Journal of Hazardous Materials 162 (2009) 498–502

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Effect of soda ash industry effluent on agarophytes, alginophytes and carrageenophyte of west coast of India

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ARTICLE INFO

Article history:
Received 28 November 2007
Received in revised form 15 May 2008
Accepted 16 May 2008
Available online 23 May 2008

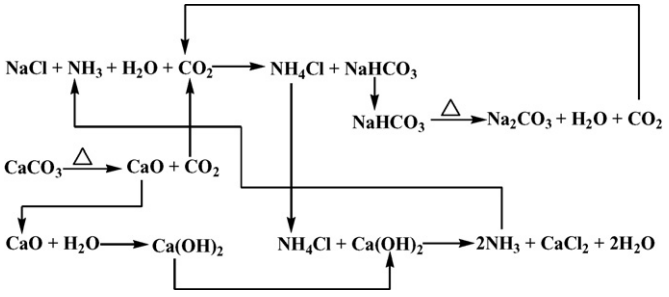
Keywords:
Soda ash
Phyco-colloid
Seaweed
Pollution ecology
Biomass

ABSTRACT

This paper presents the results of a study on the impact of the effluent released by the soda ash industry on important red and brown macro algal species *Gelidiella acerosa*, *Gracilaria corticata*, *Soleria robusta*, *Sargassum tenerrimum*, *Padina tetrastromatica* in the tidal zone around Veraval, on the west coast of India, in the lowest low water tide of December 2003. The study examined the effect of effluent discharge on availability of biomass and percentage of phyco-colloids extraction such as agar, alginic acid and carrageen of these commercial seaweeds.

1. Introduction

Soda ash is the common name for the technical grade anhydrous sodium carbonate (Na_2CO_3). In the 18th century soda ash was produced by LeBlanc process based on roasting salt cake with carbon and limestone. The synthetic procedures available for the soda ash are Solvay process, Akzo dry lime process, dual process and New Ashai process. The most accepted technology for producing soda ash is the ammonia soda or Solvay process developed by Ernest Solvay in 1861. The Solvay process is widely accepted because it requires low investment and has low maintenance costs compared to other manufacturing processes for soda ash. Of the six soda ash manufacturing units in India, four units use the Solvay process. This process produces 91.2% of the soda ash produced in India. The standard ammonia soda process is based on the following chemical reaction [1]:



The soda ash industry, where the present study was conducted, is situated at latitude 20°49′N, longitude 70°28′E. The industry manufactures approximately 1400 tons of soda ash per day (600,000 metric tons per annum) by Solvay dry liming process. In the process, it generates a large quantity of effluent, which it discharges into the sea. To meet the pollution control standard (Table 1), the actual effluent is being diluted (approximately 27 times) by seawater before it is released into deeper waters through a channel (850 m long), which allows some settling of solids. Many species of seaweed, including those, which have commercial importance, are very abundant in this region.

Seaweed, a common name for macroalgae, is a commercially valuable resource for food, fodder, soil conditioners and

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doi:10.1016/j.jhazmat.2008.05.080

Table 1
Norms for effluent disposal—Solvay process (marine recipient body)[a]

Parameter	
pH	6.5–9
Temperature	45 °C or less
Oil and grease	2 mg/L
Total suspended solids	500 mg/L
Ammonical nitrogen	5 mg/L
Bio-assay	96 h 90% survival

[a] *Source*: Central Pollution Control Board.

pharmaceuticals. Historically, seaweeds were harvested from natural populations. The increasing food demand has led to a dramatic growth of the seaweed industry since the 20th century [2]. The seaweeds are the source of phyco-colloids like agar, alginic acid and carrageenan which are extracted from the cellular wall of Rodophyceae (red algae) and Pheophyceae (brown algae). These products are difficult to synthesize chemically because of the formidable chemical barriers and therefore for these commercially important products we have to depend on seaweed resources. The economically important seaweeds (mainly the red seaweed or Rhodophyta) are under large-scale cultivation to meet the demand for important phyco-colloids. The present investigation aimed to study the effect of discharge of soda ash industry effluent on the extractable quantity of the phyco-colloids.

2. Materials and methods

The description of the study site, sampling stations, seaweed and seawater collections and analysis are recently published by us [3,4]. Samples of five species of algae of the Rhodophyta and Phaeophyta families/genus namely *Gelidiella acerosa* (Forsk.) Feldman et Hamel, *Gracilaria corticata* J. Ag., *Soleria robusta* (Grev.) Kylin., *Sargassum tenerrimum* J. Ag., and *Padina tetrastromatica* Hauck. (Fig. 1) have been collected from these stations and processed as described earlier [4]. The extraction of the phyco-colloids is done as follows:

Agar was extracted from dried samples of *G. acerosa* and *G. corticata* following the method of Roleda et al. [5]. Alkali modification [6] was done prior to extraction of agar samples. The hot homogenized extracts were filtered under pressure through Celite bed and filtrate was allowed to gel at room temperature and kept at −20 °C for 15 h. The frozen gel was thawed, the thawed liquid was squeezed off, and then the gel was washed with distilled water and air dried for 24 h at room temperature (30 °C) followed by drying in the oven at 60 °C for 4 h. The yield of agars was calculated based on received dry seaweed.

