ECOTOX - BRASIL

Ecotoxicol. Environ. Contam., v. 12, n. 1, 2017, 57-62
doi: 10.5132/eec.2017.01.07

EEC

UV-Vis spectroscopy and chemometrics applied to residues monitoring in sewage

Curti, S.M.M.; Ritter, C.M.; da Silva, L.B.; Consolin Filho, N.; Consolin, M.F.B.; Medeiros, F.V.S.; Março, P.H. & Valderrama, P.

Universidade Tecnológica Federal do Paraná (UTFPR). P.O. Box. 271, CEP 87301-899, Campo Mourão-Paraná-Brazil.

(Received April 03, 2016; Accept May 08, 2017)

Abstract

Edible oil residues (EOR) and detergents/soaps (NBDS) are a considerable problem in the water systems. The layer due to presence of these residuals covers the water surface damaging the aquatic life by hampering the sun light to touch its bottom, diminishing algae quantity and, consequently, microorganisms and fishes, which depend on it to survive, changing the local biosphere. Knowing this potential effect, the objective was monitor edible oil residues and detergents/soaps presence in two sewage treatment station located in Brazil. To this, samples were collected from 3 different sewage treatment stages and evaluated by ultraviolet-visible spectroscopy. Chemometrics was applied to recover spectra profiles and relative concentration of residuals. The results indicate that the proposed methodology is feasible to monitoring these residues in sewage.

Keywords: chemometrics, detergents, edible oil residues, MCR-ALS, resolution, sewage, soaps, UV-Vis spectroscopy.

INTRODUCTION

A significant portion of water used for public supply and production process, return dirty to the watercourses, in many cases leading to commitment of its quality for various uses. When effluent is released in a punctual or diffuse aquatic system, the chemical, physical and biological characteristics are somehow changed. As an example, an extreme increase of the organic substances can occur, inducing an increase of biochemical oxygen demand, chemical oxygen demand, total organic carbon and consequently leading to a depletion of dissolved oxygen concentration, mainly provided from the photosynthetic metabolism (Guimarães & Nour, 2001).

Edible oils have a fundamental importance on human feeding being part of a wide variety of food, besides being a resource of energy and acting over the liposoluble vitamins metabolization. However, its incorrect discard, such as on the sewage, it can generate problems to a lot of different systems such as the aquatic ones due to the fact that it has a very low solubility in water, which increases its lifetime on the environment. Moreover, when discarded in sewage it demands for higher financial expenses to the treatment because it can reach the bulk of water in different ways. For example, when discarded over the soil it can reach the groundwater causing environmental instability, while when it is discarded in the rivers it can block the water oxygenation providing catastrophic effects for aquatic species and the species around the contaminated river (Soares *et al*., 2013). Another significant problem is that the oil layer covers the water surface damaging the aquatic life by hampering the sun light to reach its bottom, diminishing algae quantity and, consequently, microorganisms and fishes, which depend on it to survive, changing the local biosphere (Manahan, 1994). Furthermore, during the decomposition process of oils and fats, a reduction of dissolved oxygen takes place leading to an increase at biochemical oxygen demand, which causes drastic changes into aquatic ecosystem (Manahan, 1994).

Nowadays, in Brazil the main source of residual oil found in sewage is the household wastewaters: edible oils are the responsible for most of the complaining reports from sewage treatment stations, and probably these residues are produced by incorrect discard on kitchen sink after frying processes. With the growing of the environmental concerns, the search for actions that could decrease the human impact

*Corresponding author: Patrícia Valderrama; e-mail: patriciav@utfpr.edu.br

over the environment is also increasing. In the Europe and other countries like Canada, United States and Japan, recommendations for proper disposal oils and fats from frying are available (Paul & Mittal, 1997). The proper residual oil collector is common in many Europe city streets, as shown in the pictures taken by one of the authors and presented in the Figure 1. It is possible to note the residual oil collectors at the street in Lisbon – Portugal (October 2010) and in Amiens – France (August 2014).

