ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XIV (XLV) 2022, No. 1
DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2022.1.04

ATR-FTIR analysis of filter paper with mass addition of seaweed *Ulva Rigida* C. Agardh

Florina Cristiana Căpriță (Filote) [1,2*], Antoaneta Ene [1,2,3], Steluța Gosav [2,3]

[1] "Dunarea de Jos" University of Galati, Doctoral School of Mechanical and Industrial Engineering, 47 Domneasca St., RO-800008, Galati, Romania
[2] INPOLDE research center, ReForm-UDJG Platform, Dunarea de Jos University of Galati, 111 Domneasca St., 800201 Galati, Romania
[3] "Dunarea de Jos" University of Galati, Faculty of Sciences and Environment, Chemistry, Physics and Environment Department, 111 Domneasca St., 111, 800201, Galati, Romania

[*] Corresponding author: caprita.f@yahoo.com

Abstract
This paper presents the results obtained from the analysis of some filter paper samples using Fourier Transform Infrared Spectroscopy (FTIR) technique. Based on the FTIR capabilities, using the infrared light to scan the samples and identify their chemical properties, organic, polymeric and inorganic materials can be characterized. The samples analysed were six filter papers with different mass additions of *Ulva Rigida* C. Agardh seaweed collected from the Black Sea, in Constanta area, SE Romania. The additions used consisted of 0.5%, 1%, 2%, 4% and 8% seaweed material, grounded to a certain grain size.

Keywords: FTIR, marine algae, filter paper.

1.INTRODUCTION

Water is a renewable natural resource that is absolutely necessary to sustain life on earth [1]. In the majority of the studies dealing with this topic, there is no mention of the fact that water can become an exhaustible resource if the quality of water is altered without the possibility of restoring it to its original quality. The composition of water has certainly changed over thousands of years and there is now talk of massive pollution of all resources.

Fresh water represents only 3% of the total amount of water on the planet, and this percentage is constantly decreasing due to pollution and over-exploitation. Industrial development, agriculture and domestic activities have intensified [2], and known methods of water purification are becoming outdated because of the large volumes of wastewater and the complexity of pollutants. Judicious consumption can help to reduce the amount of potable water that is used, but for water sources that are already polluted or whose composition has changed, new methods of purification must be found.

The aim of this work was to employ the ATR-FTIR method for analysing a series of samples consisting of filter papers with different mass additions of *Ulva rigida* C. Agardh seaweed and to investigate the possibility of using these filter papers under maximum safety conditions. The aim of manufacture this kind of filter paper was to reduce heavy metals content in wastewater and water polluted with heavy metals, and in the same time, to make use of seaweed that is currently a simply waste in Romania [3]. The FTIR analyses will complete the results obtained by SEM for microstructure characterization, as well as by SEM-EDX and ion beam techniques PIXE and PIGE for micro-composition and elemental distribution investigation in the paper and algal matrix [4].

2. MATERIALS AND METHODS

Samples of stranded seaweed of the opportunistic algal species *Ulva rigida* were collected from the Romanian part of Black Sea coast, in Constanta area [4]. They were washed with potable and demineralised water, dried in the open air, then ground to a particle size of 500 µ. This powder was introduced into the filter paper manufacturing process at laboratory level, at the company Ceprohart SA Brăila. The filter paper was obtained from hardwood and softwood pulp, from virgin fibres. The laboratory sheets were obtained using a RAPID KÖTHEN - Sheet Former, fast sheet dehydration and sheet former. The filter paper samples had different mass additions of seaweed, more specifically, 0.5, 1, 2, 4, and 8% [4].

All samples were investigated by ATR-FTIR spectroscopy technique at laboratory of INPOLDE international research network, Dunarea de Jos University of Galati (UDJG), Romania, using an a Bruker Tensor 27 FTIR spectrometer coupled with a diamond ATR device. The spectra were recorded in the 4000-400 cm^{-1} range as a mean of 32 scans and at a resolution of 4 cm^{-1}.

Fourier transform infrared spectroscopy - attenuated total reflectance (FTIR-ATR) is a method that helps in the identification of specific functional groups, as well as the chemical structure of polymeric materials. Using this method it is possible to obtain information on the presence or absence of these groups by following changes in the frequency of the absorption bands and changes in the intensity of the bands. Also, by using this method it is possible to determine changes in the chemical structure of the sample or changes in the environment around the sample [5]. FTIR-ATR spectroscopy can be used to identify the bioactive components of algae [6] and can also be used to determine the composition of different materials such as soils [7], fossil plants [8], and rocks [9].

Fig.1. The ATR-FTIR spectrometer at INPOLDE research center, UDJG

3. RESULTS AND DISCUSSIONS

The ATR-FTIR spectrum of the *Ulva rigida* seaweed sample is represented in Figure 2 and the spectra obtained for filter papers containing seaweed in different concentrations and the control paper are depicted in Figure 3. The characteristic absorption infrared (IR) bands existent in spectra and their assignments are shown in Table 1.

