



Aquaphotomics approach for monitoring different steps of purification process in water treatment systems

Muncan, Jelena
Matovic, Valentina
Nikolic, Strahinja
Askovic, Jelena
Tsenkova, Roumiana

(Citation)

Talanta, 206:120253-120253

(Issue Date)

2020-01-01

(Resource Type)

journal article

(Version)

Version of Record

(Rights)

© 2019 The Authors. Published by Elsevier B.V.
This is an open access article under the CC BY license
(<http://creativecommons.org/licenses/by/4.0/>).

(URL)

<https://hdl.handle.net/20.500.14094/90006451>





Aquaphotomics approach for monitoring different steps of purification process in water treatment systems

Jelena Muncan^{a,b,*}, Valentina Matovic^a, Strahinja Nikolic^a, Jelena Askovic^a, Roumiana Tsenkova^b

^a Nanolab, Biomedical Engineering, Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11120, Belgrade 35, Serbia

^b Biomeasurement Technology Laboratory, Graduate School of Agricultural Science, Kobe University, 1-1, Rokkodai, Nada, Kobe, 657-8501, Japan

ARTICLE INFO

Keywords:

Water treatment
Filtration
Water monitoring
Near infrared spectroscopy
Aquaphotomics

ABSTRACT

Currently, the water quality assessment is based on determination of a range of physico-chemical, and microbiological parameters, which is costly, time-consuming and requires multiple tests. Aquaphotomics strategy for water monitoring is based on the principle that the spectra of water are sensitive to all the chemical and physical perturbations, and as such reflect the state of water.

In this study, aquaphotomics approach was applied on the near infrared spectra of water samples which underwent different filtration treatments performed by a commercially available water treatment system intended for the household use. The applicability of this approach was demonstrated using difference spectra, multivariate classification analysis and by visualizing the water spectral pattern in aquagrams. The results consistently showed that water samples produced by different filtration treatments have distinctive spectral patterns which characterize the state of water molecular network, and can be used for identification of the respective treatment, tracking efficiency of the treatment and monitoring the performance of water treatment systems.

1. Introduction

Clean and safe drinking water is one of the essential requirements for human health.

One of the major strategies for ensuring continuous supply of safe drinking water is implementation of various water treatment systems. For the developing countries with the limited capital and investment potential, centralized water treatment infrastructures are difficult to achieve [1,2], and water treatment technologies for household uses present more attractive solution [3]. However, obtaining rapid and affordable assessments of the quality of drinking water is a challenge, which can be addressed with suitable monitoring techniques.

Vibrational spectroscopic techniques - near infrared (NIR) and mid infrared (MIR) spectroscopy, have been proposed as potential tools to improve the speed and reduce the cost of water quality testing [4,5]. Near infrared spectroscopy, especially, is increasingly popular due to its possibility for non-invasive, fast and simultaneous analysis of many physico-chemical parameters, replacing more frequently time-consuming laboratory methods [6]. The fast technical advancements in this field brought development of miniaturized, portable devices in response

to ever present need in the industry for novel, time- and cost-saving quality control strategies [6]. As such, near infrared spectroscopy based technology, holds huge potential for water monitoring which can be easily installed into the existing water treatment systems.

In an earlier study, a novel aquaphotomics approach to water quality control was proposed [4]. Aquaphotomics is a young scientific field which utilizes the interaction of light of various frequencies and water to acquire information about the state of aqueous systems and offers novel technological solutions based on this principle for quality monitoring of water and food, as well as in biomedicine, bi-diagnostics and biomonitoring [7,8]. Majority of aquaphotomics works are based on application of near infrared spectroscopy, which is especially convenient since it allows non-destructive measurements [9,10].

Previous works reported in the literature, which utilized aquaphotomics and near infrared spectroscopy in the field of water assessment and water quality control demonstrated that is possible to measure various solutes in water – salts, sugars, acids, pesticides, metals, nanoparticles, even the chemical properties such as acidity or pH were measured [11–16]. The main novelty in application of aquaphotomics is that contrary to the traditional spectroscopic approach, which utilizes

* Corresponding author. Nanolab, Biomedical Engineering, Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11120 Belgrade 35, Serbia.

E-mail addresses: jmuncan@mas.bg.ac.rs, jmuncan@people.kobe-u.ac.jp (J. Muncan), vmatovic@mas.bg.ac.rs (V. Matovic), strahinja.nikolic@gmail.com (S. Nikolic), jelenaaskovic@yahoo.com (J. Askovic), rtsen@kobe-u.ac.jp (R. Tsenkova).

