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Seaweed Potential in Environmental Improving

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Abstract. Owing to the effect of frequent human activities, the climate nowadays on plaxnet earth has become more and more stressed. Pollutions such as greenhouse gases are products from factories and other human activities and have become extremely severe, for the damage they could cause to both human health and surrounding environments. For decades, scientists have been seeking ways to mitigate the situation (while minimizing the cost), and seaweeds, a cheap and widespread species can be a key solution to several problems. In this paper, we demonstrate 3 uses--seaweed as forage to reduce methane production by cattle, seaweed as a heavy metal filter, and seaweed-based biofuel--and the mechanism of each. By doing research on the existing literature, we find that seaweeds have considerable potential in alleviating environmental pressure.

Keywords: Seaweed, climate change, cattle, heavy metal, biofuel, greenhouse gas.

1. Introduction

1.1. Climate change and global warming

The planet Earth has constantly been changing and forcing all lives to adapt and evolve. However, the planet Earth has undergone a drastic change in the past century and created many challenges for both humans and other living creatures. And these changes are still getting more grievous due to human activity and increased emission of greenhouse gases. A higher level of greenhouse gases in Earth's atmosphere would aggravate the greenhouse effect and trap more heat on Earth's surface. According to the Fifth Assessment Report (AR5) of the United Nations' Intergovernmental Panel on Climate Change (IPCC), "each of the last three decades has been successively warmer at the Earth's surface than any preceding decade since 1850" [1]. This long-term increase in the average surface temperature of the Earth is usually referred to as "global warming". According to NASA, the Earth's average temperatures are now the warmest in nearly 12,000 years. In the last 50 years, Earth's average surface temperature had increased by 0.13℃ (0.23°F) per decade. In the decade 2010 - 2019, the average surface temperature was 14.7℃ (58.4°F), which is 0.8℃ (1.4°F) higher than the 20th-century average. And in the year 2021, according to NASA, Earth is 1.2℃ (2.2°F) warmer than at the beginning of the Industrial Revolution, implying that the temperature has already exceeded the previous goal of controlling temperature increase

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within the range of 1.5℃ (2.7℉) [2]. The changes in temperature may seem to be mild, but any slight abnormal variation of the Earth's surface temperature can have devastating outcomes. For instance, climate change on a global scale has occurred recently and human-caused global warming is one of the biggest contributors. Although climate changes have occurred naturally throughout geologic history by reason of abnormality of solar radiation, change in oceanic and atmospheric circulation, and atmospheric chemistry; the rapid change in global temperature and climate over the last 150 years are results of human activities. Since the industrial revolution, greenhouse gas emissions including carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O), and other synthetic greenhouse gases have increased dramatically as a result of fossil fuel burning, animal husbandry, deforestation, and other human activities.