By applying an environmental politics that promote the importance of environmental education for sustainability can will be created a new mentality generation (Oliveira & Aquino, 2012). Society awareness is necessary for the negative effects of incorrect destination of oil residues used in homes and businesses while minimizing the environmental impact of waste. The need for research on alternative recycling and selective collection is a sustainable practice, to reduce damage to the environment (Soares *et al.*, 2013).

The powder soaps are sources of sodium tripolyphosphate ($Na_5P_3O_{10}$) and is directly linked to the disposal of phosphorus compounds in water systems (Silva *et al.*, 2010). When in excess, the phosphorus is one of those responsible for the eutrophication of lakes and rivers. This anion causes the nutrients enrichment for the water promoting toxic algae proliferation that can lead to excess of organic matter organic in water. The chlorination of this water form carcinogens products such as, organochlorine (Paim *et al*., 2004; Souza & Daniel, 2005; Silva *et al.*, 2010).

Powder soaps, which are consumed in much of Western Europe and industrialized regions such as North America, Japan and South Korea, do not contain tripolyphospate. In China, many regions have banned the phosphate use. However, phosphates remain as the primary structuring agent in high performance detergents and soaps, and are still found in South and Central America, Africa, Eastern Europe and Asia (Khanmohammadi *et al.*, 2007; Silva *et al.*, 2010). A methodology to determine phosphorus by flow injection analysis was proposed by Silva *et al*. (2010). However, a long time in sample preparation and several reagent quantities is necessary.

The researches about detergents/soaps from water systems also comes increased. The determination of insoluble soap in sewage sludge samples was proposed by liquid chromatography with fluorescence detection (Cantarero *et al*., 2010), while the detergent concentration in aquatic environment was determined to report the influence of different physicochemical characteristics on the distribution of linear alkylbenzene solfunate, that lead to toxicity in human beings (El-Gawad, 2014). A flow injection analysis system was proposed to determine cationic surfactants in the environmental samples (Patel & Patel, 1999) and there are earlier studies utilizing atomic absorption to determine anionic detergents in natural waters (Gagnon, 1979) and hydrophilic cobalto thiocyanate method to determine nonionic detergents in wastewater (Zoller & Romano, 1983).

When undesired substances can influence on oxygen exchange and light penetration on water systems, methodologies has to be develop in order to detect and characterize it. Some inorganic anions exhibit absorption bands in the ultraviolet region that result from nonbonding excited electrons (Holler *et al*., 2009). On the other hand, the oxidation products, formed during heating oils, present absorbance around 400 nm, while hydrolysis products produced by oxidized triacylglycerols (monomers) and dimeric and polymerized triacylglycerols during frying (Gómez-Alonso *et al*., 2003) present maximum absorbance around 380 nm (Valderrama *et al.*, 2015). However, sewage are complex samples and the direct determination of these anions or compounds by UV-Vis (Ultraviolet and Visible) spectroscopy is impossible due to lack of selectivity in the technique. Thus, to overcome the lack of selectivity problem, chemometrics have been used as complementary analytical tools in order to extract information about the UV-Vis spectra (Gonçalves *et al.*, 2014; Alves & Valderrama, 2015). In order to detect the presence of edible oils residuals and residuals from detergents/soaps, the aim of

Figure 1 – Residual oil collector on the street. (A) Lisbon – Portugal and (B) Amiens – France.

this work was to develop a fast, low cost and free of residues analytical methodology, which could be robust enough to be used for sewage treatment stations.

EXPERIMENTAL AND METHODS

Materials

Were employed a quartz cuvette (10 mm), UV-Vis spectrophotometer PG Instruments Ltd T80+. MCR-ALS (Multivariate Curve Resolution with Alternating Least Squares) algorithm code and Guidelines User Interface for MATLAB (The Mathworks Inc., MA, USA) is freely available from the MCR-ALS homepage at http://www.mcrals.info/.

Methods

Sample from three different steps of the treatment were collected at two different sewage treatment stations in the Campo Mourão – Paraná - Brazil. Sampling was carried out during three months (from March to May, 2012) with one sampling each week. First sampling point was at the entrance of the raw sewage. The second sampling point was after a pre-treatment step, precisely by the side of an anaerobic fluidic sludge reactor, and third sampling point located just after treatment, where effluent is ready to be released into the water bulk. Figure 2 present a scheme of a sewage treatment station with the points used for sampling. The samples were collected in plastic bottles and analyzes were performed on the same day.