<https://doi.org/10.1016/j.talanta.2019.120253>

Received 17 May 2019; Received in revised form 10 August 2019; Accepted 12 August 2019

Available online 13 August 2019

0039-9140/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

absorbance bands of solutes, in aquaphotomics measurements are performed indirectly, utilizing the water absorbance bands where absorbance changes due to the changes of water molecular matrix happening in response to the changes in concentration and/or composition of solutes [7]. Hydrogen bonding between the water molecules, van der Waals interactions and electrostatic effects give rise to a complex, connected water molecular system [17], which is due to all these interactions very sensitive to all perturbations. The indirect method of measurement is in aquaphotomics usually called “water-mirror approach”, meaning that the water molecular structure, revealed by the means of interaction with light (spectra), serves as a source of information on whatever solutes are present in it [18]. The proof of this concept is demonstrated clearly in a study by Gowen et al. concerned with the quantification of different types of salts in water solutions (NaCl, KCl, MgCl_2 , and AlCl_3), where the overall detection limit of 1000 ppm was reported [11]. This work showed that salts which do not even absorb near infrared light can be measured with high precision and accuracy in water solutions based on the changes they imprinted to the water molecular system. Considering just these results, the aquaphotomics approach have improved the detection limit for around five times, considering the usual 5000 ppm is roughly regarded as the general analytical limit of quantification for NIR spectroscopy [19]. Another work investigated the influence of polystyrene (aromatic hydrocarbon polymer) on water molecular structure [16]. When the first overtone of water (i.e. aquaphotomics approach) was used for quantification of polystyrene particles in aqueous suspensions (in conc. 1 %–0.0001%) measurements achieved high accuracy even in the case of very low concentrations. However, when the measurements were based on the polystyrene band near 1680 nm (C–H stretching) decrease in the concentration of particles led to substantial decrease in accuracy of prediction. This study showed that even very low concentrations of polystyrene particles, substantially change the water structure.

Aquaphotomics offered an entirely novel concept for water monitoring, radically different to the traditional concept based on measurements of individual physico-chemical or microbiological quality indices [4]. Instead of tracking individual solutes, water near infrared spectral pattern can show qualitative changes of water molecular system. This approach was successfully tested on artificially contaminated water samples and ground water [4]. In addition, results on discrimination of commercial mineral waters [20] or discrimination of filtrated and not-filtrated samples of pure water [21], based on the same principles were reported.

The main objective of this work is to evaluate the potential of NIR spectroscopy and aquaphotomics for discrimination between water samples which have undergone different filtration treatments and establish distinct spectral patterns characteristic for each step of treatment, as well as to investigate how different treatment steps change molecular structure of water.

2. Material and methods

2.1. Samples

The water samples used in this study were produced using a commercially available water treatment system (Proline Plus 5-stage RO system, ESP Water Products, Carrollton, TX). Fig. 1 schematically presents each step of water treatment (more detailed description of the product available at the manufacturer website [22]). Tap water from the city water supply (W_0) when first enters the water treatment system, undergoes 3-step filtration generating W_{1-3} water. During this phase, the water passes through polypropylene sediment pre-filter which extracts suspended materials (sediments, rust etc.) smaller than 5 μm . Secondly, two carbon filters absorb heavy chlorine and chlorine by-products, and filter out organic matter. After this phase, water W_{1-3} undergoes reverse osmosis process in which a thin film composite membrane filters impurities such as total dissolved solids, heavy metals,

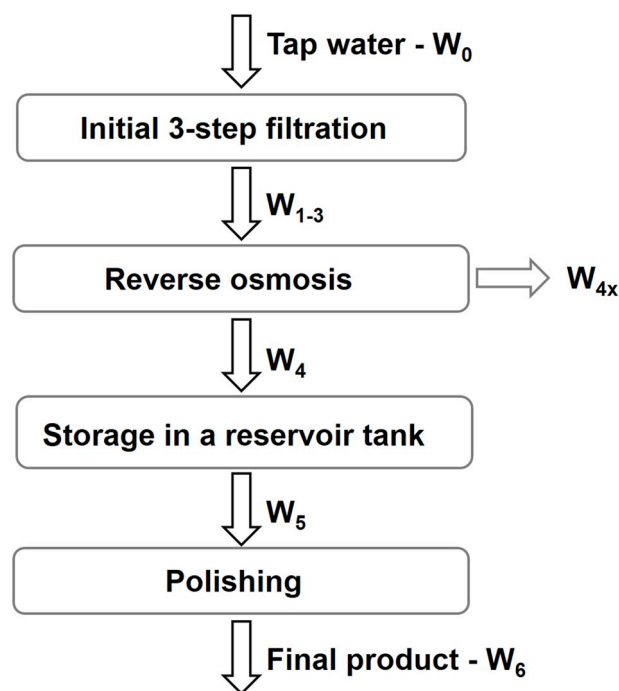


Fig. 1. The water samples (W_i) used in this study: W_0 - tap water from the city water supply; W_{1-3} - water after three-steps of mechanical filtration; W_4 - water after the initial filtration and reverse osmosis; W_{4x} - waste water; W_5 - water after filtration and reverse osmosis stored in a reservoir tank, W_6 - water after all the treatment steps, the final product.

bacteria and viruses producing W_4 . The reverse osmosis efficacy and the percentage of salts rejected during this process depend on the temperature of water and the pressure against the membrane in the system. After the reverse osmosis, the waste water containing excess salts and unwanted substances is removed from the system (W_{4x}), while the purified water after going through the check valve is being collected and stored in the reservoir tank (W_5). In the first experiment, the reservoir tank was empty, while in the two subsequent experiments, freshly produced water was mixed with the water already produced 24 h before. This water undergoes the final “polishing” process, during which coconut shell filter is used to remove dissolved gasses, bad taste and odor from the water. This is the final stage where ready for consumption water is produced (W_6). The water samples were collected after each step of the treatment and labeled according to the scheme presented in Fig. 1 (where W stands for water sample).

