Investigating Greener Alginate Extraction Methods for Bioplastic Applications

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Motivation

- Alginate-based bioplastic are promising petrochemical plastic alternatives: home compostable and good mechanical properties.[1]
- Conventional methods of extraction: often employ harsh chemicals and water and energy-intensive processes.[1]
- Limited methods tailored for bioplastic applications

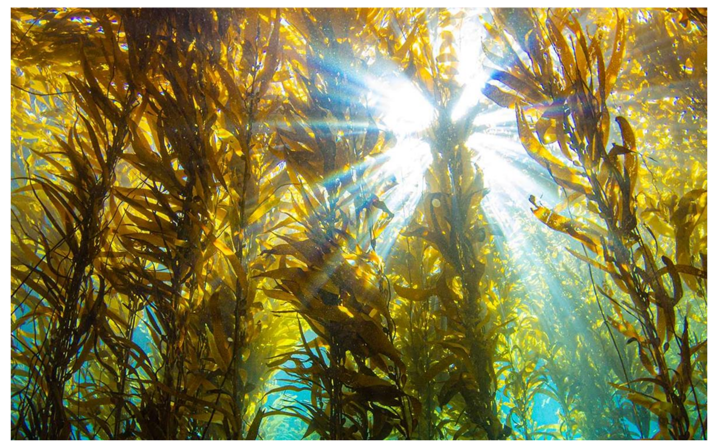


Figure 1. Kelp, a beneficial feedstock, does not require fertilizers and grows on non-arable land. [2,3]

Alginate

Alginates, derived from kelp, are copolymers composed of β-d-mannuronic acid (M) and α-l-guluronic acid (G) blocks. The M and G blocks are organized in GG or MM clock and MG or GM blocks.

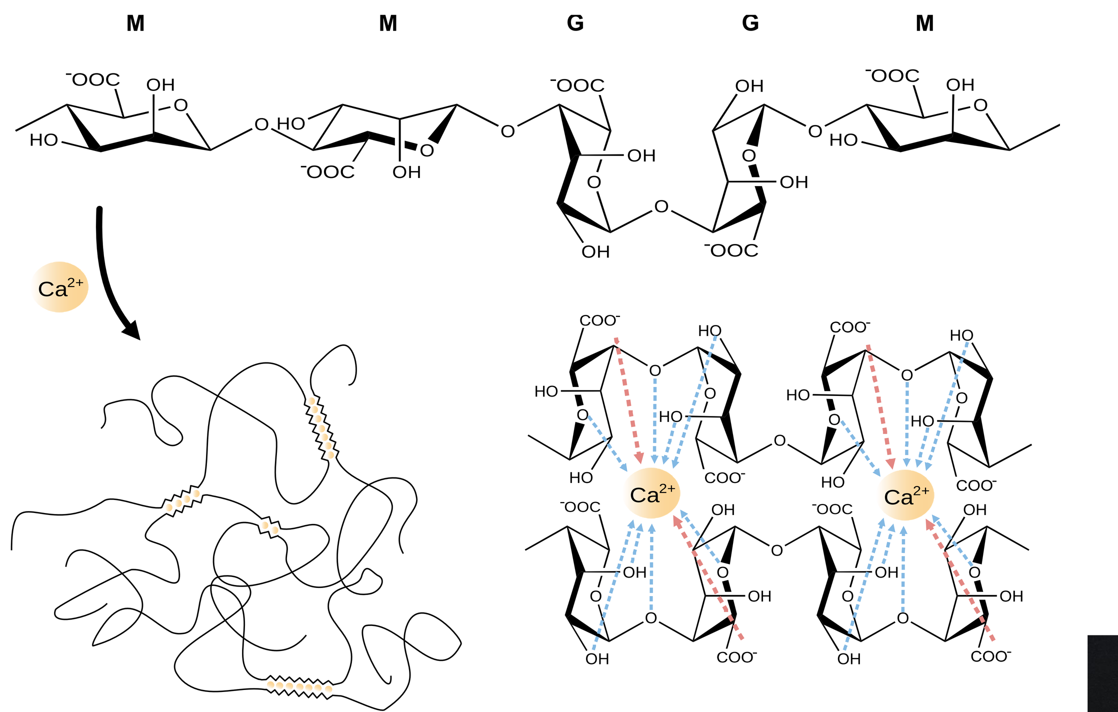


Figure 2. Chemical structure of alginate and alginate ionic crosslinking.