The spectroscopic analysis was realized, from each sample, at the range from 230 to 800 nm. The spectra results were analyzed by using the chemometric method of Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS).

Chemometric method - MCR-ALS

The main objectives of MCR-ALS are the isolation, resolution, and relative quantification of the main sources of variation in a particular data set. The outstanding feature of this method is that no a priori chemical assumption about the contribution of the different components is necessary (Izquierdo-Ridorsa *et al*., 1997). To achieve those objectives, the instrumental response (UV-Vis spectra in this case) is mathematically decompose into a mixture of pure contributions of each components of the system. The method is based on a bilinear model which assumes that the observed spectra are a linear combination of spectra of the pure components in the system (Piqueras *et al*., 2011).

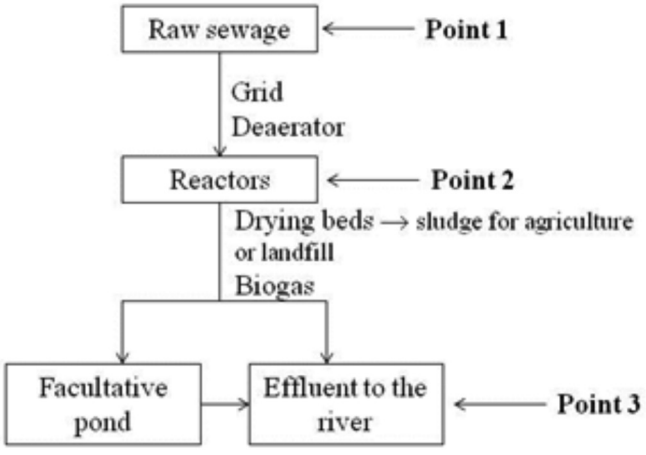

Figure 2 - Scheme of a Brazilian sewage treatment station with the three sampling points.

MCR-ALS is considered in the soft-modeling class methods, since it does not impose any mathematical model to describe the shape of the profiles in the **C** and $\mathbf{S}^T$ matrices. The algorithm steps algorithm include the determination of the number of components in **D** by rank analysis methods, such as the Singular Value Decomposition (SVD) (Março *et al*., 2014). Then, an initial **C** or $\mathbf{S}^T$ matrix with as many profiles as the number of components estimated for **D** is constructed to start the iterative resolution process. Once the initial estimate is generated, the iterative optimization step is started by Alternating Least Squares (ALS). The convergence criterion is achieved when the variation of results between consecutive iterations goes below a preset threshold value or when a certain number of iterations are exceeded (Março *et al*., 2014). Constraints are normally applied to minimize rotational or intensity ambiguity phenomenas. The most common constraints are non-negativity, unimodality, local rank, and trilinearity (Tauler, 1995).

In this research, the rank analysis was realized by SVD, initial estimates for **C** was made by PURE method that is derived from simple-to-use interactive self modeling analysis (SIMPLISMA) (De Juan *et al.*, 2004). The constraint used was non-negativity for the concentration and spectra.

RESULTS AND DISCUSSION

Before reaching the aquatic systems the wastewater, also called sewage, can should go through some kind of purification, which in Brazil is normally a combination of biological and physical-chemical process. In this research were evaluated two different sewage treatment stations named Rio do Campo and Rio Km 119, located in Campo Mourão – Paraná – Brazil. Rio Km 119 is responsible for 55% of the sewage treatment generated in Campo Mourão while Rio do Campo is responsible for the others 45% of the sewage treatment. Both sewage treatment stations together manage nineteen thousand sewage linkages, corresponding to more than seventy thousand habitants from the urban area.