2.2. Near infrared spectroscopy

NIR spectra of water samples collected after each treatment step were acquired in transmittance mode using a TG-COOLED NIR-I C9913GC spectrometer (Hamamatsu, Japan), fitted with a quartz cuvette (1 mm optical path length). Spectra were measured over the wavelength range 900–1700 nm, in 8 nm steps. Ten consecutive spectra were acquired for each sample measurement. The experiment was repeated 3 times, during 3 different days, each time with freshly prepared samples. In total, for 3 independently prepared sample replicates per water, 10 consecutive spectra acquired during each measurement (where each consecutive spectrum was an average of 10 co-added spectra) and 7 water samples, the number of acquired spectra for analysis was $n = 210$.

2.3. Data analysis

The spectral data were transformed to pseudo-absorbance units ($\log T^{-1}$, where T is transmittance). The wavelength range of the

acquired spectra was truncated to 1300–1600 nm in order to examine the 1st overtone of the water OH stretching vibration.

To explore the differences in spectra of different water samples, difference spectra were calculated and Principal Component Analysis (PCA) and Soft Modelling of Class Analogies (SIMCA) were applied. All multivariate analysis was performed using Pirouette ver.4.5 (Infometrix, Inc. USA) (Detailed description of multivariate algorithms applied in this work, is available in the Pirouette manual [23]).

Principal component analysis [24] was performed as an initial step with the purpose of examining the data and removing the outliers. Qualitative analysis – SIMCA [25] was performed with the objective of discrimination between different water samples. This algorithm employs principal components analysis of spectra for the construction of mathematical models for each sample group (class) with confidence limits. Interclass distances are calculated using between class residuals and variable importance is determined by comparing average residual variance of each class to all classes and residual variance of all classes to themselves. Variable importance, known as discriminating power was used to find variables (wavelengths) with the highest contribution to discrimination between classes.

To investigate detailed characteristics of water structural transformation after each filtration treatment, the obtained NIR spectra were subjected to analysis of the absorbance pattern at specific water bands (wavelength ranges 6–12 nm long), called Water Matrix Coordinates (WAMACS); in previous studies, Tsenkova et al. have defined 12 characteristic water wavelength ranges which cover various water molecular species and are thus useful to depict characteristic spectral pattern in the first overtone region of water [7]. The variation of WAMACS describes the water spectral pattern (WASP), which can be visualized in aquagrams [26]. The star-chart, aquagram, displays average normalized absorbance values from different water samples' spectra at 12 WAMACS related to different water molecular structures on the radial axes originating from the center of the graph. Aquagrams were calculated and visualized using Microsoft Office Excel 2013 (Microsoft Co., Redmond, WA, USA).

3. Results and discussion

The raw NIR absorbance spectra of water samples in the analyzed range 1300–1600 nm are presented in Fig. 2. The spectra of all water samples overlap and seem identical in this spectral region, whose main feature is a dominant absorbance band around 1450 nm attributed to

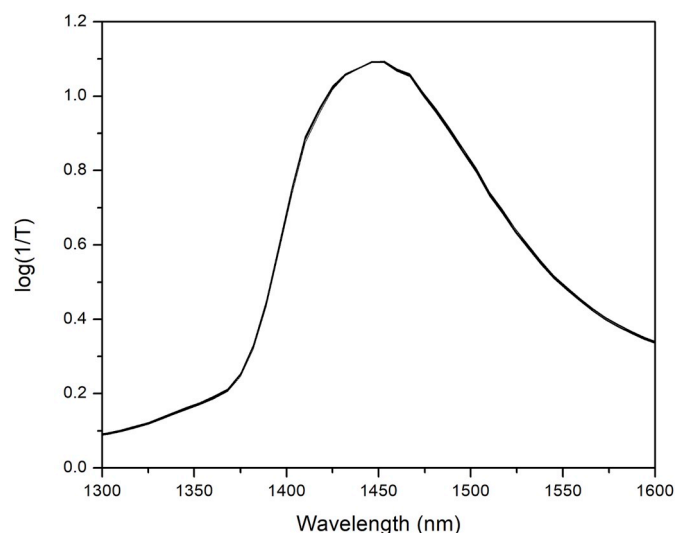


Fig. 2. Truncated (1300–1600 nm) near infrared (NIR) absorbance spectra ($n = 210$) used for analysis. All raw spectra of water samples overlap and seem identical in this region.

