ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XI (XLII) 2019, No. 1

Article DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2019.1.02

VALORIFICATION DIRECTIONS FOR MARINE ALGAE

Florina Cristiana Căpriță [1,2] , Antoaneta Ene [1,2,3]

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

Abstract
Some resources such as soil, air and water are considered inexhaustible and renewable. But in reality, due to massive pollution, the quality of these resources is affected. Increasing quantities, together with the increasing complexity of pollutants, slow the natural processes of self-purification and self-purge. Current technologies used to clean and purify fail to restore the original resource quality. In this regard, algae have been introduced into various methods of treating polluted resources to improve current technologies or to replace them. Marine algae are photosynthetic aquatic plants, which become waste if they are not valorized. In the developed countries they are used as raw or secondary material in different industries. The most important issues of marine algae usage in various industrial applications (pharmaceutical, cosmetics, food, biofuel and sewage treatment industries) are reviewed in this paper, with a focus on their biosorption properties and valorification for accumulation of heavy metals from industrial wastewater.

Keywords: marine algae, valorification, heavy metals, biosorption.

1. INTRODUCTION

According to statistical data, the population of the planet was 5.3 billion in 1990, and currently we are 7.6 billion. It is expected that in 2040 we will reach the threshold of 9 billion and life expectancy will also increase [1]. Along with the population growth, issues related to sustainable development will arise. Agriculture is the first to suffer as a result of population growth, which is already quantitative and not qualitative to cover food needs. Exploitation methods must be sustainable and in continuous progress, and in this way, viable alternatives are always sought, because irrational consumption of any kind will lead to the compromising of resources and to the exhaustion of others, so the emphasis must be on sustainable development [2]. Environmental factors will be irreversibly altered if judicious consumption is not taken into account, and it is absolutely necessary to valorize most of any waste materials and natural resources.

Marine algae are an important resource with great potential for exploitation, that has not yet been fully exploited. Algae are found in nature in marine aquatic habitats, in freshwater, but also on land. Algae are a diversified group of the Chromist Registry, the Plant Regiments, and some of the Monera Regiments.

Approximately 70% of the biomass from the seas and oceans is represented by algae, and they form the phytoplankton underlying the nutrition of the other organisms. Algae are capable of achieving the photosynthesis process with the chlorophyll or phycocyanin pigment and, after this process, algae form most of the oxygen in the water.

Up to now more than 20,000 species of macroalgae have been inventoried, the size of which differs from a few centimeters to 70 meters [3]. The largest number of macroalgae to date is the green

(Chrolophyta) over 8000 species [4], over 7000 species are red algae (Rhodophyta) [5] and the brown (Phaeophyta) over 5000 species [6]. All of these have various utilizations in several industries.

2. MARINE ALGAE- RESOURCE WITH POTENTIAL FOR VALORIFICATION

2.1. Food industry

In Asia, algae form the basis of food, which is consumed raw in salads, cooked and dried. In Ireland and Canada, it is consumed *Palma Palmaria*, and in the UK *Ulva lactuca*.

Vegetable resins, stabilizers and emulsifiers are extracted from marine algae, E 400, E 406, E 407, E 421, thickeners, additives and sweeteners [7]. Carrageenan, which is used as a stabilizer and gelling agent in products such as chocolate, powdered milk, jelly, jams, yogurt, canned meat, etc., is extracted from red algae [8,9]. An organic stabilizer (E406), called agar (agar), used as a food additive in the preparation of ice cream, candy and jam, is extracted from agarofite edible marine algae. The alginate is extracted from the brown algae, used as a thickening and gelling agent used in dairy products, processed, canned, meat products, food supplements, sweets, creams, sauces, ice cream, processed fruits and vegetables, etc. Beta-carotene extracted from green algae pigments is one of the few natural food colorants [9].

2.2. Pharmaceutical and cosmetic industry

The latest research in the field has demonstrated the efficacy of algal extracts for infections with various types of herpesvirus and pandemic influenza virus and HIV [10].

It has become certain that algae tonify the immune system, prevent cardiovascular, renal, ocular, and lung diseases. Raw consumed, marine algae prevent the risk of cancer.

