Supporting Information

Fuel intermediates, agricultural nutrients and pure water from *Kappaphycus alvarezii* seaweed

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Content list

1. FT-IR spectra of pristine κ-carrageenan extracted with seawater

The FT-IR spectrum of pristine κ-carrageenan is given in the following figure (Figure S1). The bands at 848 cm^{-1} and 928 cm^{-1} are due to 4-sulphated group and 3,6-anhydrogalactose, respectively.[1]

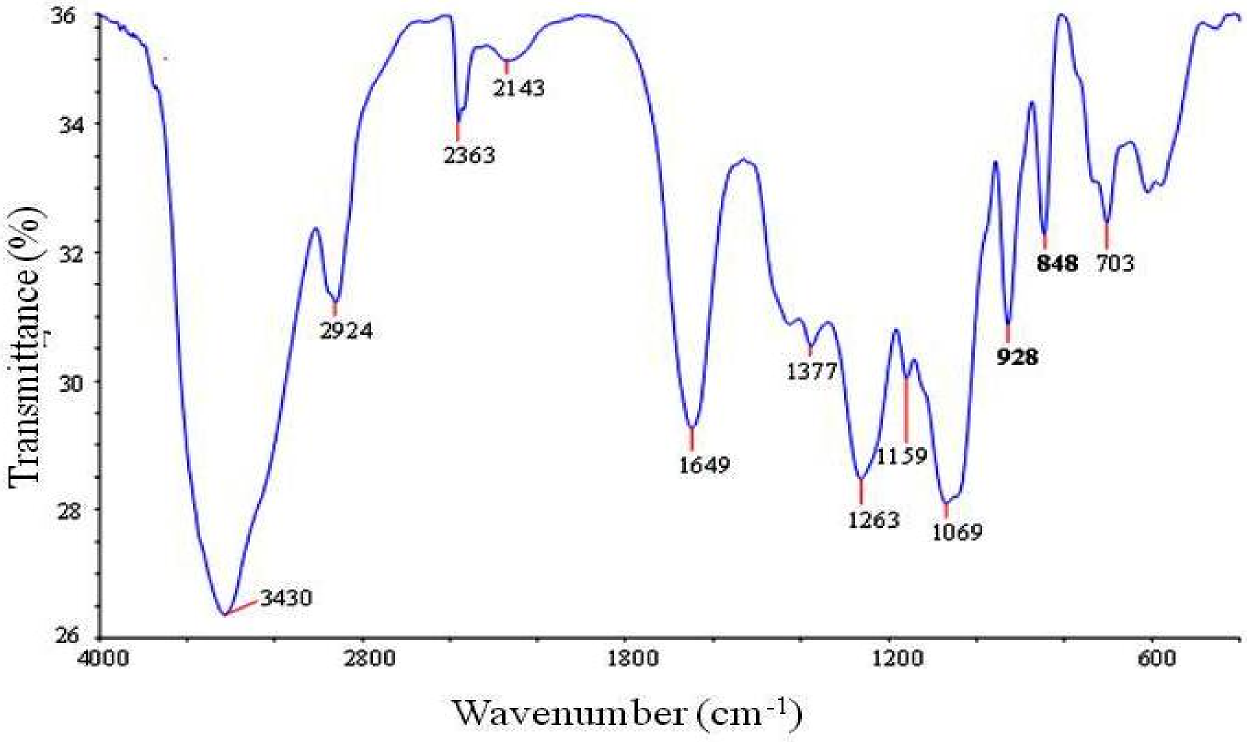
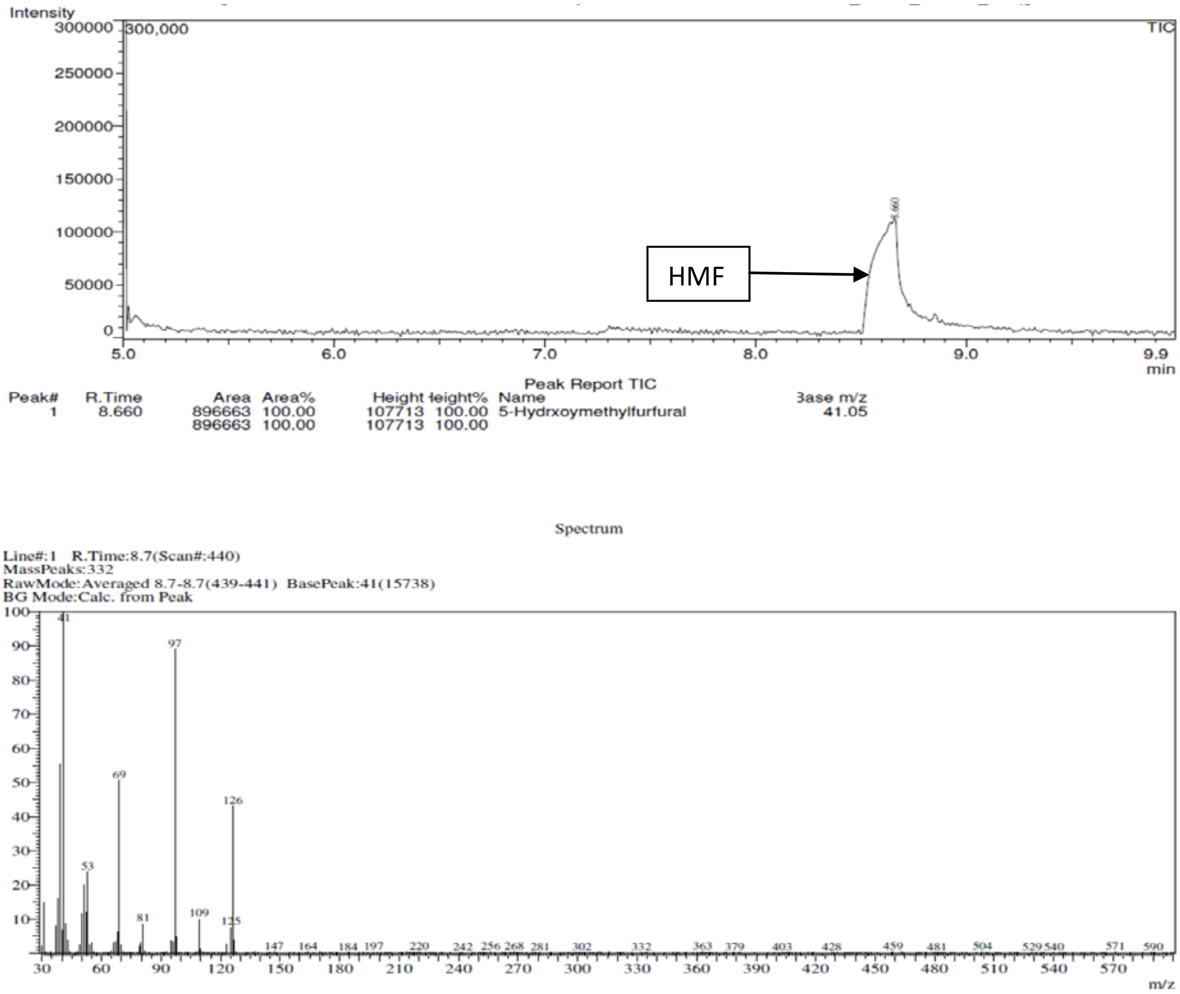


