

Biodeterioration of Coastal Concrete Structures by Marine Green Algae

S.Jayakumar^{1,*} and R. Saravanane²

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Abstract: Puducherry is a coastal region in India where the growth of *Ulva fasciata* (Delile) is very abundant on all marine structures. Though the detrimental effect of this macro algae *Ulva fasciata* is a secondary one, its effect has to ascertain. To know its effect, the basic mechanism by which *Ulva fasciata* deteriorates concrete structures, M20 grade concrete cubes were casted and kept in the coastal area where there is abundant growth of *Ulva fasciata* and also laboratory simulation has been carried out. To ascertain the detrimental effect by the macro algae on concrete surface, samples were collected from the concrete cubes kept in the coastal area and also from the laboratory simulated one. The collected samples were analyzed by SEM, EDX and XRD to establish the degree of deterioration done by marine algae on concrete surface. The SEM and EDX results showed that there is a remarkable change in the base materials viz., Ca and Si content and XRD results revealed the absence of Calcium Hydroxide. Both the results confirmed the biodeterioration of concrete by the marine green algae.

Keywords: Marine algae, marine structures, *Ulva fasciata*, concrete, deterioration

1. Introduction

About 71% of the world is surrounded by ocean. The most important herbivores in ocean are phytoplankton and benthic algae. The marine algae familiarly known as seaweeds are a diverse group of photoautotrophic organisms of various shapes (filamentous, ribbonlike, or platelike) that contain pigments such as chlorophyll, carotenoids, and xanthophylls. The growth of marine algae is abundant in coastal area since sandy beaches provide excellent attachment points in a constantly moving and dynamic environment of the sandy shore. The first type of plant life to attach itself to these structures is filamentous Macroalgae. The colonisation is likely to be, due to the constant abrasion of the lower regions by the action of the tide lifting the sand and small stones from around the base of the structure. A number of seaweeds can be found in this type of environment although there is usually

a few dominant species like *Ulva fasciata*. These green algae are classified in the phylum Chlorophyta. Many species of green algae grow attached to rocky and concrete substrates on or near the ocean's surface. In general, because they are attached to a substrate, they are not tossed up on the beach by the waves. These macroalgae are able to obtain different elements for their metabolism e.g. calcium, aluminum, silicon, iron etc by biosolubilization of materials. Such biosolubilization involves the production of organic acids by the metabolic activity of macroalgae. This acid deterioration is one of the best known biogeochemical mechanism of concrete decay [1,2,3].

To better understand the terminology and chemical process, they are explained as follows:

Biogeochemical Deterioration Mechanism [1,2].

The biogenic (produced by living organisms or biological processes) release of corrosive acids is probably the best known and most commonly investigated biogeochemical damage mechanism in inorganic materials like concrete. The process, known as biocorrosion, is known to be caused by the microbial secretion of inorganic and organic acids (acidolysis and complexation). These agents are capable of leaching the mineral matrix with subsequent weakening of the binding-

* Corresponding Author: jkss@sify.com

1 Assistant Professor, Sri Manakula Vinayagar Engineering College, Madagadipet, Pondicherry – 605 107, India.

2 Assistant Professor, Environmental Engineering Laboratory, Department of Civil Engineering, Pondicherry Engineering College, Pondicherry – 605 014, India.

system

Biocorrosion [1,2]

Kinetics of corrosion processes of metals, mineral and other materials can be influenced by biofilms. Products of their metabolic activities including enzymes, exopolymers, organic and inorganic acids, as well as volatile compounds such as ammonia or hydrogen sulphide can affect cathodic and/or anodic reactions, thus altering electrochemistry at the biofilm/metal interface. This phenomena is often referred to as “biocorrosion” or “microbially influenced corrosion” (MIC).

A **biofilm** [1] is a structured community of microorganisms encapsulated within a self-developed polymeric matrix and adherent to a living or inert surface. Biofilms are also often characterized by surface attachment, structural heterogeneity, genetic diversity, complex community interactions, and an extracellular matrix of polymeric substances.

Biodegradation [1] is any undesirable change in the properties of a material caused by the vital activities of organisms.

Phycochemistry [2] is study on natural products and chemical constituents occurring within algal thalli from biological view point. Various natural products includes fatty acids (saturated and unsaturated), sterols, terpenoids and sugars.

