Evaluation of pre-treatment conditions of biomass waste from the halophyte *Salicornia bigelovii* cultivated in sea water

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Abstract
Salicornia bigelovii is a halophyte with recent interest as feedstock for biofuel production. Salicornia biomass waste (SBW) from the haloagriculture of *S. bigelovii* can potentially be treated and converted into biogas and recycled nutrients. An evaluation of different pre-treatment conditions of SBW yielded soluble COD concentrations ranging from 11.1 to 28.71 gCODs/L for mild aqueous extraction conditions (extraction time from 10 minutes to 27 hours; concentration of 2.5 to 10% (dw/v); temperature of 50 to 95 °C) using 50 gNaCl/L solution. Maximum ammoniacal nitrogen concentrations reached 85.6 mgN/L, below the reported inhibitory values for methanogenesis. These results suggest good potential for biomethanization. Biomethane potential studies of the SBW aqueous extraction are recommended to assess the biodegradability of the solubilised COD.

Keywords
Salicornia sp.; halophyte; biomass waste; pre-treatment; COD; biogas

INTRODUCTION

Integrated processes systems, such as in an integrated seawater energy & agriculture system (ISEAS), can potentially address process shortcomings related to nutrient source, waste treatment, and environmental impacts (Warshay *et al.*, 2011).

One plant of interest for seawater agriculture (haloagriculture) is *Salicornia sp*., a halophyte found in coastal environments (salt marches, mangroves) in most continents, capable of growth while tolerating immersion in salt water containing up to 60 gNaCleq/L of salt concentration in irrigation water (Silva *et al*., 2007; Ventura *et al*., 2011). The salinity of Salicornia biomass post-harvest was measured as 30% NaCl (dry weight) (Glenn *et al*. 1992).

The seeds of *Salicornia sp*. are currently studied as substrate for biodiesel production due to its high lipid content (Glenn et al., 1991). The process of deseeding the post-harvest dried plants yields Salicornia biomass waste (SBW) composed of stems, deseeded inflorescences, and branches. The SBW is a potential source of energy and nutrients if treatable via anaerobic digestion (AD).

Little information is available in the literature regarding key characteristics of Salicornia sp. biomass, such as total COD, nutrient (organic and inorganic nitrogen, phosphorus, sulphur) concentrations, and other chemical substances of interest for the development of bioprocesses.

In AD, a wide variety of substances can act as inhibitors, leading to hindering of reactions or even reactor failure (Chen *et al*., 2008). The present work investigates if different pre-treatment conditions of SBW for BMP essays influence the concentration of such inhibitors, namely high salinity and ammonia concentration, as well as the total soluble COD concentration obtained after pre-treatment.

MATERIALS AND METHODS

Substrate preparation

Samples of *Salicornia bigelovii* plants cultivated by International Centre for Biosaline Agriculture (ICBA) in the UAE were sun and air dried, and the stems were deseeded. The resulting biomass leftover (stems, seedless inflorescences, and branches) was ground coarsely, using a blender, or finely, using a knife mill (IKA, 10 MF Basic). The ground Salicornia biomass (CGS and FGS, for coarse and fine grinding, respectively; Figure 1) was prepared prior to each extraction. Flow diagram of experiments for extraction and characterization can be seen in the Figure 2.