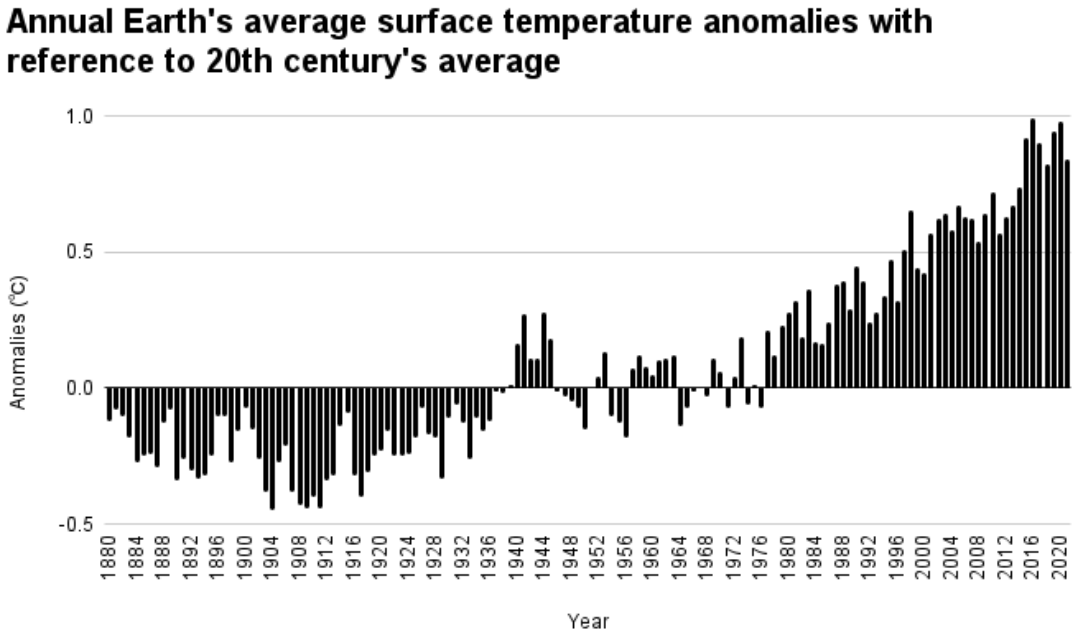


Figure 1. Annual global average surface temperature anomalies with reference to the 20th century's average global surface temperature. a distinct and rapid increase since the 1980s. (data retrieved from noaa) [35].

The greenhouse gas, carbon dioxide (CO2), increased its concentration in the atmosphere from 280 ppm (parts per million) in the pre-industrial era to currently 414.72ppm in 2021, which is a 48% increase. The concentration of methane (CH4) in the atmosphere around 1750 was 0.7ppm and it has increased to 1.84ppm currently. Nevertheless, the concentration of human-made greenhouse gases like chlorofluorocarbons (CFCs) has increased from 0 to now around 0.7ppb (parts per billion)[3]. The increase in the concentration of greenhouse gases will no doubt keep elevating global warming. The horrific outcomes include more intense climate change, more severe natural disasters, rising sea levels, etc. And they can have a devastating effect on human health, and the economy, and even cause the extinction of other species. It is urgent and it is every human's responsibility to take action now and to take care of the common home for millions of species and lives.

1.2. Seaweed

In recent years, seaweed aquaculture has become more and more important in coastal areas, not only for the considerable benefits seaweeds bring but also for their relatively low cost to grow and widespread of them on bodies of water. Seaweeds can effectively mitigate environmental pressure of their potential

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ability of photosynthesizing, absorbing a great amount of greenhouse gas (GHG). The study carried out by Yuhan Zheng, Runjie Jin， etc., has shown the substantial environmental impact seaweeds bring on Chinese coastal areas: the removal of approximately 75,563 tons of nitrogen and the absorption of 1,980,167 tons of CO2[4]. In addition, seaweeds can be consumed by either livestock or human for the rich mineral and distinct element content (iodine, calcium, magnesium), which can have potential health benefit[5]. Last but not least, seaweeds have significant potential in purifying heavy metals from water and producing biofuels, due to their special molecular structure.

There are different ways to classify seaweeds, depending on the types of dietary fibers which they contain or the basis of their color. For the latter case, they are classified as Red Seaweed, Green Seaweed, and Brown Seaweed[4][6].

1.3. Methane emission

The amount of methane emitted during the process of "enteric fermentation" is one of the largest sources of greenhouse gas emissions (GHG) and a considerable contributor to anthropogenic methane (CH4)emissions [7]. It is estimated that nearly 39% of the CH4 is produced every year in animal husbandry. In 2019, several organizations like the World Wildlife Fund (WWF) have gathered 50 related stakeholders to discuss and investigate the possibility of using seaweed, a relatively new material, as additives or directly as forage to mitigate the situation. In fact, there has long been substantial interest among scientists in using seaweeds, especially red seaweeds (*Asparagopsis taxiformis*), as fodder[8][9].

1.4. Heavy metal pollution

Along with big-scale and apparent gas emissions and pollution, metal contamination is sometimes ignored. Metals are omnipresent in human-made products, industries, and the environment. Metals are essential for the development of human society, and sometimes beneficial for human health. However, without proper disposal and processing procedures, metals can leak out and cause harm to the health of organisms and the ecosystem. Although there is no clear scientific definition that separates “heavy metals” from other metal, nonmetal, or metalloid elements, the term “heavy metal” is usually used to describe substances that frequently occurred and yet cannot be clearly defined in environmental-related topics, and most these elements have relatively high density or atomic weight. As for frequently discussed heavy metals, there is cadmium (Cd), lead (Pb), mercury (Hg), chromium (Cr), nickel (Ni), etc. Metals include cadmium, mercury, and lead bind strongly with sulfur-containing groups such as -SH and -SCH3 in cysteine and methionine which increase the bioaccumulation of these metals and cause damage to the health of humans and animals[10]. Therefore, cleaning these metals is crucial for the ecosystem and human health. There could be an easy and relatively cheap way to clean heavy metals in the aquatic and marine environment, which is to use the biomass of marine algal biomass (seaweeds) as a bio sorbent for metal contaminants. The algae and seaweed have the perfect physical and chemical structure that maximizes their biosorption ability and can be used to clean metal pollution and even recover some valuable metals from the aquatic environment.

