STUDY OF THE BIOSORPTION EFFICIENCY OF SEAWEED SPECIES COLLECTED FROM THE BLACK SEA FOR HEAVY METALS REMOVAL IN INDUSTRIAL WASTEWATERS

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Abstract
In this article, it will be presented the results obtained from research conducted in order to reduce the concentrations of metals in industrial wastewater resulted from heavy metal polluting industries, especially the metallurgical industry. Most of the world's water sources are profoundly negatively affected by human activities, and the population faces critical water supply and drinking water quality problems. Millions of people develop various diseases from drinking water from unsafe or poor quality sources, creating a global public health problem. Due to massive industrialisation, current water treatment methods are outdated, which is why water treatment and purification laws, regulations, and controls need to be updated to minimise and stop contamination of the food chain. It is the responsibility of the researchers to make the public aware of the dangers to which they are exposed due to their own negligence and to offer possible solutions to these problems. New, reliable, viable, cheap, and sustainable technologies must be developed to improve drinking water quality. One such technology that can be developed and implemented is using the biological method of biosorption. Stranded seaweed on the Romanian Black Sea coast is currently treated as waste, but it could be exploited as biomass in the biosorption process. The research aimed to investigate the possibility of valorification of macrophyte seaweed species in this direction. Five different species of stranded macrophyte seaweed were collected and used to remove selected metallic ions (Cr, Fe, Zn, Cu) from a source of wastewater resulted from the metallurgical industry processes. The wastewater samples were analyzed before and after the application of the biosorption technique using the spectrophotometric method.

Keywords: biosorption, heavy metals, wastewater, seaweed, Black Sea, Romania.

1. INTRODUCTION

From the available statistical data on the evolution of the world's population, we can see that in 1950 the world's population was 2.5 billion, today it is 7.8 billion, and predictions show that the 10 billion mark will be exceeded somewhere between the years 2050 and 2060, more precisely, in 2056 [1].

Over the next 30 years, the population will expand by a further 28.21%. This aspect needs to be taken into consideration in order to rethink how we utilise the planet's natural resources. Also, for energy-consuming industries, legislation needs to be rethought so that they are made to shift towards replacing energy consumption from non-renewable sources with energy from renewable sources.
Accelerated population growth will generate various problems [2] related to the aggressive exploitation of food and water sources and the generation of waste and pollutants. Current methods of resource exploitation, in terms of the technologies used, do not comply with the principles of sustainable development, therefore it is necessary to improve current technologies or implement new ones that operate at maximum efficiency and generate as little waste and pollutants as possible. Nowadays, society is facing an irrational consumption of resources, which will lead in time to their rapid depletion and to the degradation of environmental factors. In order to prevent this from occurring, it is necessary to implement technologies that use renewable energy and alternative fuels as a source of energy and that can use certain categories of waste. In addition to the environmental benefits of waste recovery, introducing it as a raw material in various technological processes can considerably reduce production costs [3-5].

Water constitutes a vital resource for sustaining life on earth [6] and it is not a renewable resource if its quality is altered with every human action and if its self-purification capacity is exceeded. The state of water quality has a direct environmental, social, and economic impact. The availability of limited freshwater resources worldwide is increasingly scarce due to growing pollution caused by the discharge of large quantities of inadequately treated or untreated wastewaters.

Water pollutants can be classified into organic, inorganic, biological, suspended solids, radioactive, thermal, agricultural, nutrients, and other pollutants. Organic and inorganic pollutants are found in industrial and domestic wastewater effluents [7]. Of all types of pollution, heavy metal pollution is a global concern [8] because, unlike organic pollutants, heavy metals do not degrade [9], they accumulate in living organisms [8, 10], enter the food chain, and reach the top of the food chain, causing multiple health problems to the human population [11]. The main sources of heavy metal contaminants are the mining industry, metallurgical industry, chemical industry, thermoelectric industry, pesticide and fertilizer industry, coal burning, waste water, and product waste disposal [12, 13].
Common methods for removing heavy metals from wastewater that are widely used are chemical precipitation, membrane separation, ion exchange, reverse osmosis, and activated carbon adsorption [13, 15]. All these methods are effective but they are selective and costly. One method that has come to be studied quite intensively nowadays is the adsorption technique, an efficient and economical method that provides the advantage of flexibility in design, functioning, recovery, and regeneration of adsorbates, the process being reversible [13].