Due to problems that can be caused when detergents/ soaps and edible oil residues are present in the water systems, the development of analytical methods to detect and identify these residues are extremely important. This can, for example, indicate that the sewage treatment requires a step forward in the treatment before its release in the water systems. In this research, the raw spectra obtained on April 26, 2012 from the two sewage treatment stations (Rio do Campo and Rio

Km 119) from all collection points (Figure 2) are presented in the Figure 3. A intensity difference, analytically named hyperchromic and/or hypochromic shift, in the absorbance spectra can be observed. However, due to the lack of selectivity in UV-Vis spectroscopy is difficult to draw conclusions only by regarding the spectra and the chemometric method of curve resolution, as MCR-ALS, can contribute to the reliability of the results. MCR-ALS has been proposed and extensively used to resolve multiple pure responses and concentrations of the components present in unknown mixtures. It has been applied to the analysis of the environmental samples (Peré-Trepat *et al*., 2005; Peré-Trepat & Tauler, 2006) and UV-spectral data (De Luca *et al*., 2010; Março *et al*., 2011; Jayaramana *et al*., 2012; Gonçalves *et al*., 2014a; Gonçalves *et al*., 2014b; Gonçalves *et al*., 2015).

The pseudo number of chemical components in the UV-Vis spectra was evaluated by SVD (Março *et al*., 2014), a rank analysis method. Two singular values were used, since its represent more than 90% of explained variance of the data set. In order to start the iterative resolution process the initial estimative from relative concentration profile was applied using the PURE algorithm (Windig, 1992), that is a method based on the detection of "purest" variables.

To identify and detect the presence of undesired substances in sewage, the first step was to determine where edible oils residues and detergents/soaps show spectra. About edible oils, previous research (Gonçalves *et al*., 2014; Valderrama *et al*., 2011) indicates that the absorption band located at the region around 400 nm is referred to oxidation products formed due to oil heating. This absorption band is perfect for this work, since the edible oil residues that affect sewage treatment stations, usually, is originated from fried foods and discarded at the kitchen sink. To the liquid detergents, the spectra produced when it was diluted in distillated water showed an absorption band at the region between 240 and 280 nm. For the powder soaps, a dilution in distillated water shows, besides the band between 240 and 280 nm, another band between 310 – 400 nm. The Figure 4 shown these absorptions information.

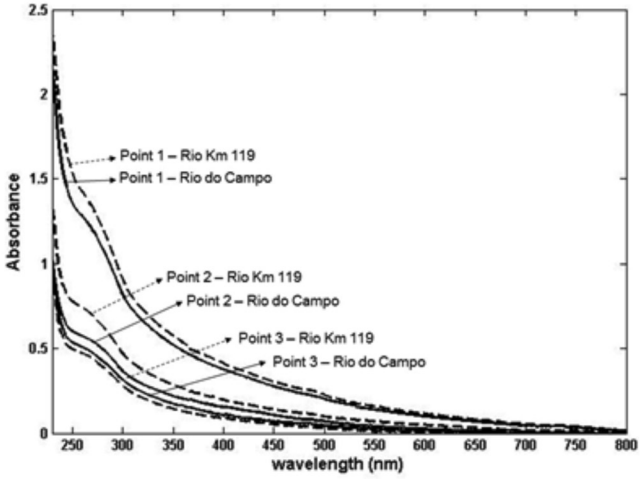

Figure 3 - UV-Vis spectra of the sewage samples from Rio do Campo (—) and Rio Km 119 (----).

By applying MCR-ALS to the UV-Vis spectra sets two spectra profiles and two relative concentration profiles were returned. Figure 5 (A) shows the spectra profile of the edible oils residues and detergents/powder soaps found in sewage recovered by MCR-ALS, on April. It's possible to observe the absorption bands resemble to detergents/soaps absorption bands and oxidation products present in the edible oil residues. Figure 5 (B) present the relative concentration of these residuals recovered by MCR-ALS. The results suggests that concentration decreases step by step of the treatment, and in the last step, which regards to the effluent ready to be released in environment, the undesired substances concentrations are considerably low, but present. These results are in accordance with a preliminary previous study (Ritter *et al.*, 2013) performed during only one week.

When making a comparison of the relative concentration values during the studied period it is found that during March 2012 the detergents/soaps concentration was higher in Rio Km 119 sewage treatment station, while during April and May 2012 it was higher in Rio do Campo sewage treatment station – Figure 6(A). In relation to oil residues its relative concentration was higher in Rio do Campo sewage treatment station during March 2012, while during April and May 2012 it was higher in Rio Km 119 sewage treatment station, as shows Figure 6(B).