Alginates were extracted according to published modified procedure [7]. The algae samples were dried to constant weight at 60 °C, and then soaked in 2% formaldehyde for 24 h, washed with water and then added to 0.2 M HCl and allowed to stand for another 24 h. Afterwards the samples were washed again in distilled water before extraction with 2% sodium carbonate. The aliquot collected was centrifuged, and the supernatants were labeled as crude extracts. The alginate sample was then obtained from the crude extract by precipitation with ethanol. The precipitate was washed twice with acetone and dried under ambient atmosphere.

Native carrageenan was extracted in distilled water at 60 °C for 4 h, under agitation [8]. The digestion product was filtered and precipitated in 85% isopropanol with 0.2% KCl solution. The coagulum was recovered and dried in an oven at 60 °C for 12 h. Native carrageenan yield was calculated on the basis of the seaweed samples dried in oven at 60 °C for 24 h and at 105 °C for 2 h to constant weight.

Elemental microanalyses (C, H, N, S) were performed in a PerkinElmer, Series II, model 2400 equipment. The accuracy of the result was checked by analyzing the standard reference material and repeating the same analysis twice or thrice.

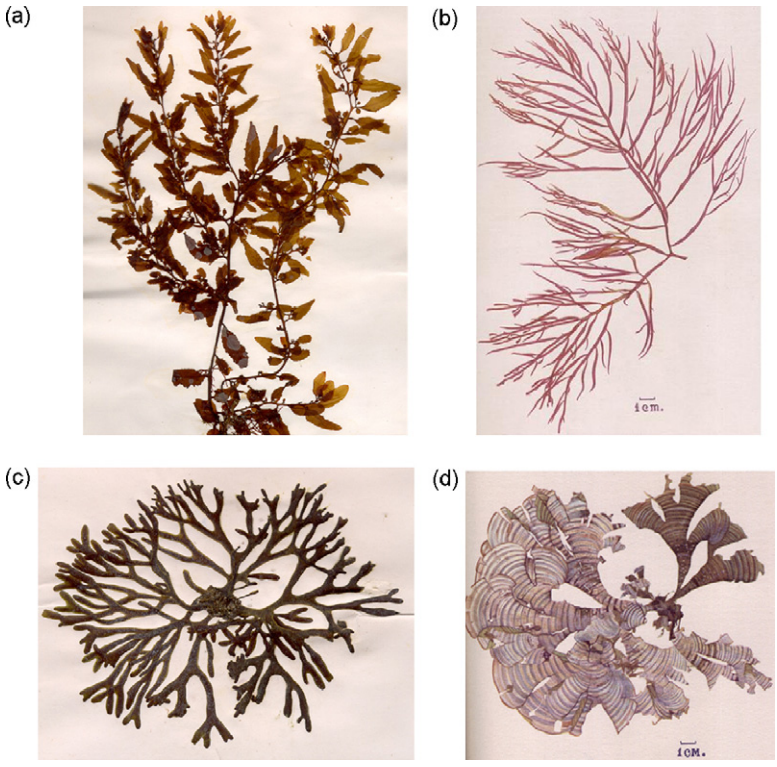

Fig. 1. The different species of seaweeds used in the present studies: (a) *Sargassum tenerrimum* J. Ag., (b) *Soleria robusta* (Grev.) Kylin., (c) *Gracilaria corticata* J. Ag. and (d) *Padina tetrastromatica* Hauck.

Table 2
Effect of soda ash industry effluent on quantity of agar, carrageenan, and alginic acid in different seaweeds

Seaweed species	Sampling location/reduction (%) with reference to control or least effected	Yield (%)
Agarophyte (agar)		
Gelidiella acerosa	3 km away from effluent discharge point	7.73 ± 0.18
	Control	9.15 ± 0.21
	Reduction	15.52
Gracilaria corticata	Near effluent discharge point	22.85 ± 0.23
	Control	25.33 ± 0.17
	Reduction	9.79
Carrageenophyte (carrageenan)		
Soleria robusta	3 km away from effluent discharge point	16.68 ± 0.81
	Control	25.50 ± 0.94
	Reduction	34.59
Alginophyte (alginic acid)		
Sargassum tenerrimum	1 km away from effluent discharge point	8.4 ± 0.23
	3 km away from effluent discharge point	12.5 ± 0.13
	Control	14.6 ± 0.17
	Reduction	42.47 (1 km)
		14.39 (3 km)
Padina tetrastromatica	1 km away from effluent discharge point	9.5 ± 0.15
	3 km away from effluent discharge point	10.3 ± 0.21
	Reduction	7.77