Figure S1: FT-IR spectrum of pristine κ-carrageenan isolated from granules of *K. alvarezii* through extraction with seawater followed by precipitation with IPA.

2. Hydrolysis of κ-carrageenan with different concentrations of sulphuric acid

1 gm of pristine κ-carrageenan was taken in a conical flask containing 20 ml of 0.1 N H_2SO_4 and the mixture was autoclaved at 105 ºC for 1 h. The product mixture was shaken thoroughly with equal volume of ethyl acetate and the organic was then subjected to GC-MS. The GC-MS spectra did not show the presence of HMF in the ethyl acetate fraction obtained from the above reaction. Then the acid strength was gradually increased to 0.9 N keeping all other reaction parameter unaltered. The highest yield of HMF (291 mg, 49 % carbon utilisation on κ-carrageenan basis) was obtained with 0.3 N H_2SO_4.



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                                   Peak Report TIC
Peak#   R.Time         Area  Area%        Height leight%  Name                          3ase m/z
    1    8.660       896663  100.00       107713  100.00  5-Hydrxoymethylfurfural          41.05
                     896663  100.00       107713  100.00
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Line#:1   R.Time:8.7(Scan#:440)
MassPeaks:332
RawMode:Averaged 8.7-8.7(439-441)  BasePeak:41(15738)
BG Mode:Calc. from Peak
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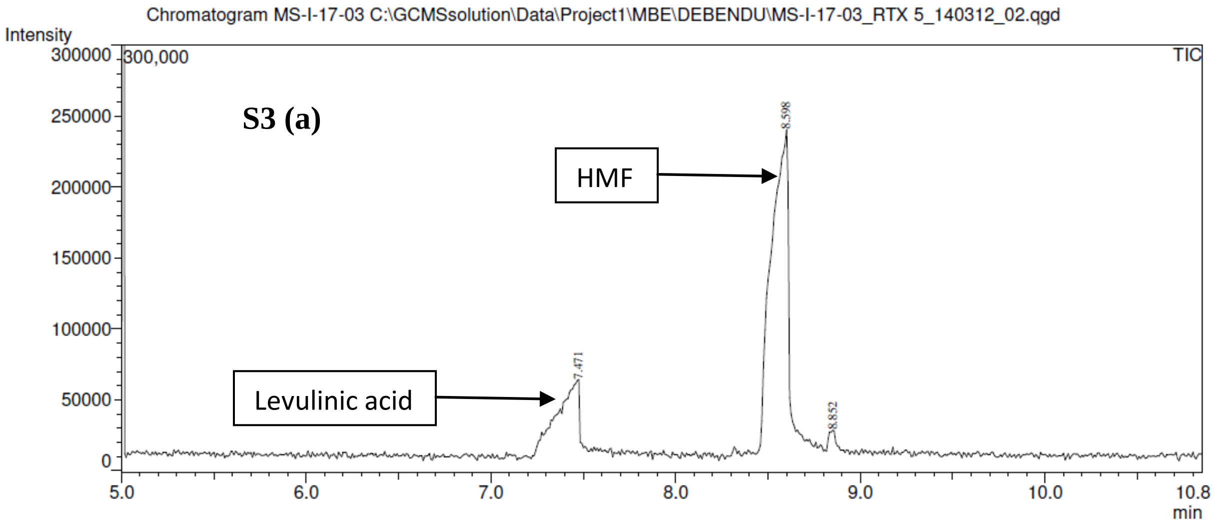
Figure S2: GC-MS data for the experiment conducted with 0.3N H_2SO_4.

2.1 Recycling of the acidic aqueous layer

10 g of the pristine κ-carrageenan was reacted under optimized condition with 0.3 N H_2SO_4 in 200ml water at 105°C under autoclaving for 1 h. The aqueous layer was extracted with ethyl acetate (1:1) and the layer was saved. Further, in the above acidic aqueous layer, 10 g κ-carrageenan was added and hydrolysed under same conditions described above followed by extraction with ethyl acetate. The cycle was repeated for 6 times. After 6 cycles the ethyl acetate fractions were analysed individually. Shown below is the GC-MS of the 6th cycle wherein HMF was found to degrade to levulinic acid.



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name	Base m/z
1	7.471	469040	23.34	54728	18.38	Levulinic acid	43.05
2	8.598	1500701	74.68	228157	76.63	HMF	97.00
3	8.852	39649	1.97	14843	4.99		126.05
		2009390	100.00	297728	100.00		

