ORIGINAL RESEARCH PAPER

APPLICATION OF EXCITATION EMISSION MATRIXES SPECTROSCOPY TO STUDY HUMIC ACIDS REJECTION WITH TiO₂ NANOFILTRATION MEMBRANE WITH ENLARGED AREA

Mihaela-Elena Dascălu[1*], Juan Antonio López-Ramírez[2], Valentin Nedeff[1,3], Emilian Mosnegutu[1], Dragos Rusu[1]

[1]*"Vasile Alecsandri" University of Bacau, Department of Environmental Engineering, 157, Calea Marasesti, 600115, Bacau, Romania*
[2]*Universidad de Cádiz, Departamento de Tecnologías del Medio Ambiente, CASEM - Polig. Río San Pedro s/n. 11510 Puerto Real, Cadiz, Spain*
[3]*Academy of Agricultural and Forestry Sciences "Gheorghe Ionescu-Şişeşti", Bucharest, Romania*

*Corresponding author: mihaeladascalu@ub.ro

Abstract: In recent years, membrane technology is increasingly being studied and thus became even more used in the production of drinking water. However, the presence of foulants in natural waters, as humic acids, affects strongly the efficiency of membrane processes. This study has been aimed to study humic acid (HA) rejection using a new TiO₂ ceramic nanofiltration membrane, with enlarged area (1.25 sqm). This membrane is a prototype and it has been chemically modified to increase its resistance to get fouled. The experiments were carried out on a pilot scale, in the laboratory within the Department of Environment ·Technologies, from the University of Cádiz, Spain. For this, ultrapure water and different HA concentrations (10 mg·L⁻¹, 25 mg·L⁻¹, 50mg·L⁻¹, 75mg·L⁻¹, 100 mg·L⁻¹) were used. For the operating conditions, a constant temperature of 20 °C, pH 7.0, a constant pressure of 7 bars and a Cross Flow Velocity of 0.7 m·s⁻¹ were used. The analytical measurements focused on the use of excitation-emission fluorescence matrix to study membrane rejection of HA. The results of the conducted experiments show that this instrumental technique helps to control the rejection of HA in water and, at the same time, highlights the potential of the prototype membrane for controlling organic matter from the water.

Keywords: *ceramic membrane, excitation emission matrices (EEM), fluorescence, humic acids, nanofiltration*

INTRODUCTION

Water is a natural resource, essential for today's society, which not only satisfies the basic needs of the human population, but also constitutes the key to the development, generation and conservation of economic resources through agriculture, energy generation, industry, transport and tourism. Thus, its quantity and good quality is a critical issue for any region or country [1, 2]. Natural waters, irrespective of their origin, contain numerous impurities, of mineral and organic nature, suspended or dissolved substances, in a higher or lower concentration, which they carry along in the course of natural circulation [3]. Of the global water resources only 3 % are fresh water resources, the most of it is ice, and it contains both inorganics, as well as organic compounds (humic substances plus man-made waste) [4]. The global water demand is expected to increase significantly in the following decennia. That is why water protection, analysis and treatment technology is of increasing importance. The consequences of discharging untreated or inadequately treated wastewater can lead to harmful effects on human health, having a negative impact on the environment and, at the same time, negative repercussions on economic activities [4]. Drinking water quality and its impact on human health populations have made of it the subject of international numerous studies [5].