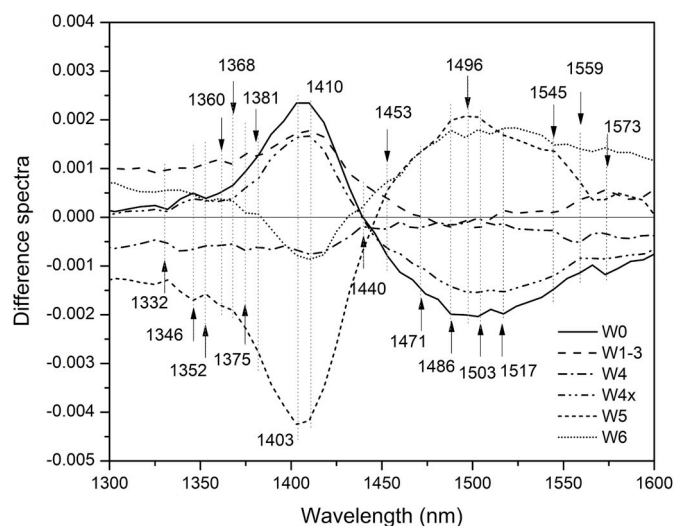


Fig. 3. Difference spectra of water samples representing basic spectral differences.

the first overtone of OH stretching vibration [10]. In order to enhance the subtle changes, at specific water absorbance bands in the spectra of different water samples, two types of calculations are usually performed in the initial evaluation of data – averaging and spectral subtraction [8].

Here, we first performed averaging across all consecutives and sample replicates spectra for each group of water samples, in order to diminish the influence on spectra of those variations which are not of interest, such as those due to the changes in parameters of the environment (temperature, pressure, humidity). Two outliers were found and their spectra removed since they worsen the average spectrum. Secondly, in order to enhance the subtle differences between the average spectra of different water samples, the average spectrum of all samples was subtracted. This is an easy and an efficient way of revealing the differences among rather similar sample groups [8].

The resulting difference spectra are presented in Fig. 3. The spectral subtraction enhanced the differences in spectra of water samples produced by different filtration treatments. The difference spectra show largest differences in values and sign in the regions around 1403–1410 nm and 1486–1517 nm, where free water molecules and hydrogen bonded water molecules absorb, respectively [7]. These spectral differences are dominantly caused by difference in temperature [27]. However, despite dominant temperature influence, many inflections and shoulders can be observed in difference spectra (marked with arrows in Fig. 3) suggesting differences in absorption of various molecular species caused by effects other than temperature [8]. It is interesting to notice that tap water W_0 and waste water W_{4x} have most similar profiles of difference spectra – the only samples which were not subjected to purification treatment. It is also noticeable, that the average spectrum of W_4 water is closest to the average spectrum of all samples.

The next step of the analysis was to apply SIMCA algorithm to determine and highlight the differences between the spectra of different water samples. The SIMCA algorithm classified all the samples accurately (100%) into their respective classes. The interclass distance values (Mahalanobis distance) reported in Table 1 show that, in all but one case, the distance between the classes is larger than 3, which indicates a reliable separation [28,29]. The interclass distance of 1.263 was found for the classes of tap water (W_0) and waste water (W_{4x}) containing concentrated waste solutes that did not pass through the reverse osmosis membrane.

SIMCA's discriminating power showed the variables with the highest contribution to the separation of classes (Fig. 4). The highest

Table 1

SIMCA interclass distance between the classes of different water samples based on the SIMCA class projections.

	W ₀	W ₁₋₃	W ₄	W _{4x}	W ₅	W ₆
W ₀	0.000	8.603	3.141	1.263	7.145	3.796
W ₁₋₃		0.000	9.096	5.374	9.904	5.012
W ₄			0.000	3.358	4.733	3.227
W _{4x}				0.000	6.115	3.666
W ₅					0.000	6.455
W ₆						0.000

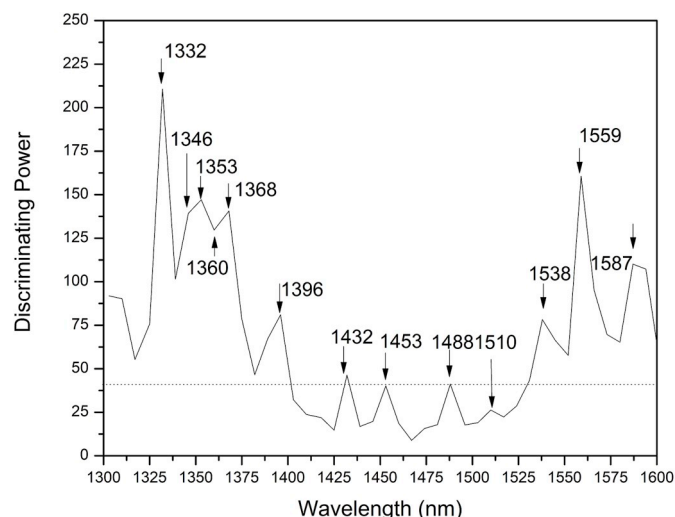


Fig. 4. Discriminating power of SIMCA classification model showing the most important wavelengths responsible for the discrimination between different water samples.

peaks in the discriminating power show that major spectral differences between water samples are found in the spectral regions corresponding to weakly hydrogen bonded water (bands at shorter wavelengths, 1332–1396 nm) and more hydrogen bonded water (bands at longer wavelengths, 1538–1587 nm). Comparatively smaller, but still with high discriminating power (> 40) 1432 nm, 1453 nm and 1488 nm wavelengths were also important for discrimination.