1.5. Alternative fuel source

Biofuel refers to fuel that is produced by biomass. It is defined as renewable energy because it is readily available. The greatest advantage of biofuel is being cost-effective and environmentally benign.

Nowadays, as the situation is turbulent, gasoline price rises simultaneously. In China, the price of high-grade gasoline had even reached over 10 yuan per liter. Thus, we can not rely only on fossil fuels. Biofuel can be a perfect alternative choice. Besides, fossil fuels are not renewable energy, with the high rate of consumption, we will be soon running out of fossil fuels within the next 25–30 years as estimated. However, biofuel is renewable energy so it won’t have any problems like this. Moreover, burning fossil fuels emits carbon dioxide which leads to the greenhouse effect and pollution, while also making the environment to be more acidic and causing diseases.

Using seaweed for biofuel production can overcome the limitation of energy and land use. Meanwhile, seaweed has no need to look after. Some seaweed species contain up to 40 percent lipids by

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weight, which can be converted into biodiesel or synthetic petroleum. There are estimates which put forward that seaweed could yield between 10 and 100 times more fuel per unit area than biodiesel.[11]

Adam Wargacki and colleagues at the Bio Architecture Lab in Berkeley, California have genetically engineered a new strain of E. coli bacteria, which can feed on the sugars found in brown seaweed and transform the sugars into ethanol. They say this method makes seaweed a "contender" for supplying the world with "real renewable biomass." They published their results in the journal Science in January 2012.[12]

2. Application

2.1. Seaweed-based forage

Enteric fermentation is a common digestive process in ruminant animals like cattle, sheep, and dairy. Together with many microorganisms, foods and forage can be broken down and decomposed for better absorption into their bloodstream system [13]. However, while enteric fermentation is essential to ruminant animals, the by-products it produces- the methane (CH4)-can do great harm to the environment. It is estimated by scientists that the CH4 emission by enteric fermentation accounts for more than 30 percent of the anthropogenic methane（CH4）emissions (AME)[14][15]（as shown in Fig.2,3).

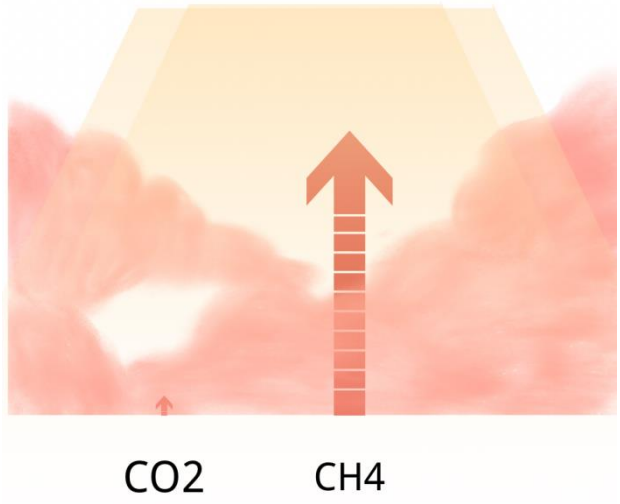


Figure 2. Greenhouse potential of CO2 vs CH4[16].

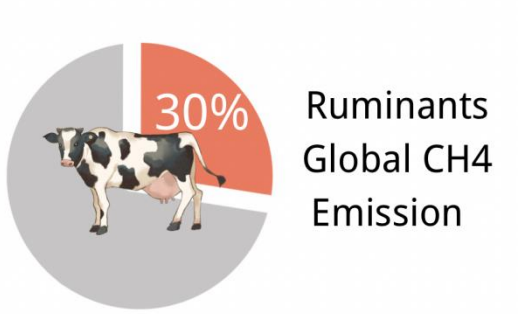


Figure 3. Ruminants Global CH4 Emission (data from reference[14]).

Factors that affect the amount of methane produced, including the type of forages used, can leave the situation unchecked if not ameliorated. The traditional forage, which is usually a mix of grain and hay,

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can worsen the problem. Therefore, scientists have turned to seaweed to mitigate the problem[17]. In fact, there has long been substantial interest among scientists in using red seaweeds (*Asparagopsis taxiformis*) as fodder for their relatively short period of growth and the wide spread of it at the junction of the sea and estuary. They can be made into fodder at a low cost, with full of nutrition and excellent ability to reduce greenhouse gas produced by ruminants like cattle[9]. In addition, studies have shown that adding seaweed to cattle forage will actually not change the flavor of either meat or milk, and can substantially reduce the greenhouse gas emission by as much as 82 percent, according to a new study conducted by researchers at the University of California, Davis[18].