Puducherry is an Indian coastal region on the Bay of Bengal. There are many marine structures located in the coastal area. These structures deteriorate due to the macro flora Figure 1 present in the sea water [4,5,6,7,8,9]. Though a secondary deterioration process, there is significant effect due to this macro flora [10,11,12]. The ambient condition prevailing in the coastal area helps the growth of *Ulva fasciata* round the year. The growth of *Ulva fasciata* on concrete structure in Puducherry region is found almost on all the structures. This study aims to ascertain the effect of marine chlorophyceae *Ulva fasciata* on concrete structure. For this, concrete cubes were immersed in the coastal area where there is abundant growth of *Ulva fasciata* and also simulated in the laboratory. Apart from this



Fig.1. Growth of Marine Seaweed on Structural Components

phychochemical analysis of *Ulva fasciata* was carried on to find the chemical constituents occurring in the algae due to secondary metabolites. The surface of the concrete cube is chipped where there is a growth of *ulva fasciata*. Their morphological characteristics were observed using Scanning Electron Microscope (SEM) and surface analysis was done using Energy Dispersive X-ray analysis (EDAX). Mineralogical analysis is done using X-ray Diffraction (XRD).

2. Materials and Methods

2.1. Concrete cubes

To ascertain the effect of *Ulva fasciata* on concrete, concrete cubes of M20 grade (Recommended in Indian Standard [13], M20 grade concrete mix is used for severe exposure condition with w/c ratio 0.5) were prepared using OPC 53 Grade cement. OPC- 53 Grade is used since it is a high quality cement prepared from the finest raw material owing to optimum water demand, it contributes to a very low co-efficient of permeability of the concrete prepared. This improves the density of the concrete matrix and increases the durability of the concrete.

2.2. Methods

The procedure followed to determine the effects of *Ulva fasciata* on concrete cubes were

- a) To culture *Ulva fasciata* naturally, several concrete cubes were kept in coastal area where there was abundant growth of *Ulva*



Fig. 2. shows the natural culture of the marine algae *Ulva fasciata* on concrete cube



Fig. 3. shows the Laboratory culture of the marine algae *Ulva fasciata* on concrete cube

- fasciata (figure-2)
- b) Concrete cubes were allowed to cure in ordinary water.
- c) Laboratory simulation has been carried out to culture the macro algae on the concrete cube. For the simulation, Humidity oven was used (Figure-3). The details of oven are as follows:

Construction

Double walled, inner S.S.304 / 316 grade & outer S. Steel or GI dully Epoxy Powder coat / finish, gap filled with Glass wool with outer metallic door provided. Chamber is illuminated

with bulb.

Cooling Facility

By Hermetically sealed branded compressor coupled with air cooled condensing unit fitted with Motor, fan blade, Electrical Accessories etc. Mounted on bottom of unit on heavy base frame.

Humidity Creation

Humidity Created with Steam and injected into working chamber.

Heating Facility

By long lasting Stainless Steel Tubular Heater with fins

Temperature Control

Electronic Digital Temperature Controller-Cum Indicator with Dry Bulb and Wet Bulb principle

The ambient condition maintained in the chamber is as follows. Samples were incubated under lighting conditions of 2000 lx, 12 h/day with a “daylight” with white fluorescent lamp. The temperature is maintained at 30 °C. The relative humidity is maintained as 90% [4].

To ascertain the detrimental effect of marine algae on concrete, 50 cubes were kept in coastal area where there is abundant growth of algae. Every three months, four cubes were tested to ascertain the effect of marine algae on the cubes. Totally 20 cubes has been tested for the past one and half years and the cubes tested after nine months only showed predominant changes in the surface analysis done using SEM and EDAX and mineralogical analysis using XRD. Moreover the concrete cubes showed a weight loss of around 0.4 kg after nine months.

The laboratory simulated concrete cubes were stated testing after six months and here also there is sustainable effect after eight months only and weight loss in this case is – 0.6 kg.

2.3. Samples and Microbiological Procedures

Concrete sample for analysis were taken from the concrete cube where *Ulva fasciata* had attached itself from natural conditions. Before chipping the concrete surface for analysis, the biomass namely the marine chlorophyceae grown on the surface was scaped and placed in sterile plastic vessel and taken to the laboratory for identification. Apart from this concrete sample was chipped from the concrete cubes immersed in ordinary water in the laboratory.