One of the most important criteria regarding the quality of water is the pollution with organic compounds. Humic acids (HA) are a major component of NOM (Natural Organic Matter) and are dominant products of plant and animal degradation through microbial activity [6, 7]. The NOM is a complex mixture of compounds, including HA, hydrophilic acids, amino acids, lipids and proteins. HA are complex NOM mixtures that are found almost anywhere in the environment, especially in soils, sediments and natural water [3, 8]. HA (Figure 1a) are macromolecules containing different kinds of acids, produced by dead organic matter biodegradation and have a dark brown to black color. A typical humic substance is a mixture of many molecules, some of which are based on a motif of aromatic nuclei with phenolic and carboxylic substituents bonded together; Figure 1b presents a typical structure [9 – 11].

a)   *b)*
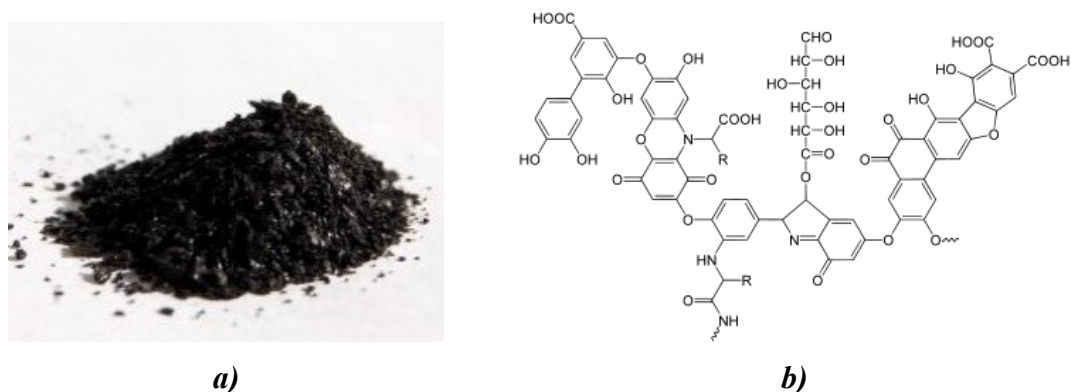
Figura 1. *Example of HA: a) product image - humic acid [12];*
b) typical molecular structure of HA [10]

HA are non-toxic compounds, but their presence in water intended for food or industrial consumption can have a significant impact on the treatability of that water and on the

success of filtration processes. The precise methods of determining HA concentrations are therefore essential to maintain the population's supply of water [2].

Concurrently, the intensity of excitation emission matrices (EEM) fluorescence has been established as the most popular tool for tracking changes in HA structures and compositions, due to its rapid measurement, non-destructive nature and high sensitivity [13 – 15]. EEM is an analytical technique that was implemented on a large scale to characterize fluorophores in the organic matter in natural water [16, 17]. It has been used in various studies, such as monitoring changes in Aquatic Humic Substances (HA$_S$) compositions and reactivity, for the photocatalytic oxidation, to investigate the chemical compositions of Dissolved Organic Matter (DOM), because it can be easily and quickly distinguished between certain DOM classes [18 – 21].

NOM can be removed from drinking water through multiple treatment options. The advances in membrane technology over the past two decades have shown membrane filtration to be an extremely attractive and efficient process for water filtration [22, 23]. Nanofiltration (NF) membranes are now widely used in the treatment of drinking waters and wastewaters, as well as in the pre-treatment of desalination due to the need to eliminate viruses, dissolved organic matter, salts, etc. [24, 25].

Ceramic membranes are suitable for applications in many areas, such as wastewater recycling, the textile industry, the food and pharmaceutical industry. They offer better properties compared to organic ions in terms of thermal, chemical and mechanical stability, as well as resistance to microbial degradation [26].

The main goal of this paper is to study the HA rejection performance of a new NF TiO₂ ceramic membrane with enlarged area and with a modified surface with antifoulant properties. HA has been used as organic model foulant.