Algae have an energizing effect on the liver, facilitating the elimination of toxins and thus lowering stress levels in the body [11]. They represent good therapy against stress, fatigue and anxiety. The use of algae in cosmetics has been a serious stepping stone with the discovery of active substances that have a rejuvenating effect. Algae are used in spa treatments, wrapping and antistress therapies. Algae extracts contribute to pore closure, skin toning, supports anti-inflammatory effect, helps to reduce spots, irritations and black spots, relieves acne and balances sebum secretion [12].

2.3. Production of biofuels

Along with worrying about climate change, the need to ensure energy security, the rise in oil prices and the fear of not exhausting some resources, the attention of scientists turned to biofuels.

The latest trends in the field research have a practical character and use algal biomass, which is considered to be a major raw material for the production of alternative fuels (biogas, biodiesel, biobutanol, ethanol, etc.) [13].

Scientists estimate that less than 3% of the world's coastal waters can provide enough algae to replace 227 billion liters of fossil fuel, and in optimal conditions, algae can produce annually 19,000 liters of ethanol per hectare, the productivity per hectare being double compared to that of sugar beet and 5 times higher than that of corn. And productivity grows when algae are growing in closed bioreactors.

Romania has a high energy potential of biomass, estimated at about 7,600 tons/year (tons of oil equivalent), or almost 19% of total primary consumption in 2000 [14].

2.4. Use of algae for industrial effluent treatment

The most severe environmental problems in the world are those of heavy metal pollution and removing these pollutants from the industrial effluents is a challenge. Because of their major toxic effects, heavy metals from industrial effluent are a major threat to the environment. With the presence of heavy metals in a concentration that exceeds the maximum limit there is the risk of endangering the health of the human beings, living organisms and the environment. The most common methods for toxic metal ions decontamination from wastewaters are ion exchange, membrane processes, chemical precipitation, lime coagulation, electroplating, solvent extraction, etc. These conventional technologies have some disadvantages such as high cost, utilization of some non-regenerable materials and generation of toxic sludge. The latest methods of wastewater treatment involve biotechnological innovation such as bioaccumulation, biosorption and adsorption processes, using plant biomass, bacteria, fungi, yeasts and algae.

This biosorption process has been defined as a property of biomolecules or biomass types to bind and concentrate selected ions or other molecules from aqueous solutions. Compared to the bioaccumulation process that is based on active metabolic transport and that has a higher degree of complexity in use, the biosorption of dead biomass is passive and is based on the compatibility of (bio-) sorbent and sorbate [15]. Biosorption is an environmentally friendly and cheap method of removing metals from the environment.

Microorganisms applications as biosorbents for heavy metal removal are the most recently studied and received growing interest due to the advantages it presents, such as rapid kinetics of adsorption and desorption, low cost, and high surface to volume ratio [16].

Researches in the field of heavy metal biosorption have led to the identification of several types of biomass, for example bacteria, fungi, algae, agricultural and industrial wastes and natural residues, efficient in concentrating these metals. For metal removal it can be used both living and dead biomass as well as cellular products such as polysaccharides [17]. Algal biomass has proven to be effective enough to be studied in a more detailed manner. Several studies have revealed that algae possess the capacity of binding heavy metal ions due to the presence of proteins, lipids or polysaccharides that are found on the wall surface of the cell which contain functional groups such as amino, carboxyl, hydroxyl and sulphate, which act as binding sites for heavy metals [18, 19].

Many of the algae species have microscopic dimensions, a characteristic that includes them in the microorganisms category, but the macroalgae species are suitable for the method of treatment of wastewater through biosorption processes due to the fact that they do not need to be grown in cultured medium and can be valorized those that come along to shore by the currents. For pollutants removing from aqueous solutions, all kinds of micro and macro algae species have been tested, and the most effective are the macroalgae, which are flexible in adapting to modified environments and can be easily determined by species, observed as they grow, can be simple handled and analyzed.

Marine algae are known to accumulate large amounts of heavy metals like Zn, Cd, Cu, Cr, Fe, Hg, Ni, Pb, and other pollutants.