These results suggest that the sewage treatment can improve the treatment by include a step before its release in the water systems. The analytical method developed from UV-Vis spectroscopy and MCR-ALS can be used in on-line monitoring after the point 2 (Figure 2) in the sewage treatment system. Furthermore, the proposed methodology is fast, low cost and free of residues, which is a great advantage that meets the requirements of green chemistry (Prado, 2003).

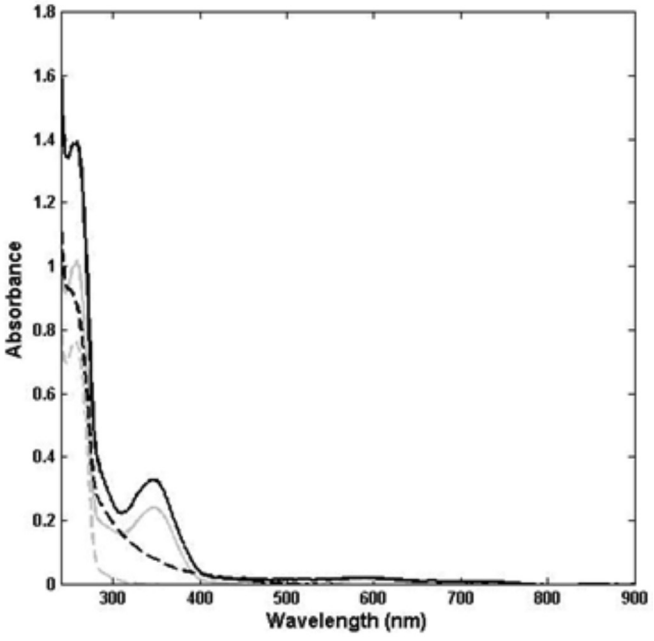

Figure 4 - Detergents and powder soaps spectra. (—) powder soaps trademark 1; (—) powder soaps trademark 2; (----) liquid detergent trademark 1; (--) liquid detergent trademark 2.

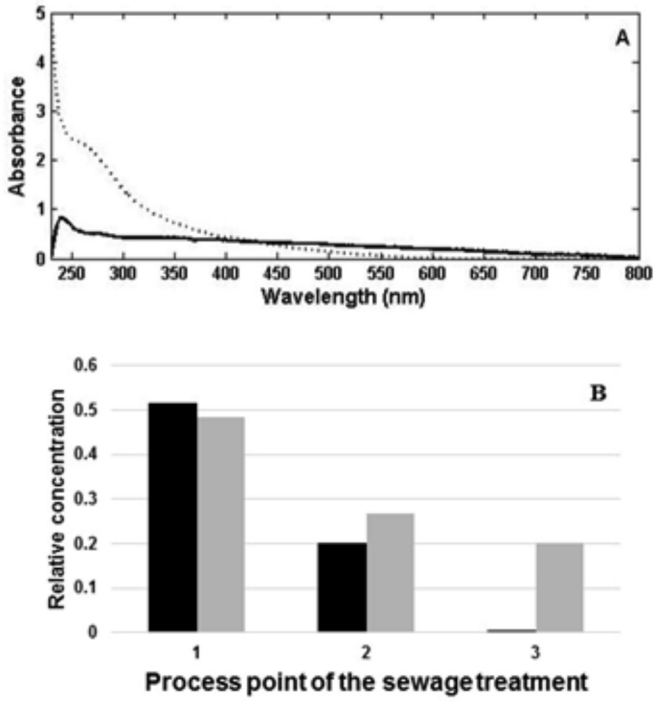

Figure 5 - MCR-ALS results for one sample from Rio do Campo. (A) Recovered spectral profile, (B) Relative concentration profiles, detergent/ soaps (….) and edible oil residues (—), (■) edible oil residues, (■) detergents/soaps.

CONCLUSIONS

The results from this study suggest that the proposed methodology can be used in sewage treatment stations in order to detect the presence of edible oil residues and detergents/soaps. The results show that UV-Vis spectroscopy data evaluated trough MCR-ALS analysis were able to clarify about those residues kinetic behavior by the observation of its relative concentrations. Moreover, the methodology proposed here has some advantages as fastness, does not require sample preparation, and does not produce toxic residues. This methodology can help sewage treatment stations to identify when a step forward in the treatment, before its release in the water systems, can be necessary.