MATERIALS AND METHODS

NF pilot plant

The experiments were carried out on a pilot plant, in the laboratory of the Environment Technologies Department, at the University of Cádiz, Spain. This plant was equipped with a NF ceramic membrane (1.2 meters long). At the Figure 2 a scheme of this plant is shown. More details can be found in reference [25].
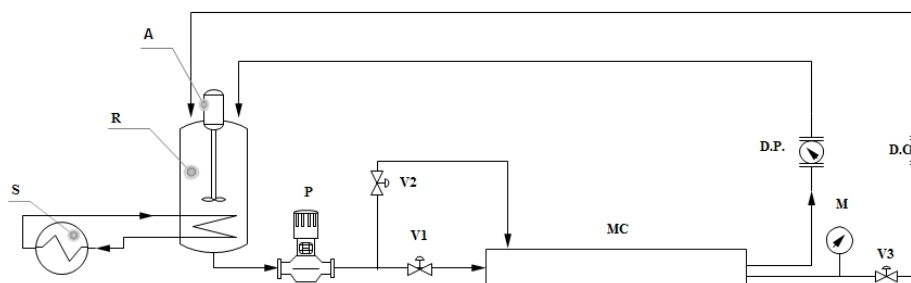
Figure 2. *Scheme of the pilot plant [25]:*
A - mixer; R - Feed water tank (capacity 100L); S - chiller; P - pressure pump;
V1 ... V3 - Valves; MC - ceramic membrane vessel; M - manometer;
D.P. - permeate flowmeter; D.C. - concentrate flowmeter

NF membrane

The membrane used is a new ceramic NF membrane of TiO_2, which had been modified in its active surface using Grignard reagents (GR) to increase fouling resistance. This membrane is an innovative prototype, developed within the FP7 Cerawater project (FP7) [23, 25, 27]. The membrane has a length of 1.2 meters and 163 tubular channels.

Analyzed indicators and equipment used

To carry out the experiments, different HA concentrations were used (10 mg·L^{-1}, 25 mg·L^{-1}, 50 mg·L^{-1}, 75 mg·L^{-1}, 100 mg·L^{-1}) and solutions with 50 L ultrapure water from a Millipore Milli-Q system were prepared for each individual experiment. Temperature was constantly kept at 20 °C using a recirculating chiller (JULABO FL601). Also, a pH value of 7.0 and a constant pressure of 7.0 bars and a cross flow velocity of 0.7 m·s^{-1} were observed.

Following the established operating conditions, experiments were carried out for every HA concentration, allowing the plant to work with the appropriate parameters for 15 minutes for each HA concentration.

Temperature, flow, pH, conductivity and TOC (Total Organic Carbon), both for the permeate and the concentrate, were measured (Figure 3a). However, analytical measurements, in particular, focused on the EEM (Emission Excitation Matrices) fluorescence, which is aimed at viewing and controlling the HA quantity in water.

The analyses for the EEM fluorescence were carried out using a JASCO FP-8300 spectrofluorometer (Figure 3b). This equipment is an advanced spectrofluorometer, equipped with approximately 50 types of sample holders to facilitate research work. The analyzed data is processed in the Spectra Manager II software. This software contains the programs required for recording the spectra on the excitation and emission part, basic kinetic measurements, quantitative measurements and measurements at a fixed wavelength [28].
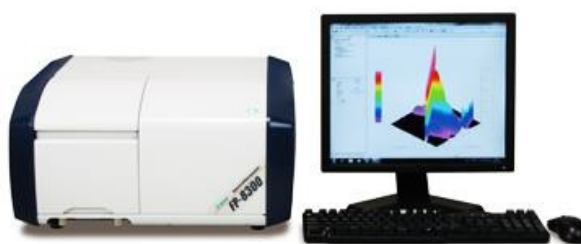
a)   *b)*

Figure 3. *Equipment for sample analysis:*
a) image during pH and conductivity analysis; b) spectrofluorometer FP-8300 [28]