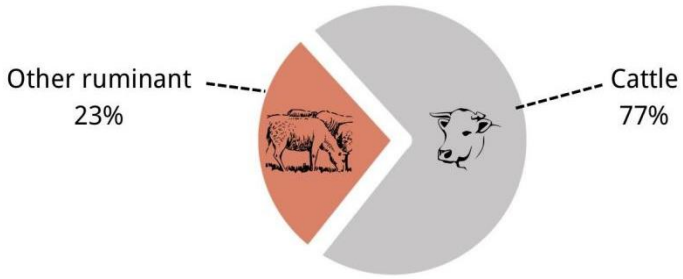


Figure 4. global ch4 emission from ruminant [%] (data from reference [14]).

2.2. Seaweed-based strategies for heavy metal bioremediation and recycling

Water is the most significant substance for all organisms, yet, with the increasing industrial activity and improper disposal of metal-contained products, heavy metal pollution is increasing. The existence of heavy metal pollutants in the aquatic environment is pernicious for the local food chain, ecosystems, and the health of both humans and other animals. Absorption is one of the most widely-used methods for removing pollutants from solution. Fortunately, algae and seaweed biomass also have a good biosorption ability to be used as a biological method to purify heavy metal pollution in water, which is more environmentally friendly and inexpensive among metal removal methods. The seaweed-based biosorbents have the properties of high uptake capacity, low cost, and high biomass abundance in the natural environment (ocean). Meanwhile, many pieces of research have shown that inactive (dead) seaweed/macroalgae biomass may be more efficient than active (living) ones in heavy metal pollution removal. Since the inactive biomass does not require energy for biological growth and can be available as waste or by-product to further reduce the cost [21].

The raw biomass often needs a little preparation before applying as a biosorbent. The general preparation includes the steps of physical, thermal, chemical, and combined activation. In the physical treatment of the raw biomass, techniques such as washing, drying, grinding, and downsizing the biomass particles will be applied (Fig. 5). Normally in the drying process, the temperature should be set below 100 ℃ to protect the natural characteristics of the biomass [3]. The heat or thermal treatment comes after physical preparation. The pyrolysis process for biomaterials is usually set below 800 ℃ and allows the biomass to have a larger surface area and more active sites on the surface for heavy metal absorption resulting in a larger absorption capacity [29]. Finally, the chemical modification of the biosorbent can provide stronger active sites and more functional groups on the surface to further improve its absorption ability. Also, with proper chemical modification, seaweed-based biosorbent can be more practical and more adaptable in a complex aqueous environment.

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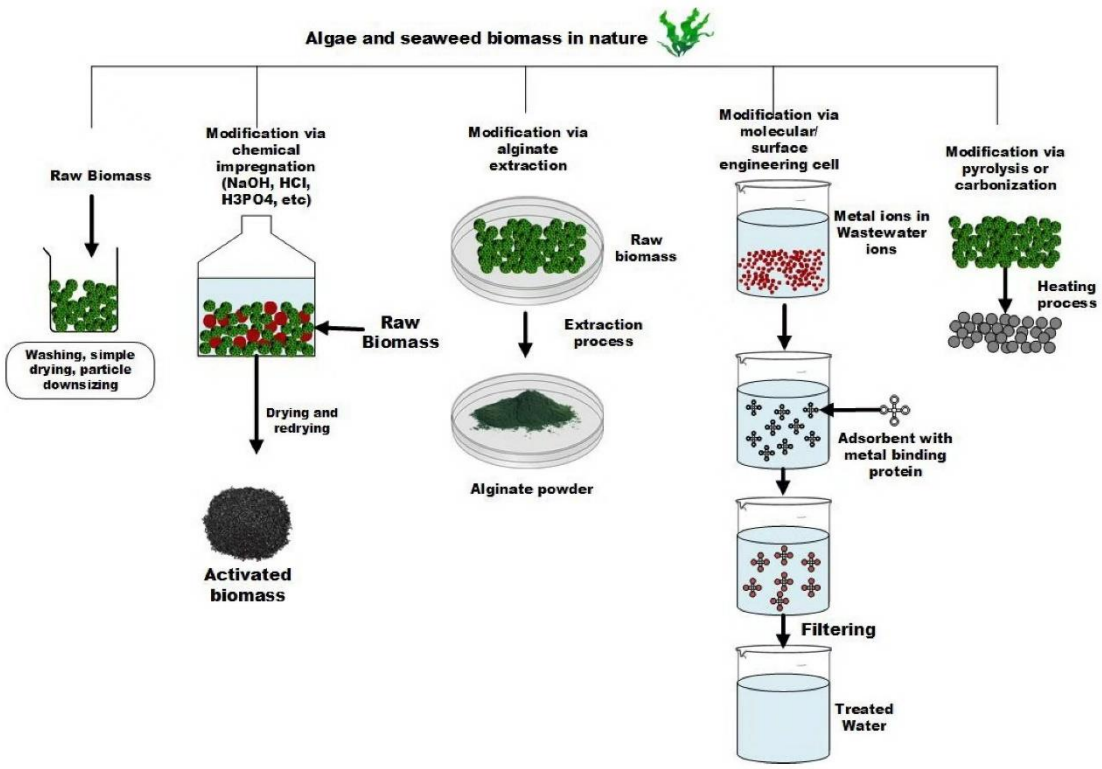