ACKNOWLEDGMENTS

The authors acknowledge Fundação Araucária for a fellowship to Cíntia M. Ritter and Letícia B. da Silva. Acknowledge CNPq for a fellowship to Suzana M.M. Curti, and thanks to SANEPAR for the samples used in this research.

REFERENCES

ALVES, F.C.G.B.S., VALDERRAMA, P. 2015. Ultraviolet spectroscopy and supervised pattern recognition methods for authentication of transgenic and non-transgenic soybean oils. Anal. Methods, 7: 9702-9706. http://dx.doi.org/10.1039/c5ay02440d

CANTARERO, S., ZAFRA-GÓMEZ, A., BALLESTEROS, O., NAVALÓN, A., VÍLCHEZ, J.L., CROVETTO, G., VERGE, C., DE FERRER, J.A. 2010. Improved sample treatment for the determination of insoluble soap in sewage sludge samples by liquid chromatography with fluorescence detection. Talanta, 82(4): 1548-1555. http://dx.doi.org/10.1016/j.talanta.2010.07.044

DE JUAN, A., NAVEA, S., DIEWOKB, J., TAULER, R. 2004. Local rank exploratory analysis of evolving rank-deficient systems. Chemom. Intell. Lab. Syst., 70(1): 11-21. http://dx.doi.org/10.1016/j.chemolab.2003.09.002

DE LUCA, M., MAS, S., IOELE, G., OLIVERIO, F., RAGNO, G., TAULER, R. 2010. Kinetic studies of nitrofurazone photodegradation by multivariate curve resolution applied to UV-spectral data. Int. J. Pharm., 386(1-2): 99-107. http://dx.doi.org/10.1016/j.ijpharm.2009.11.003

EL-GAWAD, H.A.S. 2014. Aquatic environmental monitoring and removal efficiency of detergents. Water Sci., 28(1): 51-64. http://dx.doi.org/10.1016/j.wsj.2014.09.001

GAGNON, M.J. 1979. Note on a rapid and sensitive method for the determination of anionic detergents in natural waters at the ppb level. Water Res., 13(1): 53-56. http://dx.doi.org/ 10.1016/0043-1354(79)90254-9

GÓMEZ-ALONSO, S., FREGAPANE, G., SALVADOR, M.D., GORDON, M.H. 2003. Changes in phenolic composition and antioxidante activity of virgin olive oil during frying. J. Agric. Food Chem., 51(3): 667-672. http://dx.doi.org/10.1021/jf025932w

GONÇALVES, R.P., MARÇO, P.H., VALDERRAMA, P. 2014. Thermal edible oil evaluation by UV–Vis spectroscopy and chemometrics. Food Chem., 163: 83-86. http://dx.doi.org/10.1016/j.foodchem.2014.04.109

