager II software [1]

In order to carry out the experimental determinations, the working methodology presented in figure 3 was respected.

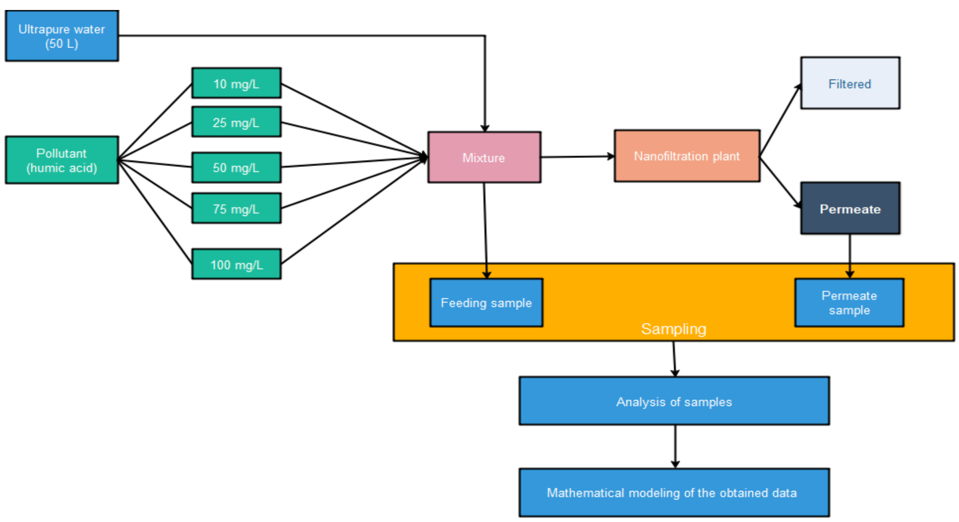

Fig. 3. Diagram of the works carried out

Results and discussions

Realization of the mathematical model

Using the TableCurve 3D program, mathematical models corresponding to the variation of the fluorescence intensity (a.u.) were made according to the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm). These models are specific for the variation of the HA content in the two areas from which the samples were taken (respectively for feedwater and for permeate) [1].

TableCurve 3D (fig. 4) is a software package for researchers, which allows the automation of the construction process of surfaces in a single processing step, where it matches and classifies about 36,000 of the more than 450 million integrated equations frequently encountered, allowing users to find the ideal model for their 3D data. Once the user has selected the best matching equation, it can issue functions and test the programming codes or generate quality reports and graphs for publications [1, 55-58].

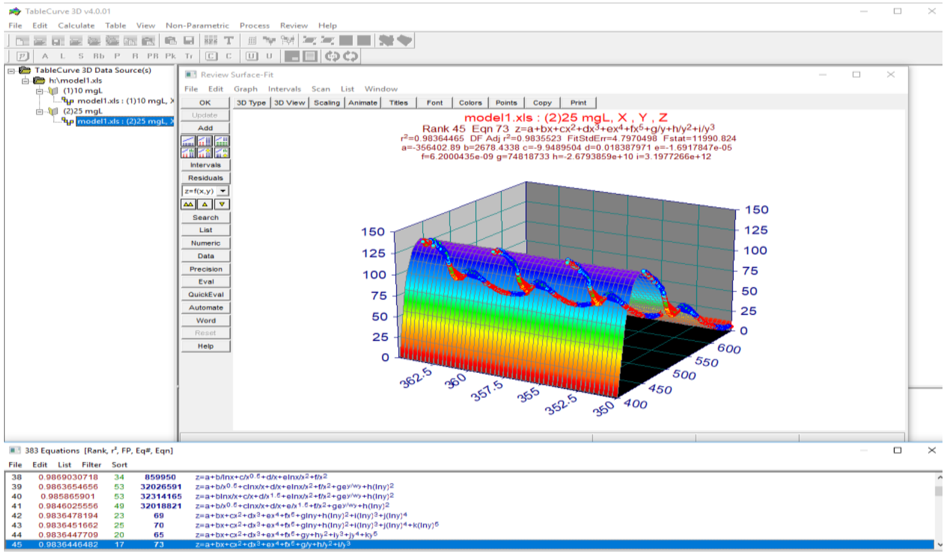

Fig. 4. Screen capture of a calculation window in the TableCurve 3D program [1]

It is worth mentioning that a number of 20,450 values were obtained, which were used for the elaboration of mathematical models [1]. Figure 5 shows the response area obtained after presenting the fluorescence intensity variation (a.u.) depending on the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm) in the case of the variation of HA content for the sample taken when supplying the filtration system [1].

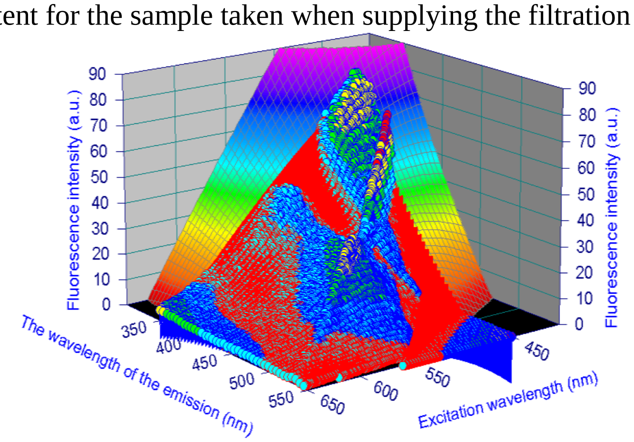

Fig. 5. Variation of fluorescence intensity (a.u.) depending on the variation of the emission wavelength (nm) and the variation of the excitation wavelength (nm) [1]

Following the modeling of the experimental data, two distinct mathematical models were obtained corresponding to the two sources from which the samples were taken:

- for the feed sample the following equation was generated:

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

- for the permeate sample the following equation was generated:

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

in which:

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, j – the coefficients of the equation (shown in Tables 1 and 2).