Biosorption, on the other hand, is a much more advantageous technique in terms of the importance of environmental protection, as it is a physico-chemical process, based on a variety of mechanisms, including absorption, adsorption, ion exchange, surface complexation and precipitation [16], using living or dead microorganisms, such as vegetal materials, agricultural and industrial wastes [17], bacteria [18,19], fungi [20], yeasts [9, 21] and seaweeds [22-27]. The biosorption technique is an ecological and cost-effective alternative for wastewater treatments. Biosorption is a process by which the biomass used has the property of retaining and concentrating heavy metal pollutants from liquid effluents. Many biological materials, such as bacteria, fungi, and algae, demonstrated their biosorption capacity, but the algae have been noted to have an increased potential [25, 28]. Today seaweeds are cultivated and exploited in the food, pharmaceutical, cosmetic, and biofuel industries [29]. Beach cast algae and wild macroalgae populations can be exploited as food and fertilizer. As regards the processing of seaweed from farming, they are subject to the legislation of the field where they will be used as raw material, but for the processing of stranded seaweed, there is no legislation or recommendations from the competent authorities, which is why, in Romania and many other countries, they are considered as simple waste [30].

There is no data on the precise estimation of the quantities of stranded seaweed on the Romanian Black Sea coast, but data provided through the media by the authorities responsible for beach management are available, and according to them, in 2021, more than 10,000 tons were collected by mid-August [31], and in 2020, 3,600 tons only in the first two weeks of August [32].

And according to statistical data provided by the National Institute of Statistics, the structure of wastewater generated in 2018 and 2019 is highlighted in Figure 3 a) and b).

![Fig. 3. Structure of wastewater generated in Romania, a) in 2018 (processed after [33]) and b) in 2019 (processed after [34])](image)

An analysis of the structure of the wastewater generated in 2019 and 2018 shows that the proportion is not very different. In 2019, compared to 2018, 0.1% less domestic wastewater was generated, 0.1% less wastewater from the mining industry, 0.1% more from the food industry, 0.8% higher volume of wastewater from the metallurgical industry, the volume of wastewater generated by the chemical and petrochemical industry remained constant, wastewater generated from the production and distribution of electricity increased by 0.7%, while 1.4% wastewater generated by other economic activities decreased.
Table 1. Average annual quantities of heavy metals from wastewater generated in 2019 and 2018 in Romania [34, 33]

<table>
<thead>
<tr>
<th>Tons/year</th>
<th>Copper</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Lead</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pollutants</td>
<td>38.9</td>
<td>7.0</td>
<td>7.3</td>
<td>22.8</td>
<td>98.7</td>
</tr>
<tr>
<td>Present in industrial wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total pollutants</td>
<td>5.3</td>
<td>1.8</td>
<td>3.5</td>
<td>4.4</td>
<td>23.2</td>
</tr>
<tr>
<td>Present in domestic wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total pollutants in 2019</td>
<td>44.2</td>
<td>8.8</td>
<td>10.8</td>
<td>27.2</td>
<td>121.9</td>
</tr>
<tr>
<td>Total pollutants</td>
<td>22.6</td>
<td>5.4</td>
<td>5.3</td>
<td>10.4</td>
<td>70.8</td>
</tr>
<tr>
<td>Present in industrial wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total pollutants in 2018</td>
<td>28.6</td>
<td>1.6</td>
<td>3.7</td>
<td>4.3</td>
<td>20.2</td>
</tr>
<tr>
<td>Present in domestic wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As can be observed in Table 1, wastewater generated at the national scale in 2019 was more loaded with chromium, nickel, lead, and zinc pollutants compared to 2018 data. Only in the case of the copper contaminant, a decrease of 7 tons was observed in 2019 compared to 2018. In 2019, compared to 2018, the 5 pollutants (copper, chromium, nickel, lead, and zinc) were found in higher quantities in wastewater generated by industries. In 2018, the amount of copper in wastewater sources resulting from domestic activities was 22.6 tons per year, while in 2019, the amount of this pollutant was reduced to only 5.3 tons per year.

In terms of wastewater treatment, Romania is in a much better situation compared to countries such as Albania, Bosnia and Herzegovina, Bulgaria, Serbia, and Turkey, according to an analysis carried out in 2017, meaning that we generate a low volume of wastewater that is discharged untreated into the effluent [35] however, some improvements are needed to reach the standards required by the European Union.

Knowing all these data, the present research aims to determine the possibility of using stranded macrophytic marine algae from the Black Sea coast of Romania as biomass used in the biosorption technique to reduce heavy metal pollutants from industrial wastewater. In this way, stranded seaweed waste can be put to use in an area where it is really needed, thus contributing to sustainable development.

### 2. MATERIALS AND METHODS

In the present research regarding the possibility of valorification of stranded macrophyte marine algae by using the biosorption technique, the biomass of five different species of macrophytes were used, samples were collected from the Black Sea shore, Modern beach, Constanta area, Romania.