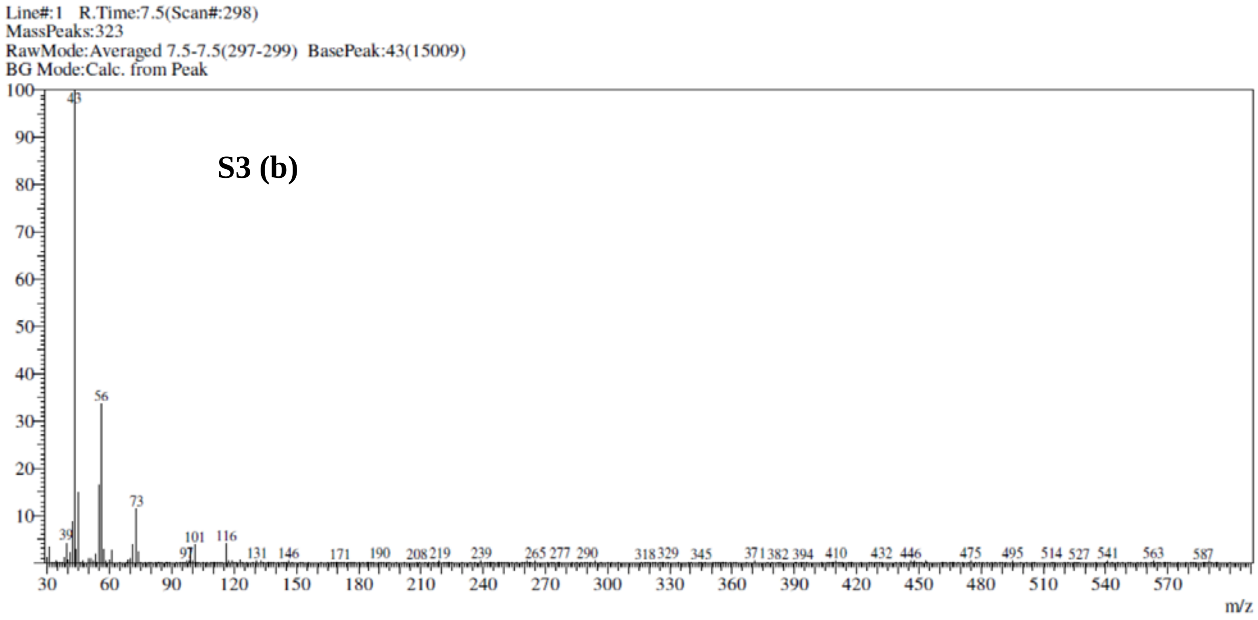
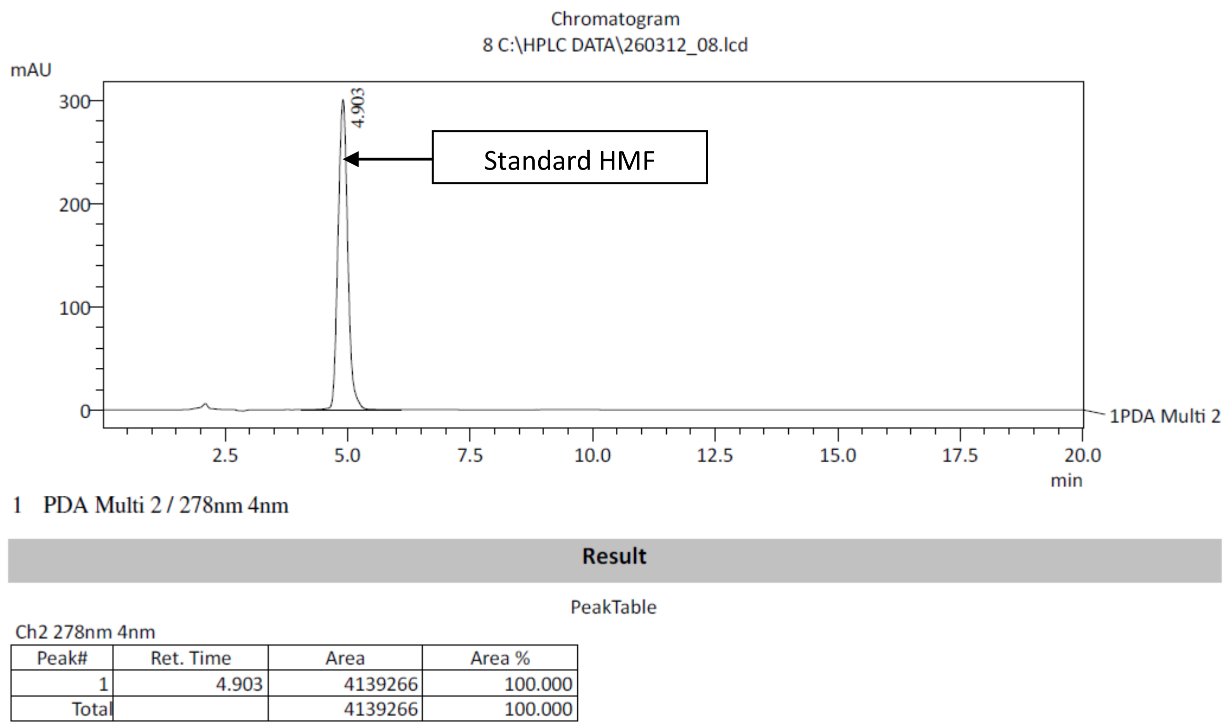


Figure S3: (a) GC of ethyl acetate fraction obtained after 6 cycle's reaction of 10 g κ-carrageenan with 200 mL 0.3 N H_2SO_4 at 105 °C under autoclave condition. (b) Mass spectra of levulinic acid.