There were tested samples of wastewater from textile industry using the biosorption method with microalgae and from the results it's concluded these are effective for removing alkali metals and industry specific chemicals [20]. In the study it was used *Chlorococcum vitiosum*, a species of microalgae. The dyeing factory from which the wastewater was used for analysis generate a quantity of 3570 liters/day of wastewater. The microalgae cultures were grown in a thermo-statically controlled environmental chamber, at 24 ± 1°C, illuminated with cool white fluorescent lamps and were microscopically examined using Olympus (HB) microscope. The algal cultures were pelleted by centrifugation at 7500 rpm for about 15 minutes and then were washed with glass distilled water, again centrifuged and dried for 24 hours in an oven until constant weight. After microalgae treatment, variations in the concentration of alkali metals and the nitrate concentration have been observed since the dyeing process uses salts to maintain alkaline state. The application of microalgae resulted in a considerable reduction of alkaline metals, Na, K, and alkaline-earth metal, Mg and Ca. The results validated the possibility of using microalgae in the treatment of alkaline metals present in the wastewater [20].

The possibilities of removing detergents and nitrites from wastewater have also been studied, with favorable results in reducing the concentrations by micro and macroalgae. In the Republic of Moldova, the species of *Cladophora glomerata (L.) kütz* and *Chaetomorpha linum (Muller) Kutzing*, species commonly found in rivers and lakes, have been tested to see how they react in contact with wastewater. A number of 7 samples were analyzed with 10 g of algae, in sample 1 drinking water was introduced, sample 2 nitrate rich solution with a concentration of 470 mg/l, sample 3 contained 5 g/l detergent, sample 4 only 2 g/l detergent, sample 5 detergent solution 2 g/l and 241 g/l nitrate, sample 6 nitrate rich solution with a concentration of 241 mg/l and sample 7 contained water from the Bâc river with a concentration of detergents - 0.3 mg/l and nitrates - 140 mg/l. The concentration of nitrates over a month decreased by approximately 130 mg/l in sample 6, in sample 7 by 90 mg/l and in sample 5 by approximately 80 mg/l. For samples 1 and 2 it was concluded that due to the high concentration of nitrates the algae suffer a state of stress and the filaments are gathered and deposited on the bottom of the vessel and in samples 3 and 4 has been noticed the death of the algal cells. Based on the results, it was concluded that the analyzed algae species can be used as efficient bio-efficacious water purifiers, presenting ecological and economic advantages, both species being able to reduce the concentration of nitrates and detergents in polluted water [21].

A group of researchers used the *Ulva lactuca* macroalga to remove a series of heavy metals from wastewater. As a result, it has been concluded that marine algae of the above-mentioned species have the ability to remove a number of heavy metals, such as As, Cd, Pb, Cu, Cr, Hg, Mn and Ni. Changing the salinity in the range of 15-35 g/l had no influence on the ability to remove the trace elements from the macroalgae. The Hg and Cr elements were accumulated in the largest proportion, while Ni, Cd and As were accumulated superficially. Analysis were performed for a series of 3 samples with different amounts of algae, 1.5 g/l, 3 g/l and 6 g/l, and the waste water had concentrations of trace elements corresponding to the maximum admissible values in waste water. The sample with 6 g/l of algae had an efficiency of 48% removal of the arsenic element and the 98% mercury element after 24 hours to 72 hours. The analysis made it clear that after the removal of metals from the waste water, Hg and Cr were found in the cell walls of the algae, and Ni, Cd and As were stored at the surface of the algae in a proportion of 60-80%. These results support the assumption that biosorbent and bioaccumulation bioreactor technologies using macroalgae could be a viable, cost-effective and greener option to reduce priority hazardous substances in contaminated waters [22].

The red algae *Gracilaria corticata* from Iran was used as a biosorbent for removing heavy metals from aqueous solutions. Heavy metals that have been analyzed for the purpose of being reduced are copper, lead, cadmium and zinc. The contact time of the samples was 40 minutes, the solutions had pH 5, and in the desorption process 0.1 N HCl was used. Stock solutions (1000 mg / l) of target metals were prepared by dissolving Cd $(NO_3)_2$, $CuSO_4$: H_2O, $ZnSO_4$: $7H_2O$ and Pb $(NO_3)_2$ in distilled water. All were stored in darkened glass flasks at 2-8 ° C and the working analyte mixtures were prepared daily by dilution with the appropriate volume of distillate water. To adjust the pH, 0.1 M HCl solutions and NaOH were used. For all experiments, the glass bottles were washed with 6.0 M HCl before use and rinsed with distilled water. The red alga *Gracilaria corticata* was prepared by cutting it into small pieces (2 mm × 2 mm), soaked in boiling water for 30 min, thoroughly washed under tap water, and left for 2–3 h in distilled water, changed 3–4 times. The washed red alga *Gracilaria corticata* pieces were ground into test tube and oven dried at 80 ˚C and used for biosorption studies. Known proportion of red alga were transferred in a centrifuge tube and 15.0 milliliters of sample solution was added to centrifuge tube. The centrifuge tube was immersed into the ultrasonic water bath for 30 min sonication at 40 kHz of ultrasound frequency and 0.138 kW of power at ambinent temperature. Then, the mixture was centrifuged at 3500 rpm for 10 min to complete phase separation. The upper solution, was withdrawn using a syringe and collected in glass test tube. Finally, the test tube solution injected into the atomic absorption spectrophotometry for analysis.