Based on the common water absorbance bands found in difference spectra and discriminating power, 12 wavelengths from WAMACS ranges were selected for representation of spectral patterns of water samples using aquagrams (Fig. 5). Each wavelength corresponds to absorption of specific water molecular species: 1346 nm - ν_3 , 1360 nm - $\text{OH}-(\text{H}_2\text{O})_n$, $n = 1, 2, 4$, 1375 nm - $\nu_1 + \nu_3$, 1382 nm - $\text{OH}-(\text{H}_2\text{O})_n$ where $n = 1, 4$ or $\text{O}_2-(\text{H}_2\text{O})_4$, 1396 nm - water trapped in the local field of ions, 1410 nm - free water molecules (S_0), 1439 nm - protonated water cluster $\text{H}+(\text{H}_2\text{O})_2$, 1446 nm - water molecules with 1 hydrogen bond; water dimer (S_1), 1460 nm - water molecules with 2 hydrogen bonds (S_2), 1474 nm - water molecules with 3 hydrogen bonds (S_3), 1488 nm - water molecules with 4 hydrogen bonds (S_4) and 1517 nm - strongly bound water (ν_1, ν_2) (for these assignments, ν_n represents vibrations of water molecules (i.e., ν_1 ; symmetric stretching, ν_2 ; bending, and ν_3 ; asymmetric stretching); assignments based on multiple sources [7,10,30–36]).

It is evident from the aquagrams of different water samples that every phase of treatment process led to the redistribution of water species, or in another words resulted in reorganization of water molecular network caused by removal of solutes.

In general, the right part of the aquagram represents free water, weakly hydrogen bonded water and water involved with hydration of solutes (solvation shells), while the left part of the aquagram (1446 nm–1517 nm) corresponds to hydrogen bonded water species

and strongly bound water.

Initially, the spectral pattern of tap water (W_0) is characterized by the presence of water molecules interacting with ions and free water molecules. The first phase of treatment, which involves three steps of mechanical filtration (W_{1-3}), results in diminished absorbance of water molecules confined in the local field of ions and free water molecules, while absorbance of water dimers and protonated clusters is increased.

The water after reverse osmosis (W_4) shows strong decrease of absorbance of weakly hydrogen bonded water species, indicating removal of solutes. Interestingly, the spectral pattern of waste water (W_{4x}) shows similarities to the spectral pattern of tap water (in agreement with the observed smallest SIMCA distance between these two classes). The spectral pattern of water stored in the reservoir tank after the reverse osmosis (W_5) shows sharp contrast to tap water; the water species are dominantly organized in hydrogen bonded formations. The final polishing step results in creation of water with slightly increased absorbance of weakly hydrogen bonded water, water dimers and protonated water clusters (W_6). However, both waters – after the reverse osmosis and final polishing are predominantly characterized with the increase of hydrogen bonded water species. This finding, that filtration process leads to increase in number of hydrogen bonded water species, is in agreement with the existing literature [21].

Taken together, these results show that each water sample, obtained after consecutive phases of filtration or storage can be characterized by its spectral pattern, distinctive for each water sample.

The spectral pattern, which in this study reflects the perturbation caused by removal of solutes during filtration, is a comprehensive marker of the state of the water as an integral system (water + solutes) which would change if the parameters of the filtration process are changed (changes in the content of tap water, changes in the efficiency of filters etc.). Instead of performing a multitude of measurements of individual physico-chemical parameters, the aquaphotomics approach offers complementary tool for a quick and cost effective screening of water that can indicate the necessity of more in-depth analysis. In addition, considering the trend of miniaturization and decreased costs of near infrared spectroscopic systems, the aquaphotomics strategy offers easy integration in water treatment systems enabling continuous, real-time screening of drinking water.

4. Conclusions

The present study demonstrated the potential of aquaphotomics strategy for monitoring of water during different steps of filtration treatment. Aquaphotomics approach to analysis of near infrared spectra of water showed subtle, but detectable and consistent differences related to the structure of molecular network of water after different types of filtration treatment. The spectral pattern of water can be used for characterization, showing the cumulative effect of changes in individual physico-chemical and microbiological indicators on water molecular network.

Real-time, online system based on the aquaphotomics near infrared spectroscopy could present an efficient, practical approach for monitoring of quality of water during treatment as well as at the point of use, signaling the changes in water quality based on detection of changes in water structure.