Alginate composition varies based on the source of kelp and the extraction process. Alginate undergoes ionic crosslinking with cations, such as calcium, at the GG-blocks (Figure 2), enabling the formation of materials like bioplastic packaging. The physicochemical properties of these materials are influenced by the block compositions, structural conformation, and molecular weight of the alginate[1,5].

Figure 3. Alginate-based packaging (Bioform).

Research Objective and Approach

This study aimed to investigate greener extraction methods and the effect on alginate properties, to advance sustainable methods suitable for bioplastic applications.

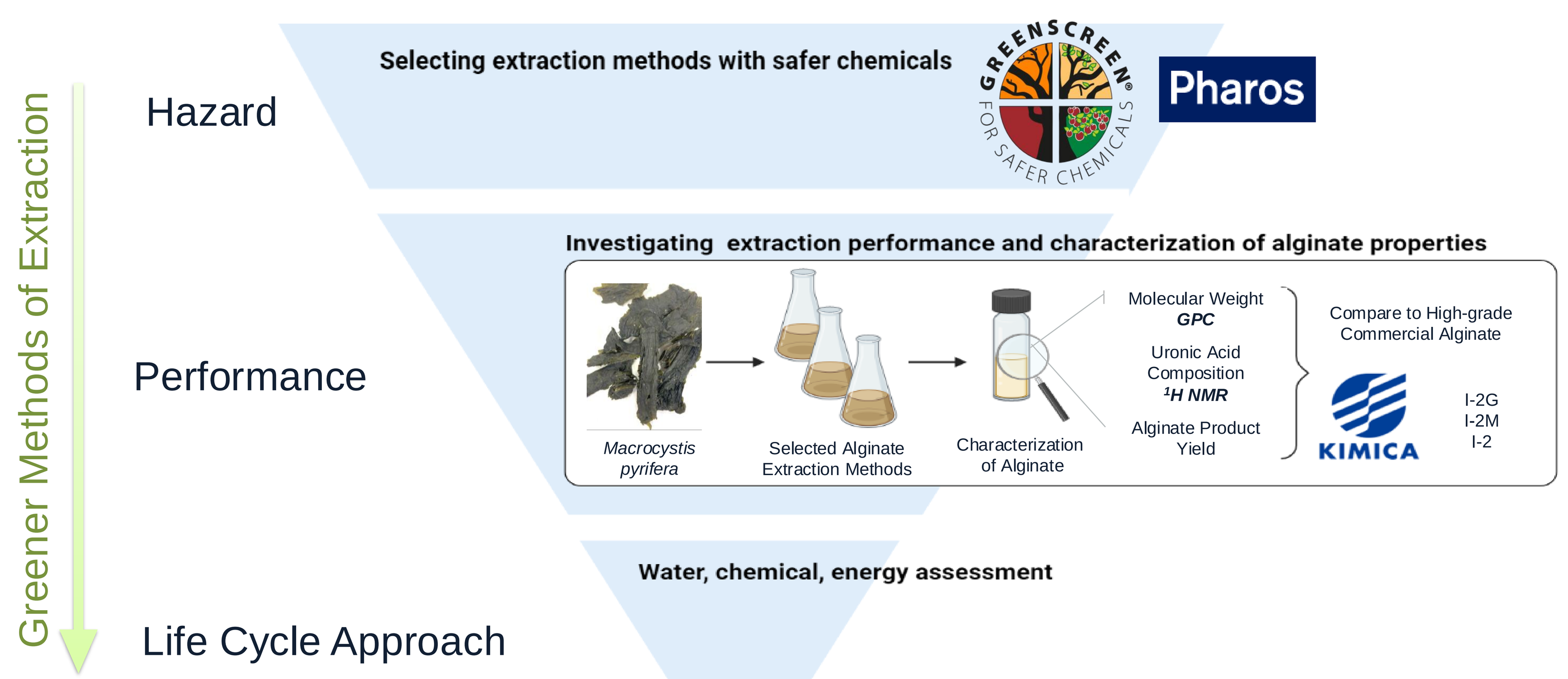
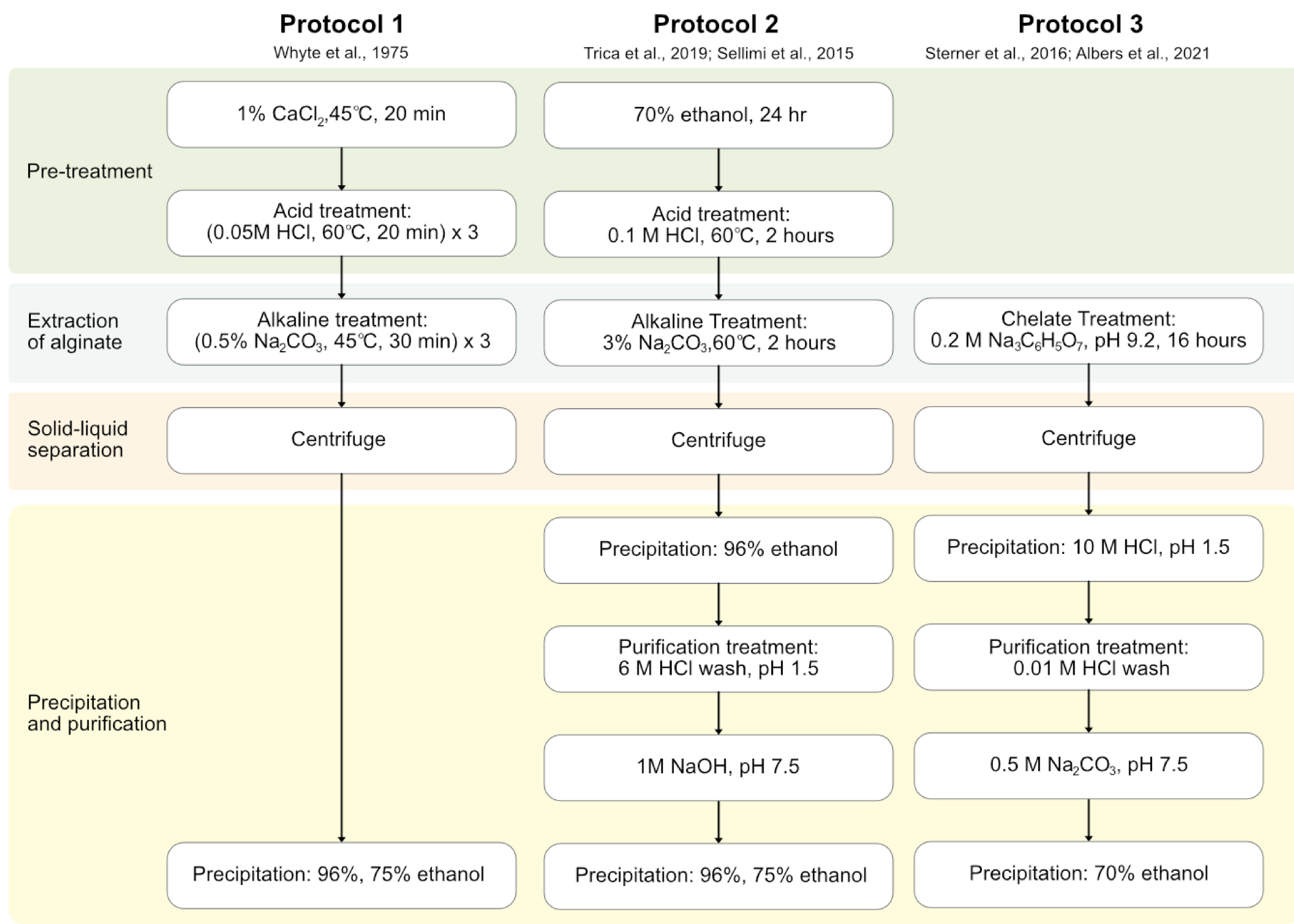


