IOSUD - „DUNĂREA DE JOS” UNIVERSITY OF GALAȚI
Doctoral School of Mechanical and Industrial Engineering

DOCTORAL THESIS

ABSTRACT

The use of marine algae to remove pollutants from industrial wastewater

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The use of marine algae to remove pollutants from industrial wastewater

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"Without school, let no one expect good parents or good sons, and therefore no well-organized and well-governed and well-kept state." (Ion Heliade Rădulescu)

Education will always remain one of the most important aspects of a society and a person's calling card, although, beyond the diplomas that a person can be proud of, it is values such as common sense, respect, integrity, wisdom, generosity, empathy, trust and love that matter most.

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Brăila, April 14th 2023 Florina-Cristiana Căpriță (Filote)

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INTRODUCTION

Since ancient times, society has found itself in a continuous and sustained development but not always the activities that man has carried out have been in accordance with the principles of environmental protection [Liton, C.V., and Tasmin, S., 2022], which can take the form of judicious consumption of resources or rational and efficient exploitation of natural resources and environmental factors [Mahmood, H., et al., 2020], [Nathaniel, S., and Khan, S. A. R., 2020]. One of the most affected resources by the development of society is water, as it is produced through two directions. Firstly through the fact that there is no judicious consumption of water, but rather excessive consumption and the fact that a very large volume of waste water, polluted, is generated as a result of consumption [Wang, Y., et al., 2022]. Water is considered to be an inexhaustible resource, but given the fact that even after treatment it does not return to its original quality, it is an exhaustible resource [Căpriță, F., et al., 2022], especially if it is not treated after use and if its properties and chemical composition are altered by adding elements or substances that disturb its balance. Industrial waste water from various uses requires initial treatment before discharge into the sewerage system. This treatment at source uses processes adapted to the nature of the pollutants, their volume and concentration and the degree of reduction and elimination of the pollutants. The technologies and techniques currently used are outdated, have low efficiency in some cases, in the form of disadvantages related to high energy consumption, reduced removal in the case of polluted water with high concentrations or complex pollutants [Căpriță, F.C., and Ene, A., 2019], [Rojanschi, V., and Ognean, T., 1989].

Motivation for the choice of research topic

Environmental pollution is a globally debated topic and in its general form it encompasses ideas, discussions and research on different topics such as soil pollution, waste generation, waste water generation, various pollutant emissions in the form of dust or gases. Researchers who have understood the urgent need to research and discover new solutions have contributed intensively through complex studies to identify various methods of treating soil, reducing the volumes of waste generated and recovering them, new technologies for purifying and treating waste water and stopping the emission of dust or various gaseous compounds. All these contributions, through the wealth of published research, through studies to improve existing technologies or develop new advanced technologies, and through examples of technology transfer, are building, step by step, a better future for all mankind.

The present doctoral thesis, entitled: "The use of marine algae for the removal of pollutants from industrial wastewater", whose main objective is the theoretical and practical research on the use of marine algae found in the Black Sea, on the territory of our country, by using them as biomaterial for the removal of pollutants from industrial wastewater, was born and conceived out of the desire to contribute to the identification of new directions of waste recovery.

General objectives of this PhD thesis are the following:

1. Literature review on the directions of seaweed valorification already identified so far worldwide;
2. Identification of seaweed species found in the Black Sea in Romania;
3. Analysis and selection of the most environmentally advantageous exploitation

direction;

4. Investigation of the properties of seaweeds involved in the reduction of some metal pollutants;
5. Identify the sources of wastewater generation requiring treatment that would be compatible with the property of algae to adsorb certain pollutants;
6. Elemental and microstructural analysis of seaweed samples of Ulva rigida species by SEM-EDX, ATR-FTIR, PIXE, PIGE techniques.
7. Integration of algal biomass waste into filter paper mass with the aim of manufacturing a product to be used in the process of reducing concentrations of some pollutants.
8. Evaluation of the strength characteristics of filter paper samples with added seaweed mass;
9. Determination of micro, macro and trace element concentrations in algae samples, and in filter papers with different seaweed mass additions, by advanced complementary spectroscopic and nuclear methods (PIXE, PIGE);
10. Determination and assessment of the metal removal capacity of some metals from industrial wastewater samples by seaweed and by laboratory produced filter papers with seaweed additions.

The present work, by means of the research topic it addresses, will contribute to the reuse of waste, to the production of a product aimed at reducing some pollutants in wastewater, by means of the results obtained in relation to the elemental composition of the seaweed species studied, as well as by describing in great detail the manufacturing steps of the filter paper with the addition of seaweed, describing the resistance characteristics of this new product and the degree of retention of the pollutants analysed.

At the same time, the present work can represent the foundation of a new direction of seaweed valorisation on the Romanian territory, by the birth of a new product.

This work was carried out in several stages, the first stage being the study of the literature initially on the species of seaweed identified so far in the Black Sea, on the territory of Romania and the study of the directions of recovery of seaweed waste known worldwide, followed by the training course carried out at the Institute of Marine "Grigore Antipa" in Constanta, the field stage of collecting seaweed samples, the stage of carrying out the first laboratory analyses and obtaining filter papers, the stage of analysis and processing of the research results, experimental data, the stage of dissemination of the results and the last stage is the writing of this PhD thesis.

The sampling phase took place during the summer periods from 2018-2022 and consisted of field trips to Constanta County for algae sampling. Seaweed samples were collected between June and September, a period when mainly opportunistic and prophylactic seaweed species sometimes grow uncontrolled.

During the laboratory phase, two further phases were identified, which were the sample preparation and treatment phase and the analytical phase for the identification of seaweed elements and verification of treatment methods, applied to wastewater samples.

Seaweed samples, wastewater samples, and samples that represented samples of filter paper with added seaweed mass produced at laboratory level were prepared for analysis at the INPOLDE Research Centre at UDJG. Samples of filter paper with added seaweed were analysed by applying physico-mechanical methods in order to determine the main physico-mechanical parameters of strength, with the aim of determining the quality of the paper and the influence of the added algal biomass, these analyses were carried out in the RENAR accredited Physical-Mechanical Testing Laboratory of CEPROHART S.A., Brăila. On seaweed samples as well as on filter paper samples with different seaweed mass additions, analyses were performed by advanced complementary analytical methods, such as scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), a method applied in the Electron Microscopy Laboratory of the Faculty of Science and Environment - UDJG, nuclear analysis techniques (PIGE and PIXE), applied at the "Horia Hulubei" National Institute of Physics and Nuclear Engineering (IFIN-HH) in Măgurele, and Fourier transform and attenuated total reflection infrared spectroscopy (ATR-FTIR), carried out at the INPOLDE-UDJG Research Centre laboratory. The application of advanced analytical methods was aimed at identifying the concentrations of elements found in the samples as well as investigating their microstructure.

Novel aspects and original contributions

The present PhD work entitled *"The use of marine algae for the removal of pollutants from industrial wastewater"* brings its contribution to the scientific sphere by presenting a new direction for the valorisation of marine algae, which has not been experimented before in Romania. Thus, it represents the first comprehensive scientific contribution on the strength characteristics of a paper with added seaweed mass. The thesis presents results on the elemental composition of the algae, as well as experiments on the reduction of some pollutants in wastewater. The studied topic provides solutions for two different environmental problems, thus identifying a use for seaweed waste that is currently not recovered and solving the problem of reducing pollutants in industrial wastewater.

Another argument in support of the novelty aspect of this work is the use of complementary advanced instrumental analysis techniques, such as spectrometric, atomic and nuclear techniques, which aim at multi-elemental varied analysis of algal and paper samples. These advanced techniques, being of high sensitivity, allowed the identification of elements that were found in the structure of the samples in different concentrations.

II PERSONAL CONTRIBUTIONS

2. RESEARCH MATERIALS AND METHODS USED IN THE EXPERIMENTAL STUDIES

2.1. Materials used during the practical research

The aim of the present work was to identify directions for the recovery of seaweed found on the Romanian territory of the Black Sea and which are not exploited, becoming simple waste. Knowing that algae have an affinity for metals and analyzing the data on metal pollution of water sources, together with the need for displacement of virgin fibre pulp from the pulp and paper industry, the direction to be presented was outlined, namely, the manufacture at laboratory level of filter papers with the addition of seaweed, with the help of which samples of waste water from the metallurgical industry were filtered, in which various metals were identified. Several materials were used in the present research work; first of all several species of seaweed were used, for which the removal capacity of some metals was analysed. Another material used was the wastewater source for which the concentrations of metals found in it were determined and the cellulose used as raw material for the manufacture of filter papers, in the mass of which various seaweed additions were immobilised in the form of powder. After the filter papers were manufactured at laboratory level, they were analysed to determine the removal/retention capacity of the studied metals.

2.1.1. Marine algae sampling

Following the analysis of the documentary sources and the scientific information collected during the documentary study, the seaweed sampling points, the species that can be found in the chosen points, the sampling interval and the identification of the wastewater sources that can be collected and used in the work were determined.

Figure 2.1. Location of macrophyte seaweed sampling points: the 4 sampling areas, Constanta Casino area, Aloha Beach; Reyna Beach and Pupa Beach (source: processing after Google Earth Pro)

2.1.2. Waste water sampling

The wastewater samples obtained and analysed in the experimental research belonged to a private company, which was active in the production of ferrous materials in primary and semi-finished forms and in the processing of metallic materials. The wastewater samples were taken directly from the generating source before entering the decanter and did not undergo any further treatment. This company uses drinking water in various technological processes and treats it by passing it through a decanter before discharging it into the municipal sewage system. [Căpriță, F.C., et al., 2021].

(a) (b) (c)

Figure 2.5. Wastewater sample from the metallurgical industry immediately after sampling (a); wastewater sample after settling (b); wastewater sample used in experiments (c), [Căpriță, F.C., et al., 2021].

2.1.3. Pulp samples from virgin fibre, softwood and hardwood sources

The pulp used was purchased directly from the producing factories that guarantee the quality of the products. The pulps used to make the filter paper samples are softwood pulp, also known as long fibre pulp, and hardwood pulp, also known as short fibre pulp. The two celluloses have been used as raw material together with mossy seaweed to obtain laboratory filter paper sheets with added *Ulva rigida* seaweed [Căpriță, F.C., et al., 2021].

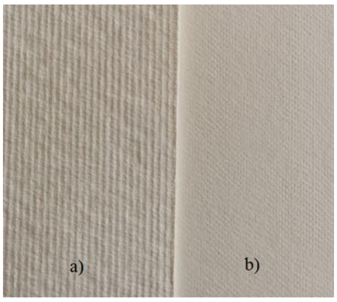


Figure 2.6. Bleached softwood kraft (BSK) (a); Bleached hardwood kraft (BHK) (b) [Căpriță, F.C., et al., 2021].

2.2. Sample preparation methods at laboratory level for the development of new products

Ulva rigida seaweed has been inserted into a filter paper because this way a filter paper can be obtained which can be used for the separation of solid and liquid parts and at the same time various pollutants can be removed by adsorption by the seaweed in the paper structure. Filter paper is a type of porous paper designed for use in the filtration of liquids and solutions. It is used to separate solid particles from liquids or to separate soluble substances from solutions. The processing of the material consisted of washing the sampled algae, initially with seawater, then with drinking water and demineralised water, dried (Figure 2.8. a-c) in the open air at a temperature of 28˚C for 6 hours and ground using a ceramic pistil mill (Figure 2.8. d) to a fine powder, (Figure 2.8. e), which was subjected to on-site dry classification. The selected material was the one with a particle size of 500 µ for an optimal surface-to-volume ratio. The processed material was then introduced into the papermaking process at laboratory level in the Fibrous Pulp Preparation and Chemical Additives Dosing Laboratory of Ceprohart SA Brăila [Căpriță, F.C., et al., 2021].

(a) (b) (c) (d) (e)

Figure 2.8. Seaweed samples collected from the Romanian Black Sea littoral and processing stages: Sample of seaweed size 20 cm long (a); Drying in the open air (b); Dried seaweed samples (c); Wetting stage with pistil mill (d); Seaweed powder obtained (e) [Căpriță, F.C., et al., 2021].

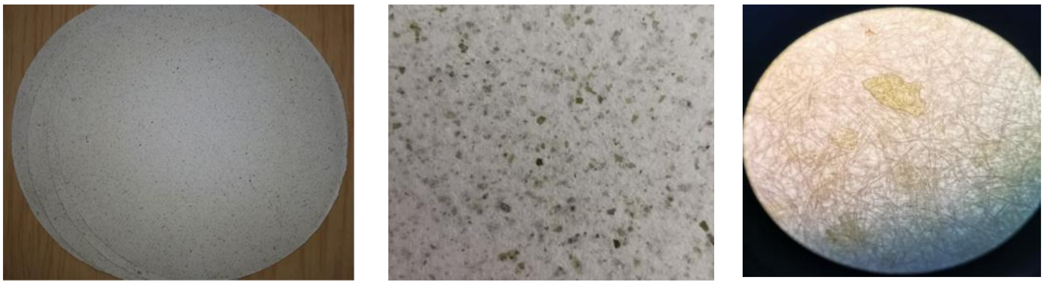
2.2.1. Technical stages and equipment used for papermaking

In order to obtain laboratory-level samples of filter paper with mass addition of seaweed, it was necessary to go through several specific steps in a dedicated laboratory. Sample preparation was carried out at Ceprohart SA Brăila, Romania, in the "Laboratory for fibrous pulp preparation and dosing of chemical additives". First, the pulps presented in section 2.1.3 were ground. The method of grinding the pulp in the laboratory was carried out using the Valley Hollander beater (Figure 2.9).

Figure 2.9. Valley beater hollander machine for pulp grinding at laboratory level (source: Căpriță, F.C., Fiber Pulp Preparation Laboratory -Ceprohart SA Brăila)

After the celluloses were prepared by grinding to the known SR grades and the working recipes were established, the homogenizer was used to dose the two types of cellulose and seaweed. The Rapid-Köthen machine [Căpriță, F.C., et al., 2021] is used to form and dry the paper sheets at laboratory level.

Figure 2.14. Rapid Köthen trainer (source: Căpriță, F.C., Fiber Paste Preparation Laboratory -Ceprohart SA Brăila)



(a) (b) (c)

Figure 2.16. Laboratory sheet of filter paper with the addition of 8% algae of the species Ulva rigida, Ø 20 cm (a); Appearance of filter paper with 8%, enlarged image (b); Incorporation of algae in the structure of the paper, sequestration of algae particles by cellulose fibres, enlarged image, magnitude 50x (c); [Căpriță, F.C., et al., 2021]

The algae were homogeneously distributed throughout the paper mass (Figure 2.16 a), there were no clumps or areas where they were not distributed (Figure 2.16 b) and after the drying step the algae dried without any drying variations. They were incorporated into the paper mass, being sequestered by the cellulose fibres (Figure 2.16 a-c).

2.3. Methods of analysis used in practical research

Seaweed samples and filter papers with seaweed addition were subjected to spectrometric and spectroscopic analysis by applying advanced methods: SEM-EDX technique for elemental and structural identification, ATR-FTIR technique for chemical structure identification and PIXE, PIGE accelerated ion beam nuclear techniques for elemental identification. Seaweed-added filter paper samples were also analysed from a physico-mechanical point of view to determine strength properties. Waste, treated and filtered water samples were analysed using the UV-VIS spectrophotometric technique.

2.3.1. Advanced spectrometric methods

- Elemental and microstructural analysis by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDX)

For the elemental, microstructural and morphological determination of the surface of the seaweed samples as well as of the filter paper with seaweed added in mass, the SEM-EDX analysis technique was applied, carried out in the Electron Microscopy Laboratory of the Faculty of Science and Environment - UDJG. The Scanning Electron Microscopy (SEM) method, coupled with Energy Dispersive X-Ray Spectrometry (EDX), is a very well known and widely used method, due to the multitude of types of materials that can be analyzed, due to the ease of sample preparation, and the very detailed results that are obtained from its application, being a qualitative and quantitative technique [Ene, A., 2006], [Pirozzi, N.M., et al., 2021], [Gupta, S., et al., 2022], [Gniadek, M., and Dąbrowska, A., 2019].

Algae and filter paper samples were analyzed using the FEI QUANTA 200 model SEM microscope (Thermo Fisher Scientific, USA) (Figure 2.17.). For all investigations, a beam accelerating voltage of 10 kV and a secondary electron (SE) signal was used to excite as many elements as possible. The samples were mounted on an aluminum support via conductive carbon tape. Elemental distribution determination was performed by the EDX microanalysis technique developed at the INPOLDE research center of UDJG [Ene, A., et al., 2013], [Ignatenko, O.V., et al., 2013], [Căpriță, F.C., et al., 2021], using a solid-state Si(Li) detector coupled to SEM. The ZAF matrix correction algorithm (Z=atomic number, A=absorption, F=fluorescence) was used to convert apparent concentrations (net spectral intensity) into (semi-quantitative) concentrations corrected for the interelement effect [Ene, A., et al., 2013]. The results have a local character, since a microarea of about 1 mm^2 was analyzed, and not the whole sample area [Căpriță, F.C., et al., 2021].

Figure 2.17. Scanning Electron Microscope (SEM) (source: Căpriță, F.C., Electron Microscopy Laboratory, Faculty of Science and Environment - UDJG)

- Chemical structure determination using Attenuated Total Reflection Fourier Transform Infrared Spectrometry (ATR-FTIR)

The Fourier transform infrared spectrometry technique was used for this determination, which is increasingly widespread and used in the study of organic and inorganic materials due to its speed in obtaining qualitative results.
The samples were investigated by the ATR-FTIR spectroscopy technique, using the Bruker Tensor 27 FTIR spectrometer coupled with a diamond ATR device (Figure 2.18.) at the INPOLDE-UDJG Research Center Laboratory [Praisler, M., et al., 2015]. The spectrum were recorded in the range 4000-400 cm^{-1} as an average of 32 scans at a resolution of 4 cm^{-1}. The attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) method helps to identify specific functional groups and the chemical structure of complex materials [Căpriță, F.C., et al., 2022].

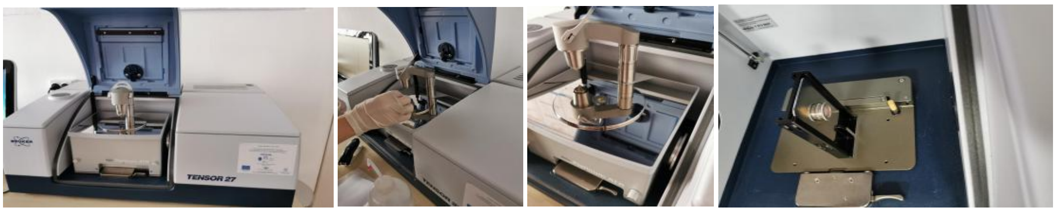
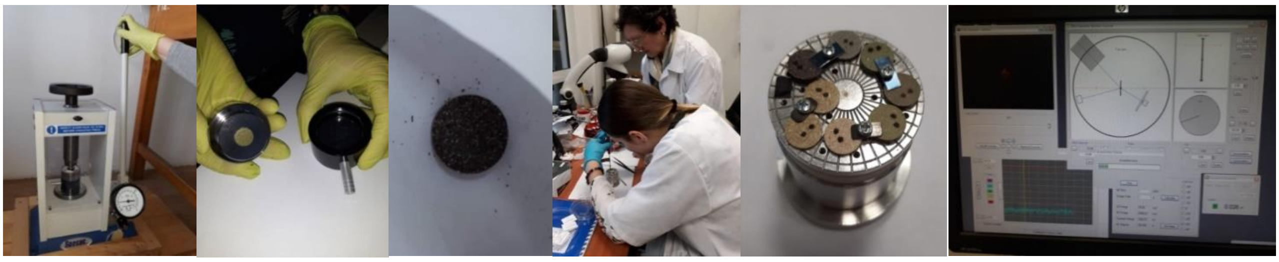


Figure 2.18. Bruker Tensor 27 FTIR spectrometer, coupled with diamond crystal ATR device [Căpriță, F.C., et al., 2022]

- Elemental analysis of samples by Gamma (PIGE) and X-ray Emission (PIXE) of charged particles

Accelerated Ion Beam Analysis (IBA) nuclear techniques have been used for the elemental determination of algal samples and some filter paper samples with mass added seaweed. This technique involves bombarding a sample with a beam of charged particles (e.g. protons, deuterons or heavy ions) to produce characteristic X-rays emitted by atoms in the sample [Ene, A., et al., 2006]. PIXE spectroscopy can be used to detect elements present in samples with high precision and very low detection limits (trace analysis) and to determine the distribution of elements in a sample [Ene, A., and Pantelică, A., 2011].



(a) (b) (c) (d) (e) (f)

Figure 2.21. Images during sample preparation for PIGE-PIXE analysis: Atlas Specac hydraulic press (a), Sample of seaweed pellet sample, genus Ulva, wetted (b) and (c); Images during the fixation of pellets on the target device for vacuum dosing (d); Device for fixation of solid samples for vacuum dosing with various samples (e); Peripheral equipment showing the running of the program allowing the beam trajectory setting and calibration (f). (source: Căpriță, F.C., IFIN-HH Măgurele Laboratory)

For the analysis of seaweed and filter paper samples with mass addition of *Ulva rigida* seaweed, the PIXE and PIGE techniques were used simultaneously, which consist of irradiating the samples in a multi-target reaction chamber with a 3 MV proton beam in vacuum for multi-element analysis of seaweed samples, the PIXE technique with external beam was additionally used. The experimental set-up includes two different detectors, one is a 20 mm^2, 8 mm thick Ortec HPGe detector for PIXE analysis in vacuum and the other is an Ortec HPGe GEM10PA-70 detector for PIGE analysis. The latter has a resolution of 1.75 keV at 1332 keV (^{60}Co) and a detection capability of 10% of the total number of incident particles. The two detectors were placed at an angle of 45° to the beam propagation direction and the sample surface. Additionally, a PIXE method was used which involved the use of an external beam [Ene, A., et al., 2019a] and an X-123 SDD Fast Amptek silicon detector. The detector has a resolving power of 140 keV at 5.9 keV, an effective area of 25 mm^2 and a thickness of 500 μm. Seaweed samples belonging to the genus Ulva were finely ground and homogenised and then pressed using an Atlas Specac hydraulic press (Figure 2.21. a) to obtain pellets (Figure 2.21. b and c), which were positioned by fixation on the target device (Figure 2.21. d and e) and then placed inside the reaction chamber on a support to perform accurate measurements in the absence of gas under vacuum conditions. In the external beam PIXE method, the samples are placed on a long thin support, called a ruler, which is placed perpendicular to the beam direction.

