

Water Quality and Chemical Analysis of Marine Cultured Pearl and its Oyster Shell

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Abstract- Environmental conditions as well as water quality are the significant factors to influence pearl oyster shell growth. Trace elements and minerals found in marine water can affect the features of the shell and eventually maybe inside the pearl. In present study we investigated, features of marine cultured pearl as well as its oyster shell controlled by water quality in which they have grown. ED-XRF was used to detect trace elements present in pearl and its oyster shell; and UV-VIS-NIR with diffused reflectance study determines the presence of chromophores. EDXRF qualitative analysis identified only calcium (Ca) as the significant element and strontium (Sr) as a minor trace element in the majority of samples. The chemical examination determined the similarity between trace elements present in nacre shells and pearls. These results may be helpful for the pearl industry that the approach to correlate pearl and oyster shell properties with marine water would be an alternative for destructive pearl testing.

Key words – Water Quality, Pearl oyster shell, Trace elements, spectroscopy

1. INTRODUCTION

Pearl is the prime gem, which is prepared entirely by nature and made famous by prehistoric people. China, Australia, French Polynesia and Japan are the major countries for pearl industry which recovered the pearls from pearl culturing. *Pinctada maxima*, *Pinctada margaritifera* and *Pinctada fucata* are the three species of pearl oysters found in all over the world. India has good assets to produce oysters and mussels in fresh as well as marine water. *Pinctada margaritifera* is black in color of the outer surface of the shell without a nacreous border. Inside the shell, due to silver nacre it appears in dark shade towards the outer rim [1]. *Pinctada maxima* is another species of pearl oyster, belongs to marine bivalve mollusk from Pteriidae and the genera *Pinctada* and Pteriidae family. There are two different color varieties: White-lipped oyster and the Gold-lipped oyster, [2]. However, in the case of *Pinctada fucata*, the color of the pearls produced may be golden yellow, pink, white or cream, depending on slight differences in the site of nuclei implantation.

In India, *Pinctada margeritifera* the pearl rich oysters found in Andaman and Nicobar Islands and *Pinctada fucata* in Palk Bay, Gulf of Kutch and Gulf of Mannar [3]. Pearl industry initially dominated the gem trade by marine water pearls. But the preventive aspects of marine water pearl were high cost of production and a long processing time, starting from 2 to 3 years [4]. The host mollusc of pearl determines its properties. Oyster type, nacre layers and may be its thickness, growth medium and trace elements present in that aquatic environment. Polluted sea water caused by acidification can influence the growth of species of marine organisms. Due to the acidification of water, pH gets reduced which ultimately affects calcifying rates and dissolution of calcified structures [5]. Owing to such processes, molluscs, structural reliability gets compromised due to reduced shell density resulting in deteriorated shell strength. Shells of pearl oyster made up of three layers, outer organic, middle prismatic and inner nacreous layer. Organic outer layer plays a vital role in protecting pearl oysters against settling of epibionts covering as well as threatening from predators like rays, octopods and starfish. It also helps to protect molluscs or oysters from harm caused due to acidified water [6].

Temperature is an important aspect concerning to genetic development of pearl oysters. It also concludes the deposition rate for shell nacre and nuclei. Thus optimum temperature range always controls pearl culture locations. Water temperature is always responsible for growth rate and development towards reproduction. Though lower temperature reduced the growth of pearl and hence culturing in the winter season nacre layers get thinner but results in improvement pearl luster. Growth and salinity are also critical factors for pearl oyster development. The weak growth rate is reported near to the surface may be due to massive movements of sea waves as well as surface environmental conditions. Thus depth affects growth, quality and color of pearl oysters. Mortality is also depends upon the salinity of the seawater. The salinity tolerance

range of pearl oyster also determines the locations of pearl implantation, their quality and color [7]. The availability of substrate is also the principal factor that restricts pteriidae distribution in environmental conditions. Currents also limit the nacre layer formation ensuing the quality of pearl oyster as well as bringing food and oxygen to the site area [8]. Water pollution also increases the mortality rate in the pearl culture farming. Oil or gas released in sea, industrialized sewage water and sometimes shrimp trawler activity can harm the water environment. The main factor for pearl oyster growth and their quality is food feeding. River water always has rich nutrients and released into sea water and those are highly accountable for the aquaculture growth [3]. Calcium rich seawater and some trace metals present also control the luster and may be color of nacre. Micro algae, bivalve eggs, larvae and some organic material present in sea water are the primary food/feed for pearl oyster [9].