RESULTS AND DISCUSSION

The collected samples, after rejection experiments, were analyzed with the Spectra Manager II software with regard to the intensity of the fluorescence (a.u - arbitrary

units), with an emission wavelength (nm) between 460 and 640 nm and an excitation wavelength (nm) between 350 and 600 nm.
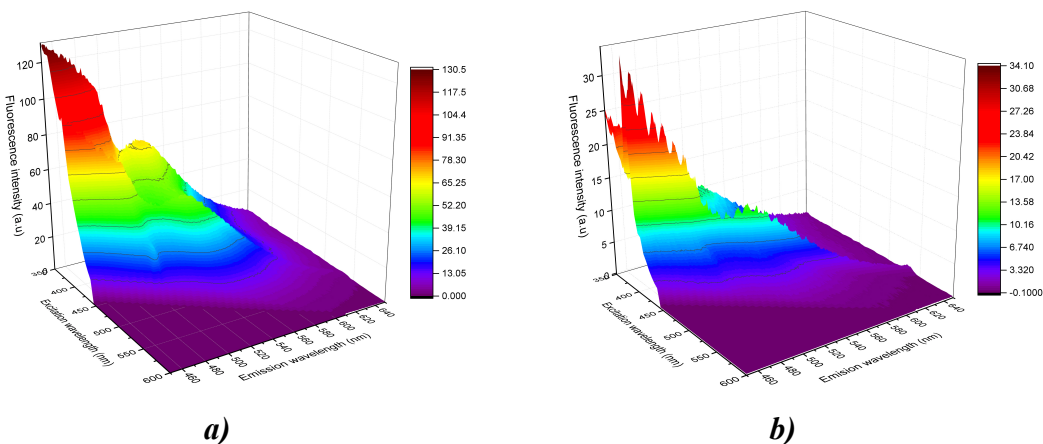
Figure 4 presents the fluorescence intensity for a sample which has a concentration of 10 mg·L^{-1} HA in the initial stage.

a)   *b)*
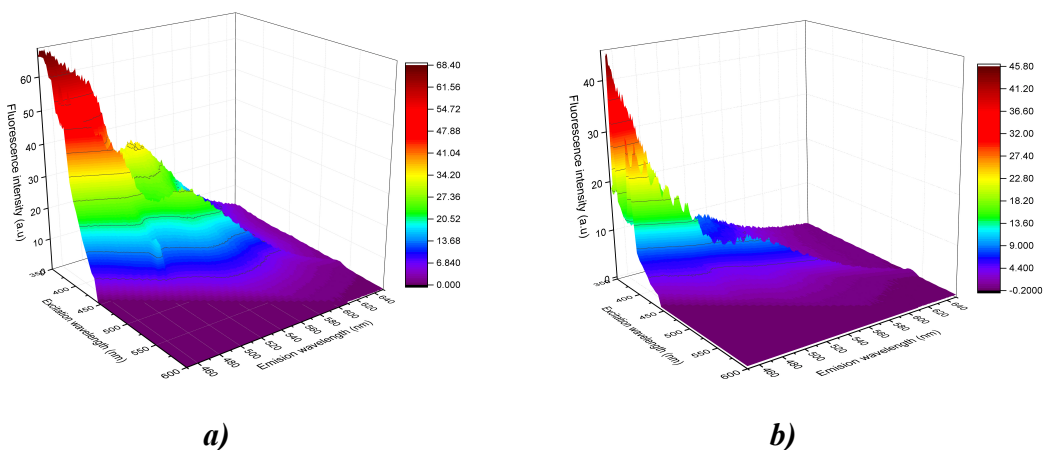
Figure 4. *EEM variation at a concentration of 10 mg·L^{-1} HA:*
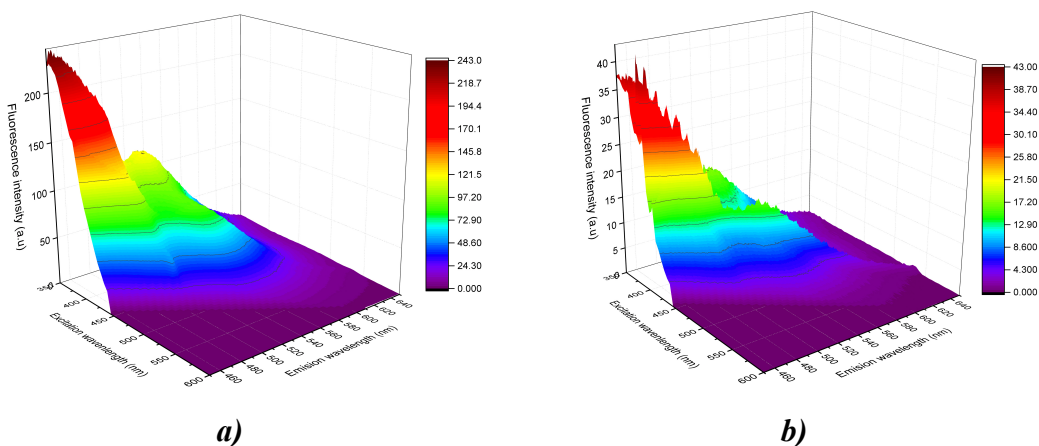*a) feed water; b) the permeate*