2.3.3. Physical-mechanical methods

The physical-mechanical tests used to determine the characteristics of the filter papers with seaweed mass addition were carried out in the "Physical-mechanical testing laboratory for pulp, paper and cardboard" accredited by the Romanian Accreditation Association (RENAR) of Ceprohart S.A. Brăila. Using the equipment from the laboratory, it was possible to determine structural characteristics of the samples, such as grammage, thickness, density, air permeability, by Gurley method, determination of smoothness, Bekk method and residue (ash content), mechanical strength characteristics, by determination of breaking strength, breaking length, tear strength by the Elmendorf method, crushing strength and bending strength, and absorption characteristics by determination of water absorption capacity, $Cobb_{60}$ method , and by determination of moisture content.

Figure 2.24.

Figure 2.25.

Figure 2.26.

Figure 2.27.

Figure 2.28.

Figure 2.29.

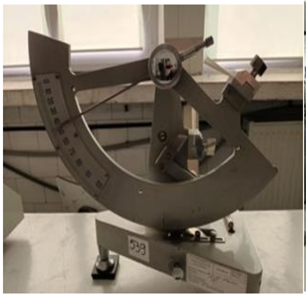


Figure 2.30.

Figure 2.31.

Figure 2.32.

Figure 2.33.

Figure 2.34.

Figure 2.24. Analytical balance type RADWAG AS 220.R2
Figure 2.25. Automatic micrometer TNB 1-A
Figure 2.26. GURLEY-Lorentzen & Wettre permeability tester type 4-1
Figure 2.27. Bekk smoothness tester
Figure 2.28. Oven for ash content determination
Figure 2.29. INSTRON 4411 dynamometer
Figure 2.30. Equipment for tearing strength determination
Figure 2.31. Frank apparatus - Bursting Strength Tester 18530 F000
Figure 2.32. Apparatus for determining the bending strength (double bending) Schopper
Figure 2.33. COBB OS absorption determination equipment
Figure 2.34. Memmert oven
(source of figures 2.24.-2.34.: Căpriță, F.C., Physical and Mechanical Testing Laboratory for Paper and Cardboard, RENAR Accredited, Ceprohart SA Brăila)

2.4. Partial conclusions

The particularities of SEM-EDX and ATR-FTIR analysis techniques for characterizing the mineralogical composition of seaweed samples and filter papers with added seaweed by mass were presented. The SEM-EDX technique allows the identification of micro and macro elements, the SEM method allows the structural, micromorphological analysis of the samples, while the EDX method allows semi-quantitative results to be obtained on the concentration of elements found in the samples under investigation. The ATR-FTIR technique allows the identification of functional groups that are characteristic of the minerals that will be found in the samples. The PIXE and PIGE nuclear techniques can be used to detect the presence of both light and heavy elements. By following the steps of paper manufacturing at laboratory level, filter papers with added seaweed can be obtained, which will be analysed in a RENAR accredited laboratory to determine the quality of the product obtained, and by spectroscopic techniques, the retention characteristics of the pollutants studied by the newly obtained product will be highlighted.

3. Research results of the analysis of the removal capacity of heavy metal pollutants by marine macroalgae used in various applications

The first step of the research was the evaluation of the materials used, the structural and elemental analysis and the analysis of the characteristics of the newly obtained material, and then the testing of the material for the adsorption capacity of the analysed pollutants. The results were disseminated through publication in articles.

3.1. Morphological and elemental characterisation of filter paper with added macrophyte seaweed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX)

With the SEM technique, microstructural changes during the incorporation and homogenization process of Ulva rigida seaweed in filter paper could be evaluated. The imaging results (Figure 3.1.) showed an optimal level of absorption depending on the content of algae added to the paper samples.

In the first part of the study, the algal powder sample obtained by dewatering and wetting was subjected to an imaging evaluation. Figure 3.1. (a) shows the microscopic images of small-sized particles of Ulva rigida algae, their structure and surface showing an irregular polygonal shape, with an average size of about 500 µm. A regular cell arrangement was observed on the particle surface, oval-shaped, densely packed cells with a microstructure similar to that of industrial foams. The sample does not show impurities in the form of sand particles, simply washing the sample with water is sufficient.

From the SEM image of the control sample (Figure 3.1.b), consisting of filter paper without added seaweed, a dense network of randomly arranged cellulose fibres could be observed. This dense network characterises the material as one with high mechanical strength and a certain microporosity.

The introduction of macrophyte particles into the sample mass consisting of filter paper changes the distribution of the fibrillar network structures. For the SEM micrographs in Figure 3.1. c-g, as the macroalgae content in the paper matrix increased from a concentration of 0.5 % to 8 %, a different arrangement of cellulose fibres was observed and the space that the algae particles occupied was observed, with the cellulose fibres that created the fibre network also incorporating the algae particles. The incorporation of algal particles was visible as dark grey polygonal plates (small pieces or aggregates) among the fibres and were outlined by yellow lines on each image for easier observation.

Based on the SEM images, it can be concluded that the materials tested presented an optimal level of incorporation of algae particles depending on their concentration, as well as a heterogeneous surface. Thus, the particles are uniformly distributed without creating agglomerations in the paper network, which indicates a high efficiency of the homogenization process. Moreover, increasing the amount of algae particles to 4% and 8% led to the formation of denser regions in algae particles (Figure 3.1. f and g), without destroying the fiber network. However, an important aspect that has attracted attention is how the algal particles and cellulose fibers interact at different stages of the synthesis process. And in the case of the addition of 8% seaweed, no significant improvements in the mechanical strength of the final material were observed along the way. This pattern of interaction confirms that the two phases do not interact in a synergistic way to form a stronger material but, on the contrary, weakens the mechanical strength, without any indication of voids in the material, even if the algae particles behave as a filler, compacting the paper structure [Căpriță, F.C., et al., 2021].

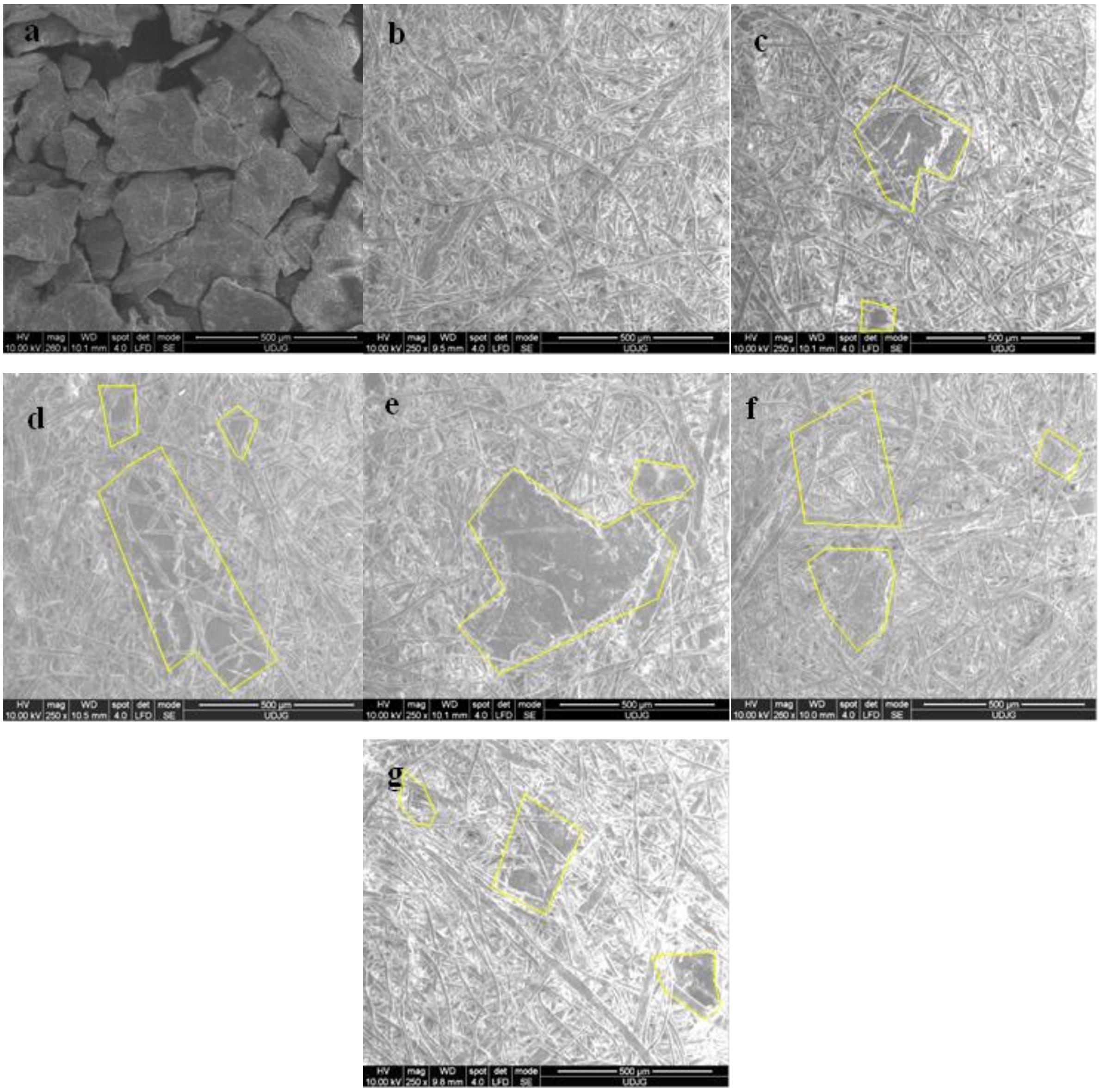


Figure 3.1. SEM images of Ulva rigida algae (a), filter paper (P0) (b), filter paper + 0.5% algae (P1) (c), filter paper + 1% algae (P2) (d), filter paper + 2% algae (P3) (e), filter paper + 4% algae (P4) (f) and filter paper + 8% algae (P5) (g) [Căpriță, F.C., et al., 2021].

Chemical microanalysis of the analysed samples consisting of seaweed, genus Ulva, and filter papers with seaweed added in mass, was performed by EDX method, and the quantitative results are presented in Table 3.1. Following the application of the method, 18 elements were identified, detected at different concentration levels. Sample P0, which consists of the filter paper control sample, does not contain seaweed, which is why the only elements present and identified are C and O. The other samples, P1, P2, P3, P4 and P5 present more elements; in particular, in higher quantities, after C and O, it was possible to identify N, S and Ca, followed by concentrations of Mg, Cu and Zn.

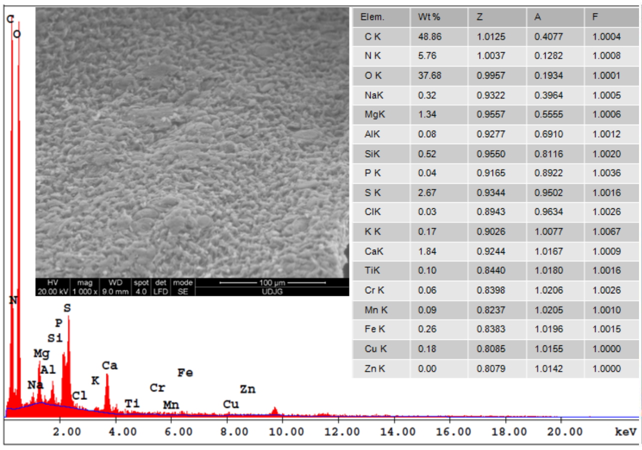
Table 3.1. *Quantitative SEM-EDX results for the chemical composition of materials synthesized from filter paper and seaweed [Căpriță, F.C., et al., 2021]*

Element	**Concentration (wt.%)**						
	Algae	**P0**	**P1**	**P2**	**P3**	**P4**	**P5**
C	48.86	60.42	55.81	56.34	57.03	56.80	54.62
N	5.76		2.50	3.05	2.41	2.63	3.01
O	37.68	39.58	32.43	32.98	35.04	34.65	33.40
Na	0.32		0.13	0.18	0.17	0.29	0.13
Mg	1.34		0.63	0.63	0.38	0.50	0.60
Al	0.08		0.00	0.12	0.12	0.14	0.08
Si	0.52		0.10	0.21	0.07	0.08	0.15
P	0.04		0.31	0.25	0.13	0.24	0.32
S	2.67		2.58	2.43	2.18	1.89	2.50
Cl	0.03		0.06	0.15	0.00	0.00	0.10
K	0.17		0.00	0.00	0.00	0.00	0.19
Ca	1.84		3.23	2.65	2.07	1.67	2.71
Ti	0.10		0.12	0.00	0.00	0.00	0.12
Cr	0.06		0.14	0.00	0.00	0.00	0.11
Mn	0.09		0.23	0.00	0.00	0.00	0.27
Fe	0.26		0.40	0.13	0.13	0.16	0.44
Cu	0.18		0.79	0.36	0.00	0.52	0.47
Zn	0.00		0.56	0.54	0.27	0.42	0.79

Quantitative analysis of the paper-algae system showed that in addition to C and O (H cannot be identified) as basic elements in paper, other major components, namely minerals and metals, are also present. Therefore, the amount of inorganic constituents was determined as follows: macroelements (N, P, K), mesoelements (Ca, Mg and S) and microelements (Na, Si, Al, Cl and Ti). First, N (in concentration of 2.41-3.05%) was observed at a higher level and S (1.89-2.58%) at a medium level. The presence of N and P nutrients suggests *Ulva rigida* as a factor for algal biomass production. Secondly, Na (0.13-0.29%), Si (0.07-0.21%) and Al (0.00-0.14%) can be bioaccumulated by *Ulva rigida* at trace levels.

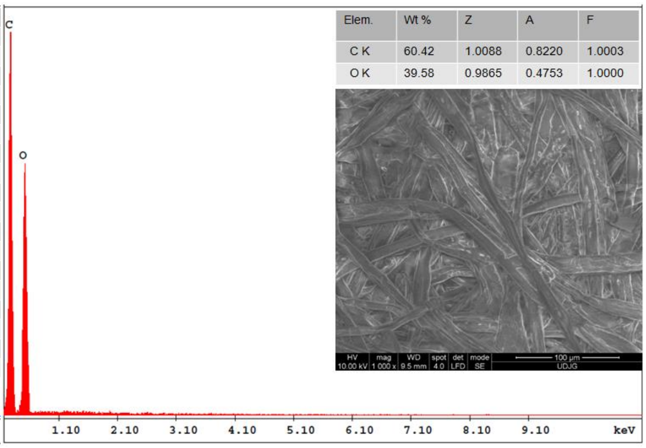
The amount of each cation (K, Na, Mg and Ca) showed the same trend of variation according to the added algae content. For all samples, Ca concentration was higher than Mg concentration. The data obtained show a difference between the concentration of elements with increasing algae content, which is also confirmed by the results on ash content in Table 3.12 [Căpriță, F.C., et al., 2021].

In addition, phosphate, nitrogen, nitrite compounds, being essential for photosynthesis, and silicon oxides in the siliceous skeleton of diatoms can be identified. By bioaccumulation, as a spontaneous process occurring in saline water, some metallic elements have been found, in different percentage concentrations, such as Zn (0.27-0.79%), Cu (0.00-0.79%), Fe (0.13-0.44%), Mn (0.00-0.27%) and Cr (0.00-0.14%), in decreasing sequence of their concentration. This may demonstrate an optimal integration process of metal ions through the cellular network of biomass. *Ulva rigida* enriched with Zn and Cu ions (maximum content of 0.79%) showed their distribution as aggregates on the macroalgal surface. The reduction of Ca, Na and K ions concentration induced the exchange of metal ions with Zn and Cu during the biosorption process [Căpriță, F.C., et al., 2021].



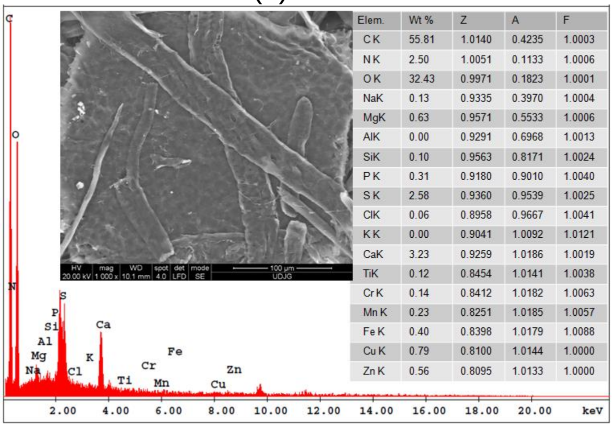
Elem.	Wt %	Z	A	F
C K	48.86	1.0125	0.4077	1.0004
N K	5.76	1.0037	0.1282	1.0008
O K	37.68	0.9957	0.1934	1.0001
NaK	0.32	0.9322	0.3964	1.0005
MgK	1.34	0.9557	0.5555	1.0006
AlK	0.08	0.9277	0.6910	1.0012
SiK	0.52	0.9550	0.8116	1.0020
P K	0.04	0.9165	0.8922	1.0036
S K	2.67	0.9344	0.9502	1.0016
ClK	0.03	0.8943	0.9634	1.0026
K K	0.17	0.9026	1.0077	1.0067
CaK	1.84	0.9244	1.0167	1.0009
TiK	0.10	0.8440	1.0180	1.0016
Cr K	0.06	0.8398	1.0206	1.0026
Mn K	0.09	0.8237	1.0205	1.0010
Fe K	0.26	0.8383	1.0196	1.0015
Cu K	0.18	0.8085	1.0155	1.0000
Zn K	0.00	0.8079	1.0142	1.0000

(a)



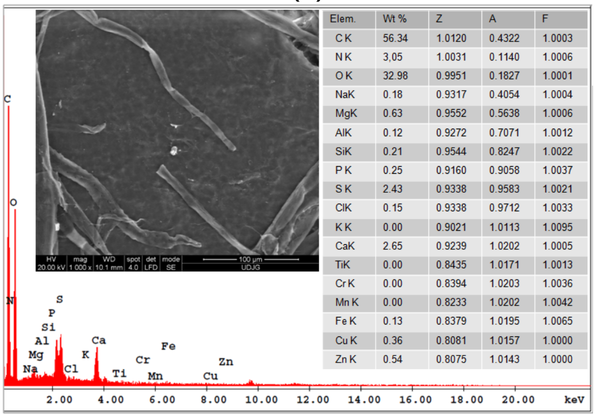
Elem.	Wt %	Z	A	F
C K	60.42	1.0088	0.8220	1.0003
O K	39.58	0.9865	0.4753	1.0000

(b)



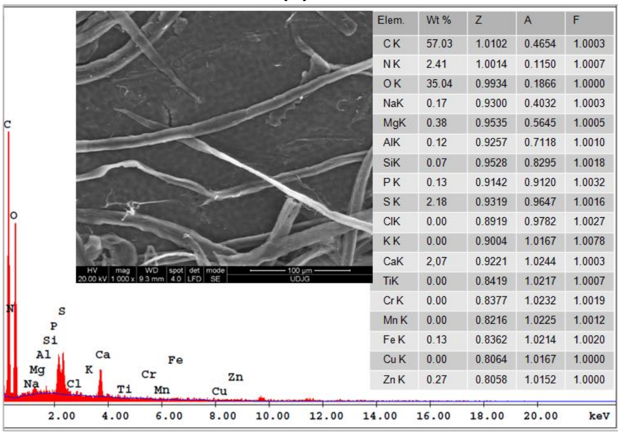
Elem.	Wt %	Z	A	F
C K	55.81	1.0140	0.4235	1.0003
N K	2.50	1.0051	0.1133	1.0006
O K	32.43	0.9971	0.1823	1.0001
NaK	0.13	0.9335	0.3970	1.0004
MgK	0.63	0.9571	0.5533	1.0006
AlK	0.00	0.9291	0.6968	1.0013
SiK	0.10	0.9563	0.8171	1.0024
P K	0.31	0.9180	0.9010	1.0040
S K	2.58	0.9360	0.9539	1.0025
ClK	0.06	0.8958	0.9667	1.0041
K K	0.00	0.9041	1.0092	1.0121
CaK	3.23	0.9259	1.0186	1.0019
TiK	0.12	0.8454	1.0141	1.0038
Cr K	0.14	0.8412	1.0182	1.0063
Mn K	0.23	0.8251	1.0185	1.0057
Fe K	0.40	0.8398	1.0179	1.0088
Cu K	0.79	0.8100	1.0144	1.0000
Zn K	0.56	0.8095	1.0133	1.0000

(c)