There are lots of impurities present in the water and the studies are carried out to document water quality in pearl culture. This experiment meant to study the essential factors which influenced marine water quality, where pearls were cultured of *Pinctada fucata* species. The water analysis and correlation of properties of marine cultured pearl and inner surface of shell nacre have been examined.

1.2 Background

In 1907, Japanese workers Koichi Mikimoto, Tokichi Nishikawa and Tatushi Mise developed the method of pearl culturing called a Mise-Nishikawa method. In this procedure, by cutting a small piece of mantle out of a live oyster, wrapping it around a mother of pearl bead and inserting it into the live tissue of another oyster. These treated oysters are placed in cages which are suspended from rafts in calm waters at variable heights. But, this procedure requires the temperature to be maintained around 10° C, the heights usually range from 2-3 meters down in spring summer and 5-6 meters down in autumn-winter. So balance can be achieved over the year. The effects of shallow water, conducive to rapid growth and greater depth all enable the pearls to acquire better colour and luster [10, 11].

2. MATERIALS AND METHODS

2.1 The method of pearl cultivation

This study was conducted at the Central Marine Fisheries Research Institute (CMFRI), located at Tuticorin, Tamilnadu, India. The potential pearl bearing oysters should be reared in safety under ideal conditions as pearl production by oyster is entirely accidental and not a normal function. And during this procedure the pearl should be protected from predators and fouling organisms which are the enemies of the oyster. The young oysters termed "spat" are reared in particular areas before being used for pearl cultivation [10, 12]. The spat is collected by hanging from rafts branches of pine trees to which young oysters cling in their early days. They are later gathered and placed in specially prepared cages where they grow undisturbed. Oyster can develop in atmospheric temperature 13°C to 25°C, we preferred to work in temperatures ranges from 20° to 25° C. 18° C is the ideal for nucleus insertion[10, 12 and 13]. Nucleus insertion ideally insertions are made between late April and early July and again from mid - September to late October. We have done this procedure in the month of October for five marine water pearls. The bead is or used to be mainly from the Gulf of Mannar, India. Several stages were required to be marked under consideration like, sacrificing of separate oyster, speed of insertion of tissue, size of nuclei, mortality rate, thickness of layers and growth duration.

2.2 Water quality monitoring

The water parameters can be effectively classified under three significant aspects, physical, chemical and bacteriological types. Multi-parameter composite field test kit (LTEK SYSTEMS, Nagpur, India) was used for monitoring physio-chemical parameters of water. The procedure used in the analysis of water samples in the field by this kit is based on the following basic principles; test for the permanent color change, color matching with standards, pH testing with strips and turbidity measurement.

2.3 Shell nacre Characteristics

In this marine water pearl culture experiment we obtained 5 marine pearls and their 5 shells. Fluoride, Iron, Nitrate, Chloride, Residual Chlorine, pH, Turbidity and Total Hardness measured with the marine water sample for each parameter.

UV-visible-near infrared (UV-Vis-NIR) reflectance spectra were collected with CARY-5000 UV VIS NIR Agilent technologies (250–3000 nm, 1 nm resolution). Point as well as elemental mapping analysis has been done Energy dispersed X-ray fluorescence (ED-XRF) has been collected on XGT-7200 x-ray analytical microscope HORIBA scientific.

3. RESULTS AND DISCUSSION

3.1 Water Analysis

Some of the standard environmental parameters to be considered are temperature, salinity, hydrogen-ion (pH) concentration and nutrient salts. Temperature is essential in many respects, particularly in regulating the metabolic rate of the animal, controlling the reproductive cycle as in sub-tropical and temperate waters which influences the quality of pearls. Nacre discharge and formation of pearl have been carried out to be severely affected by low temperature exposure (<12°C), low salinities (≤ 19 ppt), pollutants and aerial exposure [6]. The salinity of the Gulf of Mannar would generally vary from 30 to 35 ppt. Even heavy rains in the open sea would not bring about any significant variations in salinity given constant mixing of sea water that takes place by currents and tides.