Table 1. Characteristic absorption IR bands and their assignments for the *Ulva rigida*

No.	Wavenumber (cm^{-1})	Type of vibration of the chemical group [10,11,12,13]
1	3274	ν (O – H)
2	2918	ν (C – H)
3	1632	ν (C=O)
4	1416	ν (C – O – O)
5	1210	ν (S=O)
6	1032	ν (C – O – C)
7	845	ν (C – O – S)

ν – stretching vibration

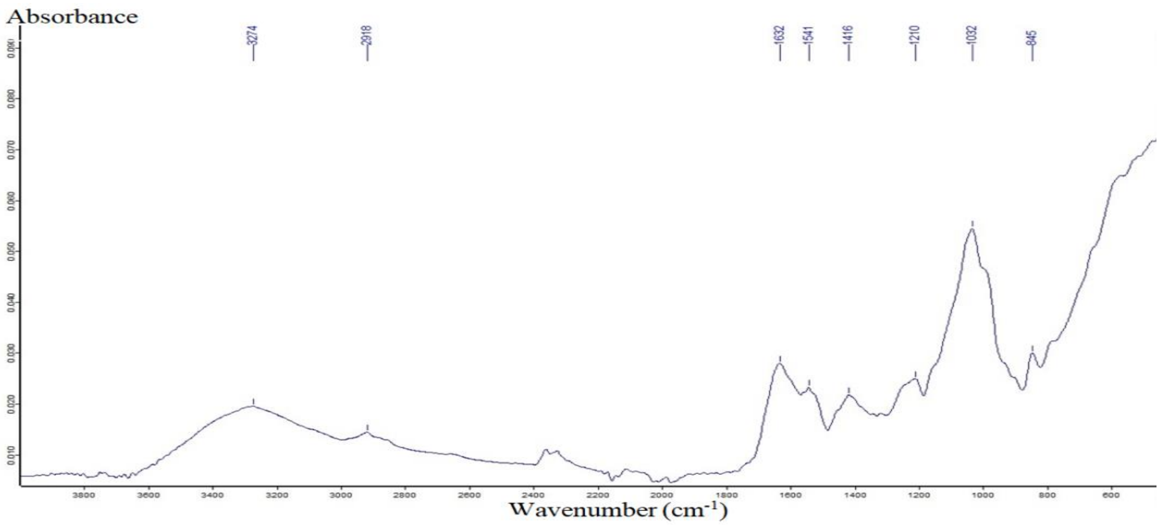

Fig. 2. The ATR-FTIR spectrum of Ulva rigida

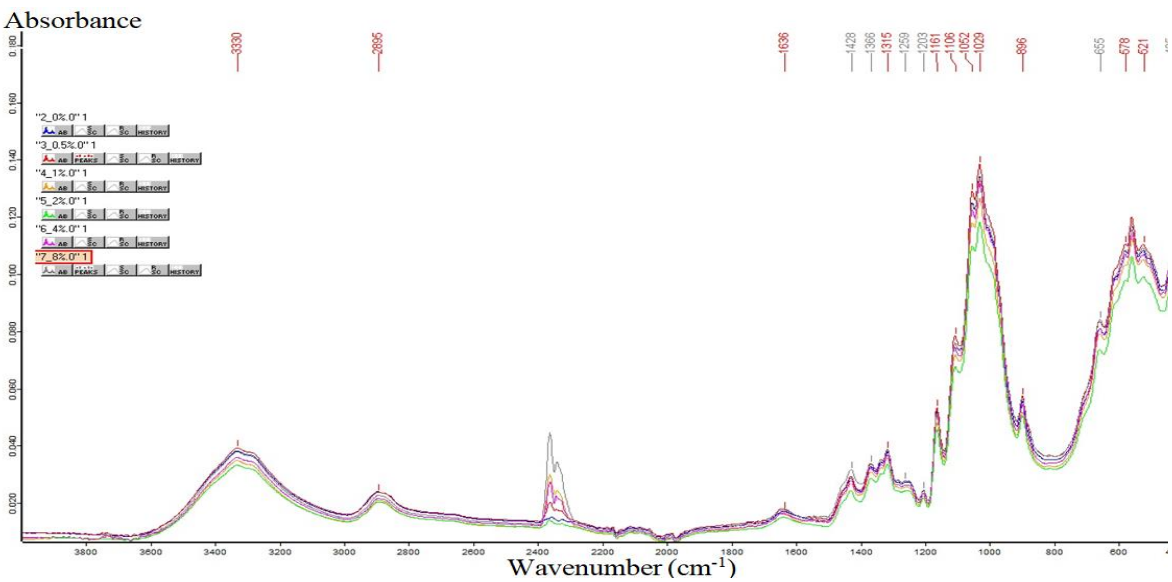

Fig. 3. ATR-FTIR spectra for the control filter paper sample (blue line) and the samples with addition of 0.5%, 1%, 2%, 4% and 8% Ulva rigida