Material and data availability

All data are available on request from the corresponding author.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal

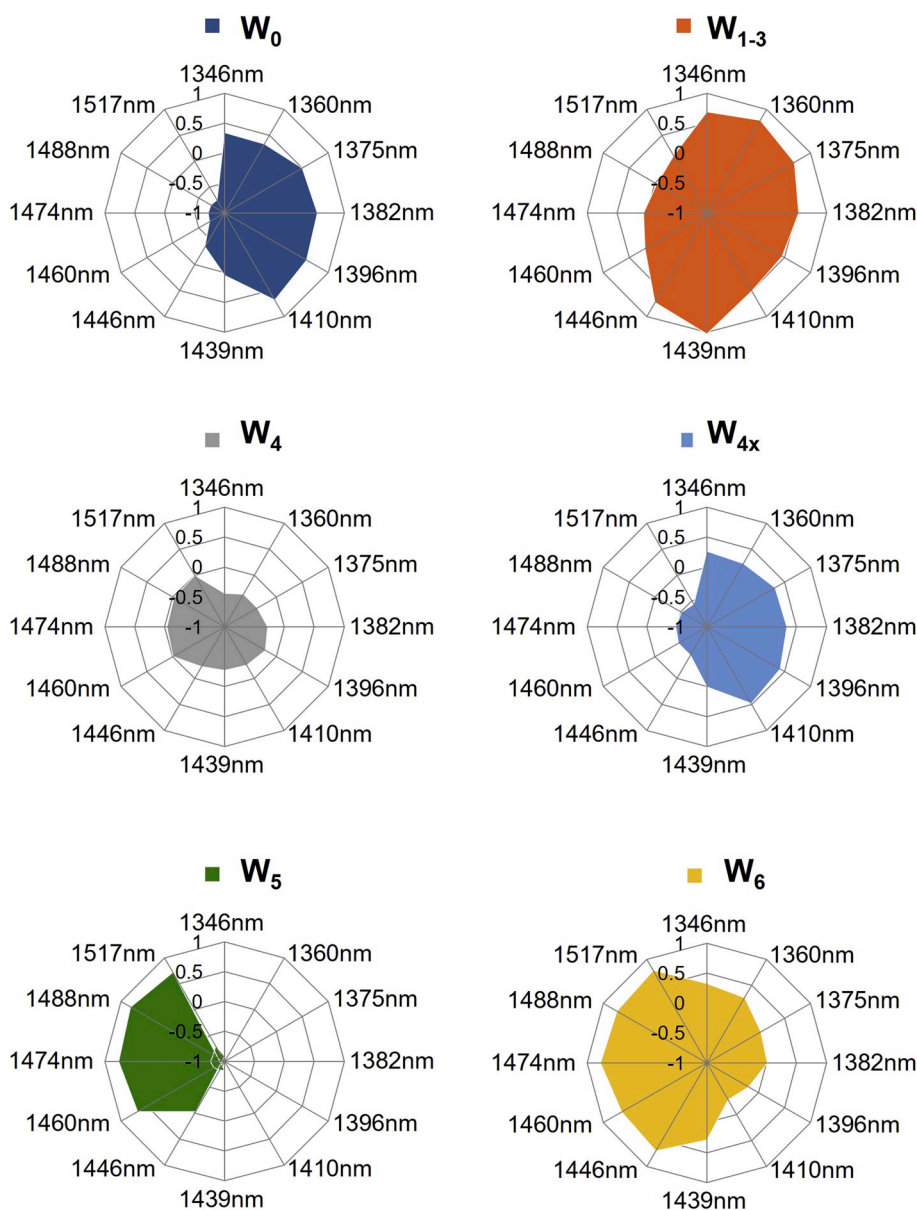


Fig. 5. Spectral pattern of water samples following different steps of treatment, visualized using aquagrams: W_0 – tap water, before treatment; W_{1-3} – water after three steps of mechanical filtration; W_4 – water after mechanical filtration and reverse osmosis; W_{4x} – waste water produced after reverse osmosis; W_5 – water after mechanical filtration and reverse osmosis stored in a reservoir tank; W_6 – final product. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

relationships which may be considered as potential competing interests:

Credit author statement

Jelena Muncan: Conceptualization; Methodology; Formal analysis; Investigation; Resources; Writing - original draft; Writing - review & editing; Visualization; Supervision; Funding acquisition; Project administration, Valentina Matovic: Investigation; Writing - original draft, Jelena Askovic: Investigation; Formal analysis; Visualization, Strahinja Nikolic: Conceptualization; Investigation; Resources, Roumiana Tsenkova: Conceptualization; Writing - review & editing; Funding acquisition

Acknowledgments

The author J.M. gratefully acknowledges the financial support provided by the Japanese Society for Promotion of Science (P17407).

Any identification of instruments and equipment used in this research, does not imply endorsement or recommendation by the authors.