Figure 5. Seaweed-based biosorbent preparations.[28].

By placing the algal-based biosorbents into the solution, metal ions accumulate onto the surface and pores of the biosorbent and finally form a layer of metal ions along with other pollutants (Fig.6) [19].

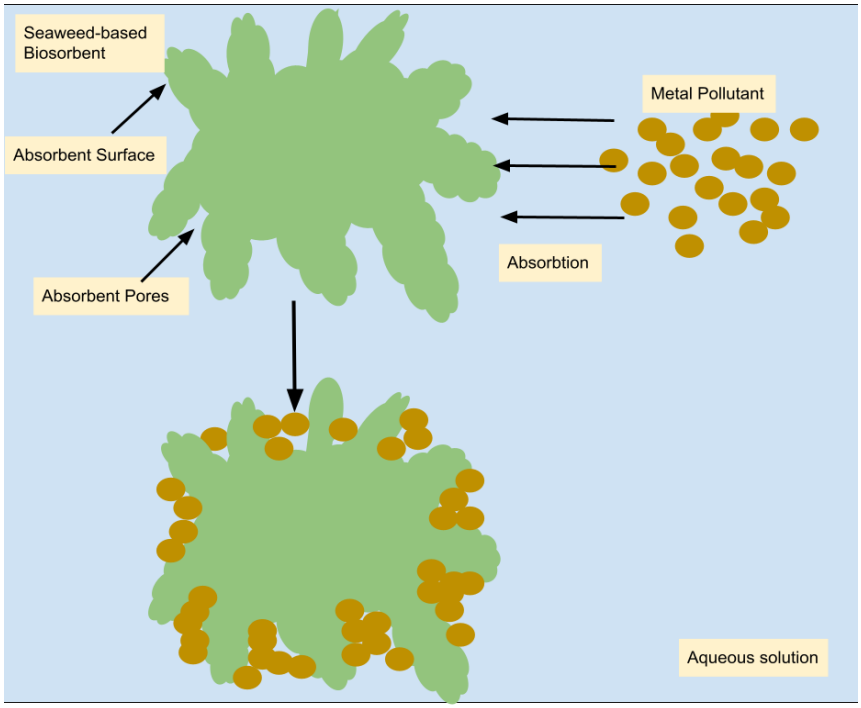


Figure 6. Seaweed-based biosorption method of removing metal pollution from water.

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A noticeable issue when using algal-based biosorption to clean metal pollution is that the solution composition will affect the metal absorbability of certain algal-based biosorbents. Some cationic chemical species in the solution would compete for the exchange site on the biosorbent and impair its biosorption capacity [20]. Recent research studied the biosorption of cadmium and copper by *Sargassum sinicola* in aqueous solutions and in saline wastewaters, indicating that the salinity of the solution caused a reduction in Cd biosorption from 89% to 5.8% [21]. Some algal-based biosorbents, especially seaweed sorbents contain many anionic sites on their surface and cause poor affinity for anions such as sulfate, phosphate, nitrate, etc. A feasible solution to solve these problems is chemical modification as discussed above. Chemically modifying the alginates, a major constituent of the seaweed biomass, allows the alginates to remove anionic pollutants from water. And it can be used to encapsulate materials such as magnetite to create a multifunctional sorbent that has magnetic properties and can remove both cationic heavy metal ions such as copper ions and anionic contaminants like arsenic [22]. The algal-based biosorption technologies for cleaning heavy metal pollution have not been fully developed at an industrial level. In the consideration of the complexity of the different aquatic environments, a large number of experiments on algal-based biosorbents are required to provide procedures and parameters for the practice of biosorption in different volumes and compositions of solutions. Over the past few decades, many experiments have been performed in order to improve the capability of obtaining biosorbents from algal biomass. In a promising future, there would be more large-scale algal-based biosorption technologies that can be used in cleaning industrial wastewater and purifying water for drinking use.