The 5 species collected and used were: *Ulva rigida*, *Punctaria latifolia*, *Pyropia leucosticta*, *Callithamnion corymbosum*, and *Cladophora sericea*. After sampling the algae were washed with potable water and distilled water to remove possible epiphytic algal debris and sand particles and dried in an oven at 105 °C with a varied time for each sample, from 2 hours and 10 minutes for *Callithamnion corymbosum* to 2 hours and 40 minutes for *Ulva rigida*. After drying, the samples were crushed and then grinded, and for determining the particle size distribution, the materials were subjected to the dry sieving process and the 500 µ particle size fraction was used.

The prepared materials were used to remove Zn, Cr, Cu, and Fe pollutants from a wastewater source originating from the metallurgical industry. Laboratory procedures were as follows: 1 g of material was introduced separately into 100 ml of wastewater. The mixture was stirred at 800 rpm using a magnetic stirrer for 30 minutes [37].

In order to show the biosorption capacity of the seaweed, the wastewater samples were analysed using the HACH DR 2800 spectrophotometer before and after the biosorption technique was applied.

The experimental data were processed in the laboratory of INPOLDE research centre, multidisciplinary platform ReForm-UDJG of “Dunarea de Jos” University of Galati, Romania.
Fig. 4. Sampling point location, Romanian coast, Constanța area, coordinates: 44° 10' 53 '' N 28° 39' 25 '' E [36]

Fig. 5. The five species of algae used to remove pollutants

Fig. 6. Ulva rigida, Punctaria latifolia, Pyropia leucosticta, Callithamnion corymbosum, and Cladophora sericea

It should be noted that no treatments were applied to the algae with the purpose of improving their pollutant retention properties, precisely in order to observe their natural capacity, and therefore the possibility of using them as such, with a few preparation steps as possible. And for the separation of the two phases, the samples were filtered on quantitative filter paper, weighing 80g/m², thus being able to recover the adsorbent.
2.1. RESULTS AND DISCUSSIONS

In accordance with the Technical Regulation NTPA-002 dated 28 February 2002 on the conditions of wastewater discharge into the sewage networks of the localities and directly into the treatment plants, the analysed wastewater shows exceedances on the maximum allowable concentrations of pollutants based on Zn, Cu, and Fe.

Tabel 2. Biosorption technique application results using seaweed.

<table>
<thead>
<tr>
<th>Determination, mg/l</th>
<th>Wastewater</th>
<th>NTPA 002</th>
<th>Ulva rigida</th>
<th>Punctaria latifolia</th>
<th>Pyropia leucosticta</th>
<th>Callithamnion corymbosum</th>
<th>Cladophora sericea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(^{2+})</td>
<td>2.13</td>
<td>1.0</td>
<td>0.6</td>
<td>0.47</td>
<td>0.6</td>
<td>0.93</td>
<td>0.84</td>
</tr>
<tr>
<td>Cr(^{3+}) &amp; Cr(^{6+})</td>
<td>0.94</td>
<td>1.5</td>
<td>0.54</td>
<td>0.55</td>
<td>0.73</td>
<td>0.62</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>4.47</td>
<td>0.2</td>
<td>1.32</td>
<td>1.15</td>
<td>3.1</td>
<td>1.21</td>
<td>1.24</td>
</tr>
<tr>
<td>Fe(^{2+}) &amp; Fe(^{3+})</td>
<td>9.81</td>
<td>5.0</td>
<td>3.95</td>
<td>2.76</td>
<td>3.7</td>
<td>2.89</td>
<td>1.12</td>
</tr>
</tbody>
</table>

**Fig. 7. Effectiveness of algae treatments in Zn\(^{2+}\) concentration reduction**

Among the five algal species analysed, species *Punctaria latifolia* reduced Zn concentration by 77.93%, with the highest efficiency, and algal species *Callithamnion corymbosum* had the lowest efficiency of 56.34%. All five algae species were able to reduce the Zn concentration below the maximum allowable limit, making them suitable for this purpose. The most effective treatments were those using: *Punctaria latifolia > Ulva rigida > Pyropia leucosticta > Cladophora sericea > Callithamnion corymbosum*.