References

- [1] C. An, S. Yang, G. Huang, S. Zhao, P. Zhang, Y. Yao, Removal of sulfonated humic acid from aqueous phase by modified coal fly ash waste: equilibrium and kinetic adsorption studies, *Fuel* 165 (2016) 264–271, <https://doi.org/10.1016/J.FUEL.2015.10.069>.
- [2] P.F. Wang, N. Geng, C. Wang, J. Qian, J. Hou, N. Qi, Evaluating the impact of long term hydrodynamic conditions on the release of metals from contaminated sediments in taihu lake, China, *J. Environ. Informatics* (2016), <https://doi.org/10.3808/jei.201500318>.
- [3] J. Huang, G. Huang, C. An, Y. He, Y. Yao, P. Zhang, J. Shen, Performance of ceramic disk filter coated with nano ZnO for removing *Escherichia coli* from water in small rural and remote communities of developing regions, *Environ. Pollut.* 238 (2018) 52–62, <https://doi.org/10.1016/J.ENVPOL.2018.03.008>.
- [4] Z. Kovacs, G. Bázár, M. Oshima, S. Shigeoka, M. Tanaka, A. Furukawa, A. Nagai, M. Osawa, Y. Itakura, R. Tsenkova, Water spectral pattern as holistic marker for water quality monitoring, *Talanta* 147 (2016) 598–608, <https://doi.org/10.1016/J.TALANTA.2015.10.024>.