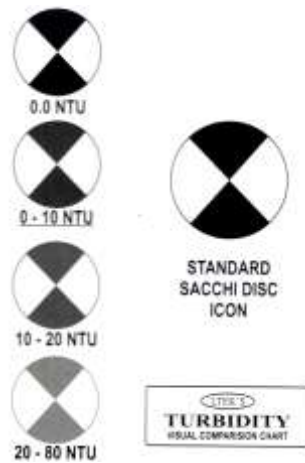


Fig 1: Standard sacchi water disc for turbidity measurement

In open sea conditions, the pH value is generally steady. In the culture location of Tuticorin, the annual range is 7.7-8.3 within the ambient range the lower pH is preferable at the time of pearl harvest, and the quality of pearl in this range is good. Other parameters have been determined with water quality monitoring with different parameters tested by the Multi-parameter composite field test kit. The details with the Gulf of Mannar parameters [14, 15] and measured parameter values of cultured pearl water are given in Table 1. As per standard test for turbidity water classified in to clear and cloudy or muddy. The Standard Sacchi Disc Icon (SSDI) is showed in figure 1. Pearl cultured 80ml water in the beaker was placed on SSDI and looked down through the sample water at the appearance of the standard icon. The appearance of the standard icon, which matched with 10 - 20 NTU icon. So we can classify the turbidity of our sample water as cloudy.

Table 1: Water quality measurement parameters tested by Multi-parameter composite field test kit

Sr. No.	Parameter	water parameters of Gulf of Mannar	Measured parameter value of cultured pearl water
1	Turbidity	No guideline	10-20 NTU
2	Chloride	15 - 5053 mg/L	75 mg/L
3	Iron	1.67 µg/L	1.7 µg/L
4	Nitrate	2.65-2.42 µg/L (July - Oct)	Oct 2.49 µg/L

5	Alkalinity	10-510 mg/L	210 mg/L
6	TDS (Total dissolved solids)	192 - 4928 mg/L	Oct 822 mg/L
7	Hardness	45-2235 mg/L	400 mg/L

Concentrations of chloride ions in the range from 15 to 5053 mg/L were reported earlier [14] and in our study we 75mg/L. The chloride pollution in an underground layer of water-bearing permeable rock may occur due to the releases from plants which are pioneer for desalination and natural salt flats in the cultured coastal area. Iron content referred earlier in two other locations [16], Thonithurai 4.60 (± 0.60) $\mu\text{g/L}$ and Chinnappalam 5.30 (± 0.90) $\mu\text{g/L}$, and we measured iron content at the cultured site near tuticorin coastal area which was around 1.7 $\mu\text{g/L}$. In sea water Nitrogen is present in dissolved state, ammonia, nitrite and nitrate also present in macrobiotic forms [14]. To produce water bodies at a higher rate alkalinity of that water is very important, it should be around 150 mg/L. The reported alkalinity of Gulf of Mannar coastal area is in the range of 10 - 510 mg/L [14, 17]. The measured alkalinity in this experiment near tuticorin pearl cultured area was 210 mg/L. Higher hardness values of sea water always obtained in pre-monsoon duration and lower values observed in post- monsoon. Higher hardness values obtained may be due to presence or absence of carbonates. The range of hardness values of Gulf of Mannar are 45 mg/L to 2235 mg/L and our determined value was 400 mg/L. Like hardness values TDS (Total dissolved solids) are maximum during pre monsoon and minimum at post monsoon. As we cultured our pearls in post monsoon season, we obtained the TDS value around 822 mg/L whereas it's from 192 mg/L to 4928 mg/L at Gulf of Mannar.