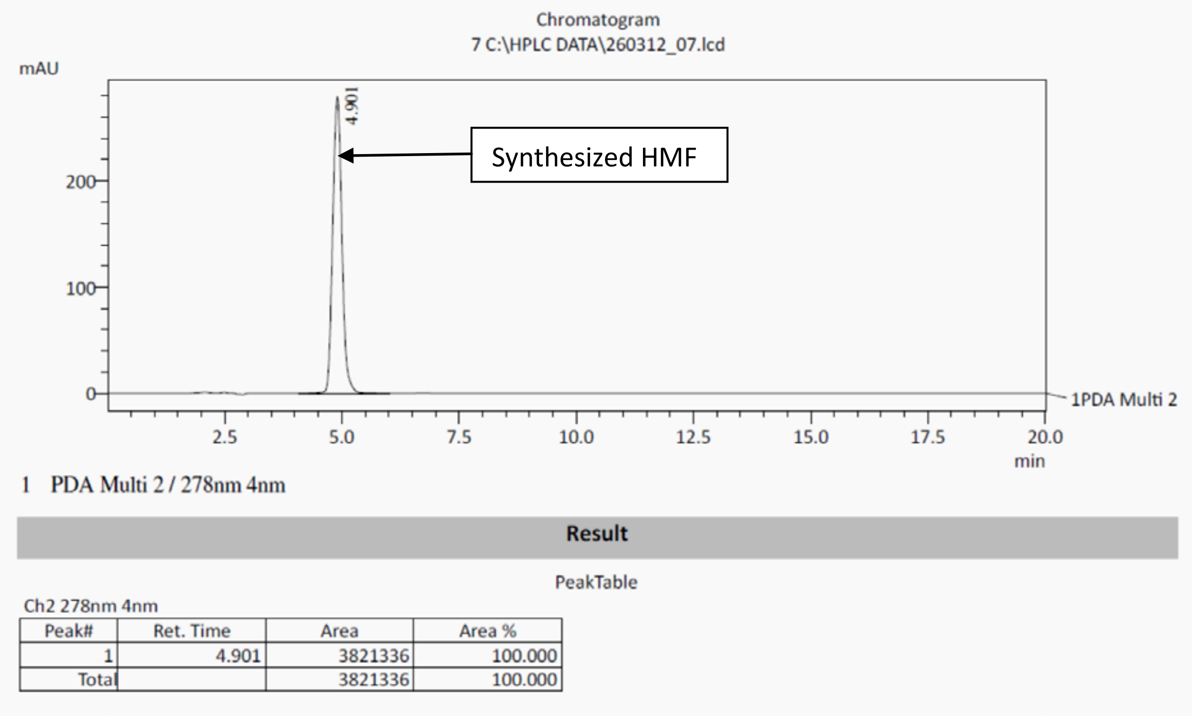
Result

PeakTable

Ch2 278nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.903	4139266	100.000
Total		4139266	100.000

Figure S4: HPLC chromatogram of standard HMF sample.



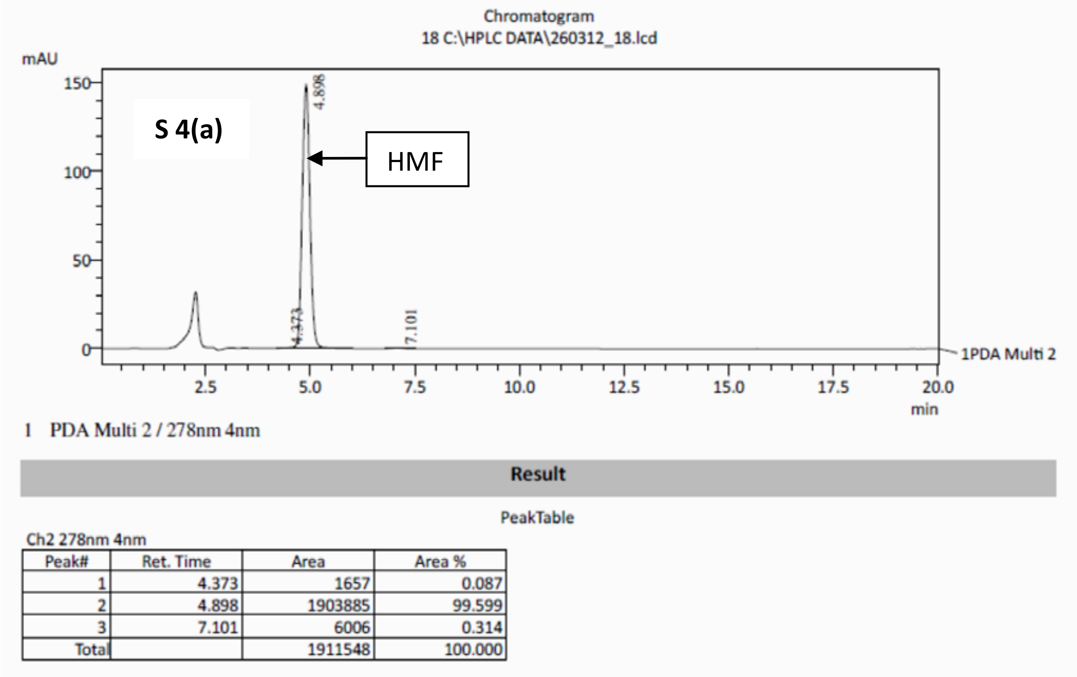
Result

PeakTable

Ch2 278nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.901	3821336	100.000
Total		3821336	100.000

Figure S5: HPLC chromatogram of HMF synthesized from κ-carrageenan, after extraction into ethyl acetate followed by removal of solvent and redissolution in HPLC grade water.