**Fig. 8. Effectiveness of algae treatments in Cr\(^{3+}\) & Cr\(^{6+}\) concentration reduction**
The initial Cr concentration found in the wastewater is below the maximum allowable limit, thus not causing an environmental problem, however, seaweed could reduce this pollutant by at least 22.34% using *Pyropia leucosticta* algae species and at most 64.89% using species *Cladophora sericea*. The most effective treatments were those using: 
*Cladophora sericea* > *Ulva rigida* > *Punctaria latifolia* > *Callithamnion corymbosum* > *Pyropia leucosticta*

![Cu²⁺ adsorption efficiency](image)

*Fig. 9. Effectiveness of algae treatments in Cu²⁺ concentration reduction*

For the Cu-based pollutant, high exceedances have been recorded and the five algal species have failed to reduce the pollutant below the maximum limit imposed by NTPA-002 but show a fairly high biosorption efficiency. Species *Punctaria latifolia* was able to reduce Cu concentration by 74.27% and the lowest efficiency was achieved by species *Pyropia leucosticta* with only 30.65%. The most effective treatments were those using: 
*Punctaria latifolia* > *Callithamnion corymbosum* > *Cladophora sericea* > *Ulva rigida* > *Pyropia leucosticta*

![Fe²⁺ & Fe³⁺ adsorption efficiency](image)

*Fig. 10. Effectiveness of algae treatments in Fe²⁺ & Fe³⁺ concentration reduction*

As a result of the determination of Fe concentration, it is observed that all five species show an affinity for Fe, with all five managing to reduce the concentration below the maximum value required by legislation. The species *Cladophora sericea* shows efficiency of 88.58% in reducing this pollutant, while the lowest efficiency was recorded by the species *Ulva rigida* of only 59.73%. The most effective treatments were those using: 
*Cladophora sericea* > *Punctaria latifolia* > *Callithamnion corymbosum* > *Pyropia leucosticta* > *Ulva rigida*
4. CONCLUSIONS

The accelerated development of industries in pursuit of profit and neglect of environmental legislation will lead to serious problems in the near future. Population growth will lead to intensive farming, draining of the planet's resources, and causing considerably more waste. Irresponsible consumption of resources and the generation of complex pollutants will reduce the capacity of pollutant removal and discharging insufficiently treated wastewater directly into the effluent will have negative effects on the aquatic environment.

Tougher environmental legislation and controls are needed to ensure progress towards the protection of the environment, natural resources, and public health. Current methods of wastewater treatment are selective and expensive and need to be improved so that they can be used in the distant future. Water quality is constantly changing and its status as an inexhaustible resource is uncertain given the decreasing degree of self-purification.

For environmental protection, it is necessary to implement new methods of reducing pollutants and newer studies in the field have focused on the use of waste for such purposes, contributing to sustainable development.

Stranded seaweed are among these wastes that can be used for this very specific goal, so they can be used to remove metals from industrial and domestic wastewater. The biosorption method has a number of advantages that make it an innovative solution. This research demonstrates that seaweed can be exploited in this direction. All five species of stranded macrophytic seaweed that have been studied, can be used to reduce Zn, Cr, Cu, and Fe concentrations from wastewater. Algae of the species Punctaria latifolia show the highest yield for the removal of the four metals studied, and algae of the species Pyropia leucostica the lowest yield.

It was observed that for the Zn concentration removal, the five algal species could have efficiencies ranging from 56 to 78%, reducing from 1.2 mg/l to 1.66 mg/l while for Cr concentration reduction, the algae had an efficiency ranging from 22 to 65%, reducing a minimum of 0.2 mg/l to 0.61 mg/l of Cr. The efficiency in reducing Cu concentration using seaweed waste varied between 31 and 74%, reducing from 1.37 mg/l to 3.32 mg/l of this pollutant and the capacity in reducing Fe concentration was in the range of 60-89%, with the algae managing to reduce from 5.86 mg/l to 8.69 mg/l of Fe. Given the very short contact time between the two phases and the fact that the algae were not subjected to additional treatments to improve the adsorption capacity, it can be concluded that seaweed can be exploited for the reduction of heavy metals. The fact that the wastewater was filtered on filter paper after the contact time to remove solid particles from the algae also contributed to these positive values, as it is known that cellulose also has the ability to adsorb various ions.

Romania disposes of quite large quantities of stranded seaweed waste during the summer. These could be recovered, the costs of using this method being very low, with a positive efficiency/cost ratio. The influent characteristics of the biosorption method can be adjusted so that their pollutant reduction efficiency is increased while incurring the lowest possible costs. Macrophytic seaweed waste stranded at the Black Sea coast could replace some adsorbents currently used, or at least be introduced as an additional treatment.

Acknowledgments
Caprita Florina Cristiana’s work was supported by the project "ANTREPRENORDOC", Contract no. 36355/23.05.019, financed by The Human Capital Operational Programme 2014-2020 (POCU), Romania.

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