Figure 4. Holistic approach for evaluating greener methods of extraction.

Selected Alginate Extraction Methods



Extractions of each protocol were completed in 8 replicates, from identical sources of *Macrocystis pyrifera*.

Figure 5. Methods of alginate extraction selected from literature, exhibiting chemicals with less hazards determined by hazard assessment.

Alginate Extraction Performance - Results

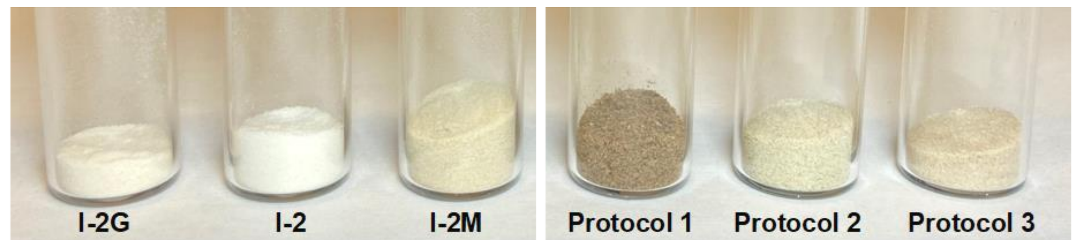
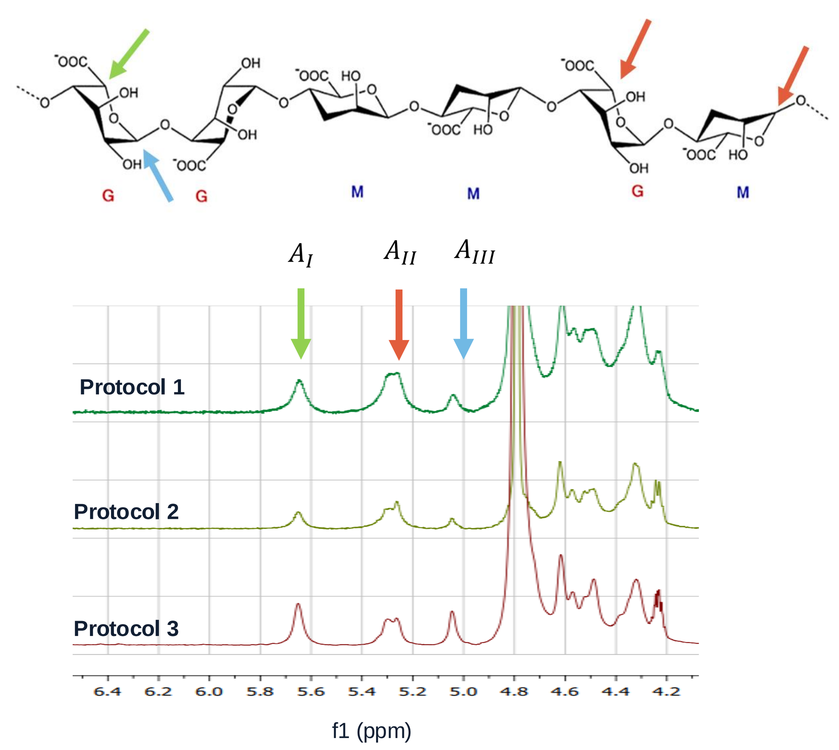


Figure 6. Isolated alginate samples compared to commercial alginate. The color of isolated alginate differed, and protocol 1 showed an undesirable dark pigment.