From the analysis of the obtained results, by means of the FP-8300 spectrofluorometer, it is found that the sample used to supply the NF plant has a maximum value of 68.40 a.u. (Figure 4a). This value corresponds to an emission wavelength of 440 nm and an excitation wavelength of 350 nm, and after the NF process this value decreases to 45.80 a.u (Figure 4b).

For the solution with an HA concentration of 25 mg·L^{-1}, the spectrofluorometer recorded a maximum value for the fluorescence intensity of 130.5 a.u, (value shown in Figure 5a) for the supply sample. This value decreased approximately 4 times after analyzing the maximum value of fluorescence intensity for the sample obtained after the NF process (Figure 5b).
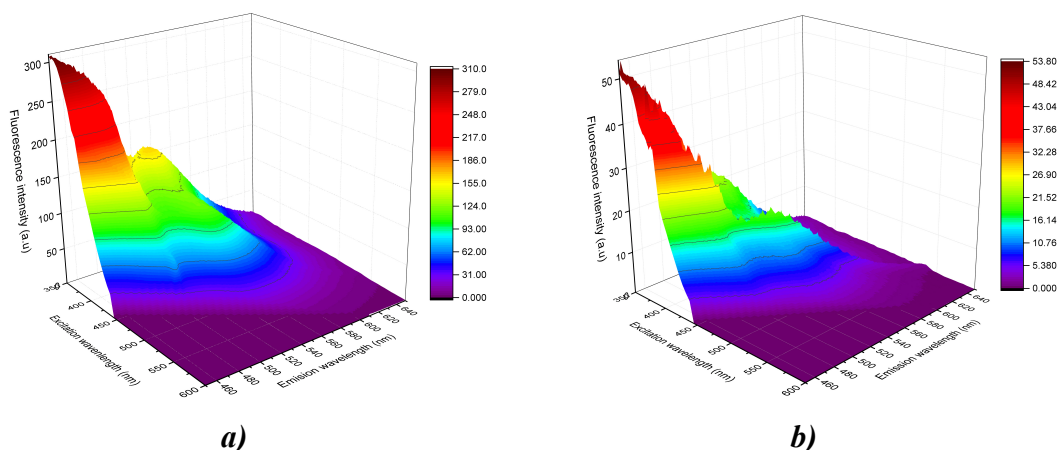

a)   *b)*

Figure 5. *EEM variation at a concentration of 25 mg·L^{-1} HA:*
a) feed water; b) the permeate