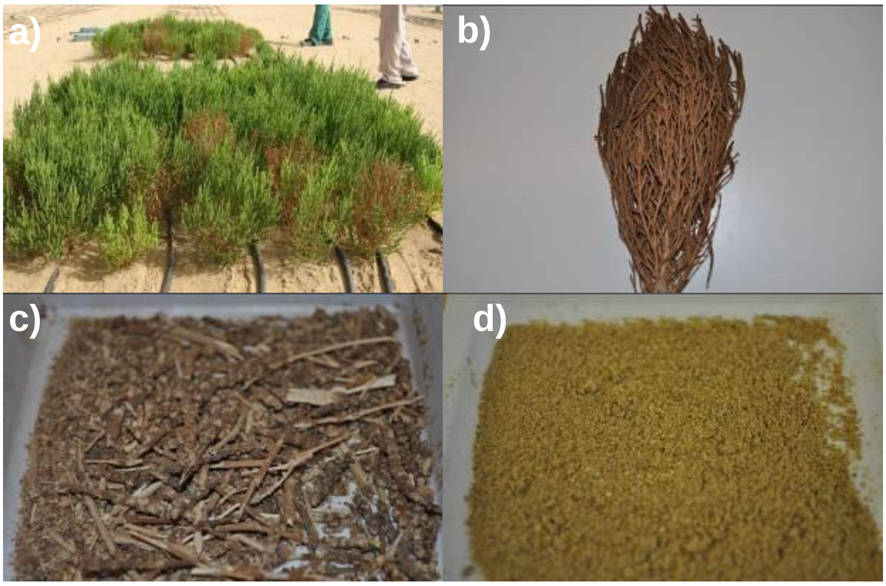

Figure 1: Different stages of substrate preparation: a) *S. bigelovii* plants in cultivation; b) dried and deseeded biomass; c) coarsely ground biomass (CGS); d) finely ground biomass (FGS).

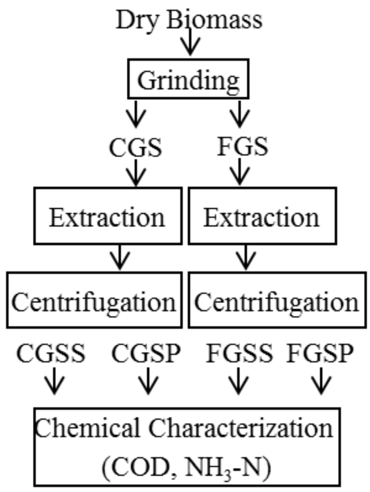

Figure 2: Flow diagram with the experiments performed and fractions generated from the substrate.

Extraction

CGS was subjected to extraction (10%, dw/v) using aqueous solution of 50 gNaCl/L, for 3-27h (at 3h intervals), at 50 °C. CGS at 10% (dw/v) concentration was also subjected to aqueous extraction for 10 minutes, at 50 °C, 70 °C, and 95 °C.

FGS was subjected to extraction (20%, 10%, 5%, 2.5%, dw/v) using aqueous solution of 50 gNaCl/L, for 1h, 12h, or 24h, at 50 °C. FGS at 10% (dw/v) concentration was also subjected to aqueous extraction for 10 minutes, at 50 °C, 70 °C, and 95 °C.

The extraction solutions were centrifuged (Centurion Scientific, K 241) at 4000 RPM, for 15 min, and the supernatant and precipitate fractions (CGSS/FGSS and CGSP/FGSP, respectively), were refrigerated and stored until further analysis.

Chemical characterization

CGSS and FGSS were analysed for soluble COD concentration (in gCODs/L) using COD measurement test kits (Hach® COD cuvette test LCK014, LCK514). FGSS was further analysed for total ammonia concentration in solution (NH_3-N total, in mg/L), using Hach® AmVer High Range Ammonia Nitrogen reagent set. All cuvette tests were measured with a spectrophotometer (Hach® DR2800). Salinity (in $gNaCl_{eq}$/L) was measured with a conductivity probe. CGSS, FGSS, CGSP, and FGSP were characterized for total solids (TS) and ash content (TFS). Measurements for all analyses were performed in triplicates.

RESULTS

Chemical characterization

Soluble COD concentration The soluble COD concentration of the CGSS fraction ranged from 11.01 gCODs/L (after 6h) to 14.15 gCODs/L (after 27h), at 50 °C, with 10% CGS (dw/v) extraction. When compared with the 3-hour extraction, each subsequent 3-hour time increase yields -2.13%, 1.07%, 3.38%, 3.02%, 9.66%, 13.63%, 22.16%, and 25.95% more soluble COD concentration (Figure 2).

Previous work (Chaturvedi *et al.* 2012) explored the influence of extraction temperature in the soluble COD concentration of CGSS, and comparable experiment was therefore performed with FGSS. Unlike in CGSS, soluble COD concentration in FGSS was found to be less impacted by extraction temperature (Figure 3).

