Distinctive Characterization of Marine water and Freshwater Cultured Pearls and Their Mother of Pearls

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ABSTRACT

The current experiment is intended to study the comparison of freshwater and marine water cultured pearls from a physico-chemical properties point of view. Water analysis, trace elements and minerals found in cultured water can influence the Mother of Pearl and pearl's properties. Marine water pearls of Pinctada fucata cultured in Gulf-of-Mannar in South-East Indian coastal area. Freshwater pearls of Lamellidens Marginalis image pearls were cultured in groundwater source near Godavari River in Maharashtra, India. Raman Spectroscopy is used as finger print to identify the material. The presence of chromophores determined with absorption spectroscopy UV-VIS-NIR with diffused reflectance study. Quantitative and qualitative chemical analysis of trace elements was obtained with ED-XRF. Comparative study has been carried out for trace elements present in pearls and their mother of pearls. This ratio always plays an important role to conclude their source of origin. The atomic percentage ratio of trace elements Manganese and strontium in marine water and freshwater pearls are different. The trace elements found in mother of pearl were equivalent with trace elements present in the pearls. This may help to avoid any destructive method of analysing pearl properties; thus shell can be destructed instead of pearl.

Keywords

Freshwater Pearl, MW Pearl, Mother of Pearl, Physico-chemical Properties, Spectroscopy

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Introduction

The pearls are organic gem grown in either the soft mantle tissue or the gonad of a living shelled mollusc, unlike gemstones produced deep inside the earth. Molluscs commonly have a soft, un-segmented body and a hard exterior shell [1]. In natural environment, the pearls are created without interference of human being. Any irritation either internal or external (between body and shell) is determined by giving it a protective coating made up of conchiolin, calcite, aragonite and some percentage of water and pearl is formed [2-4]. Shells and their pearls, both have a composite structure of aragonite and / or calcite, an organic matrix primarily of the protein conchins and water. Nacre is also known as mother of pearl (MOP).

Cultured pearls generally are formed the same way as natural pearls, the only difference is that the irritant is surgically implanted by human. Presently over 95% of the world's pearl production is cultured. Cultured pearls can be divided into two types of pearls: freshwater cultured pearls (FWCP) and marine water cultured pearls (MWCP). As their name implies freshwater pearls are formed in the mussels that lives in lakes, rivers and ponds. On the other hand, marine water pearls are formed in the oysters in the coastal sea area [2]. In the Indian coastal waters, 6 species of pearl oysters have been recorded. Among these, Pinctada fucata is the most dominant species. Pinctada fucata and Pinctada margaritifera species of pearl oysters are the most important as they produces gem quality pearls. Other 4 species of pearl oysters are not considered as gem quality. In freshwater, the Indian freshwater mussels comprising 2 genera are prosperous in value and capacity. The Genus Lamellidens is characterized by 9 species and 2 associate species, while the Genus Parreysia is represented by 35 species and 6 sub species under two sub genera out of these 52 species only Lamellidens marginalis, Lamellidens corrianus and Parreysia corrugate are significant from culturing approach [2-5]. Food feeding is the key aspect for pearl oyster's / mussel's development. Freshwater is always rich in nutrients, when freshwater stream meets into ocean; these nutrients are released into marine water. These nutrients are playing a very essential role in the growth of marine species [6]. Physico-chemical parameters and some trace metals available in culturing, are equally responsible for the lustre and may be color of inner surface of MOP / nacre / shell. Those trace metal elements may act as chromophores / coloring elements present naturally. Water temperature is playing key role towards the growth rate and reproduction of pearl oyster and / or mussels [7 and 8].

In the present study, an attempt has been made to use modern and state-of-the-art instruments to identify the pearls without destructing them, which will help to maintain the pearl's value as gemstones. The current research is also intended to compare Freshwater cultured image pearls (FWCIP) and MWCP in physico-chemical properties perspective. Water analysis, trace elements and minerals found in cultured water can influence the properties of the inner surface of MOP. The influence of these parameters on the pearl, MOP and the color of pearls are examined. Same comparison study has been carried out for MOP with Raman Spectroscopy, UV-VIS Spectroscopy and Energy dispersive X-Ray Fluorescence (ED-XRF) spectroscopy. So we can conclude that, instead of using pearl we can use MOP to obtain the same results.