Chromatogram
18 C:\HPLC DATA\260312_18.lcd

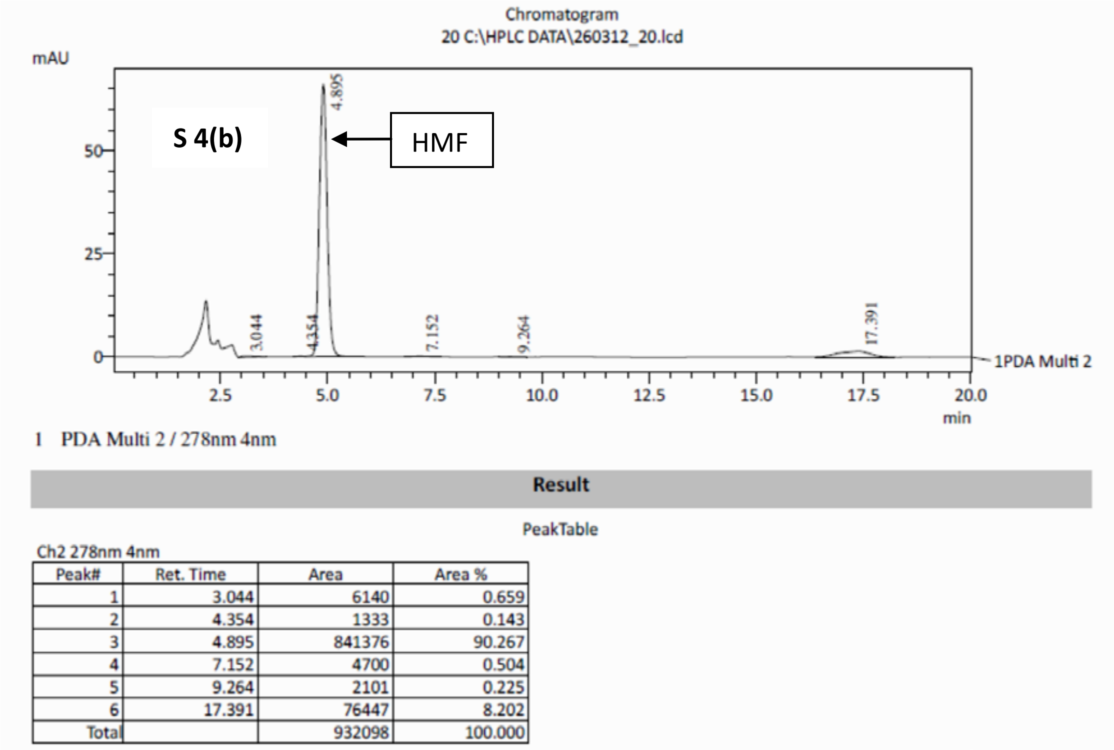
1 PDA Multi 2 / 278nm 4nm

Result

PeakTable

Ch2 278nm 4nm

Peak#	Ret. Time	Area	Area %
1	4.373	1657	0.087
2	4.898	1903885	99.599
3	7.101	6006	0.314
Total		1911548	100.000



Chromatogram
20 C:\HPLC DATA\260312_20.lcd

1 PDA Multi 2 / 278nm 4nm

Result

PeakTable

Ch2 278nm 4nm

Peak#	Ret. Time	Area	Area %
1	3.044	6140	0.659
2	4.354	1333	0.143
3	4.895	841376	90.267
4	7.152	4700	0.504
5	9.264	2101	0.225
6	17.391	76447	8.202
Total		932098	100.000

Figure S6: HPLC chromatogram of residual HMF remained in the aqueous phase for 1st cycle (a) and (b) for 2nd cycle.