The influence of pH, contact time, algae quantity and heavy metal concentrations and initial ion metal concentration were observed. In conclusion the sorption capacity of *Gracilaria corticata* biosorbent was lower under highly acidic and highly alkaline conditions. At the contact time of 60 min, the removal of copper, lead, zinc and cadmium, respectively, was 95, 93, 96 and 90%. From 10 g/l^{-1} metal ion solution, pH 7, the biosorption within 40 min sorbent–sorbate contact time, maximum adsorption was achieved with 15 g/l^{-1} red alga *Gracilaria corticata.* The study revealed that this new biosorbent could be used as a low-cost biomaterial for heavy metal wastewater treatment [23].

The industries from Suez Gulf lead to serious environmental problems like heavy metals pollution, and eutrophication. These problems can be solved by using non-living dried biomass of the most blooming algae, *Ulva lactuca* green macroalga and unicellular green alga *Dunaliella salina*, as biosorbents to remove a series of heavy metals like Zn, Cu, Cd, Fe, Mn, Pb, Ni and Cr, from industrial effluents, that belongs to fertilizers and petrochemicals production. First step for preparation of the macroalga biomass was to air-dried for four days and then oven dried for 48 h at 60°C. The microalga was harvested and rinsed several times with deionized water by centrifugation at 5000rpm for 20 minutes to remove impurities and salts. Microalgal biomass pellets were then dried at 60°C until a constant weight. The adsorption process was carried out in the next steps: in a 250 ml conical flask containing 100 ml of wastewater and 1 g of the adsorbent was added. The mixture was agitated on mechanical shaker at 250 rpm for intervals period of 30, 60, 90, 120, 150 and 180 min. The pH was adjusted at 5 and temperature at 25°C before adding the adsorbent. After that, 5 ml of each mixture was centrifuged for 15 minutes at a speed of 5400 rpm to separate the supernatants from the adsorbent. By atomic absorption was determined the residual concentration of the tested heavy metals (Cd, Zn, Cu, Mn, Pb, Fe, Cr and Ni). The results from analyzes validate that biosorption capacity of *D. salina* was more powerful for Cd, Zn and Pb especially in case of lead (22.34 mg/g) and *Ulva lactuca* was more efficient for Fe (4.07-15.86 mg/g) and Cu (0.83-11.49 mg/g). On the other hand, anent the removal efficiencies, Cu, Fe and Mn had maximum removal efficiencies by *Ulva lactuca* within both effluents (91.8, 87.2 and 84.8%). However, in case of Zn (87.4%), Pb (86.2%) and Cd (81.5%) removal, alga *Dunaliella salina* was the most efficient. Again, it was confirmed through biosorption technique the potential use of *Ulva lactuca* for removal of Cu, Fe, and Mn, and *D. salina* in removing Cd, Zn, and Pb from industrial polluted effluents [24].

In the blooming season the enormous amount of *Ulva* biomass thus becomes a troublesome waste disposal problem. On the other hand, it has been revealed that nonliving seaweed biomass, has a high capacity for assimilating heavy metals. The sorption capacity of Cd on *Ulva lactuca* biomass increased after pretreatment with alkaline solution. The material was processed and used as a biosorbent after it had been pretreated with alkaline solution to enhance its biosorption capability. An optimal pH for this process was pH=8 and Cd, Zn and Cu concentrations were in the range of 60-90 mg / l. The results of the analyzes confirm the possibility of use of the Ulva species in the processes of removing heavy metals from wastewater [25].