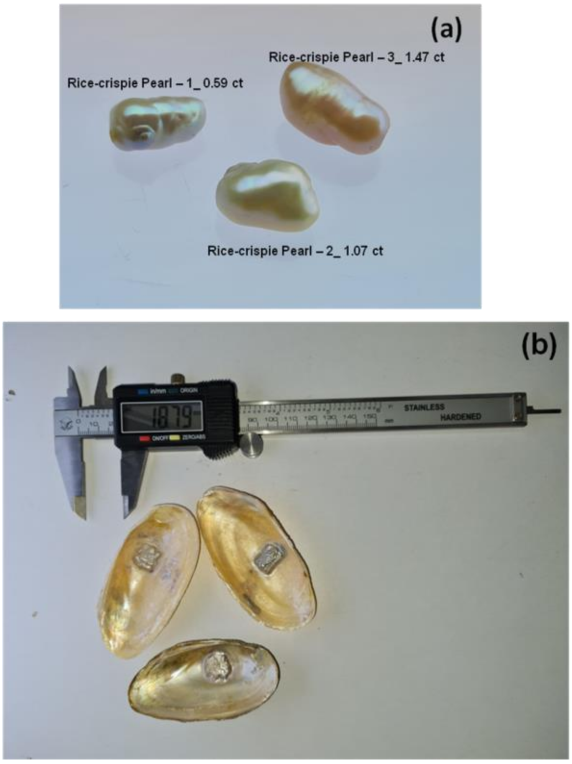


Figure 1: a. Rice-crispie shaped pearls and b. FWCIP

METHODS AND MATERIALS

This study of MWCP was conducted at the Central Marine Fisheries Research Institute (CMFRI), located at Tuticorin, Tamilnadu, India. The studies were carried out to document water quality of the area where the pearl cultivation occurred. This experiment was designed to study the critical factors that influenced MWCP quality, where pearls were cultured from Pinctada fucata species. The analysis of FWCP is planned to study 3 Lamellidens Marginalis FWCIP from the groundwater source near Godavari River in Nashik District, Maharashtra, India. In addition to this, we have taken 3 more freshwater rice-crispie shaped tissue cultured pearls from well known trade source of Indian market as it has same nature and type of origin. Images of 3 rice-crispie shaped freshwater pearls and 3 Lamellidens Marginalis FWCIP showed in Figure 1 a and b. MWCP with their MOPs and Nucleus bead is shown in figure 2. The respective nucleus bead has been taken from same batch which was used during marine water pearl cultivation. MWCPs are also displayed with their tissue appearance of the surface. Some of the MWCPs shells kept one side with sand for further examinations.

The water analysis has been done with a multi-parameter composite field test kit (LTEK SYSTEMS, Nagpur, India). It was used for monitoring physico-chemical parameters of freshwater and marine water [9]. Comparative study of marine water and freshwater parameters under physic-chemical characteristics has been determined. UV-VIS spectra were collected with CARY-5000 UV-VIS-NIR Agilent technologies (250–3000 nm, 1 nm resolution). Point analysis and mapping obtained by ED-XRF have been collected on XGT-7200 X-ray analytical microscope HORIBA scientific. Raman spectra were collected using a RamMics® RAMAN Micro-spectrophotometer.