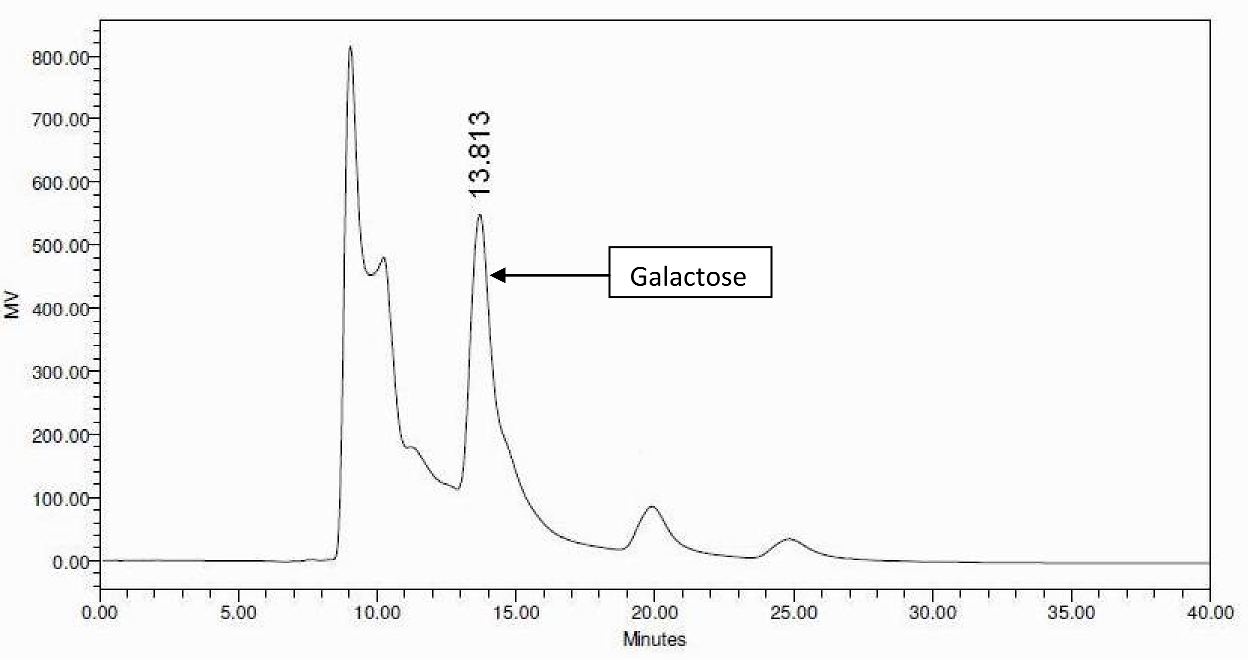


Figure S7: HPLC chromatogram of aqueous phase containing galactose obtained after HMF extraction with ethyl acetate.

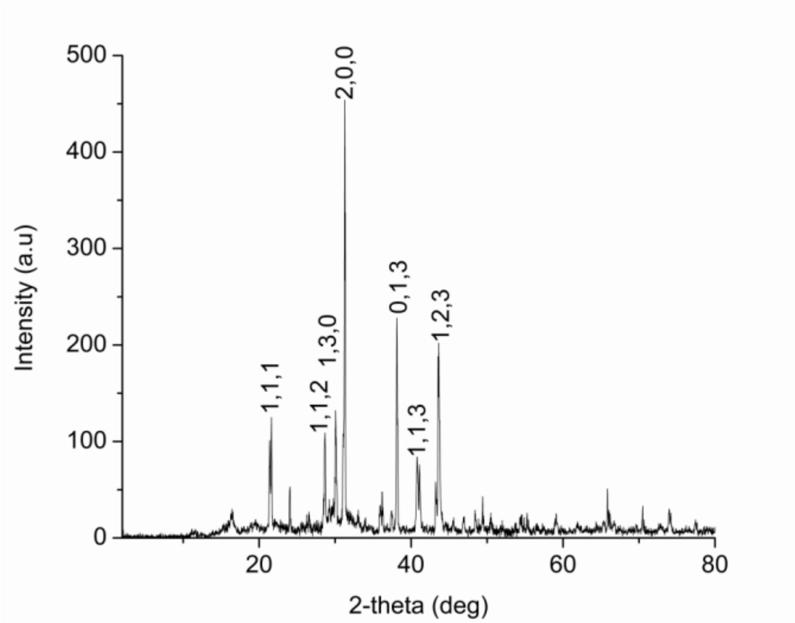


Figure S8: Powder XRD of K_2SO_4 fraction obtained after progressive evaporation of aqueous stream after HMF separation and seaweed sap. Search match analysis was performed with high score plus software using ICDD-JCPDF data base.

