# Levulinic acid production from the green macroalgae *Chaetomorpha linum* and *Valonia aegagropila* harvested in the Orbetello lagoon

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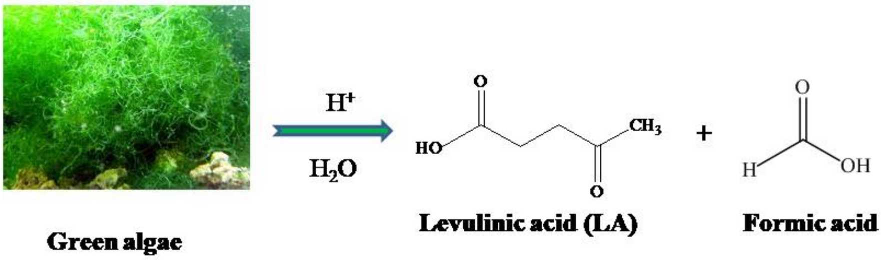
Eutrophication of coastal areas, especially estuaries and lagoons, is a global environmental problem [1]. This phenomenon can cause massive blooms of opportunistic macroalgae and drastic reduction of dissolved oxygen levels due biomass decomposition with consequent impact on aquatic ecosystems. This is true for example for the Orbetello lagoon (Italy, Southern Tuscany), a coastal shallow basin that covers a surface of about 25 $km^2$ and is characterized by low water turnover. To attempt to solve eutrophication problems, a large amount of algal biomass is removed every year from the lagoon (about 700/1000 t/year) but this practice is highly expensive and creates a disposal problem [2]. Various efforts have been made to employ the harvested biomass [2], but up to date a viable industrial application has not been found.
In this context now, for the first time, we have studied the direct conversion of two different macroalgae,harvested in the Orbetello lagoon, *Chaetomorpha linum* (Muller) Kutzing and *Valonia aegagropila* C.Agardh, to produce levulinic acid, adopting the one-pot hydrothermal treatment in the presence of aqueous diluted mineral acids ($H_2SO_4$ and HCl).
Levulinic acid (LA) is obtained in the hydrolysis of the cellulose component of biomass (Scheme below) and has been classified by the United States Department of Energy (DOE) as one of the top-12 promising bio-based building blocks.




LA is a versatile platform chemical, with a key role for movingtowards a post-petroleum society. It is a valuable intermediate for the synthesis of chemicals, for application as fuel additives, solvents, pharmaceuticals, surfactants and plasticizers [3]. LA large scale production, however, requires the use, as starting material, of cheap or, even better, negative-value biomass, as macroalgae harvested in the Orbetello lagoon. The samples of *C. linum* and *V. aegagropila* were analyzed to evaluate the carbohydrates and the acid-insoluble lignin content. *C. linum* resulted composed of 3.34 % galactan, 43.66 % glucan, 7.91% mannan, 37.50 % others components and 6.55 % Klason lignin on a dry weight basis, while *V.aegagropila* was composed of 2.62 % galactan, 33.88 % glucan, 1.23% xylan, 5.17 % arabinan, 44.35 % others components and 12.39 % Klason lignin on a dry biomass (DB) weight basis. The significant content of cellulose ascertained for both algae suggested their possible application as feedstocks for LA production.
The acid-catalyzed conversion of these algal biomasses to LA was optimized studying the effect of the main reaction parameters: biomass loading, type and concentration of the acid catalyst, temperature and reaction time. A significant yield of LA was ascertained only at temperatures in the range 170-200 °C and the use of diluted $H_2SO_4$ allowed us to reach higher performances respect to HCl. Based on this preliminary study, levulinic acid yields of 19 g LA/100 g DB for *C. linum* and 16 g LA/100 g DB for V. *aegagropila* were reached. These results confirm the significant potential of these waste green algae as a renewable starting feedstock for platform chemicals production.

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[2] M. Lenzi. J. Aquac. Res. Development 6 (2015) 291.
[3] C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A.M. Raspolli Galletti, Catalysts 6 (2016) 196-224.