3.2 UV-VIS Spectroscopy

Broad or peak absorption in UV-Vis-NIR spectroscopy is a corresponding procedure to ED-XRF for determining the trace-element content in gemstones. UV-Vis-NIR spectroscopy is a crucial procedure to know the responsible trace element for the gemstone's body color. Due to opaque appearance of pearl and their shells have to be traced in percentage reflectance spectroscopy. As this is liable to the surface of the measuring sample, this technique can play a vital role in knowing about treatment has been applied or not. The *Pinctada fucata* species pearls and their oyster shells in this experiment for which spectra were recorded showed identical curves that varied only in the reflectance absorption peaks shown in figure 2. The decreasing trend towards higher wavelengths for all pearls as well as their shells was observed. A reflectance peak absorption in the UV region at 273 nm is common to all the spectra for these pearls as well as their respective shell may be because slight grayish body appearance absorbed in UV region chromophores present naturally. Reflectance spectra for each pearl are identical with its mother oyster shell.

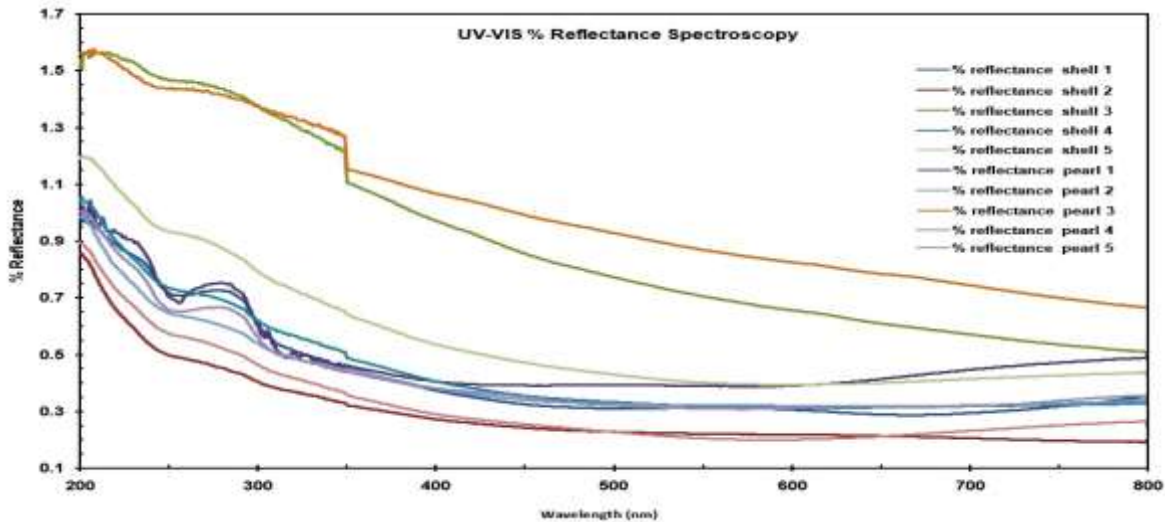


Fig 2: Optical reflection spectra of a pearl and their respective shells of *Pinctada Fucata* in UV-VIS region extended up to 800nm

3.3 ED-XRF Spectroscopy

Calcium carbonate is a principal inorganic component in pearl. Manganese (Mn) and Strontium (Sr) are other main trace elements found in pearl as well as their mother oyster. These minor elements key indicators to find out the species of their source of production. Marine water pearls can be distinguished from fresh water pearls based on their concentration of Mn and Sr [18]. ED-XRF spectroscopy provides a qualitative technique to determine chemical elements. The X-ray sampling area (1.2nm) can be centered on a tiny surface area if any color zones appears.