Figure 6a shows the variation in fluorescence intensity for the supply sample, whose maximum value is of 243 a.u., parameter which decreases after the analysis of the permeate sample with a percentage of 82.3 % (Figure 6b). This batch of analyses was carried out for a concentration of 50 mg·L^{-1} HA in the initial sample.
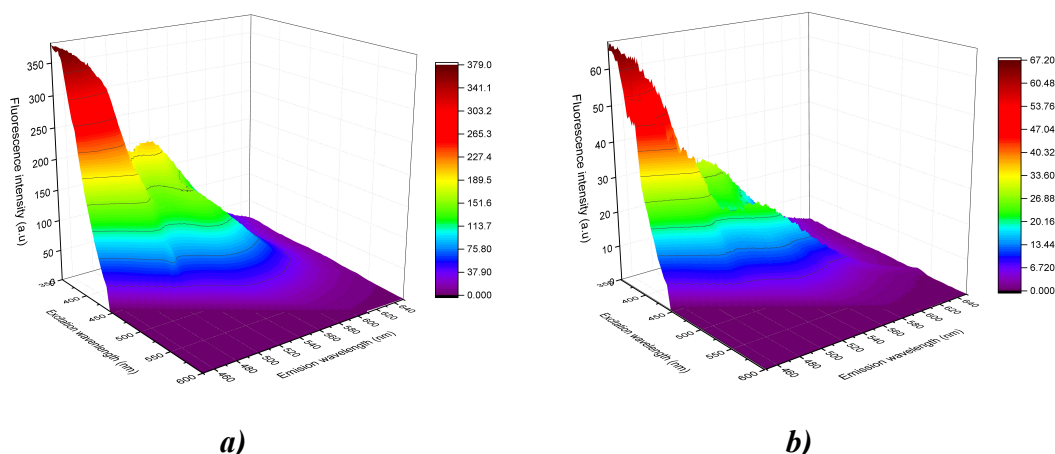

Figure 6. *EEM variation at a concentration of 50 mg·L^{-1} HA:*
a) feed water; b) the permeate

For a concentration of 75 mg·L^{-1} HA of solution used to supply the NF plant, after the sample's EEM analysis, a maximum value of fluorescence intensity of 310 a.u. was obtained for it (Figure 7a). This value dropped to 53.80 a.u. for the collected sample, after the solution passed through the NF plant (Figure 7b).

Figure 7. *EEM variation at a concentration of 75 mg·L^{-1} HA:*
a) feed water; b) the permeate

In the results obtained for a concentration of 100 mg·L^{-1} HA, present in the supply sample, a major difference is found between the fluorescence intensity value obtained in the initial sample, respectively 379 a.u. (Figure 8a) and the fluorescence intensity value obtained in the permeate sample, after filtration with the ceramic membrane (respectively 67.20 a.u. in Figure 8b).

a)   *b)*

Figure 8. *EEM variation at a concentration of 100 mg·L^{-1} HA:*
a) feed water; b) the permeate

As represented in Figure 9, the use of NF ceramic membrane for the retention of HA proves to be an efficient alternative.

$y = -0.0214x^2 + 5.5146x - 28.661$
$R^2 = 0.9978$
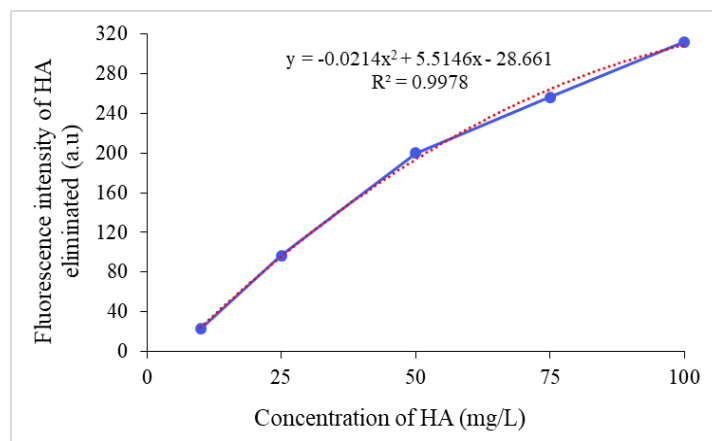
Figure 9. *Graphical representation of the amount of HA retained, after filtration with the NF ceramic membrane, as a result of data obtained by the EEM method*