The IR spectrum of *Ulva rigida* is comparable to the IR spectrum of the sulfated polysaccharides derived from marine algae [10]. The ATR-FTIR spectrum of the *Ulva rigida* (Fig.2) shows a broad absorption band at 3274 cm^{-1}, assigned to the stretching vibration of the O–H group present in the polysaccharide structure. The weak peak at 2918 cm^{-1} is related to the stretching vibration of the aliphatic C-H bond of the methyl group [11]. The 1632 cm^{-1} IR absorption band is assigned to the stretching vibration of the C=O chemical group and the 1416 cm^{-1} absorption band is attributed to the symmetric stretching vibration of the COOH group [11]. The sulfated nature of the polysaccharide is highlighted by the 1210 cm^{-1} absorption band which is assigned to stretching vibration of the S=O sulfate ester group and by the 845 cm^{-1} peak which is attributed to the C-O-S stretching vibration of sulfate group [12]. The 1032 cm^{-1} absorption peak is assigned to the stretching vibration of the C–O–C group [13].

Sulphated polysaccharides such as fucoidan and ulvan, which can be extracted from certain species of seaweed, are present both in algae spectrum and in the filter papers with algal addition (Fig.3).

4. CONCLUSIONS

Following the interpretation of the results, it can be observed in the ATF-FTIR spectrum belonging to the alga *Ulva rigida* the presence of the absorption bands belonging to the vibrational stretches of the O-H groups present in the polysaccharide structure, C-H bonds of the methyl group, and COOH groups, sulfate ester groups and C-O-C groups. It was found that there are no elements in the structure of the seaweeds analysed that make them unusable for wastewater filtration and contact with drinking water.

ACKNOWLEDGEMENTS

The work of the first authors (FCCF, AE) was financed by Dunarea de Jos University of Galati, through the internal grant with contract no. RF3621/30.09.2021.

REFERENCES

[1] Kumar, U. S., Ansari, Md. A., Greenspan, E., *Environmental Protection: Managing Fresh Water Resources*, Encyclopedia of Nuclear Energy, pp. 465-484, 2021.
[2] Thamarai S. M., Zahir H.A., An empirical analysis on the impact of metal contents on water quality, Materials Today: Proceedings, 59, 2, pp. 1349-1356, 2022.
[3] Caprita F.C., Ene A., Cantaragiu Ceoromila A., Valorification of *Ulva rigida* algae in pulp and paper industry for improved paper characteristics and wastewater heavy metal filtration, Sustainability, 13, 10763, 2021.
[4] Ene A., Caprita F.C., Pantelica A., Ceoromila A., Study of composition of seaweed of the genus Ulva and filter paper made with added algae by SEM-EDX, PIXE and PIGE, TIM 20-21 Physics Conference. AIP Conference Proceedings, 2022, in press.
[5] H.M.N. Iqbal, T.Keshavarz, *The challenge of biocompatibility evaluation of biocomposites*, in: Biomedical Composites (Editor - Ambrosio, L.), 2nd ed., Woodhead Publishing. pp. 303-334, 2017.
[6] Agatonovic-Kustri S., Ramenskaya G., Kustrin E., Ortakand D.B., Morton D.W., A new integrated HPTLC - ATR/FTIR approach in marine algae bioprofiling, Journal of Pharmaceutical and Biomedical Analysis,189, 113488, 2020.
[7] Moraru S.S., Ene A., Gosav S., Mineralogical composition assessment of soils from Covurlui and Braila plains by ATR-FTIR technique, Proceedings, 29, 80, 2019.
[8] Gosav S., Ene A., Aflori M., Characterization and discrimination of plant fossils by ATR-FTIR, XRD and chemometric methods, Romanian Journal of Physics, 64, 806, 2019.
[9] Mroczkowska-Szerszeń M., Orzechowski M., Infrared spectroscopy methods in reservoir rocks analysis, NAFTA-GAZ, 11, pp. 802-812, 2018.
[10] Aguilar-Briseno J.A., Cruz-Suarez L.E., Sassi J.F., Ricque-Marie D., Zapata-Benavides P., Mendoza Gamboa E., Rodriguez-Padilla C., Trejo-Avila L.M., Sulphated polysaccharides from Ulva clathrata and Cladosiphon okamuranus seaweeds both inhibit viral attachment entry and cell-cell fusion, in NDV infection, Marine Drugs, 13(2), pp. 697-712, 2015.
[11] Ibrahim M.I.A., Amer M.S., Ibrahim H.A.H., Zaghloul E.H., Considerable production of Ulvan from *Ulva lactuca* with special emphasis on its antimicrobial and anti-fouling properties, Applied Biochemistry and Biotechnology, 194, pp. 3097-3118, 2022.
[12] Castro R., Piazzon M.C., Zarra I., Leiro J., Noya M.,Lamas J., Stimulation of turbot phagocytes by *Ulva rigida* C. Agardh polysaccharides, Aquaculture, 254, pp. 9-20, 2006.
[13] Tian H., Yin X., Zeng Q., Zhu L., Chen J., Isolation, structure and surfactant properties of polysaccharides from *Ulva lactuca* L, from South China Sea, International Journal of Biological Macromolecules, 79, pp. 1-25, 2015.