2.4. Morphological Observations and Surface Analysis

SEM was employed in studying the morphological characteristics of the structure. For this, samples were dehydrated by using an acetone series; critical point dried; and gold coated at 10^{-3} mm Hg in sputter coat apparatus prior to SEM observations and EDAX analysis using a Hitachi S-3400N microscope.

2.5. Mineralogical Characterization

The concrete samples were analyzed by powder X-ray Diffraction using Philips PW1710 diffractometer with an automatic slit under the following conditions: emission radiation= $\text{CuK}\alpha$, voltage= 40 kV , intensity= 30 nA , goniometer speed= $0.120^\circ/\text{s}$. Goniometer calibration was performed using silica standard. Data was interpreted using X'Pert High Score. Samples were ground in agar mortar and sieved to obtain a fraction of particle size less than $53\mu\text{m}$.

2.6. Phycochemical Investigation of Marine Algae *Ulva Fasciata*

Marine algae *Ulva fasciata* was collected from the coastal area of Puducherry. It was washed

thoroughly to remove epiphytes, animal casting, attached detritus and sand particles. Then it was rinsed with distilled water and shadow dried with aeration to avoid the breakdown of secondary metabolites under sunlight and high temperature. The dried algal materials were chopped and milled. The following procedures were followed to isolate fatty acid from the dried algae:

Extraction

The dried, chopped and milled algal material was then soaked in methanol (MeOH) in a large glass jar and was kept in the solvent for one month at room temperature. The extract of the material thus obtained was then filtered to remove all solid algal particles. Next it was evaporated on a rotary evaporator under reduced pressure. This yielded a dark green, thick residue.

Saponification

An aliquot of the extract obtained was saponified with 10% KOH in 50% methanol and refluxed at 100°C for 6 hours. The mixture was then concentrated under reduced pressure and then H_2O and diethyl ester (Et_2O) were added. It was then shaken vigorously and the Et_2O layer was separated. The Et_2O layer was evaporated and used for fatty acid analysis.

Esterification

All the fatty acid fractions obtained were subjected to methylation and 1.5 -2.0 mL ethereal diazomethane was added to the fatty acid mixture. The reaction mixture was left in the fuming chamber at room temperature, over night until dissolved. The aliquots were then directly injected to a Hewlett Packard gas chromatograph

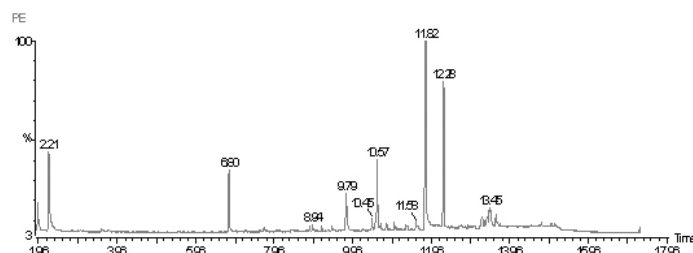


Fig.4. GC-MS of fatty acid fractions subjected to methylation obtained from *Ulva fasciata*

Table 1. Types of fatty acids present in *Ulva fasciata*

Acid type	Systematic name	Common name	Molecular formula
Saturated fatty acids			
C14:0	n-Tetradecanoate	Myristate	C ₁₅ H ₃₀ O ₂
C17:0	n-Hexadecanoate	Palmitate	C ₁₇ H ₃₄ O ₂
C19:0	n-Nonadecanoate	Nonadecylate	C ₂₀ H ₄₀ O ₂
Monoenoic fatty acids			
C13:1	Tridecenoate	Decylacrylate	C ₁₄ H ₂₆ O ₂
C19:1	Nonadecenoate	Nonadecylenate	C ₂₀ H ₃₈ O ₂
C21:1	Heneicosenoate	-	C ₂₁ H ₄₂ O ₂
C29:1	Nonacosenoate	-	C ₃₀ H ₅₈ O ₂
Dienoic fatty acid			
C17:2	9,12,15 Heptaedcaienoate	-	C ₁₈ H ₃₂ O ₂
C18:2	Octadecadienoate	Linoleate	C ₁₉ H ₃₄ O ₂

– mass spectrophotometer (GC-MS) with 11/73 DEC computer system.