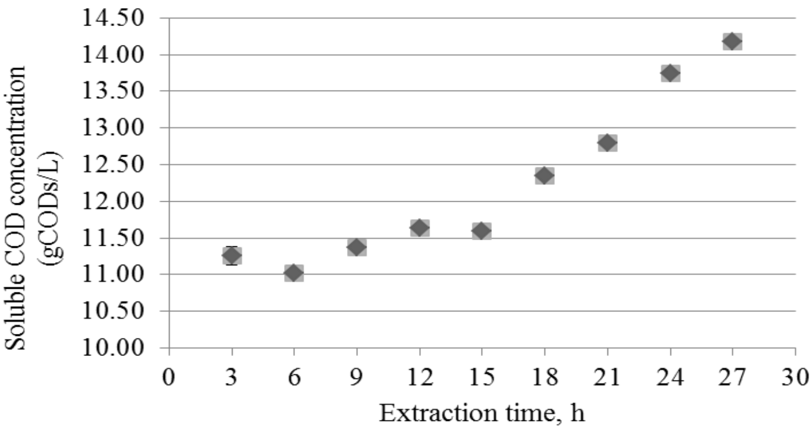

Figure 3: Soluble COD concentration measured for each extraction with an aqueous solution of 50 gNaCl/L, 10% CGS (dw/v), at 50 °C. Measurements were performed with the supernatant fractions (CGSS).

Based on CGSS soluble COD concentration results, 1h, 12h, and 24h extraction times were chosen for soluble COD measurements of FGSS. In order to compare the different extraction concentrations, soluble COD concentrations per mass of biomass extracted (in gCODs/gFGS) were evaluated. For 1h and 12h, lower initial FGS concentration in the extraction led to higher specific soluble COD concentrations. For 24h, the opposite was observed (figure 4b). Highest soluble COD concentration (28.71 gCODs/L) in FGSS was obtained with 24h, 10% (dw/v) extraction.

Ammonia concentration. The ammonia concentration in solution (in mg NH_3-N/L) for all analysed samples was below that found to be inhibitory in AD processes, as referenced from ADM1 (Batstone *et al. 2002*). CGSS was not analysed due to lower CODs values measured when compared to FGSS. Therefore, biogas production inhibition due to inorganic nitrogen initial concentration in the FGSS fraction is not expected.