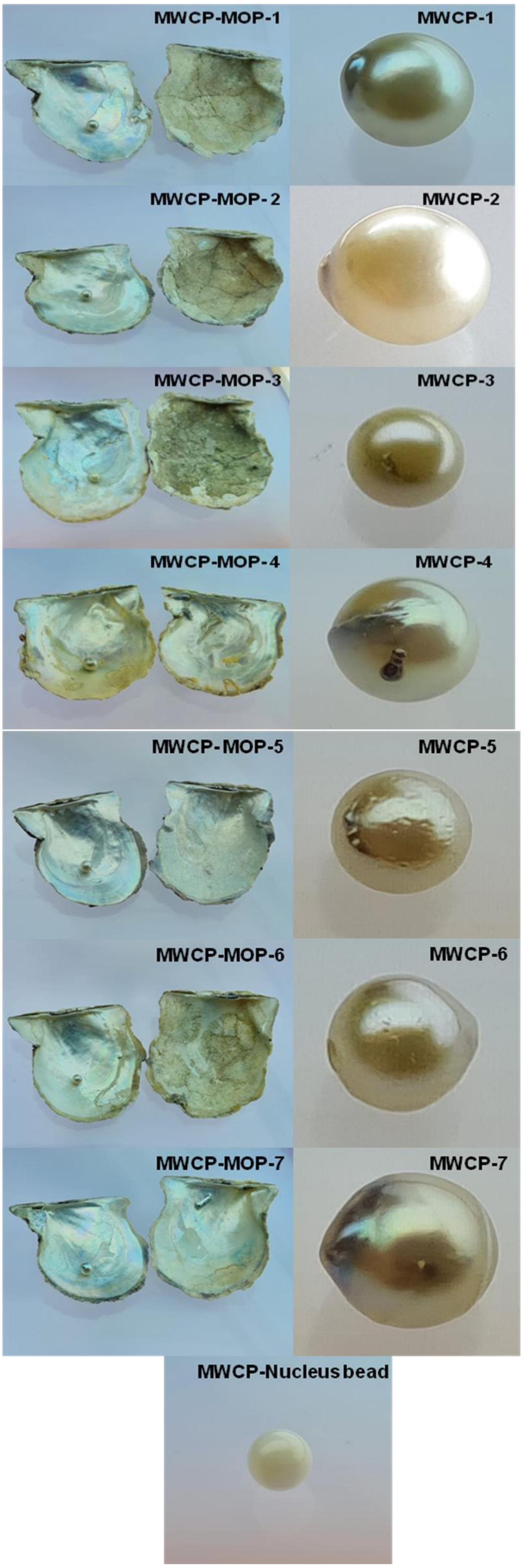


Figure 2: MWCP pearls with their MOPs and nucleus bead

I. RESULTS

Water Quality analysis

The water sample of MWCP have been collected from Tuticorin harbor for marine water analysis and FWCIP it has been collected from Godavari river ground water source. Temperature is playing a key role in regulating living bodies' metabolic rate. Environmental conditions also influence water temperature and accordingly, pearl quality. The temperature during culturing both MWCP and FWCIP was around 20 – 25 ºC. The water quality analysis with field test kit done on three principles wiz; color change; match the color with standards and pH testing with pH strips. Turbidity of freshwater and marine water samples in which pearls were cultured was measured with the Standard Secchi Disc Icon (SSDI) measurement [9]. The freshwater analysis was done with the reference of standards for drinking water (Bureau of Indian Standards (BIS) 2012; IS: 10500) [10]. The marine water testing was done with the reference of gulf of mannar water parameters [11 and 12]. The results of marine water and freshwater analysis were interpreted and compared, shown in Table 1. The water analysis parameters have demonstrated the values suitable for the cultivation of MWCP in Gulf of Mannar coastal area. Nitrate, Iron and Chloride also found satisfactory content to grow the pearls in respective water. We found the environmental conditions and / or hydrobiology is suitable for FWCIP formation in groundwater source environments near Godavari River in Nashik. The controlled metabolic rate of cultured pearls demonstrates the appropriate ecological condition to grow the marine as well as freshwater pearl.