The methanolic extract of *Ulva fasciata* revealed the presence of three saturated and six unsaturated fatty acids. The details are as below

Experimental Method – Flow Chart

The below chart 1 shows the schematic way of experimental method carried on to determine the effect of marine algae on concrete

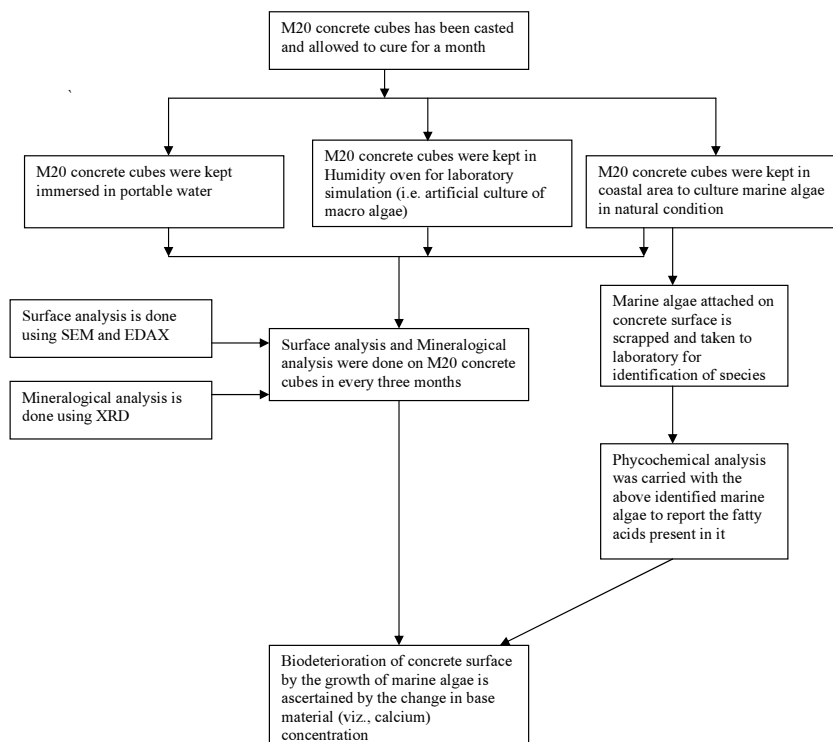


Table 1. Types of fatty acids present in *Ulva fasciata*

3. Result and Discussion

3.1. Macro-algae Results

The species collected by scarping from the surface of concrete was identified as *Ulva fasciata* Figure-5



Fig. 5. *Ulva fasciata* species

3.2. Biodeterioration Mechanisms

The release of metabolic acids is one of the best-known biogeochemical destructive mechanisms on concrete surfaces [2,3,9], with leaching of concrete binding materials [20] and consequent weakening of the crystal structure. These acids are also capable of chelating cations such as Ca, Al, Si, Fe, Mn and Mg from minerals forming stable complexes [9,14,15,16,17,18]. It has been shown that biogenic organic acids are considerably more effective in mineral mobilization than inorganic acids and are considered as one of the major damaging agents affecting concrete deterioration

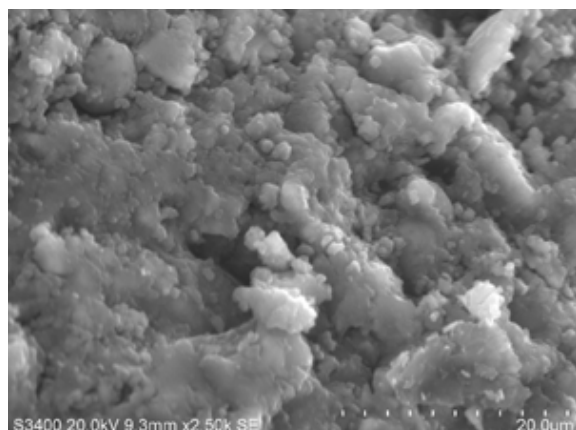


Fig. 6. SEM of concrete specimen immersed in ordinary water (magnification: x2500) - (control concrete)

The net outcome of this type of biodeterioration is the physical and mechanical break-down of the concrete matrix. (Table 2, Figure 6, Table 3, Figure 7, Table-4, Figure-8, Figure 9, Figure 10, Figure-11)