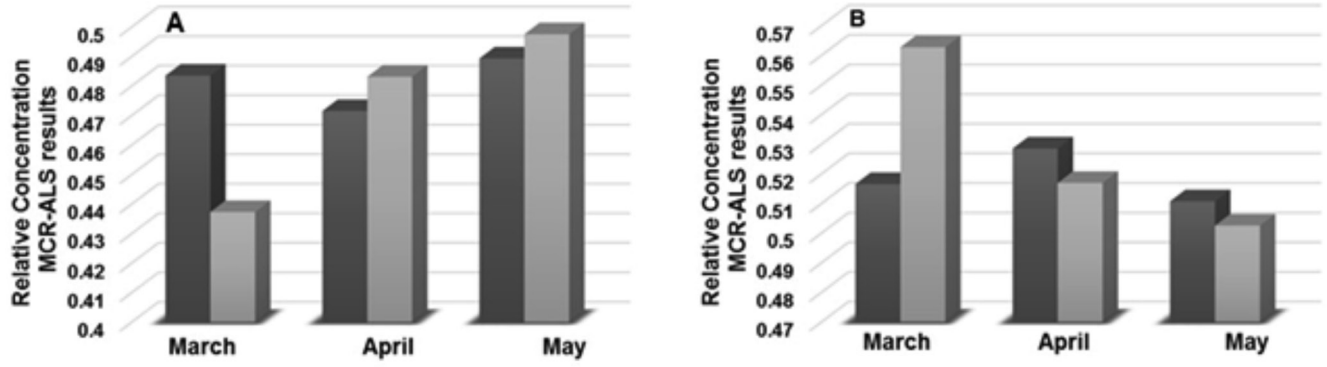

Figure 6 - Relative concentration – MCR-ALS results for (A) detergents/soaps and (B) edible oils residues obtained from the analysis during March, April and May 2012 at Rio Km 19 (■) and Rio do campo (■).

GONÇALVES, R.P., MARÇO, P.H., VALDERRAMA, P. 2014. Stability of avocado and pequi oil during heating: Study using ultraviolet visible spectroscopy and chemometrics methods of curve resolution. J. Food Process. Technol., 5(9): 365. http://dx.doi.org/10.4172/2157-7110.1000365

GONÇALVES, R.P., MARÇO, P.H., VALDERRAMA, P. 2015. Thermal degradation of tocoferol and oxidation products in diferente olive oil classes using UV-Vis spectroscopy and MCR-ALS. Quim. Nova, 38(6): 864-867. http://dx.doi.org/10.5935/0100-4042.20150074

GUIMARÃES, J.R., NOUR, E.A.A. 2001. Treating our sewage? Processes that copy nature. Quim. Nova Esc., 13: 19-30.

HOLLER, J.F.; SKOOG, D.A.; CROUCH, S.R. (2009) Princípios de análise instrumental. Editora Bookman: Porto Alegre, 6 ed., p. 384.

IZQUIERDO-RIDORSA, A., SAURINA, J., HERNÁNDEZ-CASSOU, S., TAULER, R. 1997. Second-order multivariate curve resolution applied to rank-deficient data obtained from acid-base spectrophotometric titrations of mixtures of nucleic bases. Chemom. Intell. Lab. Syst., 38(2): 183-196. http://dx.doi.org/10.1016/S0169-7439(97)00034-8

JAYARAMANA, A., MAS, S., TAULER, R., DE JUAN, A. 2012. Study of the photodegradation of 2-bromophenol under UV and sunlight by spectroscopic, chromatographic and chemometric techniques. J. Chromatogr. B, 910: 138-148. http://dx.doi.org/10.1016/j.jchromb.2012.03.038

KHANMOHAMMADI, M., ASHORI, A., KARGOSHA, K., BAGHERI GARMARUDI, A. 2007. Simultaneous determination of sodium tripolyphosphate, sodium sulfate and linear alkylbenzensulfonate in washing powder by attenuated total reflectance fourier transform infrared spectrometry. J. Surfactants and Deterg., 10(2): 81-86.

MANAHAN, S.E. (1994) Environmental chemistry. Lewis Publishers-CRC Press, Boca Raton.

MARÇO, P.H., POPPI, R.J., SCARMINIO, I.S., TAULER, R. 2011. Investigation of the pH effect and UV radiation on kinetic degradation of anthocyanin mixtures extracted from Hibiscus acetosella. Food Chem., 125(3): 1020-1027. http://dx.doi.org/10.1016/j.foodchem.2010.10.005

MARÇO, P.H., VALDERRAMA, P., ALEXANDRINO, G.L., POPPI, R.J., TAULER, R. 2014. Multivariate curve resolution with alternating least squares: Description, operation and aplications. Quim. Nova, 37(9): 1525-1532. http:// dx.doi.org/10.5935/0100-4042.20140205

OLIVEIRA, J.A.B., AQUINO, K.A.S. 2012. Óleo residual de frituras: Impactos ambientais, educação e sustentabilidade no biodiesel e sabão. Disponível em: https://ldoih.files.wordpress.com/2012/08/artigo-c3b3leo-residual-de-frituras.pdf. Acesso em: 3 dezembro 2015.

PAIM, A.P.S., PEREIRA, E.R., SANTOS, H.R., ZAIAT, M. 2004. Digestão de amostras de águas residuais para determinação de fósforo. Analytica, 3(12): 45-49.