Table 3
Concentration of C and N in seaweeds due to impact of soda ash industry effluent at different distances from effluent discharge point (mg/100 g)

Distance (km)	Name of seaweed species	C	N	C:N ratio
0	*Gracilaria corticata*	23,520	3380	6.96
1	*Padina tetrastromatica*	19,420	1190	16.32
	Sargassum tenerrimum	26,390	1340	19.69
3	*Gelidiella acerosa*	33,010	3130	10.55
	Soleria robusta	16,860	1580	10.2
	Padina tetrastromatica	20,030	1430	14.00
8	*Gracilaria corticata*	31,760	2720	11.68
	Gelidiella acerosa	25,620	2210	11.59
	Soleria robusta	16,490	1650	10.43
	Sargassum tenerrimum	27,360	1800	15.2

Both the vertical and horizontal distribution of seaweeds was studied. The measurements began from the discharge point and continued outwards. Vertical distribution was studied along a line transect perpendicular to the coastline. The biomass measurements at all the stations were performed by the quadrat method [9]. Half-meter quadrats, having 10 cm × 10 cm sub-quadrates, were placed at 5 m intervals along the vertical line transect. Species composition and biomass of individual species were determined in each quadrat. Macrophyte abundances were assessed by visually estimating their cover (%) in 0.5 m^2 quadrats at 5 m intervals along the transect. Several studies have revealed that visual cover estimation is a good method for determination of biomass and frequency of seaweed species in a study area [10,11]. Only hard substrates were sampled and quadrats that lay on sand were not included in the analysis. The survey began from the highest high water mark and walking towards the sea in the inter-tidal zone. The study included parallel tide pools to obtain a more realistic picture of the region.

3. Results and discussion

The effect of soda ash industry effluent on the extractable phyco-colloids of the different species of algae under study is presented in Table 2. The quantity of the agar [12] and alginic acid [13] extracted from the alga are in accordance with amount found in other species of economically important seaweeds.

The results show that the soda ash industry effluent has significantly reduced the extractable quantity of the different phyco-colloids from the different species of seaweed under study.

It is well known that the yield and quality of phyco-colloids produced in marine farms vary not only with the seaweed strain under cultivation but with a series of biological and environmental parameters such as age of plants, light, nutrients, temperature and salinity, amongst others [14–18]. Abiotic factors such as depth (light), salinity, substratum, nutrients, water motion, sedimentation and pollution affect the structure and distribution of algal communities at a local scale [19–25]. Interactions between algal

Table 4
Effect of soda ash industry effluent on seaweed biomass

Distance (km)	Name of seaweed species	Density (no. m^{-2})
0	*Gracilaria corticata*	168
1	*Padina tetrastromatica*	204
	Sargassum tenerrimum	92
3	*Gelidiella acerosa*	104
	Soleria robusta	14
8	*Padina tetrastromatica*	44
	Gracilaria corticata	144
	Gelidiella acerosa	92
	Soleria robusta	8
	Sargassum tenerrimum	85

Table 5
Bioaccumulation of nitrogen in *Gracilaria corticata* at 4.29 g L^{-1} seaweed density

Sr. no.	Parameter	Ammonia in seawater (mg)	Ammonia in effluent (mg)
1.	Total nitrogen in medium at 0 h	41.46	48.18
2.	Total nitrogen in medium at end of experiment	10.83	13.41
3.	Increase in nitrogen content of *Gracilaria* at end of experiment	29.65	33.65
4.	Escape of nitrogen from medium	0.98	1.12
5.	Total nitrogen in medium and *Gracilaria* (total of 2–4)	41.46	48.18
6.	Accumulation of nitrogen by *Gracilaria* (%)	71.52	69.84

species and between algae and herbivores have not been considered in this work, although they may play an important role in the distribution and abundance of seaweeds [26–29]. Considering the other factors to be constant the effect on the available quantity of phyco-colloids in these algae may directly be correlated with the effect of the effluent. The ionic waste received from the soda ash effluent has profound effect on the algal species. This waste caused: (1) plunging of the saline input, (2) chemical stratification in the surrounding region, (3) high salinity (e.g. increase in Cl^- concentration), (4) elevated precipitation and deposition of calcium carbonate and phytoplankton similar to those observed in the study of the Seneca River [30–33].