<i>Element</i>	<i>Atom %</i>
<i>Line</i>	
<i>O K</i>	58.44
<i>Mg K</i>	11.76
<i>Al K</i>	6.38
<i>Si K</i>	10.37
<i>S K</i>	1.08
<i>S L</i>	---
<i>K K</i>	0.25
<i>K L</i>	---
<i>Ca K</i>	9.18
<i>Ca L</i>	---
<i>Fe K</i>	2.55
<i>Fe L</i>	---
<i>Total</i>	100.00

Table 2. EDAX analysis of concrete specimen immersed in ordinary water- (control concrete)

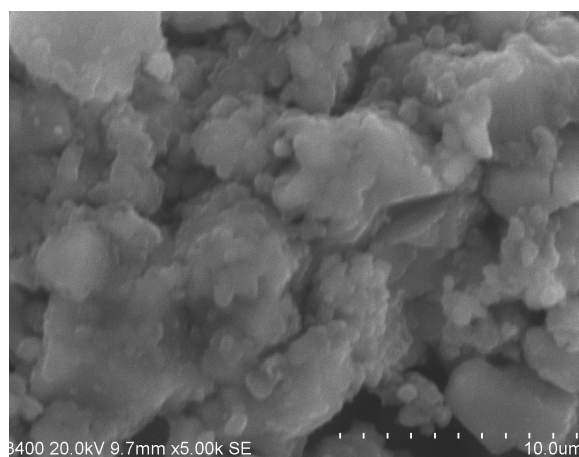


Fig. 7. SEM of *Ulva fasciata* attached concrete surface in natural condition (magnification: x2500)

<i>Element</i>	<i>Line</i>	<i>Atom %</i>
C K		34.28
O K		25.04
Mg K		1.00
Si K		0.86
Cl K		0.46
Cl L		---
K K		0.31
K L		---
Ca K		38.05
Ca L		---
Total		100.00

Table 3. EDAX analysis of *Ulva fasciata* attached concrete surface in natural condition

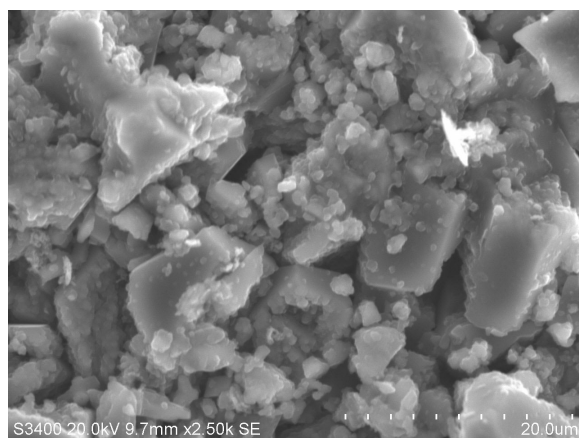


Fig. 8. SEM of *Ulva fasciata* attached concrete surface in laboratory condition (magnification: x5000)

<i>Element</i>	<i>Line</i>	<i>Atom %</i>
O	K	46.45
Na	K	1.48
Al	K	0.63
Si	K	2.79
Cl	K	2.82
Cl	L	---
K	K	1.68
K	L	---
Ca	K	44.15
Ca	L	---
Fe	K	0.00
Fe	L	---
Total		100.00

Table 4. EDAX analysis of *Ulva fasciata* attached concrete surface in laboratory condition

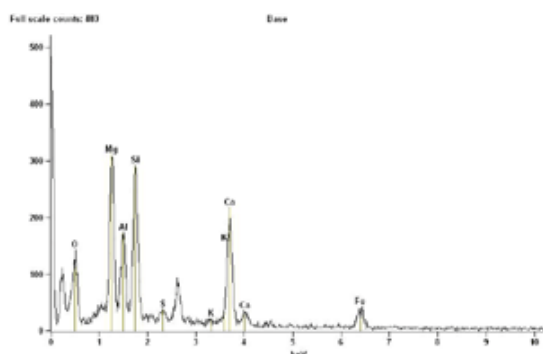


Fig. 9. EDAX of concrete specimen immersed in ordinary water (control concrete)