2.3. Seaweed-based bio-fuel production

Carbohydrates in seaweed can be converted into fuel in a variety of ways. Seaweeds can make oil by decomposing at high temperatures, ethanol by fermentation, and conversion to methane by digestion. Unlike wood, which is rough and difficult to degrade, the basic chemical composition of seaweed is composed of galactose which is easy to exploit.

The cost is another important point, seaweed doesn't need land to grow, and has no need for cultivation, making it very cheap to obtain. They only need sunlight and nutrients in the seawater. And there is inexhaustible seaweed in the sea for us to use, enabling it to be renewable energy.

Furthermore, when seaweed grows, it can absorb carbon dioxide to reduce global warming, helping to protect the environment.

Therefore, seaweed biofuel can also promote sustainable development, ensuring the coordination of the social benefit, economic benefit, and environmental benefit. Seaweed has the advantages of wide distribution, high oil content, strong environmental adaptability, short growth cycle, and relatively low production cost.

Different types of seaweed may also lead to different kinds of biofuel production. For example, in figure 4, the main products of seaweed are shown accordingly.

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Table 1. The main products of seaweed [36].

Raw material	Pretreatment	Operational conditions	Main products	Yield*	Refs.
Green seaweed					
Ulva sp.	Dilute acid	H_2SO_4 (0.6%) Temperature (120 C), time (20 min)	Carbon (reducing sugars) for thermostable cellulases, using a fungus (*Aspergillus fumigatus*)	12%	Ben Yahmed et al., 2018
Ulva rigida	Ionic liquids	SIL, DIL, LVIL, solid loading (10 wt%) Temperature (100-160 C), time (6 h)	Carbohydrates for the production of platform chemicals or biofuels	79%	Pezoa-Conte et al., 2015
Red seaweed					
Gelidium amansii	Ultrasonication	US with diluted HCl Power (30 kHz), amplitude (40%). Time (30 min)	Agarose	4.8%	Chew et al., 2018b
Kappahycus alvarezii	lonic liquids	Assisted with subcritical water extraction	k-carrageenan	79%	Gereniu et al., 2018
Kappahycus alvarezii	Deep eutectic solvents	ChCl:Urea, Ch:Ethylene:Glycol, ChCl:Glycerol Temperature (85 95 C), time (1 h)	k-carrageenan	54%	Das et al., 2016
Brown seaweed					
Ascophyllum nodosum	Irradiation	US with HCI (0.03 M), Power (750 W), frequency (20 kHz) Amplitude (114 um), Time (25 min)	Phenolics Fucose Uronic Acids	14% 8.7% 12%	Kadam et al., 2015
Fucus spiralis	Pressurized Liquid Extraction	Acetone/water (80:20) Temperature (60 °C), pressure (1000 psi)	Phenolic compounds	20%	Tierney et al., 2013
Fucus vesiculosus	Hydrothermal	Temperature (180 °C), time (20 min)	Fucoidan	18%	Rodriguez-Jasso et al., 2013
Himanthalia elongata	Pressurized Liquid Extraction	Hexane ethanol, water Temperature (100 °C), time (20 min)	Liquors with antioxidant bioacti	7.3%	Plaza et al., 2010b
Laminaria ochroleuca	Hydrothermal	Temperature (160 °C)	Fucoidan	17%	Florez-Fernandez et al., 2019
Saccharina japonica	lonic liquids	Imidazolium-based ILs Assisted with subcritical water extraction Temperature (175 °C)	Phenolic compounds	5.9%	Vo Dinh et al., 2018
Sargassum muticum	Hydrothermal	Temperature (170 °C)	Fucoidan	85%	Balboa et al., 2013

3. Mechanisms

3.1. Seaweed-based forage for cattle

During the process of enteric fermentation, methanogens are the micro-organisms contributing to the production of methane, with the catalyst of methyl-coenzyme M reductase (MCR), an enzyme that is responsible for the last step of methangenesis[8](fig.8). To reduce the CH_4 production by cattle, scientists have been seeking out ways to suppress the normal functioning of MCR, and at the same time, prevent any avoidable side effects (such as a decrease in average daily gain (ADG) or milk

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production). In recent years, researchers from UC Davis have found that seaweed additives for cattle forage can reduce CH_4 production by up to 82% by suppressing the functioning of MCR.