Table 1: Water quality analysis by Multi-parameter composite field test kit

Sr. No.	**Water Physico – chemical testing parameters**	**Measured value of MWCP**	**Measured value of FWCIP**
1.	**Salinity**	35 (Parts per thousand)	0.04 (Parts per thousand)
2.	**pH**	7.7 – 8.3	6.5 – 8
3.	**Turbidity**	10-20 NTU	0-10 NTU
4.	**Chloride**	75 mg/l	75 mg/l
5.	**Iron**	1.7 µg/l	0.3 µg/l
6.	**Alkalinity**	210 mg/l	113 mg/l
7.	**Hardness**	400 mg/l	300 mg/l

8.	**Total Dissolved Solids (TDS)**	822 mg/l	495 mg/l

Raman Spectroscopy
Raman Spectroscopy is a prerequisite for investigations of samples under test. Experimentally Raman Micro-spectrophotometer using 532 nm excitation was used to obtain the Raman spectra. It was observed that in MWCP, FWCIP and Rice-crispie shaped pearls, aragonite phase calcium carbonate ($CaCO_3$) peaks at 1086 cm^{-1} and 704.2 cm^{-1} observed. $CaCO_3$ peak indicates that the material under test is indeed a pearl. Same results we obtained for their respective MOPs. Raman spectroscopy only helps to determine the presence of $CaCO_3$ but it does not reveal the nature (Marine / freshwater) and type (Cultured / natural) of origin. This can be elucidated using ED-XRF spectroscopy.

ED-XRF Spectroscopy
The X-ray emitted from the sample is analyzed using energy dispersive method, like in nuclear radiation detection or wavelength dispersive method as in optical spectrographs. The energy spectrum of characteristic X-rays contain clear information about the atomic number, thereby the elemental composition. This unit is equipped with X-ray guided tube (XGT), made up of Beryllium which guides the X-rays helping them to focus to a spot size of 10µm. This is a unique facility of focusing X-rays without losing their intensity. Furthermore, this unit has the ability to do a two dimensional scan in transmission geometry. This gives a radiography facility together with X-ray fluorescence to map and identify different surface elements and inclusions in the sample under test. In pearls and their MOPs, Calcium carbonate ($CaCO_3$) can be easily detected and quantified. We have tested 7 MWCP, 3 FWCIP and their MOPs and three rice-crispie shaped pearls.