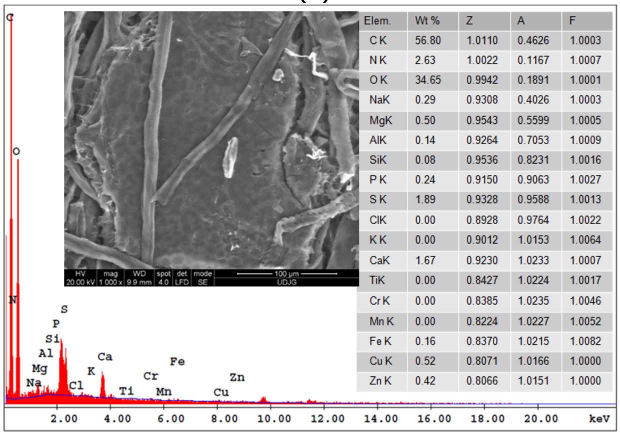
Elem.	Wt %	Z	A	F
C K	56.34	1.0120	0.4322	1.0003
N K	3,05	1.0031	0.1140	1.0006
O K	32.98	0.9951	0.1827	1.0001
NaK	0.18	0.9317	0.4054	1.0004
MgK	0.63	0.9552	0.5638	1.0006
AlK	0.12	0.9272	0.7071	1.0012
SiK	0.21	0.9544	0.8247	1.0022
P K	0.25	0.9160	0.9058	1.0037
S K	2.43	0.9338	0.9583	1.0021
ClK	0.15	0.9338	0.9712	1.0033
K K	0.00	0.9021	1.0113	1.0095
CaK	2.65	0.9239	1.0202	1.0005
TiK	0.00	0.8435	1.0171	1.0013
Cr K	0.00	0.8394	1.0203	1.0036
Mn K	0.00	0.8233	1.0202	1.0042
Fe K	0.13	0.8379	1.0195	1.0065
Cu K	0.36	0.8081	1.0157	1.0000
Zn K	0.54	0.8075	1.0143	1.0000

(d)



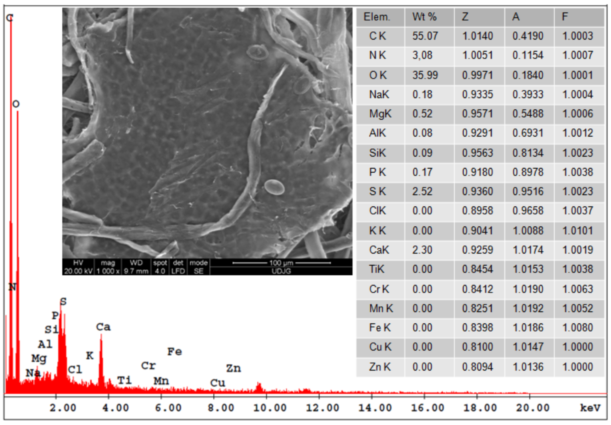
Elem.	Wt %	Z	A	F
C K	57.03	1.0102	0.4654	1.0003
N K	2.41	1.0014	0.1150	1.0007
O K	35.04	0.9934	0.1866	1.0000
NaK	0.17	0.9300	0.4032	1.0003
MgK	0.38	0.9535	0.5645	1.0005
AlK	0.12	0.9257	0.7118	1.0010
SiK	0.07	0.9528	0.8295	1.0018
P K	0.13	0.9142	0.9120	1.0032
S K	2.18	0.9319	0.9647	1.0016
ClK	0.00	0.8919	0.9782	1.0027
K K	0.00	0.9004	1.0167	1.0078
CaK	2,07	0.9221	1.0244	1.0003
TiK	0.00	0.8419	1.0217	1.0007
Cr K	0.00	0.8377	1.0232	1.0019
Mn K	0.00	0.8216	1.0225	1.0012
Fe K	0.13	0.8362	1.0214	1.0020
Cu K	0.00	0.8064	1.0167	1.0000
Zn K	0.27	0.8058	1.0152	1.0000

(e)



Elem.	Wt %	Z	A	F
C K	56.80	1.0110	0.4626	1.0003
N K	2.63	1.0022	0.1167	1.0007
O K	34.65	0.9942	0.1891	1.0001
NaK	0.29	0.9308	0.4026	1.0003
MgK	0.50	0.9543	0.5599	1.0005
AlK	0.14	0.9264	0.7053	1.0009
SiK	0.08	0.9536	0.8231	1.0016
P K	0.24	0.9150	0.9063	1.0027
S K	1.89	0.9328	0.9588	1.0013
ClK	0.00	0.8928	0.9764	1.0022
K K	0.00	0.9012	1.0153	1.0064
CaK	1.67	0.9230	1.0233	1.0007
TiK	0.00	0.8427	1.0224	1.0017
Cr K	0.00	0.8385	1.0235	1.0046
Mn K	0.00	0.8224	1.0227	1.0052
Fe K	0.16	0.8370	1.0215	1.0082
Cu K	0.52	0.8071	1.0166	1.0000
Zn K	0.42	0.8066	1.0151	1.0000

(f)



Elem.	Wt %	Z	A	F
C K	55.07	1.0140	0.4190	1.0003
N K	3,08	1.0051	0.1154	1.0007
O K	35.99	0.9971	0.1840	1.0001
NaK	0.18	0.9335	0.3933	1.0004
MgK	0.52	0.9571	0.5488	1.0006
AlK	0.08	0.9291	0.6931	1.0012
SiK	0.09	0.9563	0.8134	1.0023
P K	0.17	0.9180	0.8978	1.0038
S K	2.52	0.9360	0.9516	1.0023
ClK	0.00	0.8958	0.9658	1.0037
K K	0.00	0.9041	1.0088	1.0101
CaK	2.30	0.9259	1.0174	1.0019
TiK	0.00	0.8454	1.0153	1.0038
Cr K	0.00	0.8412	1.0190	1.0063
Mn K	0.00	0.8251	1.0192	1.0052
Fe K	0.00	0.8398	1.0186	1.0080
Cu K	0.00	0.8100	1.0147	1.0000
Zn K	0.00	0.8094	1.0136	1.0000

(g)

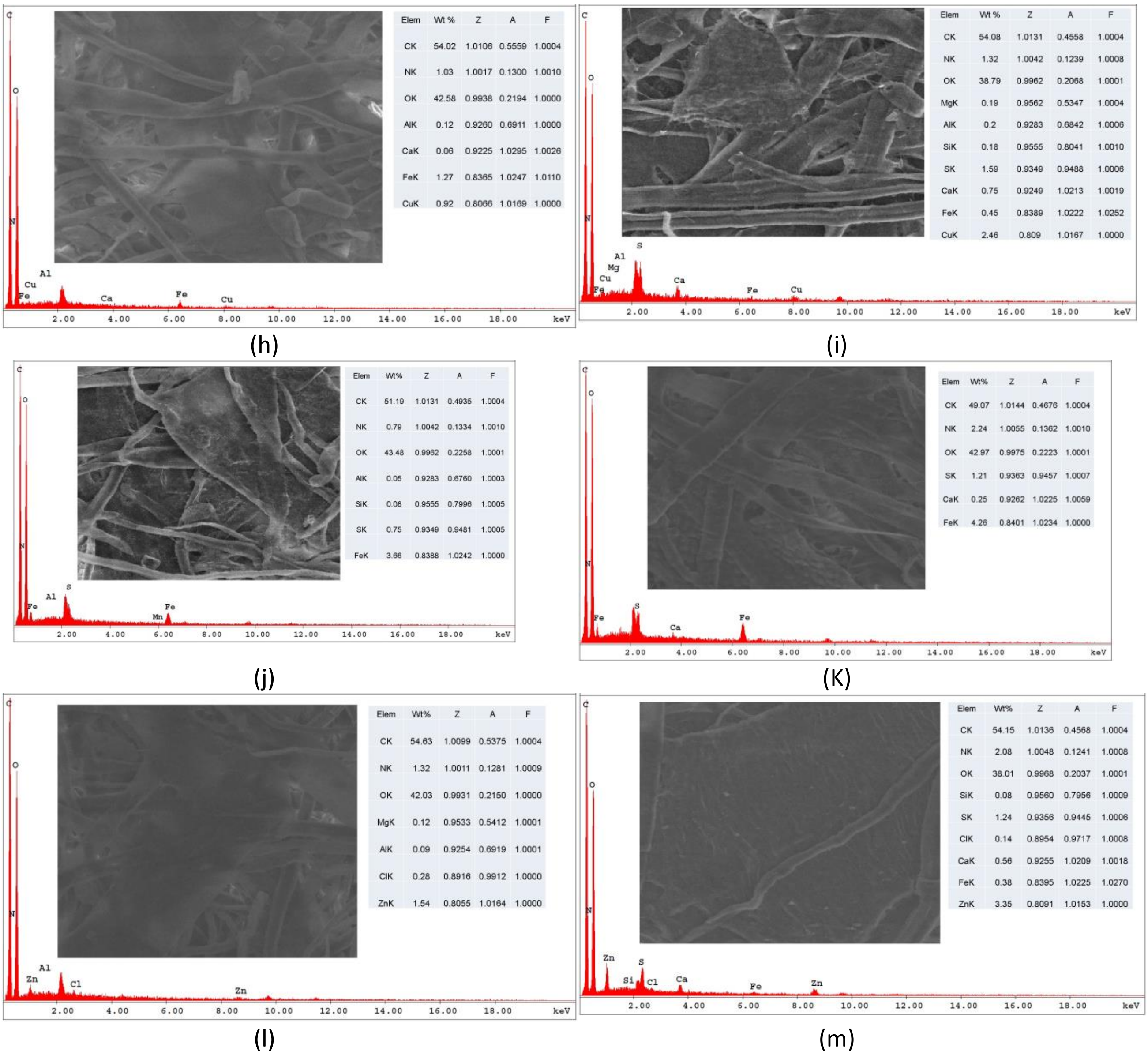


Figure 3.3. SEM-EDX results of the analysed samples: *Ulva rigida* seaweed (a); (PM) Filter paper control sample (b); (P1) Filter paper with added 0.5% seaweed (c); (P2) Filter paper with added 1% seaweed (d); (P3) Filter paper with 2% seaweed addition (e); (P4) Filter paper with 4% seaweed addition (f); (P5) Filter paper with 8% seaweed addition (g) [Ene, A. , et al., 2023], PM filter paper (h, i, j) and 30% seaweed filter papers by mass (i,k,m) used for the filtration of Cu, Fe and Zn solutions [Căpriță, F.C., et al., 2023].

From the images captured using scanning microscopy (Figure 3.3.) it can be seen that the surface of the Ulva rigida seaweed particles, the sample is homogeneous, the surfaces do not show any roughness and in the case of the images of the samples corresponding to the filter papers with added seaweed, it can be seen the bond between the fibers of hardwood and resinous cellulose and how they also form around the seaweed particles, incorporating them into the mass of the paper.

The 30% seaweed filter paper samples were tested for their filtering capacity after filtration and after drying in the open air, they were analysed by scanning microscopy and it was found that the seaweed filter paper is much more effective in removing the studied pollutants compared to the filter paper control sample. The addition of seaweed favours the retention of Cu^{2+}, Fe^{2+} and Zn^{2+} based pollutants on the sample surface and in the paper mass. The retention efficiency for Cu^{2+} increased by 167.39%, for Fe^{2+} by 16.39% and for the filtration of Zn^{2+} polluted sources, the retention efficiency is improved due to the addition of seaweed by 117.53% compared to the control sample containing no seaweed.

3.2. Chemical structure characterization by ATR-FTIR spectroscopy

ATR-FTIR technique applied on samples consisting of seaweed and filter papers with added seaweed in mass, manufactured at laboratory level aiming to reduce heavy metals from industrial polluted waters. Based on the capabilities of the FTIR technique, using infrared light to scan the samples and identify their chemical properties, organic, polymeric and, in some cases, inorganic materials can be characterised. 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 [Anderson, J.M., et al., 2010]. FTIR analyses complement the results obtained by SEM for microstructure characterization, as well as by SEM-EDX and PIXE and PIGE ion beam techniques for microcomposition and elemental distribution in the paper and algae matrix. Initial analyses on the samples, aim to identify the component elements and evaluate those that may draw attention to those with toxic potential.

Seaweeds have a complex chemical composition that differs depending on the species, with green algae being rich in chlorophyll and protein and brown algae in xanthophylls and polysaccharides, water sources and other environmental components in which they grow, seaweeds may contain more minerals and trace elements while algae that grow in freshwater sources may be richer in carbohydrates. The stage of development is another factor that determines chemical composition, so algae at an early stage of development may contain more proteins and amino acids and mature algae more carbohydrates and lipids. Even the colour of algae can indicate chemical composition characteristics, red algae contain phycobiliproteins and green algae chlorophyll.

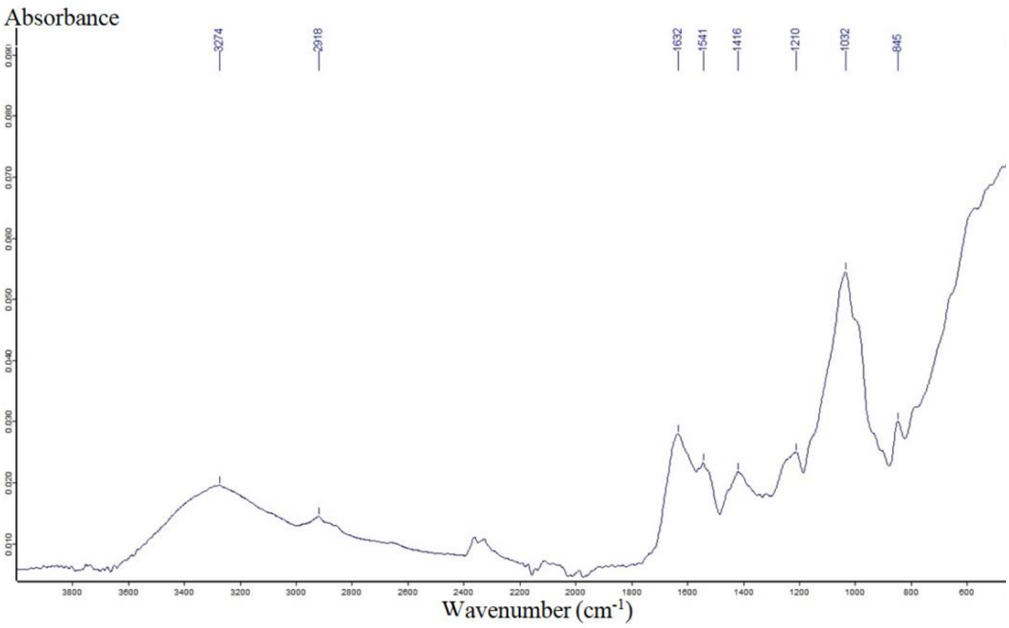


Figure 3.5. ATR-FTIR spectrum characteristic of the seaweed sample Ulva rigida, collected from the Constanta Casino area [Căpriță, F.C., et al., 2022].

Table 3.2. *Absorption bands, in the IR range, characteristic of vibrations associated with functional groups present in the seaweed sample Ulva rigida*

Crt.	**Absorption band (cm^{-1})**	**Vibrational mode**
1	3274	v (O – H)
2	2918	v (C – H)
3	1632	v (C=O)
4	1416	v (C – O – O)
5	1210	v (S=O)
6	1032	v (C – O – C)
7	845	v (C – O – S)
v- stretch vibration		

The IR spectrum of the alga *Ulva rigida* is comparable to the IR spectrum of sulphated polysaccharides derived from seaweeds [Aguilar-Briseno, J.A., et al., 2015]. The ATR-FTIR spectrum of the alga Ulva rigida (Figure 3.5.) shows a broad absorption band at 3274 cm^{-1}, attributed 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. The IR absorption band at 1632 cm^{-1} is attributed to the stretching vibration of the C=O chemical group, and the absorption band at 1416 cm^{-1} is attributed to the symmetric stretching vibration of the COOH group [Ibrahim, M.I.A., et al., 2022]. The sulfated nature of the polysaccharide is evidenced by the absorption band of 1210 cm^{-1} which is attributed to the stretching vibration of the S=O sulfate ester group and the peak of 845 cm^{-1} which is attributed to the C-O-S stretching vibration of the sulfate group [Castro, R., et al., 2005]. The absorption peak of 1032 cm^{-1} is attributed to the stretching vibration of the C-O-C group [Tian, H., et al., 2015].

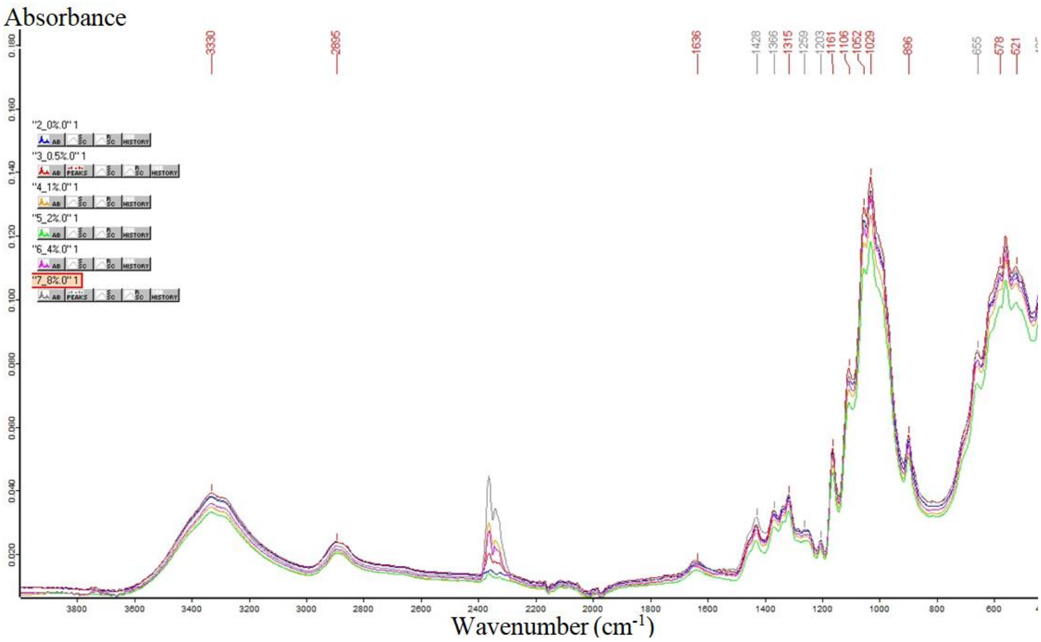


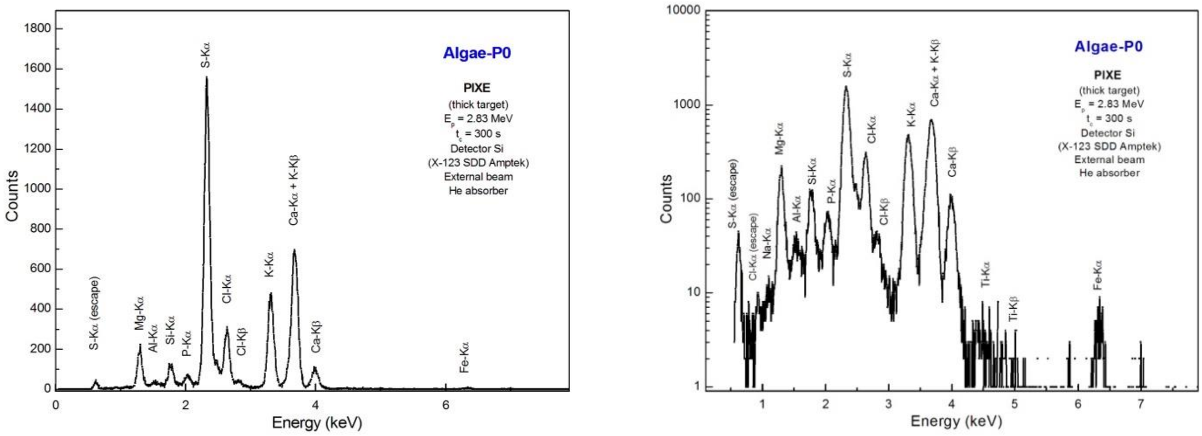
Figure 3.6. ATR-FTIR spectrums for the control sample (filter paper- (blue line) and samples containing in filter paper with seaweed addition, 0.5% (red line), 1% (orange line), 2% (green line), 4%(pink line) and 8% (black line) [Căpriță, F.C., et al., 2022].

In Figure 3.6., the ATR-FTIR spectra highlight that the absorption bands for the filter paper samples are similar, however they show small differences in peaks and based on this, the characteristic vibrations of the functional groups were assigned. Sulphated polysaccharides such as fucoidan and ulvan can be extracted from certain species of seaweed. Following the interpretation of the results, it can be seen that in the ATF-FTIR spectrum belonging to the alga Ulva rigida, absorption bands belonging to the vibrational stretches of the O-H groups present in the polysaccharide structure, the C-H bonds of the methyl group, as well as COOH groups, sulphate ester groups and C-O-C groups can be identified. It is found that there are no elements in the structure of the analysed algae that make them unusable for wastewater filtration and contact with drinking water [Căpriță, F.C., et al., 2022]. Different binding groups, e.g. OH-, COO-, NO3-, RS-, SH, PO43-, RNH2- and RO- favour the adsorption of metal ions. These groups exist externally on the cell surface and inside the cell wall in the cytoplasm and vacuoles [Bilal, M., et al., 2018].

3.3. Determination of elemental concentrations in samples analysed by IBA, PIXE and PIGE nuclear analytical methods

The PIXE and PIGE methods were applied to samples of seaweed of the genus Ulva, species Ulva rigida and filter papers with added seaweed in mass, of the same species at different concentrations, obtained at laboratory level. This method was applied to evaluate the initial samples in order to identify and quantify the elements initially found in these samples, and then to demonstrate the adsorption capacity of the pollutants in the water source by techniques such as SEM-EDX and spectrophotometry.

Both light and heavy elements could be determined using nuclear analysis techniques: Na, Mg, Al, Si, P, S, Cl, K,Ca, Ti, V, Mn, Fe, Cu, Zn. Using the PIXE method it was possible to identify the chemical elements in a number of 7 different samples, namely, seaweed of the genus Ulva, species Ulva rigida, filter paper used as a control sample, without seaweed addition and filter paper with seaweed addition, additions in mass of 0.5, 1, 2, 4, and 8%.