Table 1
THE VALUES OF THE COEFFICIENTS OF THE EQUATIONS CORRESPONDING TO THE HUMIC ACID VARIATION OBTAINED AT THE SUPPLY [1]

Nr. crt.	Parameter variation HA	The values of the constants					
		a	b	c	d	e	f
1.	10 mg/L	-13466.772	3749.721	1614681.611	-258.309	-7044652.146	-245709.396
2.	25 mg/L	-28757.635	8070.163	3251512.077	-560.974	-11860748.53	-496432.683
3.	50 mg/L	-43978.507	12363.368	4906919.546	-861.793	-21767390.49	-746253.928
4.	75 mg/L	-82157.660	23362.416	8330358.616	-1653.563	-58923018.61	-1251092.939
5.	100 mg/L	-113072.916	32418.138	10635381.98	-2321.142	-114696523.5	-1568905.904

Table 2
THE VALUES OF THE COEFFICIENTS OF THE EQUATIONS CORRESPONDING TO THE HUMIC ACID VARIATION OBTAINED FOR THE PERMEATE [1]

Nr. crt.	Parameter variation HA	The values of the constants									
		a	b	c	d	e	f	g	h	i	j
1.	10 mg/L	105026.405	-28925.885	-20883.374	501.798	-979.754	8351.528	105.984	137.077	-241.824	-416.073
2.	25 mg/L	255756.860	-52695.733	-69681.1269	-256.3469	2135.112	17641.026	253.046	106.484	-644.684	-752.734
3.	50 mg/L	253444.784	-51536.432	-69279.134	-2429.645	-114.802	21743.254	422.833	277.868	-785.586	-932.1367
4.	75 mg/L	450819.917	-99817.423	-115031.943	-1959.112	-382.117	36473.188	600.204	475.129	-1312.806	-1570.027
5.	100 mg/L	623572.518	-122375.071	-175496.849	-4562.968	2839.213	49156.570	870.323	503.675	-1902.1357	-1989.708

Table 3
ACCORDING TO THESE EQUATIONS DIFFERENT VALUES OF THE CORRELATION COEFFICIENT ARE OBTAINED [1]

Nr. crt.	Parameter variation HA	Source of sampling	The value of the correlation coefficient, r^2
1.	10 mg/L	when supplyng	0.904
2.	25 mg/L		0.908
3.	50 mg/L		0.909
4.	75 mg/L		0.903
5.	100 mg/L		0.896
6.	10 mg/L	for permeate	0.849
7.	25 mg/L		0.904

Following the analysis of the obtained mathematical models, for the set of determinations carried out, for the two samples subjected to the spectrofluorimetric analyzes, it is found that the obtained models are complex polyfactorial models, of logarithmic type [1].

Regardless of the model obtained, it is found that the value of the correlation coefficient, r2, is between 0.84 and 0.93, which leads to the conclusion that the obtained models are very close to presenting the NF process presented in this article as accurately as possible.

The mathematical models generated using TableCurve 3D were tested using the computation relation [1]:

$$e = \frac{x_{mat} - x_{expe}}{x_{expe}} \cdot 100 \quad (3)$$

in which: e represents the relative error; x_{mat} – values obtained through mathematical models; x_{expe}- values obtained experimentally.

Analyzing the values of the relative error obtained, calculated with the help of the computation relation (3), it is found that this varies so [1]:

- for supply:
  - 32.4 % from the total of relative errors is between 0 - 20%;
  - 29.8 % is between 20 – 50%;
  - 35.2 % is between 50 – 100%;
  - 2.6 % are over 100%;
- for permeate:
  - 8.3 % from the total of relative errors is between 0 – 20%;
  - 0.4 % from the total of relative errors is between 20 – 50%;
  - 54.5 % from the total of relative errors is between 50 – 100%;
  - 6.8 % are over 100%;

Conclusions

The theoretical and experimental research presented in this paper aimed to extend the knowledge about NF process performance with HA to improve water filtration.

The identification of the HA content in the water was determined using the spectrofluorimeter, a process that cannot quantitatively determine the value of a parameter but can highlight the differences between two samples. For each sample analyzed, corresponding to each set of experiences and the source of sampling, a number of 20,450 values were obtained. Following the experimental determinations, the data obtained (20,450 values for each analysis performed) were entered in the TableCurve 3D software, which aimed to design equations that have the role of describing the dependence between two input parameters that are variable and the parameters analyzed. The values of the correlation coefficients were in the range of values as close to the value of 0.84 - 0.93, which showed that the equations best represented the dependencies between the analyzed parameters, an aspect highlighted by the processing of a large number of experimental values used in the generation of mathematical model. In the verification phase it was found that the relative error calculated for the mathematical model corresponding to the sample from the feed was 97.4% for errors between 0-100%, and for the mathematical model corresponding to the sample from the permeate it is 93.1% for the same range of relative error values.

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Manuscript received: 25.11.2019