Another species of macroalga that is studied in biosorbtion processes is *Cladophora fascicularis*, a green filamentous, widely distributed in eutrophic wastewater and intertidal zones in many parts of the world. The influence of several parameters, such as initial pH, time contact, initial Pb (II) concentrations, and temperature were investigated. The kinetics and adsorption equilibrium were obtained from batch experiments. The efficiency of different desorbents (H_2O, HNO_3, Ca $(NO_3)_2$, Na_2EDTA) to remove the adsorbed Pb (II) from the biomass were also evaluated. It was analyzed the IR spectrum of the biosorbent loaded with Pb(II). It was indicated that green marine algae *C. fascicularis*, which is widely available at low cost, can be used as an efficient biosorbent material for removal of Pb(II) from wastewater. The removal rate was fast in the first 30 minute contact. The maximum adsorption capacity was 198.5 mg/g at 298 K and pH 5.0. No significant effect by co-existing cations and anions was observed, except EDTA. Desorption experiments proved that 0.01 mol/L Na_2EDTA was an efficient desorbent for the recovery of Pb(II) from biomass [26].

There are biomass pretreatment procedures which improve the biosorption capacity. They are specific to each species and involve physical and chemical treatments.

It was studied the adsorption of toxic ions of Cu^{+2}, Cr^{+3}, Cd^{+2} and Pb^{+2} using macroalga *Ulva lactuca* and its activated carbon. It was estimated the effect of several parameters such as effect of pH, contact time, algal dose, and initial concentration of metal ions on the adsorption process. The maximum removal efficiency values of algal powder and algal activated carbon for heavy metal ions were 64.5 and 84.7 mg/g for Cu^{+2}, 62.5 and 84.6 mg/g for Cd^{+2}, 60.9 and 82 mg/g for Cr^{+3}, and 68.9 and 83.3 mg/g for Pb^{+2}. The marine green alga *Ulva lactuca* was collected from the Mediterranean Sea coast it was washed with tap water and distilled water then oven dried at 60 °C for 24 h. The dried alga material was ground using a titanium milled and sieved to obtain 0.1–0.2 mm particles. For obtaining the algal activated carbon the dried algal material was carbonized at 600 °C for 3 h in a stainless steel reactor tube. The sample was soaked in potassium hydroxide for 48 h and calcined at 800 °C for 3 h. The produced activated carbon was washed several times with distilled water until a neutral filtrate was obtained and dried at 110 °C. After the important parameters and process were analyzed, the optimal adsorption condition was found to be about pH 5.0, contact time 60 minutes, adsorbent dose 0.8 g / l and initial concentration 60 mg/l KOH-active carbon has been found more efficiently than algae powder in removing heavy metals. Finally, it was concluded that KOH-activated *U. lactuca* may be used as an efficient technology to remove metal ions from the contaminated environment [27].

Marine algae in particular are very effective in removing a wide range of heavy metals (trace elements) and other elements for which reason it was studied the possibility of introducing them into industrial wastewater treatment plants. For example, in Greece, a pilot plant for phosphate removal was successfully tested using the *Ulva lactuca* species and managed to adapt it to low-salinity living environments compared to the natural development environment [28].

The most studied species is *Ulva lactuca*, a species of green leafy macroalgae, which is prone to rapid development, with elevated temperature being the environmental factor that enhances its flowering. A synthesis of biosorption possibility of different species of marine algae, including *Ulva lactuca*, to remove potentially toxic elements from aqueous solutions is presented in Table 1 (adapted after [29]).

Table 1. Biosorption possibility of different species of marine algae to remove potentially toxic elements from aqueous solutions (adapted after [29])

Potentially toxic element	**Algae used**	**Adsorption capacity**
Zn(II)	*Ulva* sp.	29.63 mg/g
Cd	*Scenedesmus quadricauda*	66%
Cd(II)	*Chlorella vulgaris* (dead)	96.8%
Cd(II)	*Chlorella vulgaris* (live)	95.2%
Cd(II)	*Ulva lactuca*	85%
Cd(II)	*Ulva lactuca*	29.2 mg/g
Cd(II)	*Chlamydomonas reinhardtii*	66.5 mg/g
Cd(II)	*Ceramium virgatum*	39.7 mg/g
Cd(II)	*Padina* sp.	90%
Cd(II)	*Durvillaea potatorum*	90%
Pb	*Scenedesmus quadricauda*	82%
Pb(II)	*Ulva lactuca*	34.7 mg/g
Pb(II)	*Chlamydomonas reinhardtii*	253.6 mg/g
Cu(II)	*Ulva fasciata*	73.5 mg/g
Cu(II)	*Sargassum* sp.	72.5 mg/g
Hg(II)	*Chlamydomonas reinhardtii*	89.5 mg/g
Cr(VI)	*Spirogyra* sp.	14.7×10^3 mg metal/kg

The method of treating wastewater by the biosorption technique is relatively simple and has advantages compared to currently used physical and chemical methods. The factors that influence the process are temperature, pH, type of biomass, algal dose, concentration of substances to be removed and contact time, parameters that can be easily identified.