(a) (b)

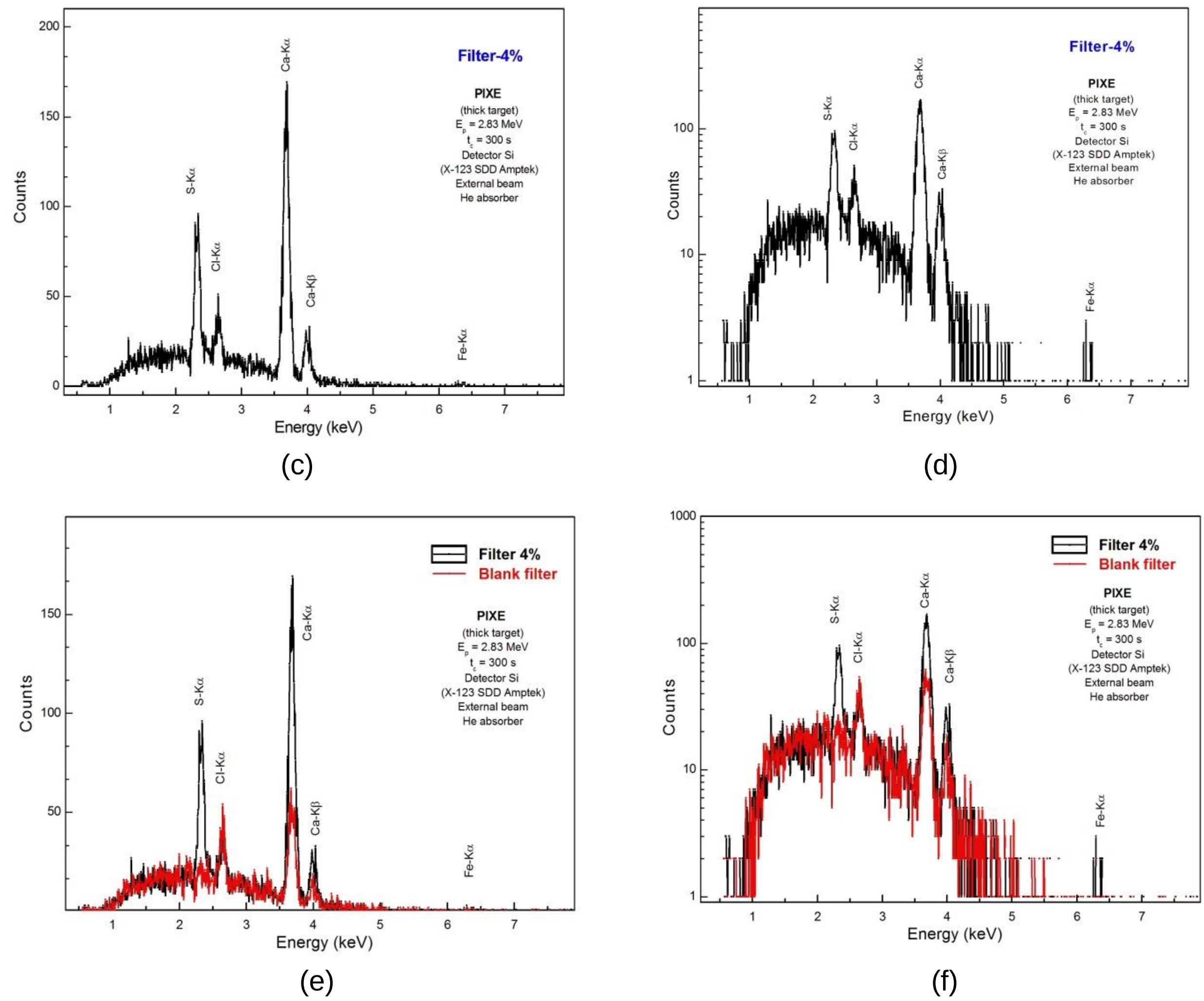


Figure 3.7. PIXE spectrum: spectra of macroalgae sample (a) and (b); spectrum of filter paper sample with seaweed mass addition at 4% concentration (c) and (d); superposition of spectra of filter paper control sample and filter paper spectrum with seaweed mass addition at 4% concentration (e) and (f) [Ene, A, et al., 2023].

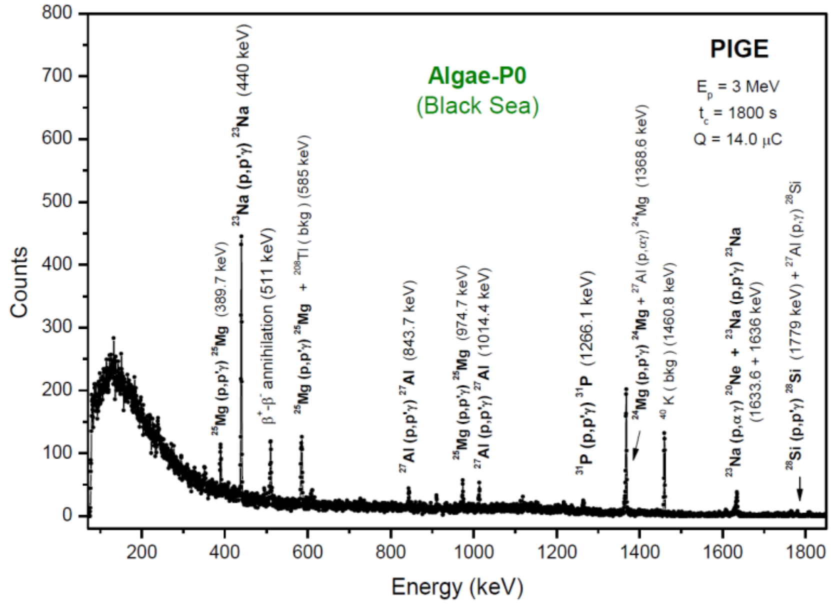


Figure 3.8. PIGE spectrum of marine algae of the genus Ulva [Ene, A, et al., 2023].

The combined use of PIXE and PIGE analysis methods confirms the presence of several chemical elements (Table 3.10.) in the algal matrix.

Table 3.10. *PIXE and PIGE analysis on algal samples - concentrations (c) and standard deviations (σ), in mg/kg [Ene, A., et al., 2023].*

Element	c (PIXE) (mg/kg)	σ (mg/kg)	c (PIGE) (mg/kg)	σ (mg/kg)
Na	1238	641	1022	82
Mg	17214	676	14800	1391
Al	482	357	330	47
Si	2149	114		
P	1730	199	1488	295
S	40018	474		
Cl	7928	229		
K	10248	203		
Ca	18865	300		
Ti	56.6	46.5		
Mn	72	48		
Fe	325	72		

By applying the PIXE method, much more detailed results could be obtained than by applying the PIGE method.

Table 3.11. *Concentration of elements in all samples analysed by the PIXE method*

Element	Marine Algae	P0	P1	P2	P3	P4	P5
		Filter paper (PM)	Filter paper with 0,5% algae	Filter paper with 1% algae	Filter paper with 2% algae	Filter paper with 4% algae	Filter paper with 8% algae
Na	1238	0	0	248.3	395	342.9	0
Mg	17214	174.69	227.5	573.4	0	239	509.2
Al	482.0	0	0	0	0	0	0
Si	2149	726.63	111.3	43.7	85.1	13.8	0
P	1730	0	0	0	0	93	0
S	40018	64.93	210.2	232.6	240.9	1752.6	1563.8
Cl	7928	8.83	706.2	632.7	582.5	531	486.3
K	10248	35.41	80.9	145.1	71.0	20.3	26.9
Ca	18865	4.31	1034.4	1480.4	1417	3367.7	2591.2
Ti	56.6	0	0	0	0	0	14.4
V	0.0	0	0	34.8	0	0	0
Mn	71.7	0	0	0	0	0	0
Fe	324.5	63.61	112.9	71.4	30.4	78.4	0
Cu	0.0	0	39.9	0	0	0	0
Zn	0.0	0	56.2	0	0	0	0
Br*	0.0	0	61.9	121.2	62.9	0	30.7
Sr*	0.0	0	0	29.9	110.4	0	135.3

* determinations using L_{α} lines

Table 3.11. contains data regarding all elements identified in the samples analysed using the PIXE external beam method. After evaluation of the element concentrations, it can be seen that there are no potentially toxic elements or high concentrations of elements that could have a negative impact on the environment.

It is observed that the highest concentrations were recorded for: S element (in seaweed and algae filter paper samples 4% and 8%), Ca (in seaweed sample and algae filter paper samples at 0.5, 1%, 2%, 4% and 8% concentration), Mg (in seaweed, filter paper control sample and algae filter paper 0.5%, 1%, 4% and 8%), Na (in the seaweed sample and in the seaweed filter paper samples at 1, 2 and 4% concentration), Cl (in all samples except the filter paper sample used as reference), Si (in seaweed and in PM filter paper), P (in seaweed).

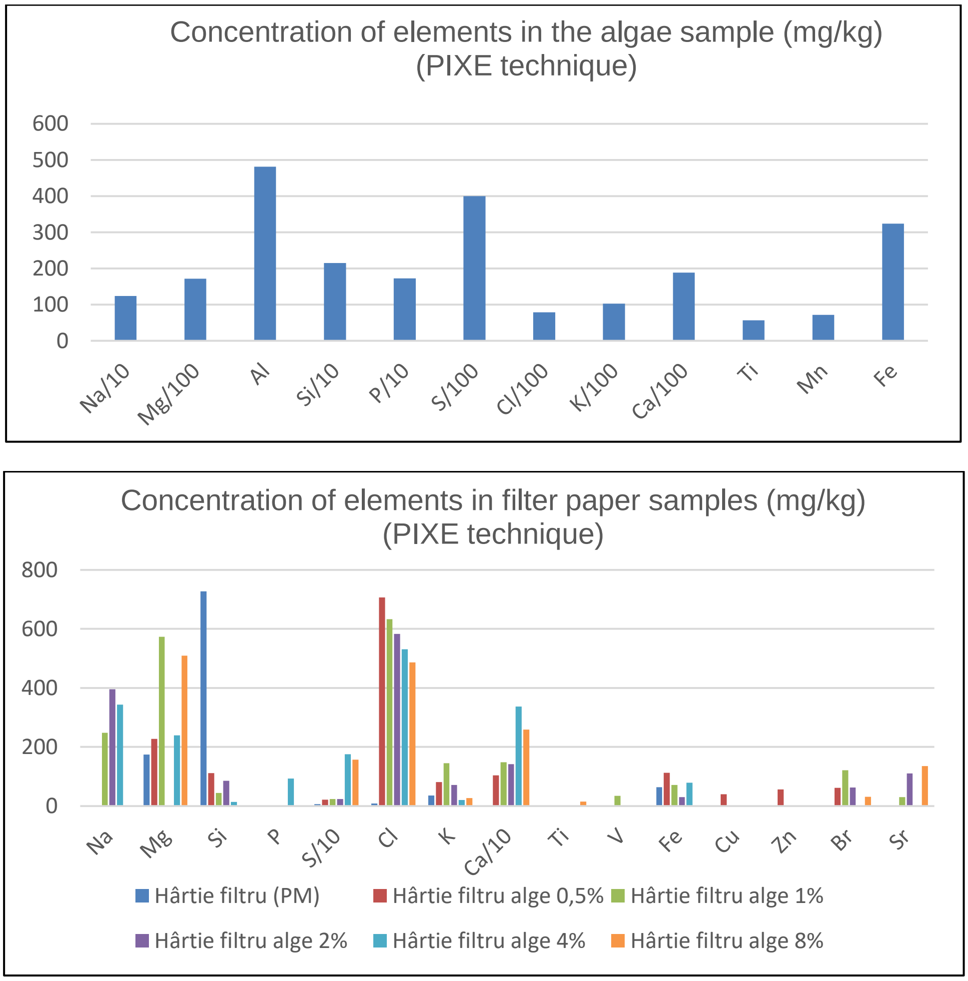


Figure 3.9. Elemental concentration variation in analysed samples

The elements Cr, Ni, As, and Pb were not found in the analyzed samples. The elements Al and Mn were found only in seaweed. Ti was found in the algae-added filter paper sample at a concentration of 8% while Zn was found in the 1% algae-added filter paper sample. The elements determined in the seaweed and seaweed-added filter paper samples could be identified on the basis of the K_{α} and K_{β} lines of the K-series of X-rays characteristic of atomic species, except for Br and Sr in the seaweed-added filter paper samples, which were quantified on the basis of the L_{α} lines of the L-series.

3.4. Identification of strength and structure and absorption characteristics of filter paper samples

Table 3.12. presents a comparative overview of the mean values of 10 determinations for each physical-mechanical characteristic of filter paper with and without the addition of dried algal biomass of *Ulva rigida* species. The algae were added in the proportions of 0.5%, 1%, 2%, 4%, 8% (P1-P5) [Căpriță, F.C., et al., 2021], 10%, 20% and 30% (P6-P8) [Căpriță, F.C., et al., 2023] calculated to the absolute dry material of the filter paper composition with a grammage of 80 g/m^2. The aim of these tests was to determine the possibility of incorporating stranded macroalgae into the paper mass and to evaluate how they influence the physical-mechanical characteristics of the paper.

Tabel 3.12. *Centralization of the results of the analyses performed on samples of filter papers with added seaweed (average of 10 determinations for each parameter analyzed) [Căpriță, F.C., et al., 2021].*

Sample coding	Addition	Grammage	Thickness	Density	Air permeability		Smoothness	Ash content	Breaking Load		Breaking strength		Tearing	Bursting Resistance	Folding Endurance	Water Absorptiveness	Moisture
					s				N		m						
	% Alge	g/m^2	µm	g/cm^3	Front side	Back side	s	%	Dry	Wet	Dry	Wet	mN	kPa	No.	g/m^2	%
P0	0	80.62	144	1.789	1.9	1.9	6	0.4	40.6	3.62	3.422	0.305	560	143	13	165.38	4.95
P1	0.5	80.33	142	1.768	2.5	2.3	6	0.42	41.01	3.78	3.470	0.320	560	143	14	170.38	5.04
P2	1	80.81	145	1.794	2.6	2.5	6	0.44	41.34	4.03	3.476	0.338	580	147	15	176.63	5.14
P3	2	80.63	143	1.774	2.6	2.5	6	0.49	43.96	4.16	3.705	0.351	620	141	15	177.31	5.23
P4	4	80.66	144	1.785	2.8	2.8	6	0.67	44.27	3.82	3.729	0.322	600	141	15	185.06	5.45
P5	8	80.47	142	1.765	3.2	3.1	6	0.93	39.73	2..35	3.355	0.198	540	127	11	179.12	5.27
P6	10	80.87	148	1.83	2.4	2.3	6.5	1.14	38.23		2.574		580	80	8	207.3	4.36
P7	20	80.93	151	1.866	2.0	1.9	6	2.39	33.23		2.578		580	90	6	206.1	5.42
P8	30	80.74	138	1.709	5.3	5.1	7.5	3.16	53.54		4.256		880	199	90	188.4	6.65

3.4.1. Determination of the structural characteristics of filter paper with added macrophytic seaweed

- Determination of grammage of filter paper samples

The results of the samples are close in terms of values because the whole manufacturing process was controlled in order to obtain papers with a grammage of 80 g/m^2 and this was quite straightforward at laboratory level; however, obtaining an accuracy of two decimal places is difficult even at industrial level but the values obtained have a maximum deviation of 0.21 g/m^2. The presence of dried seaweed added en masse did not affect the grammage of the samples by absorbing moisture from the environment. The average of all samples is 80.67 g/m^2. The grammage of the samples was analysed in order to draw conclusions about the other characteristics and their relationships

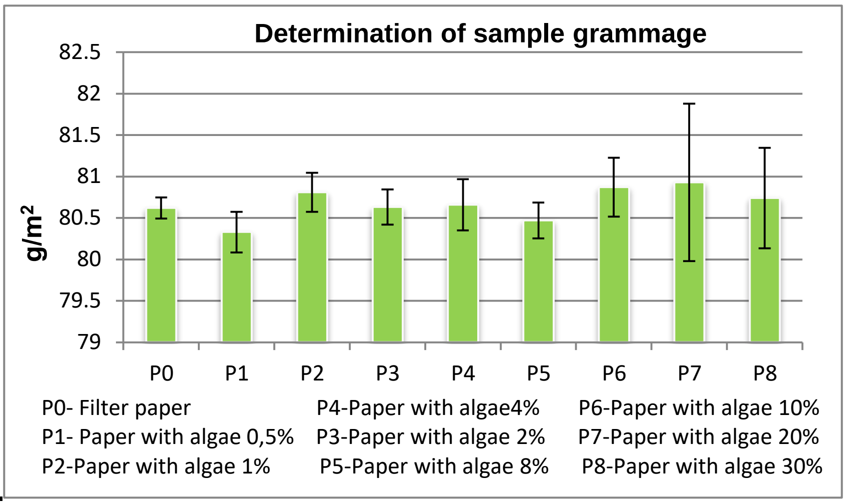


Figure 3.10. Results of sample grammage determination

All samples consisting of filter papers, including the laboratory control sample, have grammage values slightly above 80 g/m^2 (Figure 3.10.), sample P7 has the highest value, quite close to the value of 81 g/m^2 while sample P1 has the lowest value. The grammage has an influence on the samples through the fact that the higher the grammage of the samples than the one programmed to be obtained, other characteristics such as strength and structure are also conditioned [Căpriță, F.C., et al., 2021].

- Thickness determination

This property is closely related to the grammage of the sample and can be modified depending on the end use, from the paper recipe, at the industrial level the technological parameters of the paper machine, the linear pressure at the wet presses and the value of the vacuum at the suction boxes can be modified.

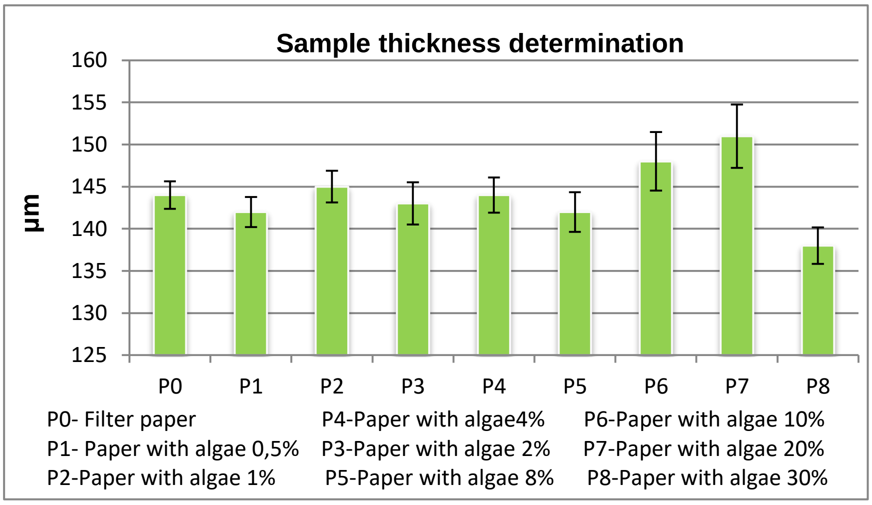


Figure 3.11. Sample thickness results

It can be observed as the results of the determination of the filter paper thickness correspond to the results of the grammages. The difference between the maximum value recorded for sample P7 and the minimum value of sample P8 is only 13 µm. Depending on the specific application, the grammage and therefore the thickness of the filter paper can be modified from the recipe. From the analysis of the statements of manufacturers of various paper grades on the market, it was observed that the thickness characteristic may vary between similar paper grades and this is due to several factors, such as the manufacturing recipe, the proportion of cellulose fibers from softwood sources, moisture, etc [Căpriță, F.C., et al., 2021].

The first 5 samples were more stable in terms of thickness [Căpriță, F.C., et al., 2021], while samples P6, P7, P8 had different oscillations due to the fact that they contain higher concentrations of seaweed that influence the manufacturing process, the laying of the cellulose fibers, the creation of the fiber network and the algae particles that were trapped in the fibrillar network (Figure 3.11.). Samples P7 and P8 show the largest difference and this can be interpreted through the differences in the concentrations of seaweed found in the cellulose fibers that interconnect with each other through hydrogen bonds.

- Sample density determination

As filter paper is used to separate fine solid particles from liquids, it must constitute a semi-permeable barrier. Since density is a characteristic resulting from the correlation between grammage and thickness, it can be easily modified according to requirements by adjusting grammage, pulp consistency and thickness by adjusting the linear pressure on the machine's wet presses at industrial level. Analysing the data provided by paper manufacturers on the market, it was observed that this characteristic has values between 0.34 and 0.55 g/cm3.

The results obtained for the determination of this characteristic are uniform, directly proportional to the thickness of the samples and influenced by the grammage and thickness of the samples. This characteristic of the filter papers provides important information on the porosity properties, filtration efficiency. The higher the density of the material, the more efficient the filtration, meaning that the liquid phase passing through the material penetrates a network of more densely bound, condensed fibers, with no voids through which the phases to be retained on the surface or in the mass of the filter paper can slip.