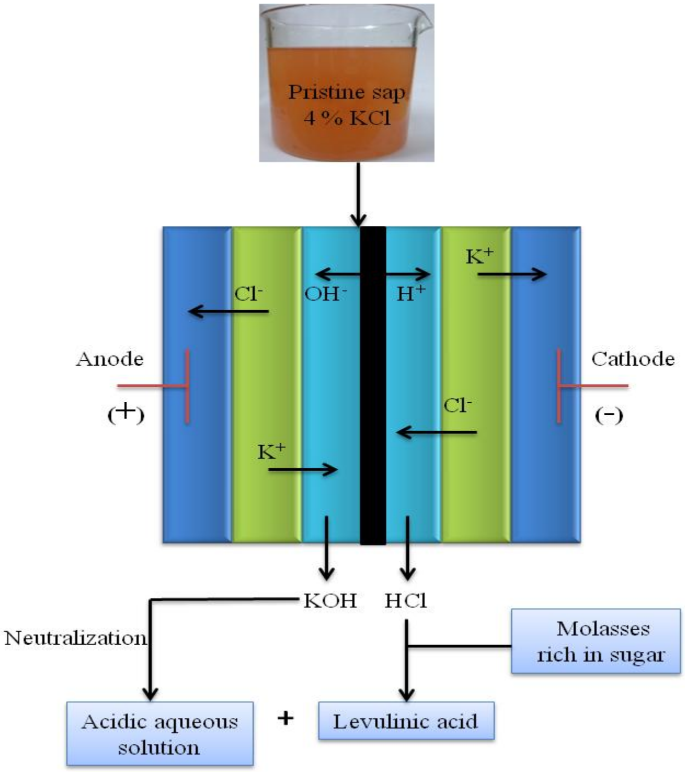
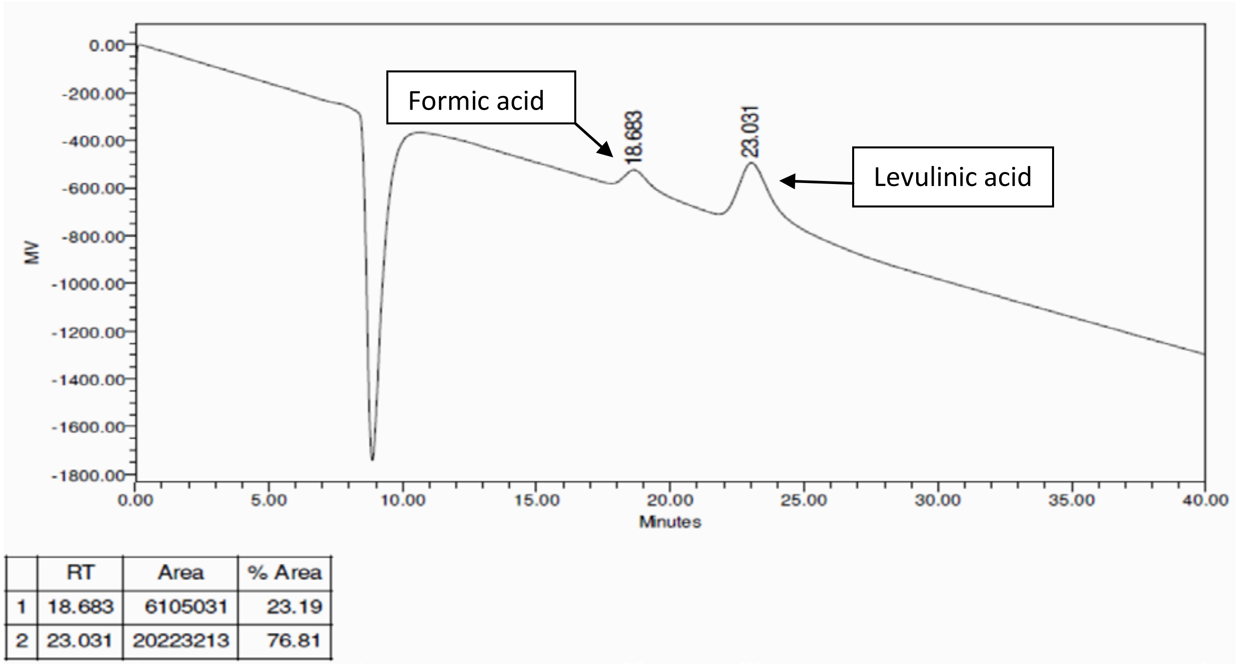


Figure S9: Schematic representation of bipolar electrodialysis process for the generation of HCl and KOH from KCl rich seaweed juice.



	RT	Area	% Area
1	18.683	6105031	23.19
2	23.031	20223213	76.81

Figure S10: HPLC chromatogram of levulinic acid and formic acid.

Table S1. Table for composition of different salts obtained during the course of progressive forced evaporation of spent aqueous stream containing seaweed juice for K_2SO_4 recovery.

Entry no	Specific gravity	Volume (ml)	Remarks	Solid obtained if any/(g)	Solution Composition (moles per 1000 moles H_2O)			
					[K_2SO_4]	[$MgSO_4$]	[$MgCl_2$]	[K_2Cl_2]
1	1.33	250	Aqueous phase after 10 cycles neutralized with $Mg(OH)_2$	0.0	8.47	42.05	0.0	0.0
2	1.13	2000	After addition of 1.8 L of sap into aqueous phase in entry 1followed by evaporation	0.0	5.35	0.0	4.98	1.53
3	1.15	650	Concentration through forced evaporation	0.0	16.8	0.0	15.6	4.8
4	1.17	400	“	6.2 K_2SO_4	25.8	0.0	25.28	7.9
5	1.172	350	“	10.2 K_2SO_4	25.9	0.0	27.7	9.04
6	1.19	300	“	16.5 K_2SO_4	27.14	0.0	32.14	9.28
7	1.2	250	“	33.6 K_2SO_4	13.56	0.0	34.27	17.5
8	1.22	150	“	13.3 KCl (with some K_2SO_4 impurity)	19.8	0.0	64.3	16.17

References

1. N. Rasool, T. Yasin, J.Y.Y. Heng, Z. Akhter, *Polymer*, 2010, **51**, 1687-1693.