Romania has a favorable context for the application of such an innovative treatment method, thus achieving two possible objectives, namely the purification of the currently scarcely scarce waters and the valorisation of algae as biomaterials. This recovery route presents several advantages over the currently exploited methods for removing pollutants from water.

The most known and used adsorbents for removing pollutants from wastewater are: active coal, granulated coke, ash from blast furnaces, district heating plants, fossil coal, various granular minerals (limestone, dolomite, etc.) of synthetic resins. However, compared to the algal biomass that can be successfully used as an adsorbent, they present a number of cost / cost-effectiveness disadvantages and cannot be recovered.

Future research will be carried out in the frame of doctoral stage on algae species harvested from Black Sea, Romanian part, and their potential use for cleaning selected toxic metals from industrial wastewater.

3. CONCLUSIONS

Population growth, intensive farming development and industrialization have irreversible consequences on the aquatic environment, many of which are destroyed. The inefficient use, irresponsible water consumption and the introduction of pollutants into the circuit affects the entire food chain. And the increasing volumes of polluted waters and the complexity of pollutants make the methods currently used for purification obsolete. Wastewater removal methods of large-scale wastewater currently used are physical and chemical processes, but the most advantageous are biological processes. Processes applied at industrial level are the purification in granular filters and filtered filters, ultrafiltration, electrodialysis, and adsorption with activated carbon, granulated coke, granular minerals. From chemical purification processes we mention neutralization, coagulation, flocculation and ion-exchange oxido-reduction. All of these currently used methods are very costly, laborious and not selective.

It is known that water is an inexhaustible resource, but the excessively high volume of wastewater loaded above the maximum permissible limits leads to the impossibility of water self-purification, permanently changing its quality. Discharges of wastewater into natural receptors can lead to the degradation or destruction of the fauna and flora of the receptor by lowering the amount of oxygen dissolved in the receptor water with negative effects on the organisms of the ecosystem. This may favor negative effects on the receptor and the forms of life on which contains (intoxication, eutrophication, etc.).

The use of marine algae in heavy metal removal processes by biosorption is a relatively simple method for removing pollutants from wastewater. Algae can be used as low-cost sorbents for removing heavy metals from wastewater compared to currently used coal that requires high processing costs.

Algae are an important agent in the fight against pollution and are already used in the world for the treatment of wastewater, especially in the removal of heavy metals, nitrates and phosphorus. Their use has two great advantages over the traditional practices: reducing the amount of chemicals and energy costs.

In Romania, these are not capitalized, becoming waste that is stored in the ecological landfill. Algae are currently used at an industrial level for the production of biofuels in the pharmaceutical, cosmetic, food and chemical industries.

REFERENCES

1. United Nations Department of Economic and Social Affairs, UN projects world population to reach 8.5 billion by 2030, driven by growth in developing countries, https://news.un.org/en/story/2015/07/505352-un-projects-world-population-reach-85-billion-2030-driven-growth-developing, 2013.
2. The Rio Declaration on Environment and Development, http://www.unesco.org/education/pdf/RIO_E.PDF, 1992.
3. El Gamal A., Biological importance of marine algae, Saudi Pharmaceutical Journal, 18(1), 1-25, 2010.
4. Michael D. Guiry, How many species of algae are there?, Phycological Society of America, 48(5), 1057–1063, 2012.
5. Guiry, M.D, "*Algaebase*". www.algaebase.org, 2016.