Table 1. Isolated alginate average yield and characterization of alginate properties

	Avg. Yield (%)	Weight Avg. Molecular Weight, M_w (kDa)	Polydispersity Index, PDI
Protocol 1	24.3 ± 0.7	240.53 ± 100.81	1.30 ± 0.03
Protocol 2	22.3 ± 1.2	228.20 ± 57.83	1.30 ± 0.10
Protocol 3	26.7 ± 0.6	59.51 ± 13.33	2.20 ± 1.50
I-2M	-	211.90 ± 7.18	1.34 ± 0.11
I-2	-	248.70 ± 8.32	1.25 ± 0.07
I-2G	-	276 ± 58.00	1.25 ± 0.12

- Protocols 1 and 2: high M_w comparable to commercial alginate. Beneficial for tough materials
- Protocol 3: low M_w and high PDI, indicating degradation during the extraction process.



$$M/G = \frac{A_{II} + A_{III}}{A_I} - 1$$

values > 1, higher M content
values < 1, higher G content

$$F_{GG} = \frac{A_{III}}{A_{II} + A_{III}}$$

Figure 9. Key signals for determining alginate composition, ^1H NMR spectrum and uronic acid composition equations.[5,10]

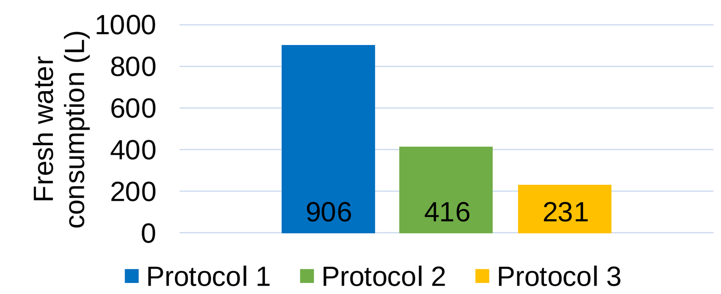
Table 1. Uronic Acid Composition of isolated alginate and commercial alginate

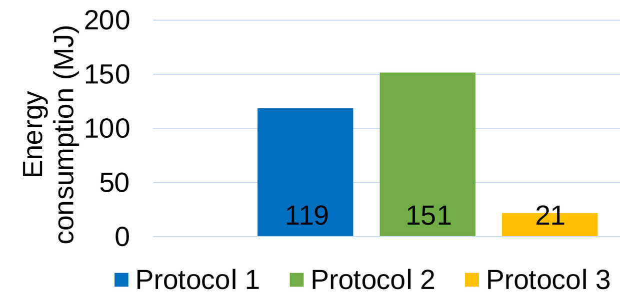
	M/G Ratio	Fraction of GG Blocks
Protocol 1	1.23 ± 0.03	0.18 ± 0.00
Protocol 2	1.53 ± 0.07	0.17 ± 0.01
Protocol 3	0.63 ± 0.03	0.34 ± 0.01
I-2M	1.98± 0.07	0.13 ± 0.00
I-2	1.01 ± 0.07	0.20 ± 0.00
I-2G	0.24 ± 0.06	0.51 ± 0.01

- Protocol 1 and 2: high M content.
- Protocol 3: low M/G ratio and a high fraction of GG blocks, which is advantageous for crosslinking.
- Potential M block degradation occurring during Protocol 3.

Life Cycle Approach - Results

Chemical, energy, and water assessment, evaluating the input requirements to produce 1 kg of alginate. The material inputs were adjusted based on experimental yield. Impact on Climate Change determined using the ReCiPe method.