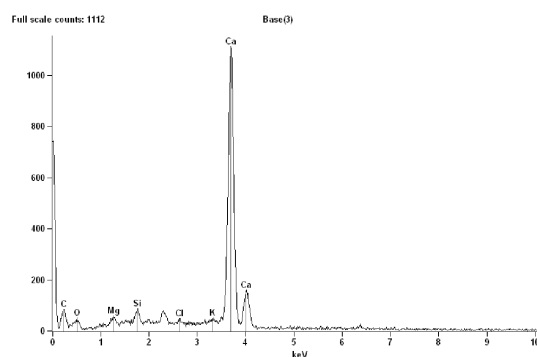


Fig. 10. EDAX of *Ulva fasciata* attached concrete surface in natural condition

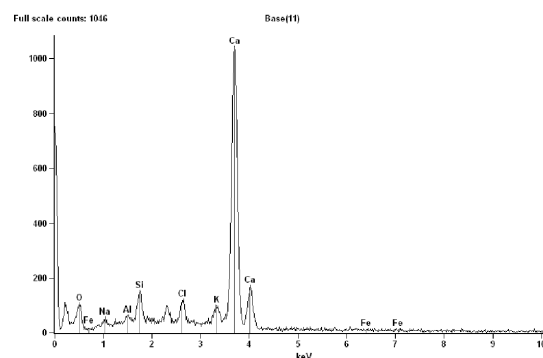


Fig. 11. EDAX of *Ulva fasciata* attached concrete surface in laboratory condition

3.3. Discussion

All surfaces in natural environments either aerial or sub-aerial are colonized by microorganisms and sub-aerial structures are colonized severely. Concrete is one such material that can be readily colonized by macro algae [19] as is revealed in this work. Macro algae are able to obtain several elements they need for their metabolism (e.g. calcium, aluminium, silicon, iron and potassium) from the concrete [9,14,15,16,17,18] by biosolubilization in the presence of sea water. This biosolubilization process generally involves the production of various organic acids (listed in table-1) by marine algae. The release of aggressive acids is one of the best known biogeochemical destructive mechanisms [1,2,3,9] on concrete surfaces. It occurs through the leaching of binding materials with the consequent weakening of the crystal structure

[20]. The final result of this type of biodeterioration is the physical and mechanical breakdown of the concrete [3,9].

3.3.1. Surface analysis by EDAX

EDAX results depicted above table 2, 3 and 4 elucidate that the base material has been modified. In the case of concrete cubes cured in ordinary water (control concrete) the silica level is 10.37% atom while calcium level is 9.18% atom. The EDAX results of the algal affected concrete in natural condition shows that the calcium level has tremendously increased to 38.05% atom while silica level has been decreased to 0.86% atom [8,9,12]. While in the case of simulated condition, calcium level has tremendously increased to 44.15% atom while silica level has been decreased to 2.79% atom. This proves that the calcium level in the algal affected concrete surface in natural condition has increased tremendously. This high level of calcium is due to dissolution of calcium in concrete by organic acid produced by marine chlorophyceae *Ulva fasciata* and precipitation of the organic salt upon dehydration. This is an indication of the alteration of the base material.

3.3.2. Mineralogical analysis by X-ray diffraction

Figure 12 shows the mineralogical analysis of concrete by XRD. The following are the crystals

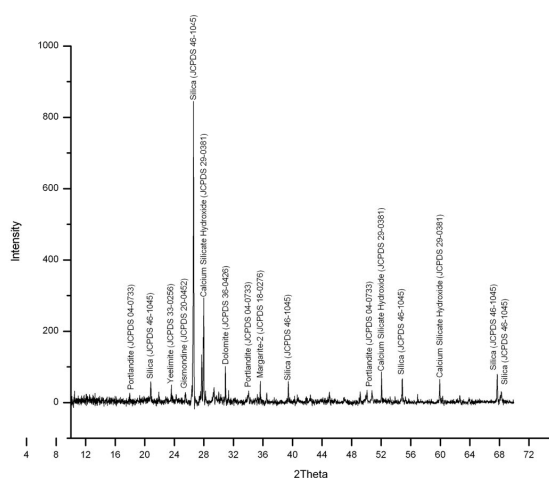


Fig. 12. XRD of concrete specimen immersed in ordinary water (Control concrete)