Table 2: Comparative qualitative analysis from ED-XRF spectroscopy of marine water pearls and their mother oyster shells

Trace elements	1 st Sample		2 nd Sample		3 rd Sample		4 th Sample		5 th Sample	
	Pearl %	Shell %	Pearl %	Shell %	Pearl %	Shell %	Pearl %	Shell %	Pearl %	Shell %
Ca	98.83	98.78	99.06	98.99	98.98	99.05	97.81	97.95	97.56	97.65
Sr	0.29	0.31	0.30	0.31	0.29	0.29	0.31	0.3	0.30	0.31
Mn	0.01	0.01	0.01	0.01	0.02	0.03	0.01	0.01	0.02	0.01
Fe	0.04	0.05	0.06	0.05	0.05	0.05	0.11	0.09	0.04	0.05
Ni	0.09	0.1	0.11	0.1	0.07	0.09	0.08	0.1	0.09	0.1

All of 5 pearls and their shell samples listed in Table 2 were investigated by ED-XRF point analysis as well as mapping (Showned only one comparison here), and the results are presented in figure 3. The mother of pearl showed a high resemblance in trace elements level with their respective pearls. Figure 3 showed the mapping images of one of the marine water pearl and its mother oyster shell. Calcium (Ca) is a significant trace element, and Stauntium (Sr), Iron (Fe), Nickel (Ni), Manganese (Mn) are minor trace elements found in the analysis. ED-XRF can be a vital technique to identify the pearl and their mother oyster shell.

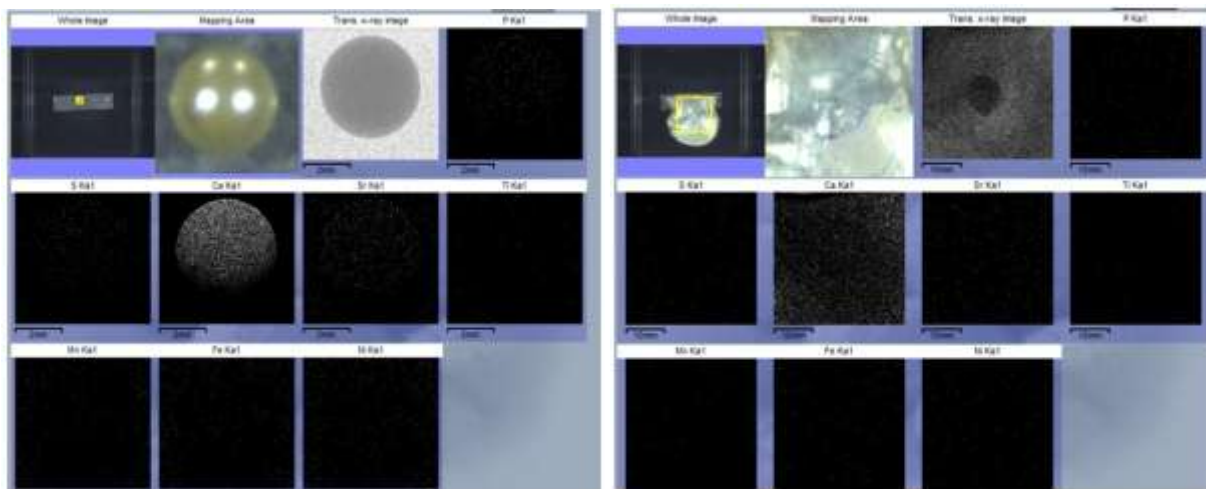


Fig 3: ED- XRF mapping for pearl and its mother oyster shell with Major elements Ca, Sr, Mn, Fe and Ni.

4. CONCLUSION

In the present investigation, water quality analysis has been done to know the physio-chemical water parameters present in the cultured water sample. Alkalinity, turbidity, pH, TDS and Hardness were showed appropriate conditioned values that are suitable for marine water pearl culturing in the Gulf of Mannar coastal area. Nitrate, Iron and Chloride showed the controlled content in the respective water where pearls were grown. UV – VIS optical reflectance spectroscopy revealed of natural-color of nacre shell as well as Pinctada Fucata species pearl. This spectrum also indicated the absence of any surface treatment on the pearl. ED-XRF showed an identical qualitative analysis of shell nacre and pearl, Strontium is the major

element present after Calcium as a trace element in both shells as well as pearl. The comparative analysis of trace element present in both shells and their respective pearls will be helpful for the pearl industry that the move toward comparing pearl and oyster shell characteristics with marine water would be a substitute for destructive pearl testing. This can be further authenticated by doing more samples.

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