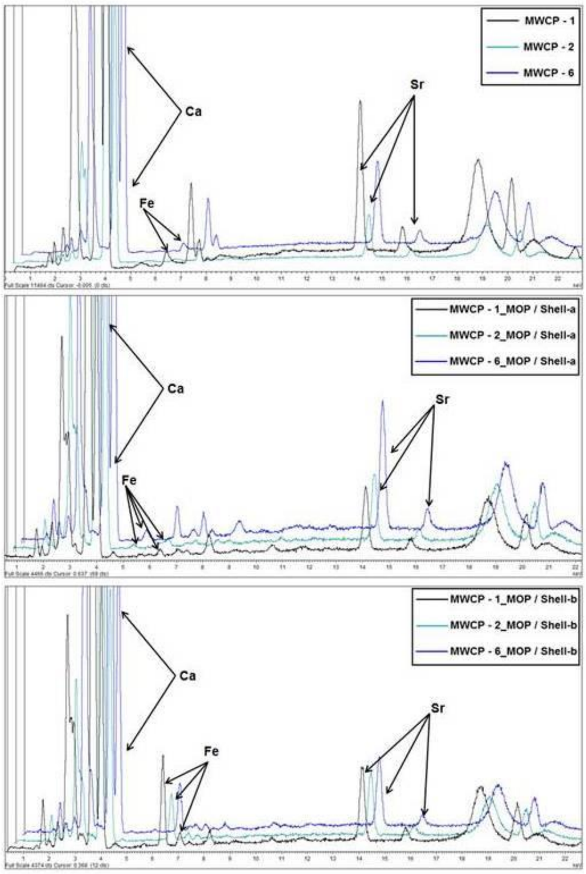


Figure 3: ED-XRF spectra of three pearls and their MOPs

Calcium (Ca), Strontium (Sr), and Manganese (Mn) are the primary trace elements found in MWCP and FWCIP as well as their MOPs and Rice-crispie shaped pearls. The ratio of atomic mass % of Mn and Sr elements for MWCP is around 1:30 and for FWCIP it was obtained around 1:3. The X-ray fluorescence data analysis of marine water and freshwater pearls, reveals the atomic mass % for Ca is around 98%. Metal element like Iron (Fe) was also observed. However, its atomic mass % in both marine water and freshwater pearls is different. MWCP showed atomic mass %: Mn < Sr but Mn ≤ Fe. We have also taken point as well as mapping analysis for their MOP shells. The obtained qualitative analysis and lustre of MWCP - 3 to 7 are identical, but the lustre of MWCP 1 and 2 is slightly varied. Thus we have shown here spectra of MWCP 1, 2 and 6. Furthermore, we kept some MWCP's MOPs with one side uncleaned holding the marine sand to understand their elemental analysis. So we entitled the one side which appears eye-clean as shell-a and other as shell-b. In figure 3, it was observed that a very negligible amount of Mn in

MWCPs. There were some minor peaks also observed in the graph, which could be due to overlapping of similar elements. However their quantification of the same is absent. But the atomic mass % of Sr and Fe were noticeable. This may be because this shell of MOP holds marine soil indicating Fe content present in the marine environment.