CONCLUSIONS

A study was designed in which a solution of 50 L ultrapure water with various HA concentrations (10 mg·L^{-1}; 25 mg·L^{-1}; 50 mg·L^{-1}; 75 mg·L^{-1}; 100 mg·L^{-1}) was used, solution which was passed through a NF plant with ceramic membrane.
Based on the analysis of the experimental results, respectively following the analysis of the fluorescence intensity variation the following conclusions can be drawn:
  a) EEM fluorescence spectroscopy can be used to study membrane rejection after filtration.
  b) Regardless of the value of HA concentration used in the experimental determinations, it is determined that the fluorescence intensity value for the

initial (supply) sample differs from the final one (after the filtration process), with a positive difference between the two values.

REFERENCES

1. Song, Z., Fathizadeh, M., Huang, Y., Chu, K.H., Yoon, Y., Wang, L., Xu, W.L., Yu, M.: TiO$_2$ nanofiltration membranes prepared by molecular layer deposition for water purification, *Journal of Membrane Science*, **2016**, **510**, 72-78;

2. Trellu, C., Péchaud, Y., Oturan, N., Mousset, E., Huguenot, D., van Hullebusch, E.D., Esposito, G., Oturan, M.A.: Comparative study on the removal of humic acids from drinking water by anodic oxidation and electro-Fenton processes: Mineralization efficiency and modelling, *Applied Catalysis B: Environmental*, **2016**, **194**, 32-41;

3. Kim, H.-C., Park, S.-J, Lee, C.-G., Han, Y.-U., Park, J.-A., Kim, S.-B.: Humic acid removal from water by iron-coated sand: a column experiment, *Environmental Engineering Research*, **2009**, **14** (1), 41-47;

4. http://www.who.int/mediacentre/news/releases/2017/launch-version-report-jmp-water-sanitation-hygiene.pdf, Progress on Drinking Water, Sanitation and Hygiene Update and SDG Baselines 2017, accessed February 21, **2018**;

5. http://unesdoc.unesco.org/images/0024/002475/247552e.pdf, The United Nations World Water Development Report 2017, Instructions for Authors, accessed February 17, **2018**;

6. Valencia, S., Marín, J.M., Restrepo, G., Frimmel, F.H.: Application of excitation–emission fluorescence matrices and UV/V is absorption to monitoring the photocatalytic degradation of commercial humic acid, *Science of the Total Environment*, **2013**, **442**, 207-214;

7. Rodríguez, F.J., Schlenger, P., García-Valverde, M.: A comprehensive structural evaluation of humic substances using several fluorescence techniques before and after ozonation. Part I: Structural characterization of humic substances, *Science of the Total Environment*, **2014**, **476-477**, 718-730;

8. Orsi, M.: Molecular dynamics simulation of humic substances, *Chemical and Biological Technologies in Agriculture*, **2014**, **1** (10), 14 p., https://doi.org/10.1186/s40538-014-0010-4;

9. de Melo, B.A.G., Motta, F.L., Santana, M.H.A.: Humic acids: Structural properties and multiple functionalities for novel technological developments, *Materials Science and Engineering: C*, **2016**, **62**, 967-974;

10. https://en.wikipedia.org/wiki/Humic_acid, accessed March 23, **2018**;

11. http://karnet.up.wroc.pl/~weber/kwasy2.htm, accessed March 23, **2018**;

12. https://www.kelp4less.com/shop/humic-acid-omri/, accessed March, **2018**;

13. Liu, T., Chen, Z.-L., Yu, W.-Z., You, S.-J.: Characterization of organic membrane foulants in a submerged membrane bioreactor with pre-ozonation using three-dimensional excitation emission matrix fluorescence spectroscopy, *Water Research*, **2011**, **45** (5), 2111-2121;