PAUL, S., MITTAL, G. S. 1997. Regulating the use of degraded oil/fat in deep-fat/oil food frying. Crit. Rev. Food Sci. Nutr., 37(7): 635-662.

PATEL, R., PATEL, K.S. 1999. Simple and specific method for flow injection analysis determination of cationic surfactants in environmental and commodity samples. Talanta, 48(4): 923-931. http://dx.doi.org/10.1016/S0039-9140(98)00306-3

PERÉ-TREPAT, E., LACORTE, S., TAULER, R. 2005. Solving liquid chromatography mass spectrometry coelution problems in the analysis of environmental samples by multivariate curve resolution. J. Chromatogr. A, 1096(1-2):111-122. http://dx.doi.org/10.1016/j.chroma.2005.04.089

PERÉ-TREPAT, E.; TAULER, R. 2006. Analysis of environmental samples by application of multivariate curve resolution on fused high-performance liquid chromatography-diode array detection mass spectrometry data. J. Chromatogr. A, 1131(1-2):85-96. http://dx.doi.org/10.1016/j.chroma.2006.07.047

PIQUERAS, S., DUPONCHEL, L., TAULER, R., DE JUAN, A. 2011. Resolution and segmentation of hyperspectral biomedical images by multivariate curve resolution alternating least squares. Anal. Chim. Acta, 705(1-2): 182-192. http://dx.doi.org/10.1016/j.aca.2011.05.020

PRADO, A.G.S. 2003. Green chemistry, the chemical challenges of the new millennium. Quim. Nova, 26(5): 738-744.

RITTER, C.M., CURTI, S.M., VALDERRAMA, P. 2013. Monitoramento mensal da presença de detergentes não biodegradáveis e resíduos de óleos comestíveis nas estações de tratamento de esgoto da cidade de Campo Mourão, Paraná. Tópos, 7: 51-57.

SILVA, F.S.V.C.B., SILVA, V.L., LAVORANTE, A.F., PAIM. A.P.S. 2010. Evaluation of sample preparation of the detergente powder using factorial design. Quim. Nova, 33(5): 1199-1203.

SOARES, V.S., DAL PUPO, D., MOURÃO, R.C. 2013. Produção de sabão artesanal no município de Sorriso – MT: Alternativa sustentável ao óleo usado. In: Anais do IV Congresso Brasileiro de Gestão Ambiental. Salvador.

SOUZA, J.B., DANIEL, L.A. 2005. Comparação entre hipoclorito de sódio e ácido peracético na inativação de *E. Coli*, *colifagos* e *C. perfringens* em água com elevada concentração de matéria orgânica. Eng. Sanit. Ambiental, 10(2): 111-117.

TAULER, R. 1995. Multivariate curve resolution applied to second order data. Chemom. Intell. Lab. Syst., 30(1): 133-146. http://dx.doi.org/10.1016/0169-7439(95)00047-X

VALDERRAMA, L., GONÇALVES, R.P., MARÇO, P.H., RUTLEDGE, D.N., VALDERRAMA, P. 2016. Independent Components Analysis as a means to have initial estimates for Multivariate Curve Resolution-Alternating Least Squares. J. Adv. Res., 7: 795-802. http://dx.doi.org/10.1016/j.jare.2015.12.001

VALDERRAMA, P., MARÇO, P.H., LOCQUET, N., AMMARI, F., RUTLEDGE, D.N. 2011. A procedure to facilitate the choice of the number of factors in multi-way data analysis applied to the natural samples: Application to monitoring the thermal degradation of oils using front-face fluorescence spectroscopy. Chemom. Intell. Lab. Syst., 106(2): 166-172. http://dx.doi.org/10.1016/j.chemolab.2010.05.011

WINDIG, W. 1992. Self-modeling mixture analysis of spectral data with continuous concentration profiles. Chemom. Intell. Lab. Syst., 16(1): 1-16. http://dx.doi.org/10.1016/0169-7439(92)80073-D

ZOLLER, U., ROMANO, R. 1983. Determination of nonionic detergents in municipal wastewater. Environ. Int., 9: 55-61.