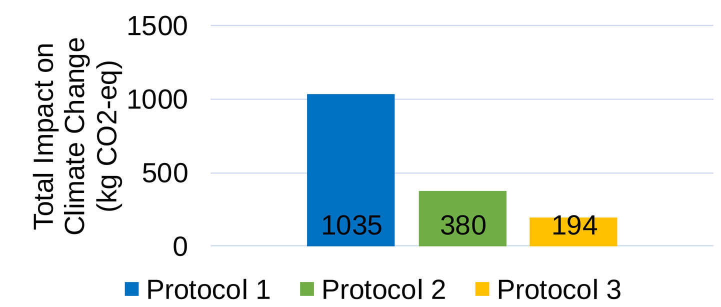


Figure 8. Comparison of chemical, energy, and water assessments of extraction protocols.

Table 3. Impact on Climate Change (kg CO2 eq). Highest contributors include ethanol and sodium citrate

	Protocol 1	Protocol 2	Protocol 3
Energy	9.6	12.4	1.7
Freshwater	1.3	0.6	0.4
Ethanol	1020.5	364.1	116.1
Hydrochloric acid	0.1	1.3	1.0
Sodium carbonate	0.7	1.2	0.1
Sodium citrate	-	-	75.2
Calcium chloride	2.3	-	-
Sodium hydroxide	-	0.0	-

Optimization of Protocol 3 - Preliminary Results

Investigated reduced extraction time for Protocol 3. Trialed extraction times at 1, 4, 10 hours.

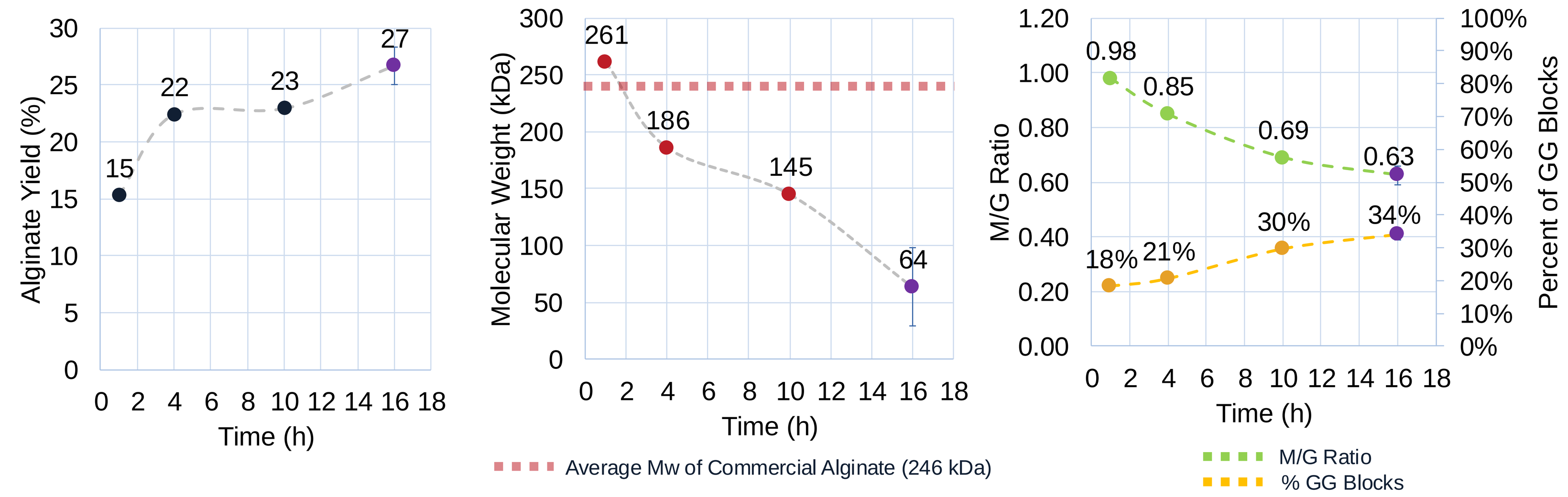


Figure 9. Isolated alginate yield and characterization of properties at varying extraction times.

Conclusions and Future Work

This work aimed to evaluate greener alginate extraction methods, investigating the safety and environmental impact, and investigate the isolated alginate properties for bioplastic applications.