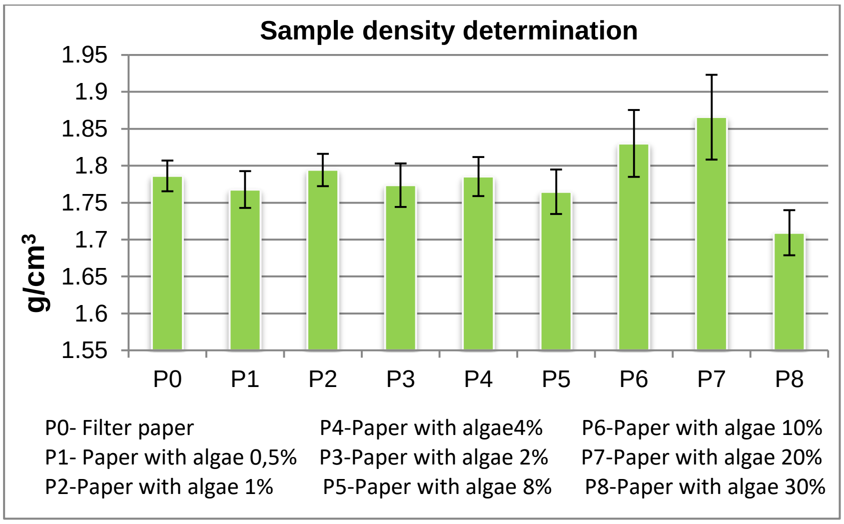


Figure 3.12. Sample density determination results

As with the thickness determination, the results of this determination are fairly uniform, the most obvious differences being between samples P7 and P8 (Figure 3.12). The differences are only 0.157 g/cm^3, which is a very small value to obviously influence either this characteristic or the porosity and filtration properties.

- Determination of air permeability, Gurley method

The air permeability determinations show increasing values, directly proportional to the increasing seaweed addition in the paper mass for the first 5 samples, containing 0.5, 1, 2, 4 and 8% additions [Căpriță, F.C., et al., 2021]. A different behaviour is observed for 10, 20 and 30% algae additions. Comparing the reference sample, which has no algae content, with the first 4 samples with algae content, it can be seen how this characteristic improved, from the minimum value of 1.9 s for the control sample, to 2.5, respectively 2.3 s for the sample with 0.5% algae addition, to 3.2, respectively 3.1 s for the sample with 8% algae addition. From the data obtained on the air permeability determination for both sides of the filter paper sheets, it can be seen that there are no noticeable differences. Considering the average values obtained for the two faces of the paper and comparing them with P0, we observe that the addition of only 0.5% improved the characteristic by 26.32%, P2 by 34.21%, P3 shows the same percentage of improvement as P2, P4 by 47.37%, and the highest increase was found for sample P5, 65.79%. Samples P6 and P7 show slightly improved values compared to sample P0, but not noticeable, with P7 showing similar values to P0. The 10% and 20% algae additions act variably in the paper mass compared to the lower additions, dislodge a higher percentage of cellulose fibres and behave differently. For sample P8, the 30% algae addition acts positively, improving this characteristic by 173.6% for one side of the paper and 168.4% for the other side of the sample compared to the control sample. The permeability characteristic also provides information about the absorbency of the paper (Figure 3.13.). The differences between the two sample faces show similar values with very small differences. For some types of paper, waterproofing treatments are applied which increase the permeability value, making it impermeable to water penetration into the paper mass.

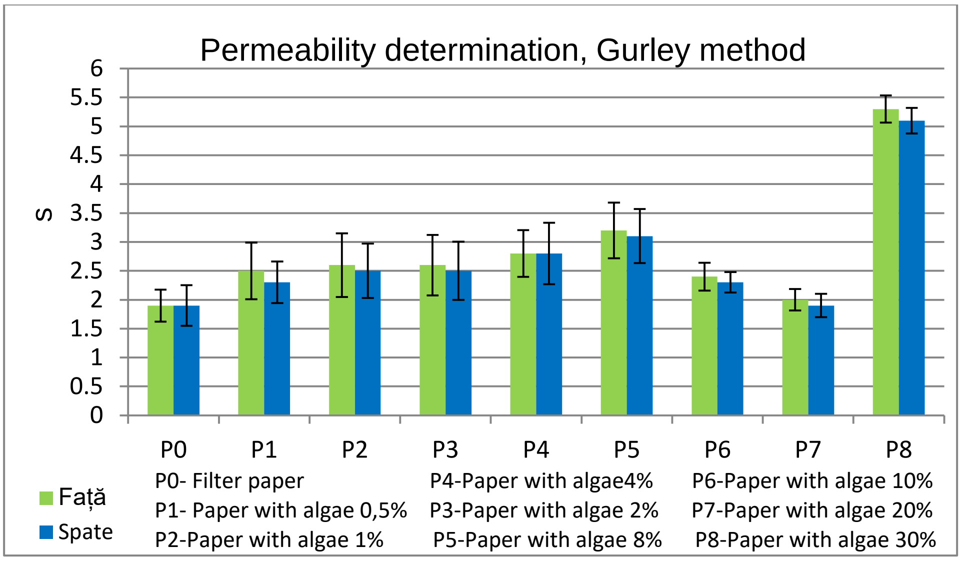


Figure 3.13. Permeability results, Gurley method

When comparing samples P5 and P8, for which the permeability values are high, we observe an increase of 62.5 percent in sample P8. The addition of seaweed to the paper mass does not negatively influence this characteristic.

- Determination of smoothness, Bekk method

Values with insignificant influence were obtained for the determination of Bekk smoothness, where, as can be seen in Figure 3.14. for the first 5 samples consisting of filter papers with seaweed additions of 0.5, 1, 2, 4 and 8 % [Căpriță, F.C., et al, 2021], even for sample P7 with 20% addition, the values of these determinations are 6 s. Samples P6 and P8 show values of 6.5 and 7.5 s, respectively (Figure 3.14). The addition of seaweed does not affect the smoothness characteristic of the paper, but neither does it improve this characteristic for these samples with very low additions. For the 30% addition a slight improvement is observed, a 25% higher value compared to the control sample and to samples P1, P2, P3, P4, P5 and P7. It seems that the small seaweed particles did not cover the spaces between the fibres, allowing air to pass between them in the case of the low addition samples and for the high addition samples the effect is not very obvious, the mass added seaweed particles may be an impediment to the fiber network, weakening this fiber relationship.

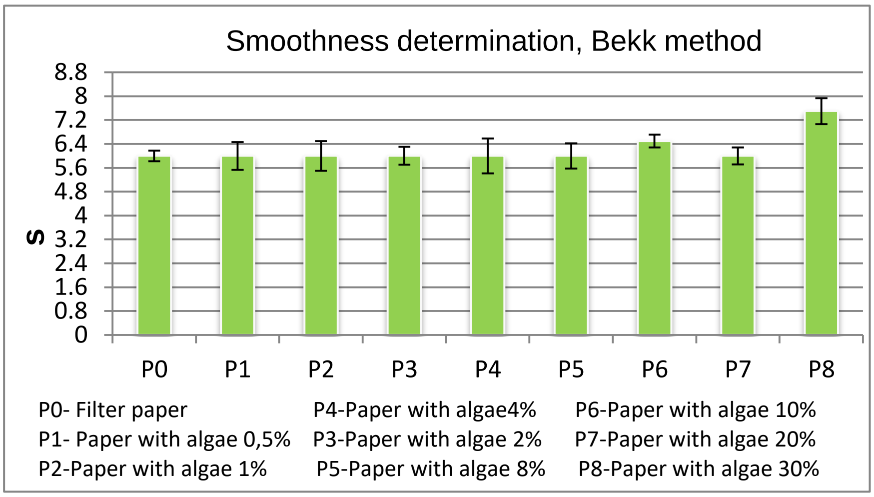


Figure 3.14. Results of smoothness determination, Bekk method

- Residue determination (ash content)

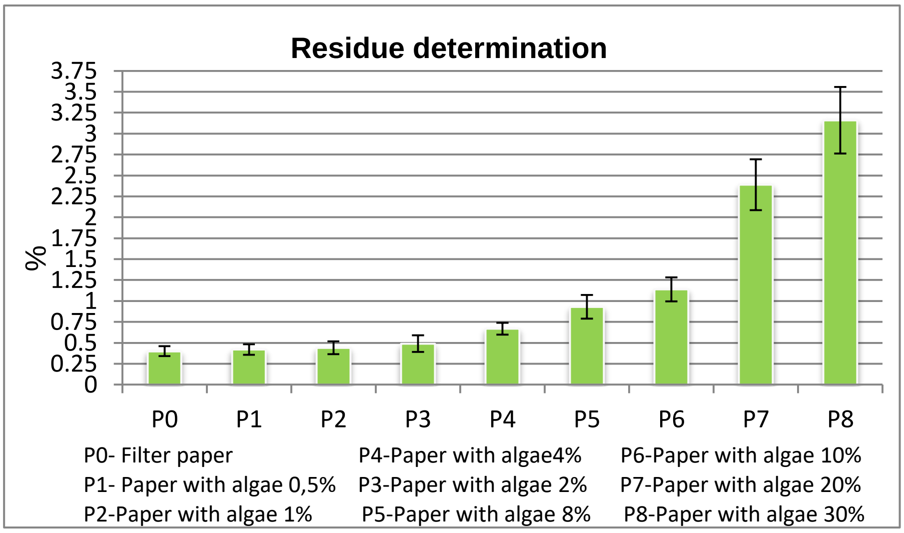


Figura 3.15. Results of ash content determination

The ash content increases in relation to the biomass addition, one of the main reasons being that seaweed has a high content of mineral, inorganic elements. From the analysis of the values we can see that, compared to P0, the ash content for P1 increases by 5%, for P2 by 10%, P3 by 22.5%, P4 by 67.5%, P5 by 132.5% [Căpriță, F.C., et al., 2021], P6 by 185%, P7 by 497.5% and for P8 by 690% (Figure 3.15). The increase in ash content does not show perfectly exponential values because the ash content in these samples depends on the algal content, which varies according to the minerals in the algae.

Samples P1, P2, P3 and P4 do not show very large changes compared to the control sample P0 [Căpriță, F.C., et al., 2021]. This determination is very representative, in the context that some determinations, such as the determination of smoothness and permeability, do not show linear increases in values, thus the correctness of the algae addition can be questioned.

3.4.2. Mechanical strength characteristics of filter paper with added macrophyte seaweed

- Determination of breaking load

Comparative analysis of the results of the breaking load determination of the dry samples shows that the results are increasing for the first 4 samples, P1, P2, P3 and P4 containing small additions of 0.5, 1, 2 and 4% seaweed in the filter paper mass. Percentage wise, the value for sample P1 improved compared to the control sample by 1.01%, P2 shows an increase of 2.04%, P3 an increase of 8.28%, P4 shows an increase of 9.04% and P5 shows lower values compared to P0, by 2.14%, P6 decreased by 5.84% and P7 by 18.15%, which leads to the conclusion that an addition of 8%, 10% and 20% seaweed in the paper mass affects the structure of the fiber network, thus weakening the bonds formed and destabilizing their strength. However, in the case of sample P8, the determination result is improved by 31.87% compared to the control sample P0; thus, this percentage gives stability to the paper structure, being optimal to provide paper strength (Figure 3.16.).

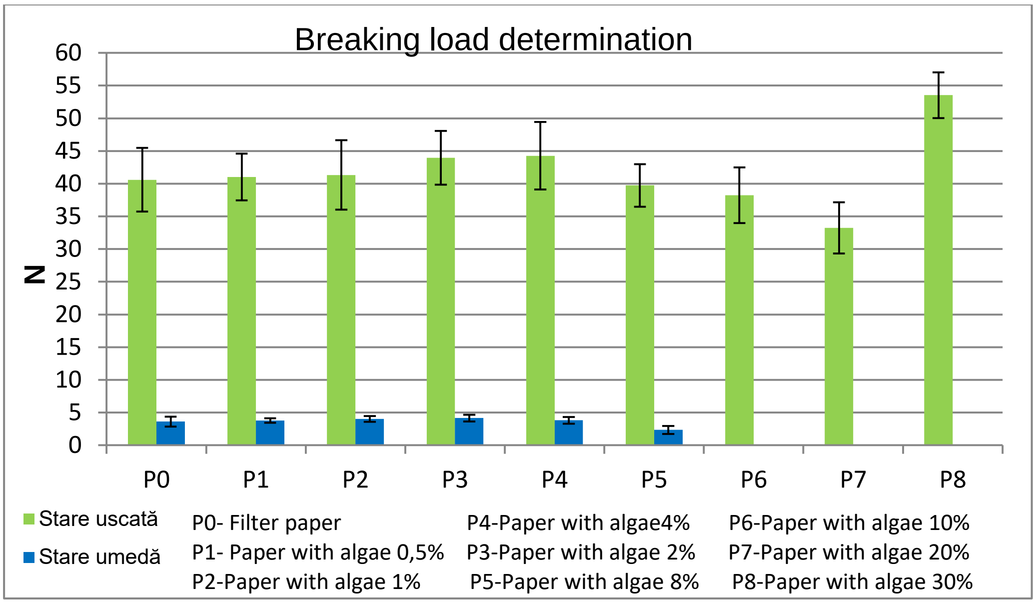


Figure 3.16. Results of the breaking load determination

For the determination of the breaking load of the samples in the wet state, the values are slightly improved compared to the control sample: for samples P1 by 4.42%; to 1.19% for P2; to 14.92% for P3; to 5.8% for P4; and P5 showing a decrease of 35.08% [Căpriță, F.C., et al., 2021]. It can be seen that, in the wet state, the samples P4 and P5 tested show the lowest values. In the case of sample P5, the same phenomenon occurs as in the case of the determination of the breaking loads in the dry state, i.e. the weakening of the fiber bonds due to the addition of 8% algae. For samples P6, P7 and P8, the determination of the wet tensile strength was difficult to perform because the samples do not have the strength to handle the specimens and clamp between the clamps of the apparatus used for this test.

- Determination of breaking length

Following the determination of the breaking length in the dry state, results were obtained which were compared with the control sample, P0. In the case of sample P1, an increase of 1.37% is observed, in P2 by 1.61%, in P3 by 8.27% and in P4 by 9%, P5 shows an increase of 1.96%, but a decrease compared to P3 and P4 [Căpriță, F.C., et al., 2021]. In the case of sample P6, it seems that the value is lower compared to P0 by 24.78%, and sample P7 shows a value 24.66% lower. Sample P8 has an improved breaking length compared to the control sample by 24.37%. Small additions of seaweed to the paper mass improve the strength for determining the breaking length by small percentages, but do not give noticeable improvements. Additions of 8, 10 and 20% algae act negatively because they are percentages that destabilize the formation of the fibre network, but the 30% algae addition is high enough to create stronger bonds.

Analysing the results of wet breakage length determination, compared to P0, P1 shows an increase by 4.92%, P2 by 11.15%, P3 by 15.08% and P4 by 5.57%, and P5 shows a decrease by 34.75%. The determination of breaking length is closely related to the determination of breaking load and sample weight. The addition of 8% seaweed also seems to harm this characteristic, but the other additions improve this determination. The addition of 4% seaweed had a positive influence on the tensile strength; however, in the case of the sample with the addition of 8%, the influence was negative because the seaweed particles weakened the bonds between the fibres, so that the results of sample P5 were also lower compared to the control sample (Figure 3.17.) [Căpriță, F.C., et al., 2021]. For samples P6, P7 and P8 this determination was difficult to perform because the clamping of the paper specimens between the dynamometer clamps could not be achieved.

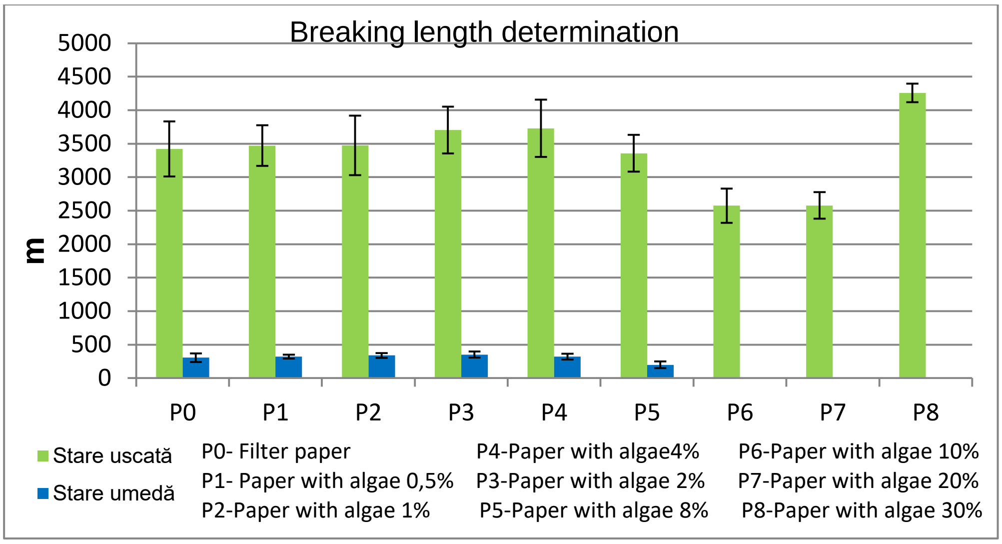


Figure 3.17. Results of the breaking length determination

- Determination of the tear strength, Elmendorf method

The values of the tearing strength oscillate for the 8 samples which can be noticed is in the case of sample P8. Comparing the samples with the filter paper without algae addition, the one used as reference sample, it was observed that P1 shows no change, P2 shows an increase of 3.57%, P3 an increase of 10.71%, P4 shows an improvement of 7.14% and P5 shows a decrease of 3.57% [Căpriță, F.C., et al., 2021], P6 and P7 have similar results as sample P2, the increase being only 3.57% compared to the reference. Sample P8 the one with the highest concentration of seaweed by mass, 30%, has an increased tear strength value of 57.4% compared to the reference sample (Figure 3.18). The addition of 30% seaweed significantly improves the tear strength of the material, while the addition of 8% decreases the quality of this paper characteristic.

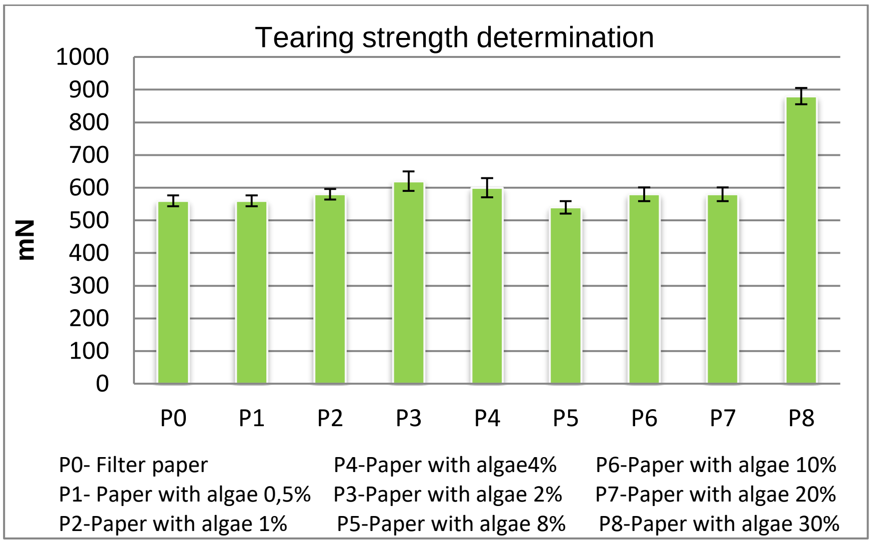


Figure 3.18. Results of tear strength determination

- Determination of the bursting strength

The results of the tests for the determination of the resistance to bursting are comparable with those obtained from the tests for the determination of the resistance to tearing. This analysis shows identical results for samples P0 and P1, the addition of only 0.5% did not influence this characteristic, but for P2 compared to P0 an increase of 2.8% was observed. In the case of samples P3 and P4 a decrease of 1.4% was recorded and for P5 a decrease of 11.2% [Căpriță, F.C., et al., 2021]. Obvious results were recorded for samples P6, P7 and P8. Samples P6 and P7, those showing additions of 10 and 20%, were evaluated and compared with the reference sample P0, and the values of this determination are decreasing by 44.06% and 37.06%, respectively. Sample P8 shows an improved value of 39.16% of this strength characteristic, compared to the reference sample, P0. The samples with significant results, from which important conclusions can be drawn, are samples P5, P6, P7 and P8 (Figure 3.19). The very low additions do not obviously affect the paper's crimp strength and the additions of 8, 10 and 20% contribute to the weakening of the fiber network, but the addition of 30% is an optimal one, by which a better strength of the paper is obtained, and we can conclude that it is a new material.

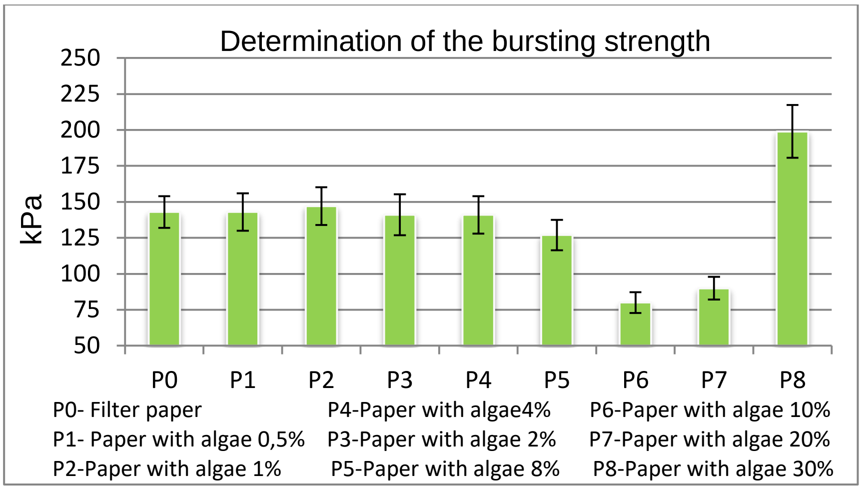


Figura 3.19. Results of the determination of the resistance to bursting

- Determination of folding endurance

Analysing the results of the determination of the folding endurance, the same trends as for the determination of the tear and bursting strength are observed. Following the tests for the determination of the bending strength, the following results were obtained compared to the reference sample P0: an increase of 7.7% for P1, and 15.38% for P2, P3 and P4, while samples P5 [Căpriță, F.C., et al., 2021], P6 and P7 show a decrease of 15.38%, 38.46% and 53.85% respectively. Sample P8 shows the most significant result, i.e. an increase by 592.31% (Figure 3.20). It can be concluded that for this determination the optimum addition of seaweed added to the paper structure is 30%.