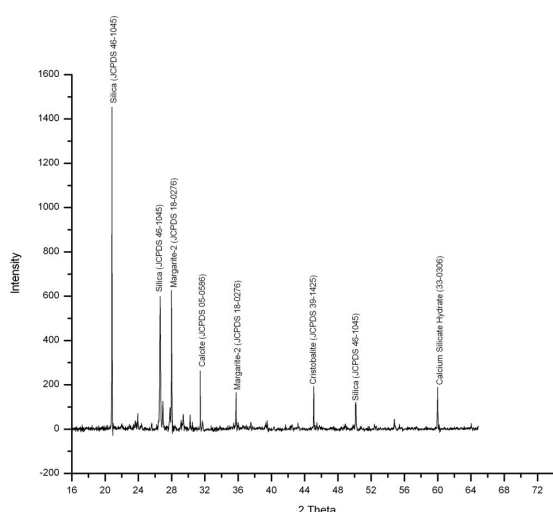


Fig. 13. XRD of *Ulva fasciata* attached concrete surface in natural condition

present in concrete specimen immersed in ordinary water Portlandite ($\text{Ca}(\text{OH})_2$), Silica, Yeelimite ($\text{Ca}_3\text{Al}_6\text{O}_{12} \cdot \text{CaSO}_4$), Gismondine ($\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$), Dolomite ($\text{CaMg}(\text{CO}_3)_2$), Margarite-2 ($\text{CaAl}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$), Calcium Silicate Hydroxide ($\text{Ca}_4\text{H}_2\text{O}_{15.5}\text{Si}_5$). The intensity of Portlandite is 34 at 18° , 34° , 50° while silica has a maximum intensity of 846 at 26° and Calcium Silicate Hydroxide has a intensity of 294 at 28° .

The above figure 13 shows XRD pattern for algal attached concrete in natural condition. Compounds like Silica, Margarite-2, Calcite (CaCO_3), Cristobalite (SiO_2), and Calcium

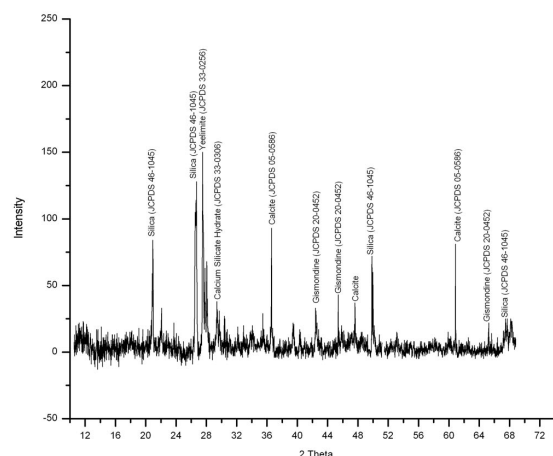


Fig. 14. XRD of *Ulva fasciata* attached concrete surface in laboratory condition

Silicate Hydroxide are present in this condition. Apart from this, it is noticed that the Silica intensity (1447) is very high at 21° compared to 26° which is 846 only. Compounds like Yeelimite, Gismondine and Portlandite are completely absent here. The absence of Portlandite (i.e. Calcium Hydroxide) shows that the alga has utilized it for its metabolic activity.

The above figure-14 shows the XRD pattern for algae attached concrete in simulated condition. It is notified that the intensity of Yeelimite is very high (151) while there are two Silica peaks at 21° and 27 ° with intensities of 84 and 129. Apart from this, Calcite which is present here is also noticed in natural condition which is not present in the control concrete. Three peaks are noticeable for portlandite in control concrete which is totally absent in this case. Similarly Margarite-2 is not noticeable here. This shows that algae have utilized this calcium hydroxide for its metabolic activity [9,17,18].

4. Conclusion

Samples obtained from the concrete cubes immersed in ordinary water and from the *Ulva fasciata* attached concrete surface in natural as well as laboratory simulated condition was studied in order to identify the effect of metabolic activity of macro algae *Ulva fasciata* on concrete. Surface analysis by EDAX suggests that biodeterioration may be performed through a biosolubilization mechanism involving the production of metabolic acids by algae. EDAX results elucidate us that the calcium level is tremendously increased to 38.05 % in natural and 44.15% in laboratory simulation while the silica level decreased remarkably. Also from XRD we are able to see that crystals of Portlandite which are present in control concrete is completely absent in algal attached concrete and this shows that the marine algae has utilized it for its metabolic activity. Hence, it is concluded that the base material has been altered severely. Thus the presence of chlorophyceae would serve as a primary support for heterotrophic biofilm, providing organic matter for growth through photosynthesis.

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