6. Hoek C. Mann D.G., Jahns H.M., *Algae : an introduction to phycology* Cambridge University Press, Chapter 12, Heterokontophyta Class Phaeophyceae (brown algal), United Kingdom, 165-175, ISBN 9780521316873, 1995.
7. https://sites.google.com/site/naturamedicala/farmacia-verde/algele
8. http://www.agargel.com.br/carrageenan.html
9. Alba K., Kontogiorgos V., Seaweed Polysaccharides (Agar, Alginate Carrageenan), Encyclopedia of Food Chemistry, 240-250, 2019.
10. Sureshbabu N., Manikannan M., Emerging Novel Anti HIV biomolecules from marine Algae: An overview, Journal of Applied Pharmaceutical Science, 5(9), 153-158, 2015.
11. Jai K., Algae in Medicine. Medicinal Plants: Various Perspectives, Pub. Department of Botany & Publication Unit, ISBN 81-87259-85-X, 31-50, 2012.
12. Surabhi J., Roshani K., Upasani V., Applications of algae in cosmetics: an overview, International Journal of Innovative in Science, Engineering and Technology, 7(2), 1269-1278, 2018.
13. Scientific and Technical Report (RST), Development and Validation of Reliable Solutions for Biogas Production from Algal Biomass in the Danube Delta Biosphere Reserve, Implementation Phase No.1 / 2017 Research Studies, Demonstration Model Concept, Sampling and Assessment biomass, procurement of materials and equipment National Institute for Research and Development for Electrical Engineering, 2017.
14. https://www.descopera.ro/dnews/9164090-o-reusita-revolutionara-aduce-biocombustibilul-din-alge-mai-aproape-de-realitate
15. Volesky B., Biosorption and me, Water Research, 41(18), 4017-4029, 2007.
16. Abbas H., Ismail M., Mostafa M., Sulaymon H., Biosorption of heavy metals: a review, Journal of Chemical Science and Technology, 3(4), 74-102, 2014.
17. Wang J., Chen C., Biosorbents for heavy metals removal and their future, Biotechnology Advances, 27(2), 195–226, 2009.
18. Ramelow G.J., Fralick D., Zhao Y., Factors affecting the uptake of aqueous metal ions by dried seaweed biomass, Microbios, 72(291), 81–93, 1992.
19. Holan Z.R., Volesky B., Biosorption of lead and nickel by biomass of marine algae, Biotechnol. Bioeng. 43(11), 1001-1009, 1994.
20. Jaya C., Ashutosh D., Mukesh G., Ravikumar K., Microalgae Application for Treatment of Textile Effluents, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 4(4), 1602-1606, 2013.
21. Gînju E., Fuştei R., Water purification with Cladophora glomerata and Chetamorpha linum - a hygienic and economical perspective, The Scientific Annals of "Nicolae Testemitanu" State University of Medicine and Pharmacy, 113-119, 2010.
22. Henriques B., Teixeira A., Figueira P., Reis A., Almeida J., Vale C., Pereira E., Simultaneous removal of trace elements from contaminated waters by living Ulva lactuca, Science of The Total Environment, 652, 880-888, 2019.
23. Teimouri A., Eslamian S., Shabankare A.,Removal of heavy metals from aqueous solution by red alga Gracilaria corticata as a new biosorbent, Trends in Life Sciences, 5, 236-243, 2016.
24. Mofeed J., Biosorption of Heavy Metals from Aqueous Industrial Effluent by Non-living Biomass of Two Marine Green Algae Ulva lactuca and Dunaliella salina as Biosorbents, The Egyptian Society for Environmental Sciences, 16(1), 43-52, 2017.
25. Suzuki Y., Kametani T., Maruyama T., Removal of heavy metals from aqueous solution by nonliving Ulva seaweed as biosorbent, Water Research, 39(9), 1803-1808, 2005.
26. Deng L., Su Y., Su H., Wang X., Zhu X., Sorption and desorption of lead (II) from wastewater by green algae Cladophora fascicularis, Journal of Hazardous Materials, 143, 220-225, 2007.
27. Wael I., Asad H., Yahia A., Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon, Egyptian journal of basic and applied sciences, 3(3), 241-249, 2016.
28. Tsagkamilis P., Danielidis D., Dring M., Katsaros C., Removal of phosphate by the green seaweed Ulva lactuca in a small-scale sewage treatment plant (Ios Island, Aegean Sea, Greece), Journal of Applied Phycology, 22(3), 330-339,2010.

29. Bilal M., Rasheed T., Sosa-Hernández J.H., Raza A., Nabeel F., Iqbal H., Biosorption: An Interplay between Marine Algae and Potentially Toxic Elements—A Review, Marine Drugs, 16(2) 1-16, 2018.