14. Li, W.-T., Chen, S.-Y., Xu, Z.-X., Li, Y., Shuang, C.-D., Li, A.-M.: Characterization of dissolved organic matter in municipal wastewater using fluorescence PARAFAC analysis and chromatography multi-excitation/emission scan: a comparative study, *Environmental Science & Technology*, **2014**, **48** (5), 2603-2609;

15. Lee, B.-M., Seo, Y.-S., Hur, J.: Investigation of adsorptive fractionation of humic acid on graphene oxide using fluorescence EEM-PARAFAC, *Water Research*, **2015**, **73**, 242-251;

16. Coble, P.G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Marine Chemistry*, **1996**, **51** (4), 325-346;

17. Park, M., Snyder, S.A.: Sample handling and data processing for fluorescent excitation emission matrix (EEM) of dissolved organic matter (DOM), *Chemosphere*, **2018**, **193**, 530-537;

18. Martin, M.V., Gebühr, C., Mártire, D.O., Wiltshire, K.H.: Characterization of a humic acid extracted from marine sediment and its influence on the growth of marine diatoms, *Journal of the Marine Biological Association of the United Kingdom*, **2014**, **94** (5), 895-906;

19. Senga, Y., Moriai, S., Naruoka, C., Nedachi, R., Terui, S.: Characterizing the photochemical degradation of aquatic humic substances from a dystrophic lake using excitation-emission matrix fluorescence spectroscopy and parallel factor analysis, *Limnology*, **2016**, **18** (1), 97-110;

20.   Shao, S., Liang, H., Qu, F., Yu, H., Li, K., Li, G.: Fluorescent natural organic matter fractions responsible for ultrafiltration membrane fouling: Identification by adsorption pretreatment coupled with parallel factor analysis of excitation–emission matrices, *Journal of Membrane Science*, **2014**, **464**, 33-42;
21.   Guo, J., Liu, H., Liu, J., Wang, L.: Ultrafiltration performance of EfOM and NOM under different MWCO membranes: Comparison with fluorescence spectroscopy and gel filtration chromatography, *Desalination*, **2014**, **344**, 129-136;
22.   Mohammad, A.W., Teow, Y.H., Ang, W.L., Chung, Y.T., Oatley-Radcliffe, D.L., Hilal, N.: Nanofiltration membranes review: Recent advances and future prospects, *Desalination*, **2015**, **356**, 226-254;
23.   Mustafa, G., Wyns, K., Vandezande, P., Buekenhoudt, A., Meynen, V.: Novel grafting method efficiently decreases irreversible fouling of ceramic nanofiltration membranes, *Journal of Membrane Science*, **2014**, **470**, 369-377;
24.   Quang, V.L., Kim, H.-C., Maqbool, T., Hur, J.: Fate and fouling characteristics of fluorescent dissolved organic matter in ultrafiltration of terrestrial humic substances, *Chemosphere*, **2016**, **165**, 126-133;
25.   Dascalu, M.E., Amaya Vías, D., Nedeff, V., López-Ramírez, J.A.: Characterization studies of a new ceramic nanofiltration membrane with fouling resistant properties for efficient water treatment, *Environmental Engineering and Management Journal*, **2016**, **15** (7), 1629-1634;
26.   Chougui, A., Belouatek, A., Rabiller-Baudry, M.: Synthesis and characterization of new ultrafiltration ceramic membranes for water treatment, *Journal of Water Process Engineering*, **2018**, Article in press, https://doi.org/10.1016/j.jwpe.2018.04.017;
27.   Hosseinabadi, S.R., Wyns, K., Buekenhoudt, A., Van der Bruggen, B., Ormerod, D.: Performance of Grignard functionalized ceramic nanofiltration membranes, *Separation and Purification Technology*, **2015**, **147**, 320-328;
28.   https://www.jasco.de/uploads/files/Brochure-Jasco-FP-8000-Series-LQ.pdf, Features of the FP-8000 Series, accessed March 23, **2018**.