- [5] A.A. Gowen, R. Tsenkova, M. Bruen, C. O'Donnell, Vibrational spectroscopy for analysis of water for human use and in aquatic ecosystems, *Crit. Rev. Environ. Sci. Technol.* 42 (2012) 2546–2573.
- [6] C.W. Huck, Theoretical and technical advancements of near-infrared spectroscopy and its operational impact in industry, *NIR News* 28 (2017) 17–21, <https://doi.org/10.1177/0960336017738174>.
- [7] R. Tsenkova, Aquaphotomics: dynamic spectroscopy of aqueous and biological systems describes peculiarities of water, *J. Near Infrared Spectrosc.* 17 (2009) 303–313, <https://doi.org/10.1255/jnirs.869>.
- [8] Tsenkova, J. Munčan, B. Pollner, Z. Kovacs, Essentials of aquaphotomics and its chemometrics approaches, *Front. Chem.* 6 (2018) 363, <https://doi.org/10.3389/fchem.2018.00363>.
- [9] D.A. Burns, E.W. Ciurczak, *Handbook of Near-Infrared Analysis*, CRC Press, 2008.
- [10] Y. Ozaki, Applications in Chemistry, in: H. Siesler, Y. Ozaki, S. Kawata, H. Heise (Eds.), *Near-Infrared Spectroscopy: Principles, Instruments, Applications*, Wiley, Chichester, UK, 2002, pp. 179–211.
- [11] A.A. Gowen, F. Marini, Y. Tsuchisaka, S. De Luca, M. Bevilacqua, C. O'Donnell, G. Downey, R. Tsenkova, On the feasibility of near infrared spectroscopy to detect contaminants in water using single salt solutions as model systems, *Talanta* 131 (2015) 609–618, <https://doi.org/10.1016/J.TALANTA.2014.08.049>.
- [12] G. Bázár, Z. Kovacs, M. Tanaka, A. Furukawa, A. Nagai, M. Osawa, Y. Itakura, H. Sugiyama, R. Tsenkova, Water revealed as molecular mirror when measuring low concentrations of sugar with near infrared light, *Anal. Chim. Acta* 896 (2015) 52–62, <https://doi.org/10.1016/J.ACA.2015.09.014>.
- [13] A.F. Omar, H. Atan, M.Z. MatJafri, NIR spectroscopic properties of aqueous acids solutions, *Molecules* 17 (2012) 7440–7450, <https://doi.org/10.3390/molecules17067440>.
- [14] A.A. Gowen, Y. Tsuchisaka, C. O'Donnell, R. Tsenkova, Investigation of the potential of near infrared spectroscopy for the detection and quantification of pesticides in aqueous solution, *Am. J. Anal. Chem.* 2 (2011) 53–62, <https://doi.org/10.4236/ajac.2011.228124>.
- [15] A. Putra, H. Meilina, R. Tsenkova, Use of near-infrared spectroscopy for determining the characterization metal ion in aqueous solution, 2nd Annu. Int. Conf. Syiah Kuala Univ. - Life Sci. Eng. Chapter. 2, 2012, pp. 154–158.
- [16] R. Tsenkova, E. Iso, M. Parker, C. Fockenberg, M. Okubo, Aqua-Photomics: a NIRS investigation into the perturbation of water spectrum in an aqueous suspension of mesoscopic scale polystyrene spheres, 13th Int. Conference on Near Infrared Spectroscopy, Umea-Vasa, Sweden, 2007.
- [17] M. Chaplin, Liquid water, *Water Struct. Sci.* (2019), http://www1.lsbu.ac.uk/water/liquid_water.html, Accessed date: 26 July 2019.
- [18] G. Bazar, Z. Kovacs, M. Tanaka, R. Tsenkova, Aquaphotomics and its extended water mirror concept explain why NIRS can measure low concentration aqueous solutions, *Aquaphotomics, "Understanding Water in Biological World"*, The 5th Kobe University Brussels European Centre Symposium "Innovation, Environment, and Globalisation, Brussels, Belgium, 2014.
- [19] C. Pasquini, Near infrared spectroscopy: a mature analytical technique with new perspectives – a review, *Anal. Chim. Acta* 1026 (2018) 8–36, <https://doi.org/10.1016/J.ACA.2018.04.004>.
- [20] J.S. Munčan, L. Matija, J.B. Simić-Krstić, S.S. Nijemčević, D.L. Koruga, Discrimination of mineral waters using near-infrared spectroscopy and aquaphotomics, *Hem. Ind.* 68 (2014) 257–264, <https://doi.org/10.2298/>
- HEMIND130412049M.
- [21] T.M.P. Cattaneo, S. Vero, E. Napoli, V. Elia, Influence of filtration processes on aqueous nanostructures by NIR spectroscopy, *J. Chem. Chem. Eng.* 5 (2011) 1046–1052.
- [22] EPS Water Products, Proline Plus five stage RO system, <https://www.espwaterproducts.com/proline-plus-five-stage-ro-system/>, (2019), Accessed date: 1 September 2019.
- [23] Infomatrix Inc, Soft independent modeling of class analogy, *Pirouette Multivariate Data Analysis Software - User's Manual*, Infomatrix, Inc., Bothell, WA, 2014, pp. 14–31.
- [24] H. Martens, M. Martens, *Multivariate Analysis of Quality: An Introduction*, John Wiley & Sons, Chichester, England, 2001.
- [25] S. Wold, M. Sjostrom, SIMCA: A Method for Analyzing Chemical Data in Terms of Similarity and Analogy, (1977), pp. 243–282, <https://doi.org/10.1021/bk-1977-0052.ch012>.
- [26] R. Tsenkova, Aquaphotomics: water in the biological and aqueous world scrutinised with invisible light, *Spectrosc. Eur.* 22 (2010) 6–10.
- [27] V. Segtnan, S. Šašić, T. Isaksson, Y. Ozaki, S. Sasic, T. Isaksson, Y. Ozaki, Studies on the structure of water using two-dimensional near-infrared correlation spectroscopy and principal component analysis, *Anal. Chem.* 73 (2001) 3153–3161, <https://doi.org/10.1021/AC010102N>.
- [28] G. Blomquist, E. Johansson, B. Söderström, S. Wold, Data analysis of pyrolysis—chromatograms by means of simca pattern recognition, *J. Anal. Appl. Pyrolysis* 1 (1979) 53–65, [https://doi.org/10.1016/0165-2370\(79\)80005-4](https://doi.org/10.1016/0165-2370(79)80005-4).
- [29] R.G. Brereton, *Multivariate Pattern Recognition in Chemometrics: Illustrated by Case Studies*, Elsevier Science, New York, 1992.
- [30] D. Kojić, R. Tsenkova, K. Tomobe, K. Yasuoka, M. Yasui, Water confined in the local field of ions, *ChemPhysChem* 15 (2014) 4077–4086, <https://doi.org/10.1002/cphc.201402381>.
- [31] A.A. Gowen, C. Esquerre, C.P. O'Donnell, G. Downey, R. Tsenkova, Use of near infrared hyperspectral imaging to identify water matrix co-ordinates in mushrooms (*Agaricus bisporus*) subjected to mechanical vibration, *J. Near Infrared Spectrosc.* 17 (2009) 363–371.
- [32] H. Maeda, Y. Ozaki, M. Tanaka, N. Hayashi, T. Kojima, Near infrared spectroscopy and chemometrics studies of temperature-dependent spectral variations of water: relationship between spectral changes and hydrogen bonds, *J. Near Infrared Spectrosc.* 3 (1995) 191–201, <https://doi.org/10.1255/jnirs.69>.
- [33] E. Chatani, Y. Tsuchisaka, Y. Masuda, R. Tsenkova, Water molecular system dynamics associated with amyloidogenic nucleation as revealed by real time near infrared spectroscopy and aquaphotomics, *PLoS One* 9 (2014) e101997, <https://doi.org/10.1371/journal.pone.0101997>.
- [34] Weber, Kelley, Nielsen, Ayotte, Johnson, Isolating the spectroscopic signature of a hydration shell with the use of clusters: superoxide tetrahydrate, *Science* 287 (2000) 2461–2463.
- [35] J.M. Headrick, E.G. Diken, R.S. Walters, N.I. Hammer, R.A. Christie, J. Cui, E.M. Myshakin, M.A. Duncan, M.A. Johnson, K.D. Jordan, Spectral signatures of hydrated proton vibrations in water clusters, *Science* 308 (80) (2005) 1765–1769, <https://doi.org/10.1126/science.1113094>.
- [36] D. Wei, D.R. Salahub, Hydrated proton clusters: ab initio molecular dynamics simulation and simulated annealing, *J. Chem. Phys.* 106 (1997) 6086–6094, <https://doi.org/10.1063/1.468256>.