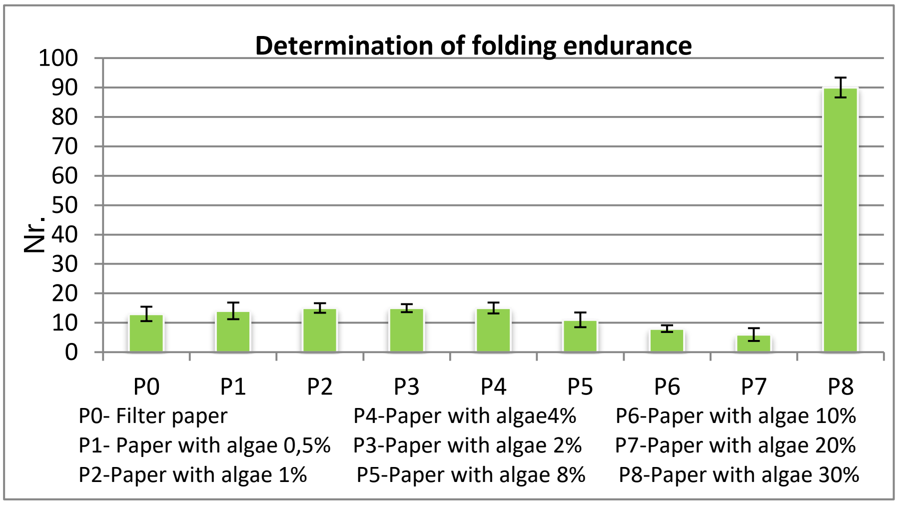


Figure 3.20. Results of the determination of folding endurance (double bending)

3.4.3. Absorption characteristics of filter paper with added macrophyte seaweed in the mass

- Determination of water absorption capacity, Cobb$_{60}$ method

Increasing the addition of algae in the paper mass improves this characteristic by 3.02% for P1, 6.8% for P2, 7.21% for P3, 11.9% for P4 and 8.31% for P5 [Căpriță, F.C., et al., 2021].

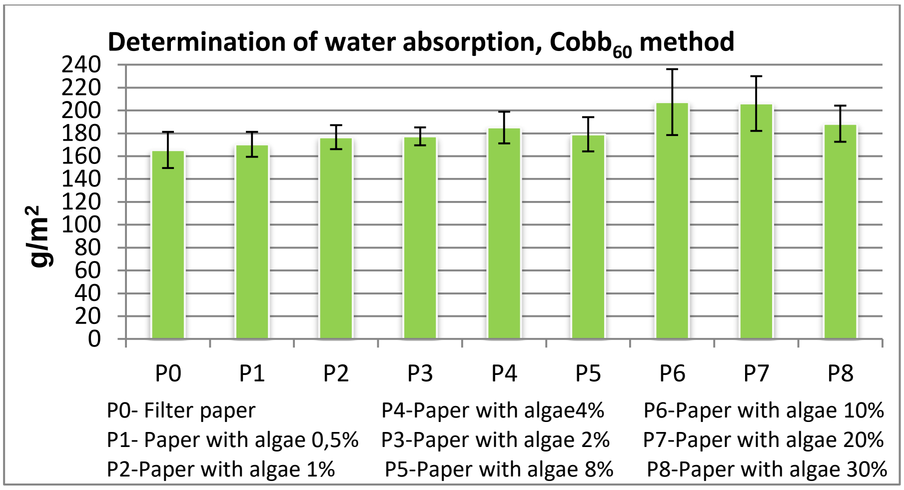


Figure 3.21. Results of water absorption determination, $Cobb_{60}$ method

The additions of 10, 20 and 30% seaweed show more improved values than the lower additions. For sample P6 an improvement of 25.35% was obtained compared to P0, for P7 an increase of 24.62% and for sample P8 the result improved by 13.92%. Compared to sample P6, which showed the highest value, sample P8 differed by a decrease of 9.12 percent (Figure 3.21.). A paper made of 100% hardwood pulp with a basis weight of 70 g/m2 has a water absorption capacity determined by the Cobb60 method of 150 g/m2, while a paper made of 100% softwood pulp with the same basis weight has a Cobb60 of 120 g/m2 [Todorova, D.A. and Lasheva, V.G.. 2020].

- Moisture determination

In order to determine the moisture content of the samples, they were conditioned in order to establish the relationship between the seaweed introduced into the filter paper and the moisture they could absorb from the air. Following this analysis, in the case of sample P1 there was an increase of 1.82% compared to P0, the reference sample containing no seaweed, while in the case of sample P2 there was an increase of 3.84%, P3 of 5.66%, P4 of 10.1%, P5 of 6.46% [Căpriță, F.C., et al., 2021]. For the sample with an addition of 10%, an increase of 8.28% in humidity was obtained compared to P0, and for P7 of 9.49%. The sample P8 which has an addition of 30% seaweed by mass, the moisture content increased noticeably by 34.34% (Figure 3.22.).

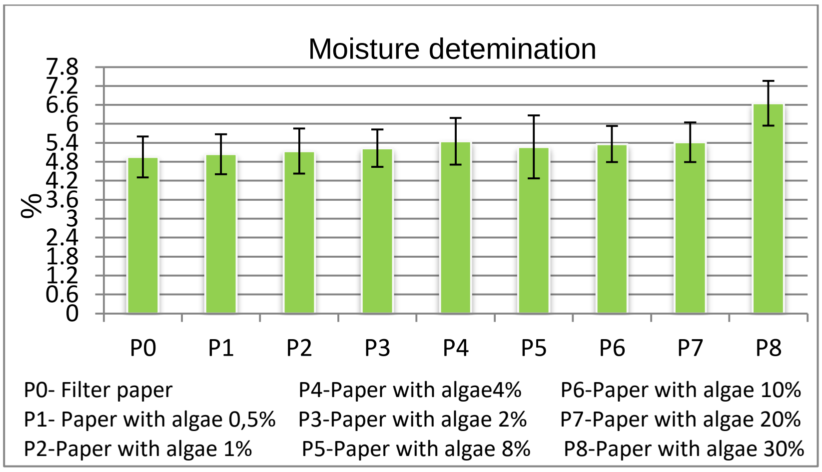


Figure 3.22. Moisture determination results

3.5. Filtration capacity determination of heavy metals, TDS and TSS from wastewater using seaweed and seaweed filter papers

The materials used in the thesis research were also analysed by spectrophotometric techniques in order to demonstrate the removal capacity of some metals by seaweed and by the newly created material. Table 3.13. shows the results obtained for the initial concentrations of some metals in the industrial wastewater source and after filtering the water through filter papers with different additions of stranded seaweed, compared to the national technical regulations NTPA-001 and NTPA-002. NTPA-001 sets pollutant limits for industrial and municipal wastewater discharges to natural receptors while NTPA-002 defines the conditions for wastewater discharges to municipal sewer systems and directly to sewage treatment plants and to comply with these regulations, factories must control technological processes and apply abatement and water treatment treatments prior to discharge. The initial concentrations for Cu, total Fe, Zn and TSS exceed the maximum allowable limits imposed by NTPA 001 and NTPA 002 and this can be seen from Table 3.13.

Table 3.13. *Concentrations of some metals in wastewater and after filtration using filter paper with different additions of stranded seaweed compared to national regulations NTPA-001 and NTPA-002, expressed in mg/dm3 [Căpriță, F.C., et al., 2021]*

Metal	Waste water	NTPA 001	NTPA 002	P0	P1	P2	P3	P4	P5
Cr total	0.37	1.0	1.5	0.15	0.09	0.08	0.09	0.07	0.07
Cu	1.8	0.1	0.2	0.2	0.2	0.21	0.18	0.15	0.11
Fe total	6.14	5.0	-	0.07	0.04	0.05	0.03	0.03	0.03
Zn	1.92	0.5	1.0	0.22	0.17	0.10	0.11	0.08	0.09
TDS	468	-	-	436	434	422	422	419	420
TSS	2495	-	350	5	2	3	0	0	0

- Determination of total Cr concentrations in analysed waste water

The results obtained for the filtration of total chromium from the wastewater source using filter paper samples can be seen from Figure 3.23. and Table 3.13. Comparing the data obtained from filtration using the reference sample P0, it can be seen that P1 shows a 40% improvement in pollutant reduction, P2 improves by 46.7%, P3 reduces by 40%, while P4 and P5 improve by 53.3% the water quality. All the values resulting from filtration with the 6 filter paper samples are below the maximum permissible limit required by legislation. Analysing the results according to the initial concentrations of the wastewater sample, we observe that the filter paper samples reduced the pollutant concentrations by a minimum of 59.46% using P0 and a maximum of 81.08% using P4 and P5 [Căpriță, F.C., et al., 2021].

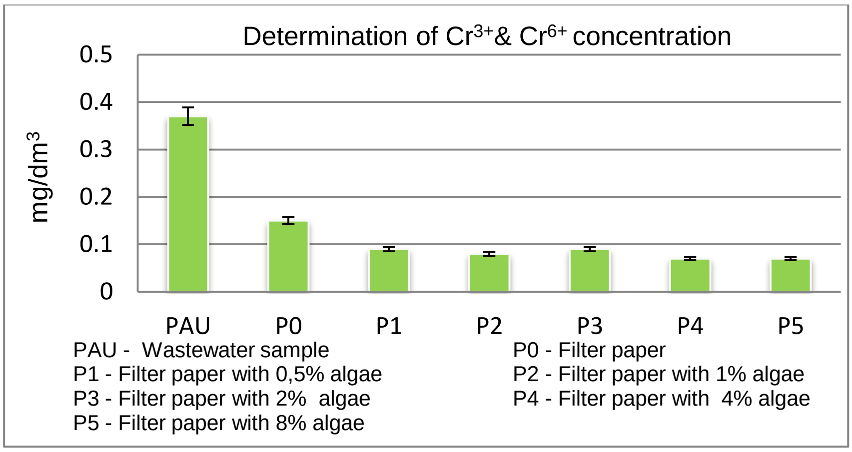


Figure 3.23. Results of Cr^{3+} and Cr^{6+} concentrations obtained after filtration of industrial wastewater using filter papers with different additions of *Ulva rigida* algae [Căpriță, F.C., et al., 2021].

- Determination of Cu^{2+} concentrations in industrial wastewater

Considering the data presented in Figure 3.24. and Table 3.13. we can conclude that all filter paper samples are effective in reducing Cu2+ pollutant concentrations in wastewater. Comparing the results of the control sample P0 with the other samples, P1 makes no qualitative contribution in reducing the concentration, P2 shows a decrease by 5%, P3 is more effective by 10%, P4 by 25% and P5 by 45%. Analyzing by comparison with the initial Cu concentration in the wastewater sample, we observe that P0 and P1 have an efficiency of 88.88%, P3 of 88.33%, P4 of 90% and P5 shows the best efficiency in reducing the pollutant of 91.67% [Căpriță, F.C., et al., 2021].

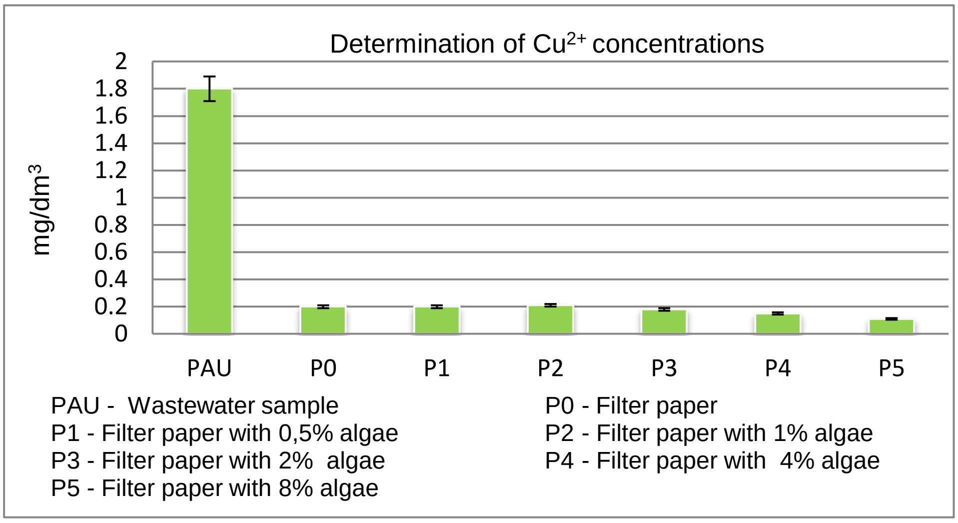
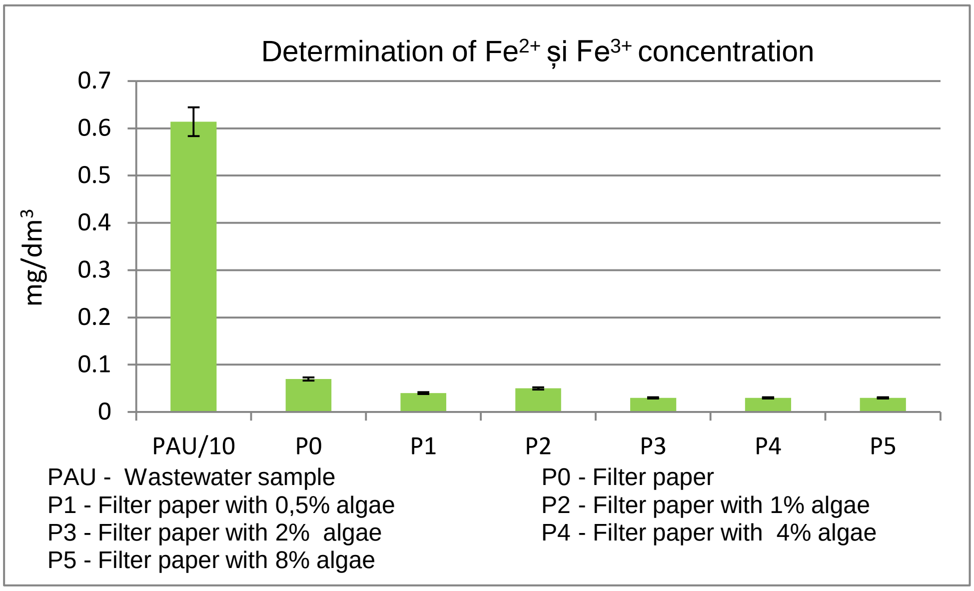


Figure 3.24. Results of Cu^{2+} concentrations after application of the industrial wastewater filtration method using filter paper samples with different additions of *Ulva rigida* algae in mass [Căpriță, F.C., et al., 2021].

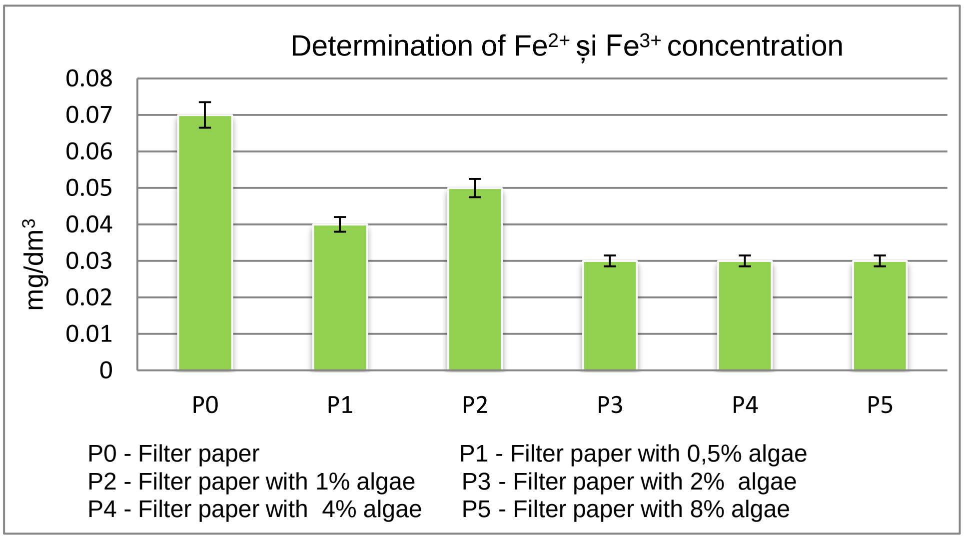
- Determination of total Fe concentrations in wastewater

Figure 3.25. presents the efficiency of samples consisting of filter papers obtained at laboratory level in which different seaweed additions were incorporated in terms of reducing iron concentrations. Comparing the efficiency of the filter paper samples with mass addition of algae with the control sample P0 containing no seaweed but only cellulose fibers, it is observed that P1 shows an efficiency of 42.86% in reducing total Fe concentration, P2 has

an efficiency of 28.57%, and samples P3, P4 and P5 show an improvement in Cu concentration reduction capacity of 57.14%. Comparing the reduction capacity with the initial wastewater pollutant concentration, P0 shows an efficiency of 98.86%, P1 99.3%, P2 99.19%, and samples P3, P4 and P5 99.51%. All 6 samples can reduce total Fe concentrations by more than 98% (Table 3.13.) [Căpriță, F.C., et al., 2021].



(a)



(b)

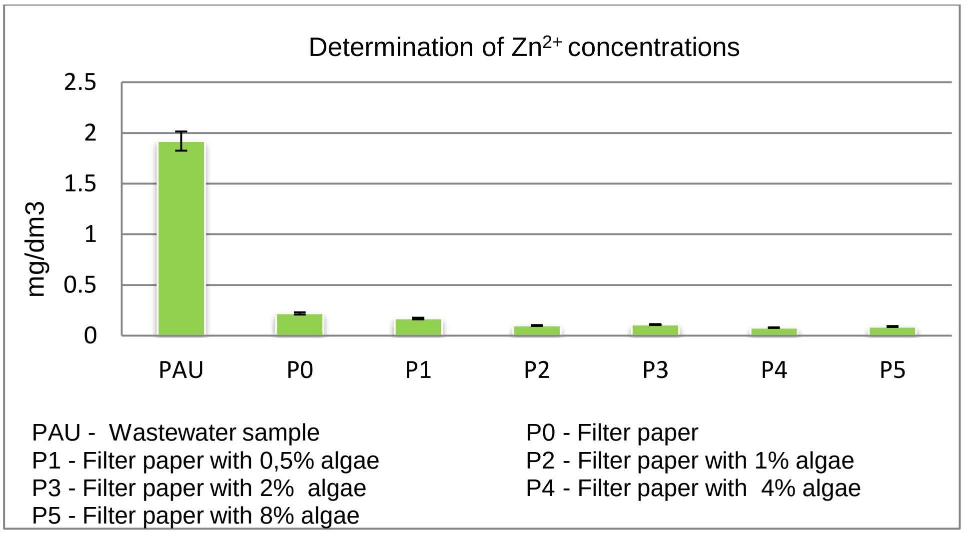
Figure 3.25. Total Fe concentrations obtained after filtration of industrial wastewater using filter papers with different additions of Ulva rigida macrophytes in mass (a) and (b) [Căpriță, F.C., et al., 2021].

In order to demonstrate the reduction capacity of Fe concentrations by seaweed-containing papers, Figure 3.25. b is shown, where the initial Fe concentration found in industrial wastewater was not included.

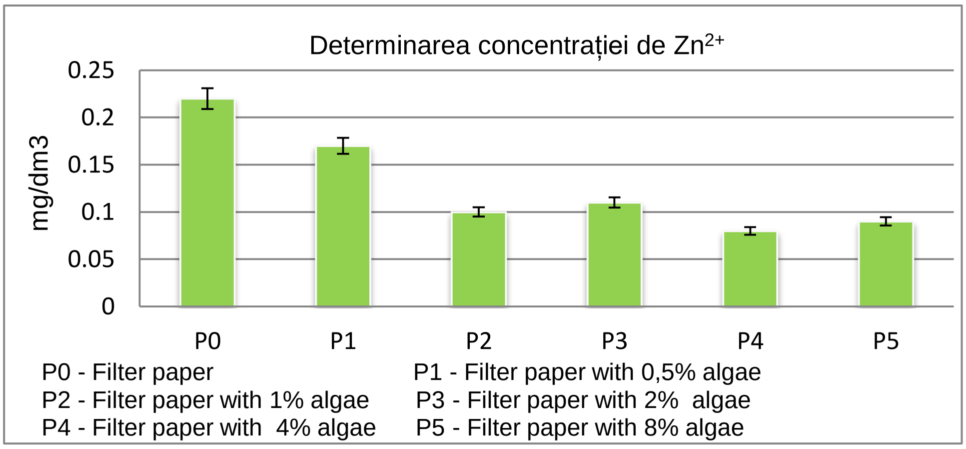
- Determination of Zn^{2+} concentrations in industrial wastewater

For the determination of the reduction concentration potential of Zn2+, sample P1 shows an efficiency of 22.73% when compared to the reference sample P0, P2 shows an efficiency of

54.55%, P3 50%, P4 reduces Zn concentration by 63.64% and P5 by 59.1%, Compared to the baseline concentration of the wastewater sample, P0 reduced the concentration of the pollutant by 88.54%, P1 by 91.15%, P2 by 94.79%, P3 by 94.27%, P4 by 95.83% and P5 by 95.31%. A better retention capacity is observed for the seaweed-added filter paper samples, above 91% for all 5 samples (Figure 3.26; Table 3.13.) [Căpriță, F.C., et al., 2021]. Figure 3.26. b, highlights the reduction capacity of the Zn concenrations of the seaweed-added filter paper samples, without further comparison with the initial concentration in the wastewater sample.