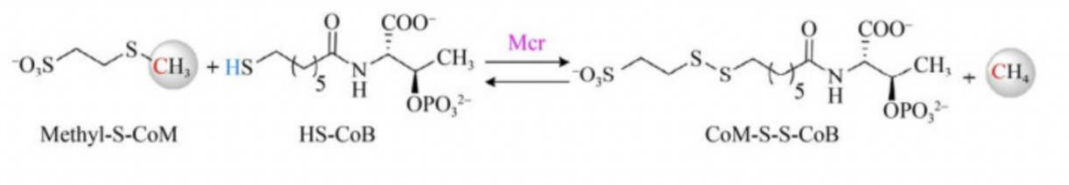


Figure 8. CH4-forming reaction catalyzed by Mcr (adapted from [23]).

Among various species of seaweeds, the red seaweed (*Asparagopsis taxiformis)* is proved to be the most promising species in its potential of reducing CH_4 production, with 98.9% of CH_4 cut down when applied at 17% OM in vitro. As anti-methanogen, *Asparagopsis taxiformis* is able to naturally synthesize halogenated compounds, such as 2-bromoethanesulphonate, 3-bromopropanesulphonate, contributing to the inhibition of methanogen production by isolating the prosthetic group required by MCR in the formation of CH4[25][26]. In addition to that, further studies have shown that the mode of action of red seaweed will not influence the total VFA concentrations or digestibility of cattle, achieving the goal of not changing the average daily gain (ADG) or milk production[8][24].

3.2. Mechanism of seaweed biosorption of metals

The high affinities between the seaweed biomass and metal ions allow the biomass to remove metal pollutants. There are several sub-groups of seaweed, which are brown seaweed, red seaweed, and green seaweed. They have a lot in common, but the main difference among them is the cell wall which is dominant for biosorption. The cell walls of the brown seaweed contain cellulose, alginic acid, and polymers (e.g., mannuronic and guluronic acids) complexed with light metals such as sodium, potassium, magnesium, calcium, and polysaccharides. The alginic acid and some sulfated polysaccharides such as fucoidan are important components of the cell walls of brown seaweed and they are also the predominant active groups in brown seaweed. Green seaweed also has cellulose in the cell wall. The difference is that a high content of proteins is bonded to the polysaccharides. These compounds are rich in organic ligands or functional groups such as amino, carboxyl, sulfate, and hydroxyl, which are significant in binding with metal ions to remove heavy metal pollutants. There is cellulose in red seaweed's cell walls as well, however, its biosorption ability is mainly given by the sulfated polysaccharides. The functional group in red seaweed is not as abundant as those in brown and green seaweed [29]. The metal removal ability of the biomaterials is highly dependent on the porosity level and the abundance of functional groups.

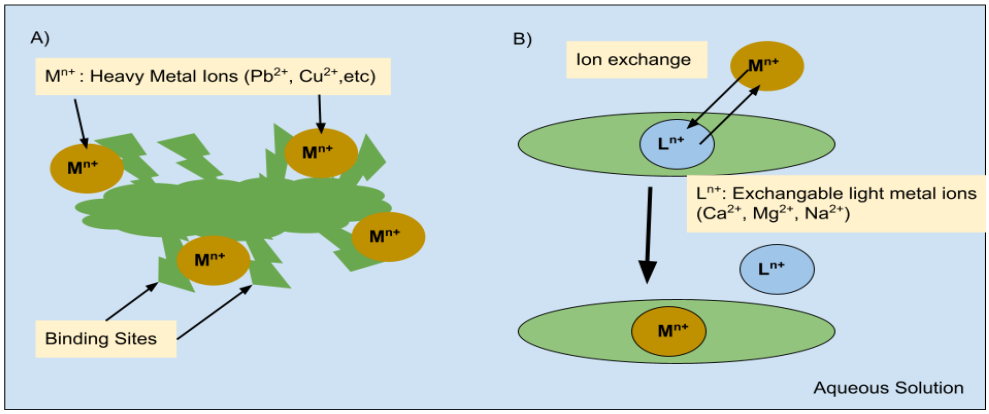


Figure 9. Ion binding and ion exchange with seaweed-based biosorbents.