The yield of agar per biomass of *Gracilaria* is known to decrease with increasing tissue nitrogen concentrations and accordingly agar yield was lower in *Gracilaria* from effluent affected station as compared to control [34,35]. The other independent studies also show the negative correlation between nitrogen content and agar yield in the *Gracilaria* species [36,37].

Table 3 lists the concentration of elemental C, N and C:N ratios in the tissues of different seaweeds. The C:N ratio in almost all seaweeds decreased in the effluent affected region and not in the control. However, a greater quantity of tissue N found may be attributed to the uptake of the effluent which is very rich in N [4].

The discharged effluent is highly alkaline and contains CO_3^{2-} and HCO_3^- salts. Most of algae posses CO_2-concentrating mechanisms (CCM) that is associated with the ability to utilize, directly or indirectly, the bulk HCO_3^- pool in seawater. Most of the seaweeds have been found to be able to use the HCO_3^- as their principal source of inorganic carbon (Ci) for photosynthesis [38–41]. HCO_3^- is usually dehydrated extracellularly as mediated by surface-bound carbonic anhydrase to generate CO_2, which is then taken up into the cell. Another important way by which the ionic Ci from utilization is the direct HCO_3^- uptake through the plasma membrane facilitated by an anion exchange protein [42–44]. The tissue inorganic carbon content of the algae (Table 3) is varying based on their ability to take up the inorganic carbon. However, in general, the tissue N content in the algae is found to be more in the polluted condition then in the control mainly because effluent is very rich in N content and thus many of the algae accumulate this nitrogen directly by assimilation [4]. The availability of nutrients for biological uptake is an important factor controlling algae species composition and biomass in shallow coastal waters, and various algae show the different growth strategies, life forms and distribution along nutrient gradients [45–47]. Thus algae able to use of an increase in ambient nutrient concentration, are either nutrient limited or capable of 'luxury uptake', i.e., able to incorporate excess nutrients for later use.

The seaweed biomass was also affected by the soda ash industry effluent. The seaweed density per meter square observed in the effluent affected region and in the control is given in Table 4.

The result shows that there is more biomass available (nearly 56% more) near effluent affected region than the control. Seaweed productivity in effluent affected areas is higher due to the greater nutrient availability provided by the effluent discharge.

There is a considerable difference in the biomass availability at the effluent affected station and control station (cf. Table 4). The differences may be due to the combined effect of the quality of effluent, turbidity, topography and other environmental variables [48,49]. However, the above workers have clearly shown that a difference in biomass is primarily due to pollutants and the effects of other parameters are secondary in nature. Similar observations were also reported for *Gracilaria* spp. at Itamaraca Island (Brazilian Northeast) [50].

The abundance of *G. corticata* near the effluent discharge point shows that this alga has a mechanism to utilize the ammonical waste generated from the soda ash. Thus by cultivating this alga in effluent affected water large quantity of nutrient can be removed as *Gracilaria* is a good biofilter for nutrients [51–53] and at the same time generating agar, an important phyco-colloids, as a by-product. This kind of experiments with *Gracilaria chilensis* are already in use in Chile to reduce the nutrient load from fish farms and have shown very good results [54,55]. Several studies have shown that *Gracilaria* with high levels of tissue nitrogen produces high quality agar [36,56] which is important from a commercial point of view.

To demonstrate the environmental cleaning capacity of the present species of *Gracilaria*, i.e., *G. corticata*, the independent laboratory experiment was carried out in which the freshly collected biomass of the alga was subjected to high ammonia containing seawater prepared from liquor ammonia, as well as, undiluted soda ash industry's effluent. The ammonium ion concentration was measured periodically. The result of this experiment is listed in Table 5. The results show that the alga has removed almost 70% of the NH_4-N from the medium and thus considered as a good candidate for cleaning the environment polluted from soda ash industry's effluent.

4. Conclusion

There is a considerable effect on extractable quantity of phyco-colloid of the seaweeds due to uptake of polluted water. The per gram yield of phyco-colloids decreased due to effect of soda ash industry effluent but overall yield will be more because of greater biomass production in the effluent affected region. All the species exhibit tolerance against the effluent affected environment especially *G. corticata* and thus can be cultivated on a large scale in effluent affected area to get a double benefit of cleaning the environment while producing a phyco-colloids as a by-product. While there are potential economic benefits and environmental cleaning processes taking place due to the presence of the Solvay discharge, there are significant impacts on the structure and functioning of the wider aquatic ecosystem at this location. More research efforts are necessary to understand these phenomenons.

Acknowledgements

The authors acknowledge the financial assistance of the Council of Scientific and Industrial Research (CSIR), New Delhi, India to this work. They express their gratitude to Dr. P.K. Ghosh, Director, CSMCRI for his constant help and encouragement during the work.

Sincere thanks are due to Chaitali Vaishnav, The Maharaja Sayajirao University of Baroda for language editing.

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