(a)



(b)

Figure 3.26. Reduction efficiency of Zn^{2+} concentrations after industrial wastewater filtration using filter papers with different mass additions of *Ulva rigida* algae [Căpriță, F.C., et al., 2021].

- Determination of TDS concentrations in wastewater

Determination of TDS in water reveals the total amount of dissolved substances in the water, including salts, minerals and other organic and inorganic substances. For the determination of TDS concentrations, sample P1, which consists of filter paper with 0.5% seaweed added, shows a reduction efficiency of only 0.46% compared to the control sample, P2 and P3 of 3.21%, P4 of 3.9% and P5 of 3.67%. Comparing the results with the original data on TDS concentration in the wastewater sample used in the experiment, P0 shows an efficiency of 6.84% improvement in TDS retention, P1 an efficiency of 7.26%, P2 and P3 an efficiency of 10.47% and P5 an improvement of 10.26% (Figure 3.27; Table 3.13.) [Căpriță, F.C., et al., 2021].

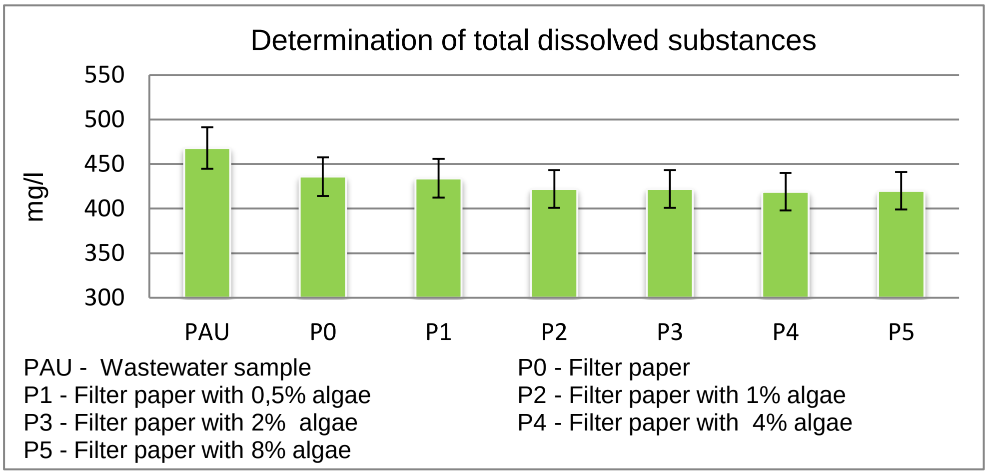


Figure 3.27. TDS determination results obtained after filtration of industrial wastewater using filter papers with different mass additions of *Ulva rigida* algae [Căpriță, F.C., et al., 2021].

- Determination of TSS concentrations in industrial wastewater

Through the use of this method it was possible to show the total amount of solids that remain suspended in water or other liquid and do not dissolve completely. From the analysis of the data obtained, it can be accepted that P0 reduces TSS concentrations by 99.8%, P1 by 99.91% and P2 by 99.87%; and the last samples, P3, P4 and P5, show 100% efficiency. Comparing the samples of interest with P0, P1 shows a high efficiency of 60%; P2 40%; and P3, P4 and P5 100% (Figure 3.28.) [Căpriță, F.C., et al., 2021].

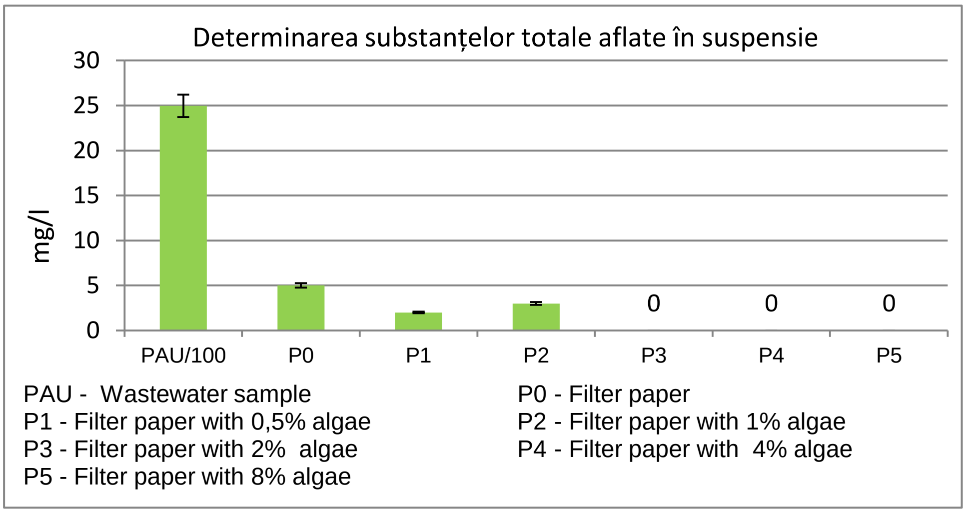


Figure 3.28. Values obtained from TSS determination using filter paper filtration with different mass concentrations of *Ulva rigida* macrophytes [Căpriță, F.C., et al., 2021].

Due to the fact that the results of analyses of wastewater filtration containing metals using samples consisting of filter papers with additions of up to a maximum of 8% seaweed of the species Ulva rigida added by mass are promising [Căpriță, F.C., et al., 2021], filter papers with higher additions of seaweed added by mass to the samples were manufactured in order to also evaluate their capacity to retain the studied pollutants. Filter papers with additions of 10, 20, 30 and 50% algae incorporated in the sample mass were manufactured at laboratory level. For the analysis of these paper samples, substances of known concentrations of Cu^{2+}, Fe^{2+} and Zn^{2+} were prepared in order to have more control over the experiment [Căpriță, F.C., et al., 2021]. The results of this research phase are presented in Table 3.14. [Căpriță, F.C., et al., 2023].

Table 3.14. *Results obtained from filtration of samples of solutions of different metals, known concentrations, expressed in mg/l*

Sample name	Samples	Cu^{2+}	Fe^{2+}	Zn^{2+}
PS	Solution of known concentration	1	2	1,5
P0	Filter paper without added seaweed	0,41	0,76	0,72
P6	Filter paper with 10% seaweed added	0,43	0,49	0,67
P7	Filter paper with 20% seaweed added	0,3	0,55	0,38
P8	Filter paper with 30% seaweed added	0,24	0,67	0,40
P9	Filter paper with 50% seaweed added	0,77	1,8	0,97

- Determination of Cu^{2+} concentrations in 0.5 g/l solution

For this determination a solution was prepared using $CuSO_4$. $CuSO_4$ is the chemical formula for an inorganic compound known as copper(II) sulphate. It consists of a positively charged copper ion (Cu^{2+}) and a negatively charged sulphate ion (SO_4^{2-}). Copper sulphate has a solid crystalline structure and is blue in colour. This compound is used in various fields such as the chemical industry, agriculture, medicine and electroplating processes.

$CuSO_4 \times 5H_2O$ Molecular weight= 249,68 g
Cu^{2+} Molecular weight= 63,546 g

249,68 g $CuSO_4 \times 5H_2O$ ……………… 63,546 g Cu^{2+}
X ……………………………… 0,5 g

X g= $\frac{249,68\ x\ 0,5}{63,546}$= 1,965 g of $CuSO_4$ was dissolved in one litre of demineralised water. To obtain a solution of concentration 1 mg/l, 2 ml of the 0.5 g/l Cu^{2+} solution was diluted in one litre of demineralised water.

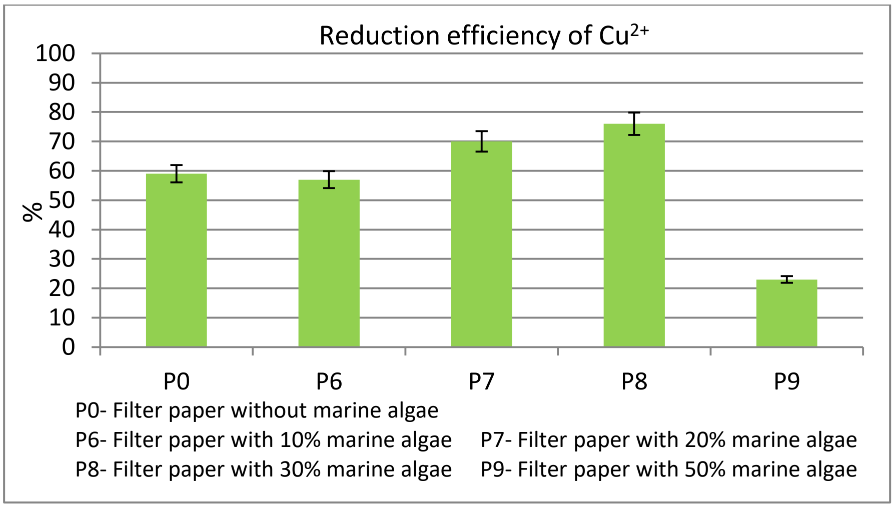


Figure 3.29. Filtration efficiency of Cu^{2+} solution using filter papers with different mass additions of *Ulva rigida* algae

From the analysis of the results of this stage of the research, it can be seen that all 5 samples show low values compared to the water sample consisting of 1 mg/l Cu^{2+} solution.

Thus, sample P0, which consists of the filter paper sample without added seaweed, and is the reference sample, reduced the concentration of Cu^{2+} in the analysed solution by 59%, while sample P6, which consists of the filter paper with added seaweed of 10%, reduced it by 57%. Samples P7 and P8, filter papers with 20 and 30% seaweed added respectively, reduced the concentration of this metal by 70 and 76% respectively, while sample P9, filter paper with 50% seaweed added, reduced the concentration of Cu by only 23%. One of the reasons for this phenomenon is that the strength of the fibre network is weakened by the high addition of seaweed particles. It can be seen that the filter paper, P0, reduces the concentration by a similar percentage to sample P6, and if we compare samples P7, P8 and P9 with the control sample, we see that the results are as follows, -26.8%, -41.5% and +87.8%. The sample with the highest addition of algae is ineffective in reducing Cu^{2+} concentration (Figure 3.29.).

- Determination of Fe^{2+} concentrations in the 0.5 g/l solution

In order to determine the Fe^{2+} concentration that the filter paper samples with added algae can retain, a solution with known Fe^{2+} concentration was used. For the chemical solution, $FeSO_4$, an inorganic compound consisting of an iron ion (Fe^{2+}) and a sulphate ion (SO_4^{2-}), was used. It is found as blue-green crystals or crystalline powder and is soluble in water. $FeSO_4$ has various uses. For example, because of its iron content, it is used as a food supplement, in the textile industry and in the production of pigments and paints, as a soil fertiliser because it supplies iron to plants, helping to improve plant health and agricultural production; in addition, because of its oxidative and antibacterial properties, it is an active ingredient in cleaning products.

$FeSo_4 \times 7H_2O$ Molecular weight= 278,028 g
Fe^{2+} Molecular weight= 55,845 g

278,028 g $FeSO_4$........................... 55,845 g
X g .... 0,5 g

$Xg=\frac{278{,}028x\ 0{,}5}{55{,}845}$ = 2,489 g $FeSo_4$ was dissolved in one liter of demineralized water. To obtain a solution of concentration 2 mg/l, 4 ml of the 0.5 g/l Fe^{2+} solution was diluted in one liter of demineralized water.

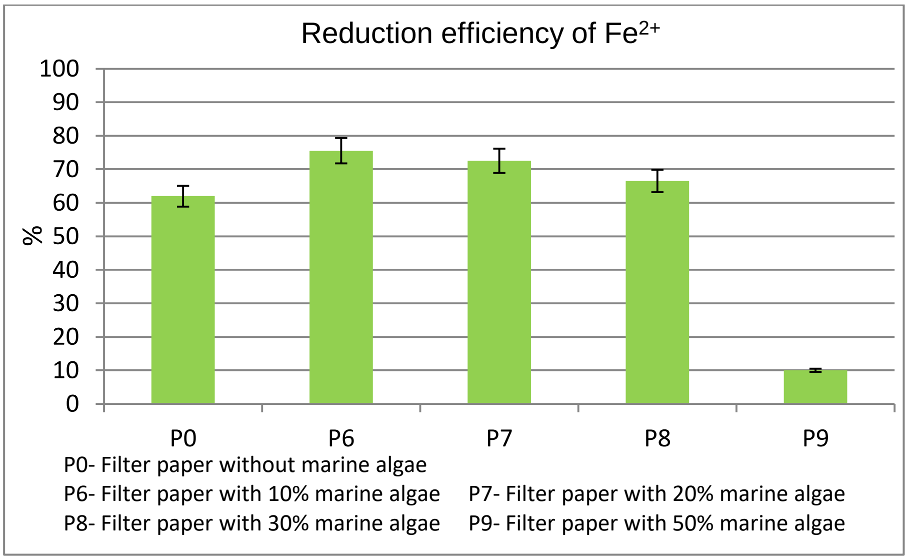


Figure 3.30. Reduction efficiency of Fe^{2+} concentration by filtration using filter papers with different mass additions of *Ulva rigida* algae.

The chart in Figure 3.30. illustrates the reduction in Fe2+ concentration for all samples subjected to the filtration process. Sample P0, the reference sample consisting of a common filter paper, reduced the Fe2+ concentration in solution by 62%, sample P6, the filter paper with 10% addition reduced the concentration by 75.5% while the less efficient sample P7 reduced the concentration by 72.5% and sample P8 by 66.5%. Again, the sample identified with the notation P9 was the least effective, reducing the concentration by only 10%. This draws attention to the fact that the dosage of 50% seaweed introduced into the paper mass, affects the filtration efficiency.

- Determination of Zn^{2+} concentrations in the 0.5 g/l solution

In order to analyse the zinc retention capacity of zinc-containing water sources by the studied samples of seaweed filter papers, a Zn^{2+} solution of known concentration was first obtained. To obtain the solution, $ZnCl_2$, a chemical made of zinc and chlorine atoms, was used. It occurs as white solid crystals and has many industrial uses, including textiles, disinfection, wood processing and battery production. It is also used as an active ingredient in some cosmetics and medicines.

$ZnCl_2$ Molecular weight = 136,315 g
Zn^{2+} Molecular weight = 65,409 g

136,315 g $ZnCl_2$........................... 65,409 g
X g .... 0,5 g

$Xg=\frac{136,315 \ x\ 0,5}{65,409} = 1,042$ g of $ZnCl_2$ was dissolved in one litre of demineralised water. To obtain a solution of concentration 1.5 mg/l, 3 ml of the 0.5 g/l Zn^{2+} solution was diluted in one litre of demineralised water.

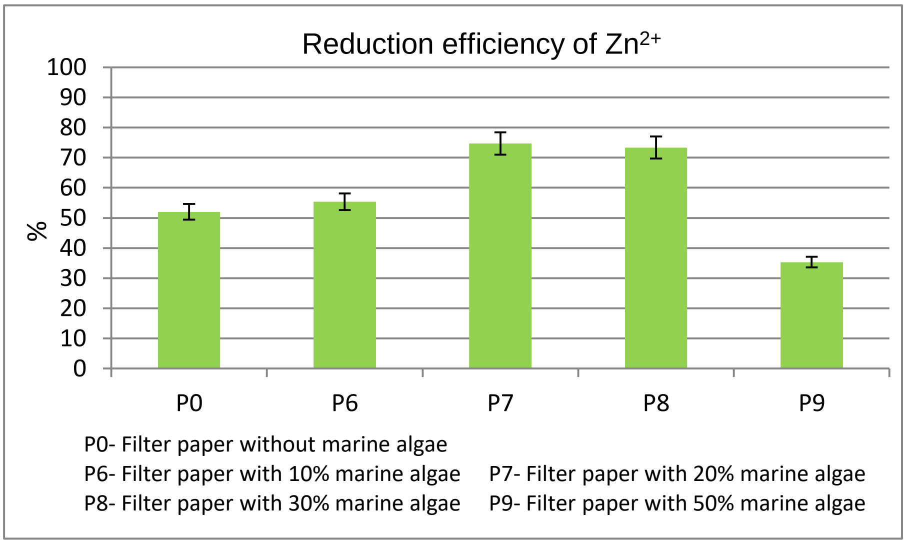


Figure 3.31. Filtration removal efficiency of Zn^{2+} concentration using filter papers with different macroalgae mass additions.

Considering the graph in Figure 3.31., the removal capacity of zinc from the prepared solution is observed for all 5 samples subjected to filtration. The control sample, P0, reduced the concentration of this metal by 52%, while samples P6, P7 and P8 were more effective in reducing the concentration, with 55.33%, 74.67% and 73.33% respectively. Sample P9, which is the filter paper with the highest seaweed content of 50%, is not as practical as the other filter paper samples with lower seaweed content. It can easily be seen that it is less productive even compared to sample P0 (the reference sample). During the determinations, two of the samples even got punctured by the 100 ml volume of sample that was filtered out, requiring the experiment to be repeated.

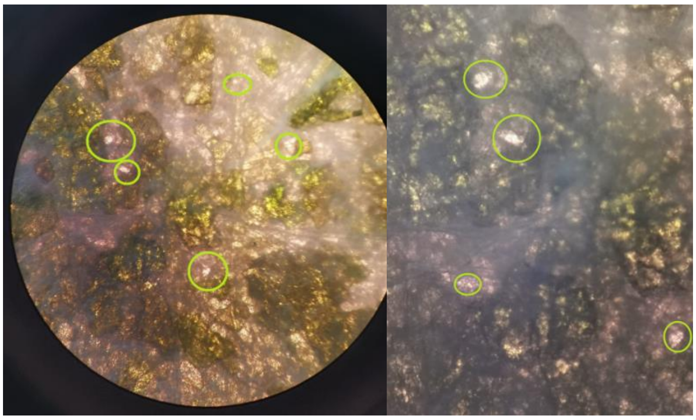


Figure 3.32. Microscopic analysis of the surface of filter paper samples with the addition of 50% seaweed (source: Căpriță, F.C., Microscopy Laboratory Ceprohart SA Brăila)

The poor efficiency of the filter paper samples obtained with the highest concentrations of seaweed, 50%, is due to the presence of voids in their structure (Figure 3.32).

3.6. Metal removal/retention capacity of different seaweed species

In order to highlight the metal removal/retention capacity of seaweeds, seaweeds that have not undergone mechanical processing steps towards incorporation into the filter paper mass were also studied. Five different species of macrophytic seaweeds, collected from the Black Sea coast, Constanta area, Romania, were analysed in the research on the possibility to recover stranded macrophytic seaweeds by using them for metal removal. The samples collected and used as biomass were: *Cladophora sericea*, *Ulva rigida*, *Punctaria latifolia*, *Callithamnion corymbosum* and *Pyropia leucosticta* [Căpriță, F.C., and Ene, A., 2021]. The collected macrophytes were washed with drinking water and distilled water to remove any epiphytic algae, sand particles or other debris and were dried in an oven at 105°C. The drying time was variable for each sample, depending on the moisture content of each sample, from 2 hours and 10 minutes for Callithamnion corymbosum to 2 hours and 40 minutes for *Ulva rigida* algae. After drying, the samples were wetted, and to determine particle size distribution, the materials were subjected to the dry sorting process on sites with different mesh diameters using the 500 µ particle size fractions.

After preparation of the materials, they were used to remove Cu^{2+} metals, Cr^{3+} and Cr^{6+}, Fe^{2+} and Fe^{3+} and Zn^{2+}, which were found in the wastewater source from the metallurgical industry. As a working procedure, 1 g of biomass material was used, introduced separately into 100 ml of wastewater. The mixture was stirred at 800 rpm using a magnetic stirrer for 30 min [Căpriță, F. C., and Ene, A., 2021].

In order to analyze and demonstrate the removal capacity of the studied metals by the selected seaweed species, the wastewater samples were analyzed using the HACH DR 2800 spectrophotometer before and after the seaweed application. The experimental data obtained were processed in the laboratory of the INPOLDE research centre, multidisciplinary platform ReForm-UDJG of the Danube University of Galati, Romania.

Table 3.15. *Results of research on the metal removal capacity of different species of seaweeds, results expressed in mg/l [Căpriță F. C., and Ene A., 2021].*

Metals	Waste water	NTPA 002	*Ulva rigida*	*Punctaria latifolia*	*Pyropia leucosticta*	*Callithamnion corymbosum*	*Cladophora sericea*
Cu^{2+}	4.47	0.2	1.32	1.15	3.1	1.21	1.24
Cr^{3+} & Cr^{6+}	0.94	1.5	0.54	0.55	0.73	0.62	0.33
Fe^{2+} & Fe^{3+}	9.81	5.0	3.95	2.76	3.7	2.89	1.12
Zn^{2+}	2.13	1.0	0.6	0.47	0.6	0.93	0.84

According to the Wastewater Discharge Regulation, approved by Government Decision No. 188/2002, NTPA 002, the concentrations of copper, iron and zinc exceed the maximum allowable limits (Table 3.15.) for discharge into the city's sewage system, which is why it is necessary to apply abatement techniques. The company that generated this industrial wastewater was equipped with a decanter, but it is obvious that it was undersized and further pollutant removal steps are needed. In the case of metals, the most common techniques are chemical precipitation, where a precipitating agent such as calcium hydroxide is added to aid sedimentation, ion exchange, adsorption using various adsorbents such as activated carbon, electrocoagulation, ozonation or reverse osmosis membranes, but these are expensive to apply.