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The key functional groups can be adequately found in green and brown seaweed, such as amine, carbonyl, hydroxyl, thiol, carboxyl, and other natural compounds that support metal-binding like lignins, cellulose, lipids, hydrocarbons, proteins, and tannins [30]. Generally, the alginate and sulfated polysaccharides (fucoidan) in seaweed cell walls are the keys to the heavy metal binding. The alginate in brown seaweed is discovered to have high uptake for divalent cations such as Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} [31]. Furthermore, the studies show that the affinity of metal ions to alginate and fucoidan is related to the stereochemical effect. The larger ions would fit better in a binding site with two distant functional groups, and following the affinity sequence: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Ca^{2+} > Mg^{2+}$ [30]. In conjunction with metal binding, seaweed biomass, especially in light metal riched brown seaweed biomass, can trap heavy metals by ion exchange. Ion exchange usually occurs between light and heavy metals. Common exchangeable metal ions found in seaweed biomass are Na^{2+}, Ca^{2+}, and Mg^{2+}. The heavy metal ions in the water will be exchanged with the light metal ions in the biosorbent (Fig. 9) [32]. Meanwhile, the adsorption capacity and adsorption speed are also affected closely by the exchange capacity of surface cation along with the aforementioned particular operating conditions.

3.3. Seaweed-based bio-fuel production

Seaweed biofuel's mechanism is to alter the carbon dioxide into a bio-product of its own to fix carbon and stimulate the carbon in the seaweed to react into oil, then bring the oil inside the cells outside. After that, the oil will go through a refining process to become gasoline. This process enables the nutrition and the carbon dioxide to translate into biofuel and protein through photosynthesis. Some other ways such as organic solvent extraction, liquefaction, and catalyzing are also theoretically feasible.

Dilute acid treatment and hydrothermal treatment followed by enzymatic saccharification showed a higher product yield. As a result, the use of an acidic catalyst is recommended to get a higher yield and be cost-effective.[27] Biofuel is produced by transesterification process in which fats and oils from seaweed are broken apart to yield very long molecules that contain the oxygen.

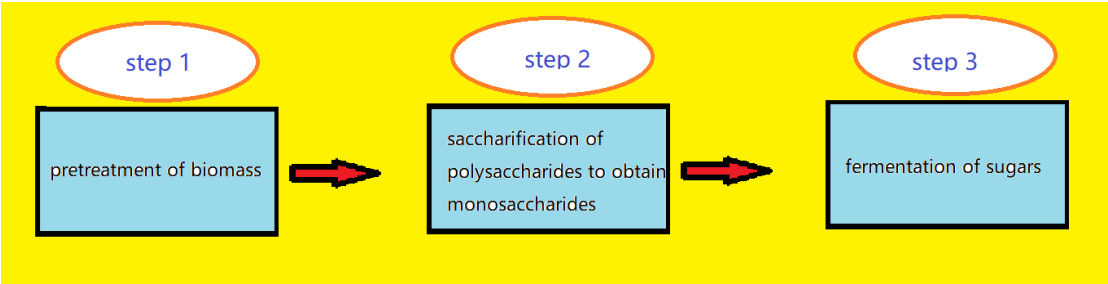


Figure 10. steps to obtain bioethanl or biobutanol from seaweed [37].

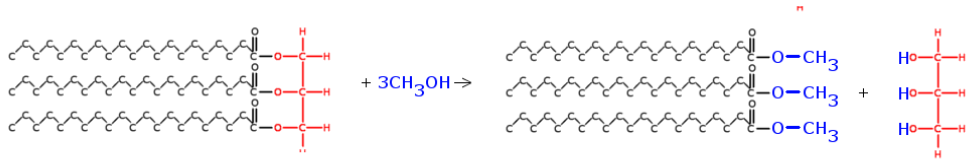


Figure 11. Transesterification of fatty acid [38].

In the figure above, glycerol is shown in red and methanol in blue. This figure shows the reaction of how biofuel is produced. Taking a triglyceride (made of three fatty acids and a glycerol molecule that is shown in red) and react that with methanol (shown in blue) yields a mixture of fatty acid esters (black and blue) that can be used as biodiesel as well as a glycerin (blue and red).

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4. Conclusion

The research above shows that seaweeds have potential in many aspects, such as their application to cattle forage, usage as heavy metal 'filter', and can be made into biofuel. Thus, we should focus more attention on seaweeds to mitigate the mounting environmental crisis.

5. Acknowledgement

Su Qiyun, Han Lilin, and Yu Xincheng contributed equally to this work and should be considered co-first authors.

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