- Three greener alginate extraction methods were selected and evaluated.
- Protocol 1 and 2: molecular weight similar to commercial alginate, and high M content.
- Protocol 3: high G content, and lowest environmental impact.
  - Reduced extraction time resulted in higher molecular weight and higher M content.

The next steps include:

- Design of experiment (surface response methodology) to further optimize protocol 3 for desired alginate molecular weight.
- Investigate the relationship between alginate properties and alginate film mechanical properties.

Acknowledgements and References

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(1) Saji, S.; Hebden, A.; Goswami, P.; Du, C. A Brief Review on the Development of Alginate Extraction Process and Its Sustainability. Sustainability 2022, 14 (9), 5181. https://doi.org/10.3390/su14095181. **(2)** Underwater Cathedrals: Shooting Magnificent Kelp Forests. Ikelite. https://www.ikelite.com/blogs/advanced-techniques/underwater-cathedrals-shooting-magnificent-kelp-forests (accessed 2023-05-31). **(3)** Devadas, V. V.; Khoo, K. S.; Chia, W. Y.; Chew, K. W.; Munawaroh, H. S. H.; Lam, M.-K.; Lim, J.-W.; Ho, Y.-C.; Lee, K. T.; Show, P. L. Algae Biopolymer towards Sustainable Circular Economy. Bioresour. Technol. 2021, 325, 124702. https://doi.org/10.1016/j.biortech.2021.124702. **(4)** Davis, T.; Llanes, F.; Volesky, B.; Diaz-Pulido, G.; McCook, L.; Mucci, A. 1H-NMR Study of Na Alginates Extracted from Sargassum Spp. in Relation to Metal Biosorption. Appl. Biochem. Biotechnol. 2003, 110, 75–90. https://doi.org/10.1385/ABAB:110:2:75. **(5)** Abasalizadeh, F.; Moghaddam, S. V.; Alizadeh, E.; akbari, E.; Kashani, E.; Fazljou, S. M. B.; Torbati, M.; Akbarzadeh, A. Alginate-Based Hydrogels as Drug Delivery Vehicles in Cancer Treatment and Their Applications in Wound Dressing and 3D Bioprinting. J. Biol. Eng. 2020, 14 (1), 8. https://doi.org/10.1186/s13036-020-0227-7. **(6)** Zhang, H.; Cheng, J.; Ao, Q. Preparation of Alginate-Based Biomaterials and Their Applications in Biomedicine. Mar. Drugs 2021, 19 (5), 264. https://doi.org/10.3390/md19050264. **(7)** Whyte, N. C. Alginate Degradation in Situ Accompanying Thermal Drying of the Marine Algae Nereocystis Luetkeana and M~crocystis Integrifolia. 38. **(8)** Trica; Delattre; Gros; Ursu; Dobre; Djelveh; Michaud; Oancea. Extraction and Characterization of Alginate from an Edible Brown Seaweed (Cystoseira Barbata) Harvested in the Romanian Black Sea. Mar. Drugs 2019, 17 (7), 405. https://doi.org/10.3390/md17070405. **(9)** Albers, E.; Malmhäll-Bah, E.; Olsson, J.; Sterner, M.; Mayers, J. J.; Nylund, G. M.; Rupar-Gadd, K.; Abdollahi, M.; Cvijetinovic, S.; Welander, U.; Edlund, U.; Pavia, H.; Undeland, I. Influence of Preservation Methods on Biochemical Composition and Downstream Processing of Cultivated Saccharina Latissima Biomass. Algal Res. 2021, 55, 102261. https://doi.org/10.1016/j.algal.2021.102261. **(10)** Grasdalen, H.; Larsen, B.; Smidsrød, O. A p.m.r. Study of the Composition and Sequence of Uronate Residues in Alginates. Carbohydr. Res. 1979, 68 (1), 23–31. https://doi.org/10.1016/S0008-6215(00)84051-3.