Figure 3.35. Macrophytic seaweed species sampled from the Romanian Black Sea coast, *Ulva rigida, Punctaria latifolia, Pyropia leucosticta, Callithamnion corymbosum* and *Cladophora sericea* [Căpriță, F. C., and Ene, A., 2021].

- Cu^{2+} removal by the five species of seaweed

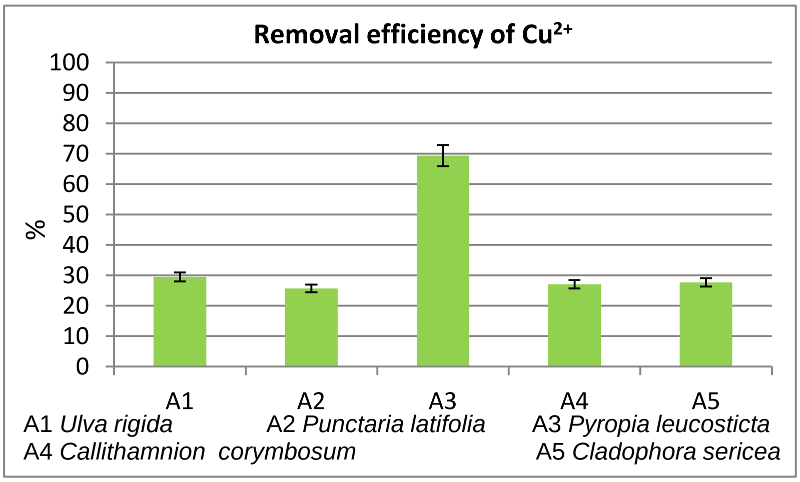


Figure 3.36. Determination of Cu^{2+} removal capacity by macroalgae harvested from the Black Sea.

The determination of the copper concentration reduction capacity of the selected species of seaweeds shows the performance of all the species in assimilating this metal, but the decreases in concentrations were not sufficiently efficient to record values below the maximum allowable limit of NTPA 002. The best efficiency was recorded for the species

Punctaria latifolia, 74.27% and the lowest efficiency for the species Pyropia leucosticta, only 30.65%. All species, not including Pyropia leucosticta, have a yield above 70% (Figure 3.36). The utility of the species, is as follows: *Punctaria latifolia>Callithamnion corymbosum>Cladophora sericea>Ulva rigida>Pyropia leucosticta* [Căpriță, F. C., and Ene, A., 2021].

- Chromium removal efficiency by selected algal species

The initial concentration of chromium identified in the industrial wastewater source analysed shows a value below the maximum limit allowed for discharge into the sewage system; however, research was also carried out on this metal to determine the possibility of removal and the maximum capacity the algae have without being stimulated by pretreatment or process modifications. The highest assimilation efficiency of this metal could be observed for Cladophora sericea species, 64.89%, and the lowest for Pyropia leucosticta species, only 22.34%. The ranking of the samples according to the degree of removal achieved places the algal species in the following order: *Cladophora sericea>Ulva rigida>Punctaria latifolia>Callithamnion corymbosum>Pyropia leucosticta* (Figure 3.37.) [Căpriță, F. C., and Ene, A., 2021].

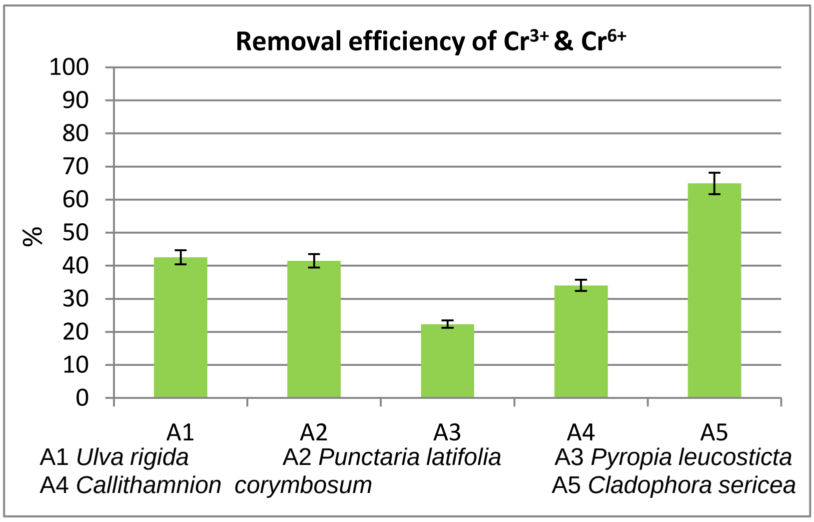


Figure 3.37. Determination of Cr^{3+} and Cr^{6+} removal capacity of macroalgae harvested from the Black Sea [Căpriță, F. C., and Ene, A., 2021]

- Analysis of total iron concentration reduction by marine algae

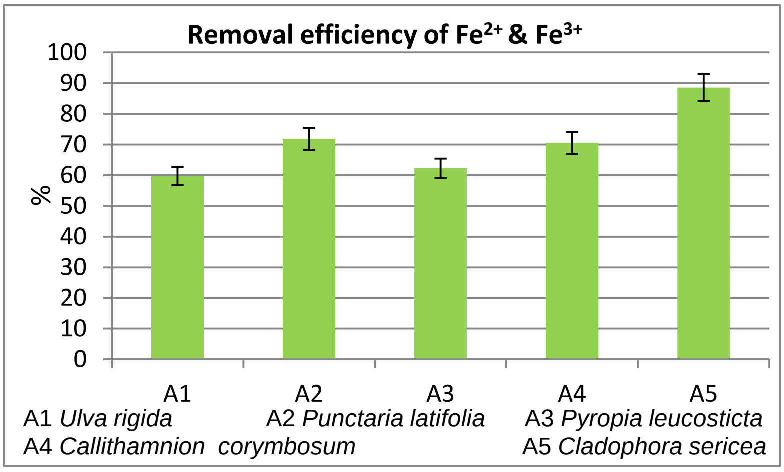


Figure 3.38. Reduction capacity of Fe^{2+} and Fe^{3+} concentration by marine macroalgae collected from the Black Sea [Căpriță, F. C., and Ene, A., 2021].

Following the determination of iron in the analyzed water source, the potential for iron reduction by all five algal species was observed. The results obtained include values below the maximum permissible limit, highlighting the affinity for this metal. Using the Cladophora sericea species, an efficiency of 88.58% was obtained in the reduction of total iron, while the Ulva rigida species showed the lowest efficiency, only 59.73%. The order of the samples according to iron removal capacity is as follows: *Cladophora sericea>Punctaria latifolia>Callithamnion corymbosum>Pyropia leucosticta>Ulva rigida* [Căpriță, F. C., and Ene, A., 2021].

- Study of zinc concentration reduction by marine algae

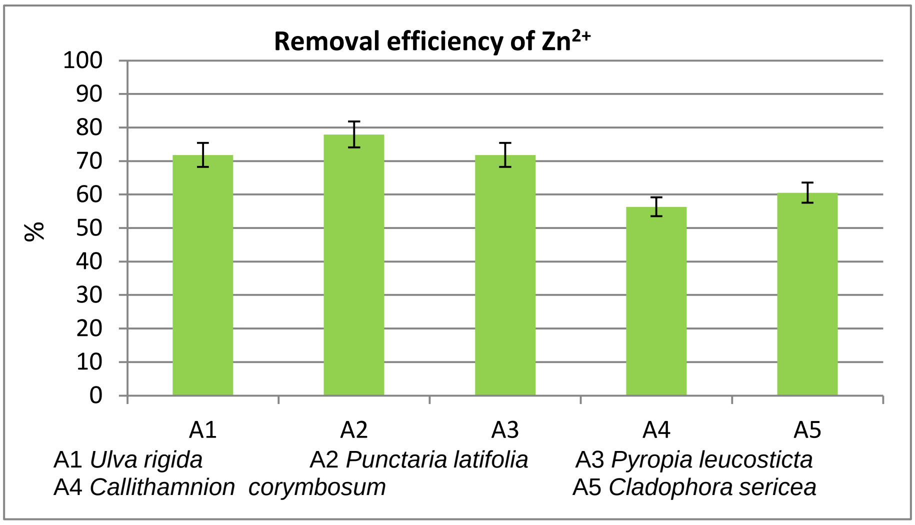


Figure 3.39. Determination of Zn^{2+} concentration reduction property by marine macroalgae collected from the Romanian Black Sea shore [Căpriță, F. C., and Ene, A., 2021].

All the five species analysed show a performance in reducing zinc concentration of over 56%, and the new values obtained are below the maximum limit imposed by the Romanian legislation, making them suitable materials for this purpose. Of the five algae species analysed, the species Punctaria latifolia removed Zn concentration by 77.93%, with the highest efficiency, and the algae species Callithamnion corymbosum had the lowest efficiency of 56.34%. Establishing the order of zinc removal efficiency by the analyzed seaweed species places them consecutively as *Punctaria latifolia>Ulva rigida>Pyropia leucosticte>Cladophora sericea>Callithamnion corymbosum* [Căpriță, F. C., and Ene, A., 2021].

Partial conclusions

A new direction of seaweed recovery has been identified, by incorporating seaweed into paper pulp. The laboratory has succeeded in adding different percentages of seaweed, 0.5, 1, 2, 4, 8, 10, 20, 30 and 50% to the filter paper mass. The utilization of algae by this method has the benefit of displacing the pulp raw material. The newly obtained product has been successfully used for the removal of Cu, Cr, Fe and Zn pollutants from an industrial wastewater source. The characteristics of filter paper samples were determined. For some characteristics some improvements can be observed. The addition of 50% seaweed displaces too much fibre, making the filtration resistance unstable. SEM-EDX methods for the identification of chemical elements found in the samples, ATR-FTIR method for the identification of functional chemical groups, as well as PIGE and PIXE nuclear methods for the complementary analysis of chemical elements were applied on the new products obtained.

4. General Conclusions, Personal Contributions and Perspectivese

General Conclusions

The PhD work entitled "The use of marine algae for the removal of pollutants from industrial wastewater" investigated the possibility of using marine algae for the reduction of Cu, Cr, Fe and Zn pollutants from wastewater sources by obtaining a new product at industrial laboratory level.

Seaweed collected from the Romanian Black Sea coast was processed and introduced into the structure of filter papers, and the newly obtained product was subjected to complex analysis by combining classical methods of investigation and advanced spectroscopic and nuclear techniques for the analysis of environmental samples. Thus, the steps to be carried out to obtain filter paper samples were identified, a series of samples were manufactured at laboratory level, with different seaweed mass additions, from 0.5% to 50%. The strength characteristics of the samples consisting of newly obtained filter papers were evaluated.

The research is the first study of its kind in Romania, and the results obtained contribute to the inclusion of a new method of seaweed recovery.

Accelerated Ion Beam Nuclear Spectrometry (AIBP and PIXE) are advanced, complementary techniques, which were used to analyse seaweed samples and those consisting of filter papers with seaweed mass addition for multi-element analysis, aimed at identifying and quantifying chemical elements, in order to highlight the metal removal capacity of the wastewater source used.

The SEM method allowed micromorphological and structural analysis of the samples using a primary electron beam. The SEM-EDX method provided semi-quantitative information on the concentration of elements in the samples analysed, and the following elements were identified: C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu and Zn.

An important feature of this method is the image magnification, which exceeds the capability of optical microscopy, and the much greater depth of field. The SEM technique also provides information about the topography of the sample surface via the secondary electron detector and the backscattered electron detector. Using this method, it was possible to observe the structure of filter paper samples with different seaweed additions, as well as the original seaweed samples. In addition, the EDX technique allows elemental analysis of the material, for elements with atomic number $Z > 6$, by interaction with the primary electron beam.

EDX spectrum and elemental distribution maps showed mainly C and O as dominant elements in the matrix of the paper samples, while higher concentrations of N, S and Ca were also found in algae.

Using the ATR-FTIR molecular spectrometry technique, important data on the characteristic functional groups of the samples were obtained.

Thus, by analysing the absorption bands attributed to the characteristic vibrations of the functional groups present in the samples, absorption bands belonging to the vibrational stretches of O-H groups, C-H bonds of methyl groups, as well as COOH groups, sulphate ester groups and C-O-C groups were identified. These groups favour the adsorption of metal ions.

The PIGE and PIXE techniques allowed complementary determination of the chemical elements present in the samples analysed, identifying the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn and Fe.

After corroborating the results, it was concluded that seaweed filter paper can be used in the process of heavy metal wastewater filtration without introducing hazardous chemical elements.

Following the analysis of samples of filter papers with seaweed incorporated in the mass, it was observed that the density, permeability and ash content of the samples are influenced by the percentage of seaweed introduced. Breaking load and breaking length undergo changes at additions above 8%, and an addition of 50% increases these values, which can also be observed for tear, tear and fold strength.

It can be stated that at 50% algae addition, the paper is a completely different product, with algae considerably increasing these characteristics. Water absorption and moisture content show higher values compared to papers with lower concentrations of seaweed. However, it has been shown that the dislocation of such a high percentage of fibres creates an imbalance in the fibre network structure, weakening the pollutant retention capacity after filtration. After viewing the structure of the samples using a microscope, voids were observed on all surfaces of the 50% seaweed filter paper sample.

Samples consisting of 4 and 8% filter papers show positive results for the removal of pollutants such as Cu, Cr, Fe and Zn. Higher additions of seaweed to the filter paper mass dislodge too high percentages of cellulose fibres, resulting in a lower retention efficiency of the analysed metals.

The study of metal reduction by the macrophytic seaweed species *Ulva rigida, Punctaria latifolia, Pyropia leucosticta, Callithamnion corymbosum* and *Cladophora sericea* revealed their affinity for the retention of copper, chromium, iron and zinc, especially for species belonging to the genus Ulva and Cladophora.

It should be noted that no treatment was applied to the algae to improve their pollutant retention properties, precisely in order to observe their natural capacity and therefore the possibility of using them as such, with as few preparation steps as possible.

This has demonstrated the possibility of exploiting seaweed waste and obtaining a new industrial product with the capacity to reduce some pollutants in waste water.

Personal contributions and future perspectives

- The research has examined the possibility of exploiting macrophytic marine algae found in our country.
- A series of samples of filter papers with added seaweed incorporated in their mass were obtained at laboratory level.
- The maximum concentration of seaweed that can be introduced into the paper structure was evaluated and the characteristics of the samples and the interaction between the two materials were followed.
- The mechanical strengths of the papers and the influence of seaweed in the paper structure were determined.
- Filter paper samples were tested for filtration of a wastewater from the metallurgical industry.
- The reduction capacity of copper, chromium, iron and zinc metal pollutants was evaluated.
- The elements that are found in the structure of the newly obtained product were determined.

Future research directions can be identified, such as:

- Advanced study to assess the removal capacity of several pollutants, e.g. organics, nutrients such as nitrogen and phosphorus, chemicals such as detergents, pesticides and pharmaceuticals, even bacteria.
- Other seaweed species are also used in the pulp and paper industry.
- Exploitation of seaweed through pulp extraction.
- Pre-treatment of algae to improve the adsorption capacity of metals from wastewater sources.
- Use of marine algae for the removal of pollutants from domestic wastewater.
- Extending research to identify other directions of seaweed exploitation.
- Transfer the laboratory model of the concept and process for algae-added filter papers to pilot scale to demonstrate the maturity of the technology.

"Thousands have lived without love, not one without water." W. H. Auden

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PARTICIPATION IN NATIONAL AND INTERNATIONAL PROJECTS

Project Joint Operational Programme Black Sea Basin 2014-2020, code BSB165, Creating a system of innovative transboundary monitoring of the transformations of the Black Sea river ecosystems under the impact of hydropower development and climate change (HydroEcoNex), (2018-2021), Grant contract 105067/14.09.2018, Project coordinator (Partner PP3) Ene Antoaneta (Dunarea de Jos University of Galati); Project Manager: Elena Zubcov (Institute of Zoology, Chisinau) (implementation period: 21 September 2018-20 March 2021). **Student doctorand, voluntar proiect**

Project JINR-Romania no. 63/2019, Assessment of industrial impact on agroecosystems and human health risk in Romania using nuclear and related analytical techniques, JINR Theme no. 03-4-1128-2017/2019, Order JINR 397/27.05.2019, Leaders from Romania: Ene Antoaneta (Project Director, UDJ Galati), Project Responsable: Stihi Claudia (Valahia University of Targoviște); **student doctorand, membru**; 2018-2019.

Project JINR-Romania nr. 64/2019, Assessment of air and soil quality using biomonitoring, neutron activation analysis and related analytical techniques, JINR Theme no. 03-4-1128-2017/2019, Order JINR 397/27.05.2019, Leaders from Romania: Stihi Claudia (Project Director, Valahia University of Targoviste), Ene Antoaneta (Project Responsible partner P1, UDJ Galati); **student doctorand, membru**; 2018-2019.

RESEARCH GRANT JINR-Romania no. 21/2018, Development of laboratory infrastructure for applications of nuclear and magnetic techniques on characterization of agricultural soils and content of potentially toxic elements, Theme no. 03-4-1128-2017/2019, Order IUCN 321/21.05.2018, Director Romania: Ene Antoaneta (UDJ Galati); **student doctorand, membru**; 2018-2019.

Project Joint Operational Programme Black Sea Basin 2014-2020, code BSB27, Black Sea Basin interdisciplinary cooperation network for sustainable joint monitoring of environmental toxicants migration, improved evaluation of ecological state and human health impact of harmful substances, and public exposure prevention (MONITOX) (2018-2021), Grant contract 105070/14.09.2018, Project Manager (Leader Partner) Ene Antoaneta (UDJG); **student doctorand, voluntar,** 2018-2021.

Project JINR-Romania no. 63/2019, Assessment of industrial impact on agroecosystems and human health risk in Romania using nuclear and related analytical techniques, JINR Theme no. 03-4-1128-2017/2019, Order JINR 397/27.05.2019, Leaders from Romania: Ene Antoaneta (Project Director, UDJ Galati), Project Responsable: Stihi Claudia (Valahia University of Targoviște); **student doctorand, membru;** 2018-2019.

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RESEARCH GRANT JINR-Romania no. 26/2019, Development of laboratory infrastructure for applications of nuclear and related techniques on the characterization of agricultural soils andtransfer of potentially toxic elements in plants, Theme no. 03-4-1128- 2017/2019, Director Romania: Ene Antoaneta (UDJ Galati); **student doctorand, membru;** 2018-2019.

RESEARCH PROJECT 2020 JINR-Romania no. 71, Neutron activation analysis and related analytical techniques for the assessment of sediment quality in the Danube River and its deltaic areas, JINR Theme no. 03-4-1128-2017/2022, Investigations in the Field of Nuclear Physics with Neutrons, Leaders from Romania: Ene Antoaneta (Project Director, UDJ Galati), Stihi Claudia (Project Responsible, Valahia University of Targoviste), **membru**.

RESEARCH PROJECT 2020 JINR-Romania no. 68, Air pollution assessment by neutron activation analysis and related atomic methods using biological indicators, JINR Theme no. 03-4-1128-2017/2022, Investigations in the Field of Nuclear Physics with Neutrons, Leaders from Romania: Stihi Claudia (Project Director, Valahia University of Targoviste), Ene Antoaneta (Project Responsible, UDJ Galati), **membru.**

RESEARCH GRANT JINR-Romania no. 32/2020, Development of laboratory infrastructure for applications of nuclear and related techniques for the assessment of soil and sediment quality (metals, radionuclides, microplastics) in Danube and Black Sea region, Theme no. 03-4-1128-2017/2022, Director Romania: Ene Antoaneta.

Grant intern UDJG nr. RF 3621/30.09.2021, Tehnici avansate de cercetare și modelare/simulare utilizate în mediu, medicină și protecția contra radiațiilor nucleare (TASIMEDPRO), Director proiect – Prof.dr. Ene Antoaneta, **membru**.

Grant FDI UDJG – centrul de cercetare INPOLDE, Tehnici radiometrice, spectroscopice și imagistice aplicate în studiul materialelor avansate, mediu și sănătate (RADIOSIMS), Contract nr. 17094/31.05.2022, proiect CNFIS-FDI-2022-0205, 2022, Susținerea cercetării de excelență în activitatea CDI din Universitatea „Dunărea de Jos” din Galați - CEREX UDJG 2022, Director proiect – Prof.dr. Ene Antoaneta; **membru.**

Grant intern UDJG nr. 9187/29.03.2023, Cercetări privind aplicații interdisciplinare ale tehnicilor avansate de analiză și control în studii de mediu, sănătate și știința materialelor (INTERVENT), Director proiect – Prof.dr. Ene Antoaneta; **membru.**.

Proiectul Excelență, performanță și competitivitate în activități CDI la Universitatea “Dunărea de Jos” din Galați, EXPERT (ID 345); Programul 1-Dezvoltarea sistemului național de cercetare-dezvoltare, Subprogram 1.2-Performanță instituțională- Proiecte de finanțare a excelenței în CDI; Cod proiect:14PFE/17.10.2018; Coordonator: Prof.dr. ing. Bahrim Gabriela-Elena; **student doctorand, grup țintă**, 2019-2020.

Proiect „Excelența academică și valori antreprenoriale - sistem de burse pentru asigurarea oportunităților de formare și dezvoltare a competențelor antreprenoriale ale doctoranzilor și post doctoranzilor” – ANTREPRENORDOC Contract nr. 36355/23.05.2019 POCU/380/6/13 - Cod SMIS: 123847, **Membru grup țintă 2 proiect**

Axa prioritară 6 – Educație și competențe

Titlul proiectului: „Excelența academică și valori antreprenoriale - sistem de burse pentru asigurarea oportunităților de formare și dezvoltare a competențelor antreprenoriale ale doctoranzilor și postdoctoranzilor – ANTREPRENORDOC”

Contract nr. 36355/23.05.2019 POCU/380/6/13 - Cod SMIS:123847