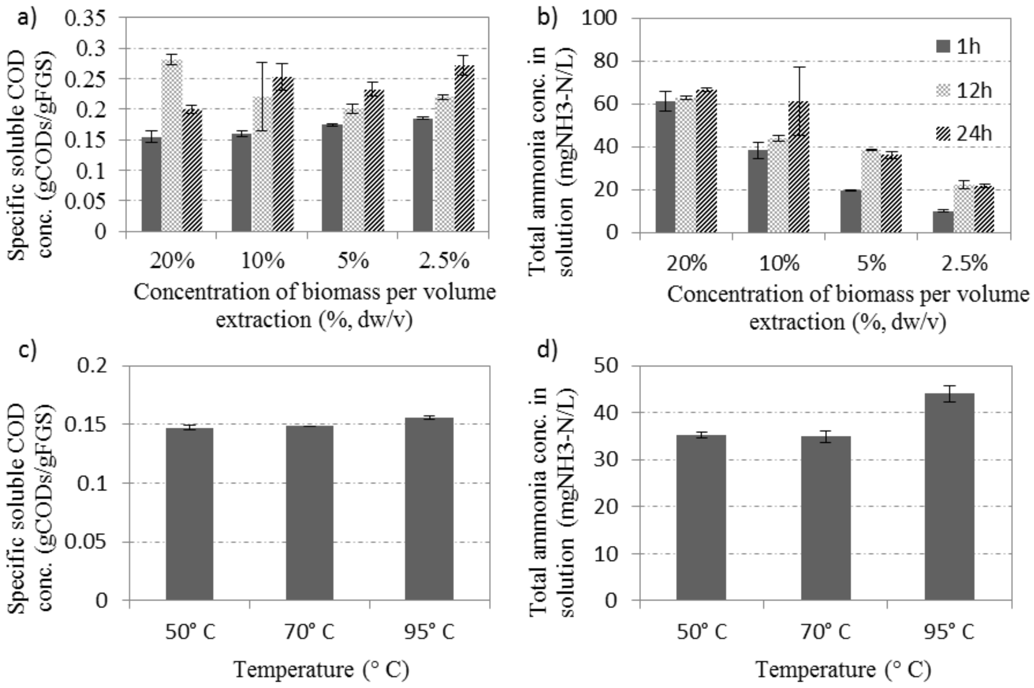

Figure 4: a) Soluble COD obtained for different temperatures, with 10-minute, 10% FGS (dw/v) extraction using an aqueous solution of 50 gNaCl/L; b) Total ammonia concentration in solution for different temperatures, with 10-minute, 10% FGS (dw/v) extraction using an aqueous solution of 50 gNaCl/L c) soluble COD obtained for different concentrations and extraction times, using an aqueous solution of 50 gNaCl/L d) total ammonia concentration in solution for different concentrations and extraction times, using an aqueous solution of 50 gNaCl/L.

Total solids concentration. Total solids and total volatile solids concentration analyses results can be seen in Table 1. The increased initial biomass concentrations show a corresponding increase in the total volatile solids post extraction. This suggests that higher concentrations of initial biomass can be further experimented which could be explored for different dilution rates.

Table 1: Total solids (TS) and total volatile solids (TVS) measurements for each of the FGSS fractions obtained for different extraction times and initial biomass concentrations.

Initial biomass concentration (%, dw/v)	Extraction time (h)	Total Solids after extraction ($gTS/100g_{Solution}$)	Total Volatile Solids (gTVS/100gTS)
2.5%	1	5.95	8.83
	12	6.17	8.84
	24	6.43	9.77
5%	1	6.79	11.80
	12	7.58	19.64
	24	7.09	16.65
10%	1	8.48	15.48
	12	9.77	23.49
	24	10.96	23.14
20%	1	11.64	19.72
	12	11.77	21.41
	24	11.97	23.14

CONCLUSIONS

Salicornia biomass waste can be easily hydrolysed under mild conditions, using aqueous solutions of 50 gNaCl/L. The soluble COD concentration of the resulting extractive reached up to 0.305 gCODs/gDM at 20% dw/v in 12h extraction time. No clear trends were observed in the resulting soluble COD concentrations under the different extraction times. Dilution did not appear to have limited the pretreatment and therefore less diluted extractions are suggested for further investigation. Ammonia nitrogen concentrations remained below reported inhibitory levels for methanogenesis in all cases. The results obtained with mild hydrolysis conditions seem to indicate that industrial scale-up may be achievable with low energy requirements (heating), capital costs (Volume, HRT due to hydrolysis time) and operational costs (use of seawater, minimal additives).

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REFERENCES

Batstone, D.J., Keller J., Angelidaki I., *et al.* 2002. The IWA Anaerobic Digestion Model No 1(ADM 1). *Water Science & Technology* **45**(10), 65 –73.

Chaturvedi, T., Baldwin, R.M., Schmidt, J.E., Thomsen, M.H., 2012 Bioenergy potential from high salinity lignocellulosic biomass of *Salicornia bigelovii*. *20th European Biomass Conference*, Milan, Italy.

Chen, Y., Cheng, J.J., Creamer, K.S. 2008 Inhibition of anaerobic digestion process: A review. *Bioresource Technology* **99**, 4044-4064.

Glenn, E.P., Coates, W.E., Riley, J.J, Kuehl, R.O., Swingle, R.S. 1992 *Salicornia bigelovii* Torr: A seawater irrigated forage for goats. *Anim. Feed Sci Technology* **40**, 21-30.

Glenn, E.P., O'Leary, J.W., Watson, M.C., Thompson, T.L., Kuehl, R.O., 1991. Salicornia bigelovii Torr: an oil seed halophytes for sea water irrigation. *Science* **251**, 1065–1067.

Silva, H., Caldeira, G., Freitas, H., 2007 Salicornia ramosissima population dynamics and tolerance of salinity. *Ecological Research* **22**(1),125–134.

Ventura, Y., Wuddineh, W.A., Myrzabayeva, M., et al. 2011 Effect of seawater concentration on the productivity and nutritional value of annual Salicornia and perennial Sarcocornia halophytes as leafy vegetable crops. *Scientia Horticulturae* **128**(3),189 –196.

Warshay, B., Pan, J., Sgouridis, S. 2011 Aviation industry's quest for a sustainable fuel: considerations of scale and modal opportunity carbon benefit. *Biofuels* **2**(1), 33-58.