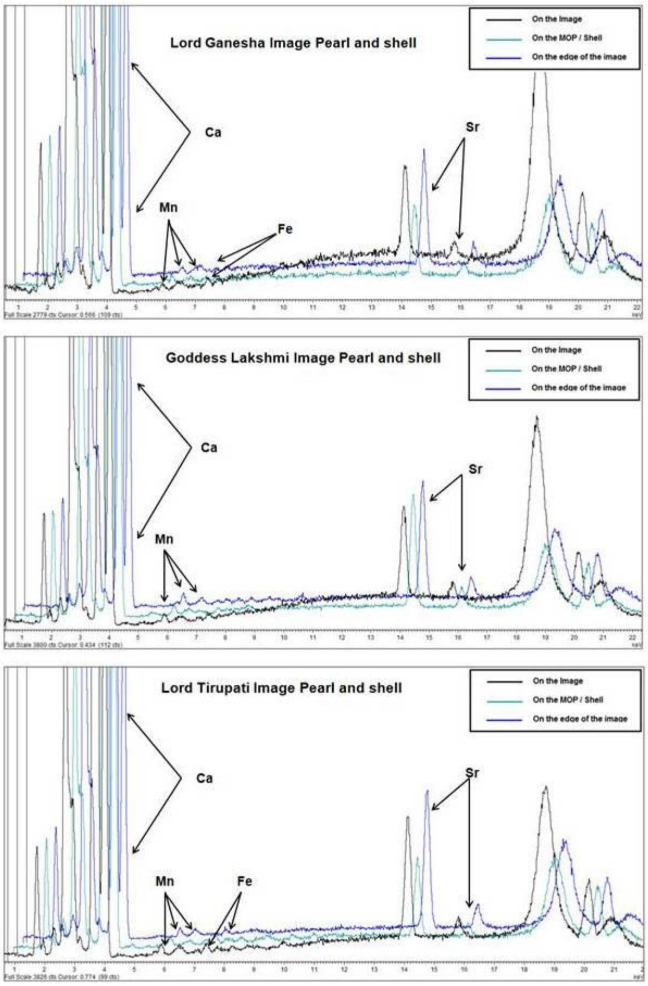


Figure 4.a: ED-XRF of 3 FWCIP

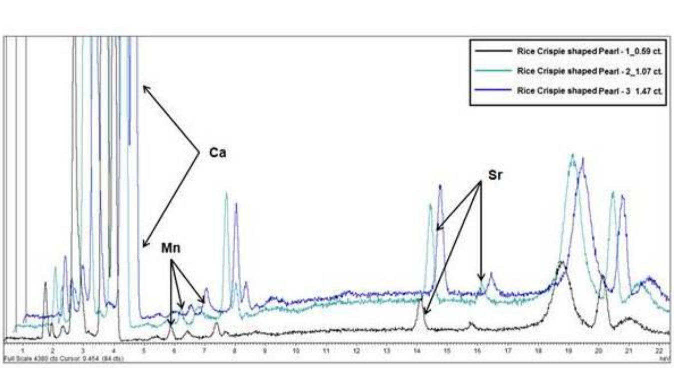
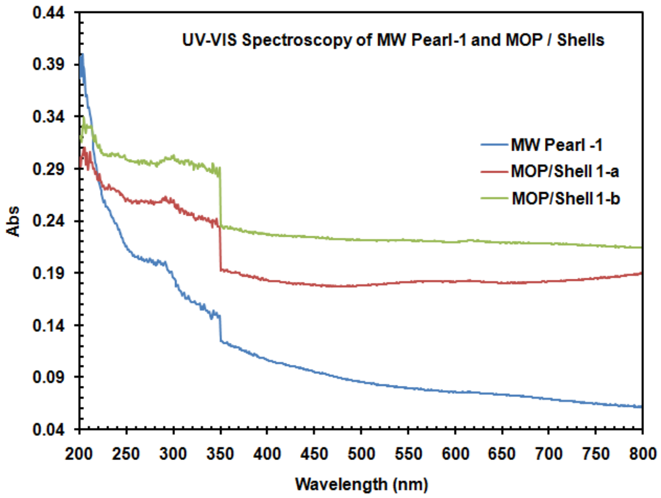


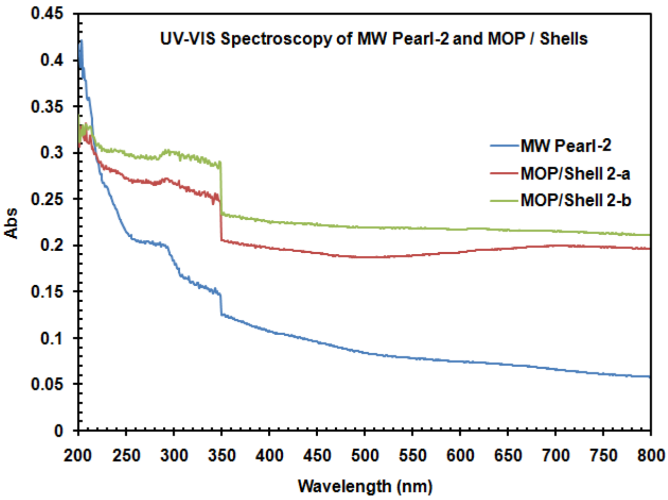
Figure 4.b: ED-XRF of 3 freshwater Rice-crispie shaped pearls

Figure 4.a and b showed graph of 3 FWCIP and 3 rice-crispie shaped freshwater pearls. There were two peaks also obtained in figure 4.b near Fe peaks which may be due to overlying other elements like Cobalt (Co), Nickel (Ni) and Copper (Cu) spectra but their quantification were absent. The ratio of atomic mass % of elements Mn and Sr for freshwater pearls it was obtained around 1:3. In quantitative analysis we found the atomic mass % of Fe is less than Mn. However, when we focused at the edge of all image pearls, we found Mn $\leq$ Fe which can act as coloring elements during formation of FWCIP. As we found a significant amount of Fe in river water, this can be accountable for the presence of Fe content in image pearls and bluish color / metalic lustre appearance at the edge of image pearls. In figure 4.b, rice-crispie shaped pearls are showed Mn $\geq$ Fe. Regarding rice-crispie shaped pearls, the water source may have significantly less or negligible amount of Fe content, leading to its external appearance. As we purchased rice-crispie pearls from trade source, we could not test the water parameters where rice-crispie shaped pearls originated.

UV-VIS Spectroscopy

UV-VIS absorption spectroscopy technique is used to determine the optical properties of pearl and their MOPs / shells. The trace elements are responsible for gemstone's body color and can co-relate with broad or sharp absorption. As pearl and MOPs are opaque, UV-VIS absorption spectroscopy can be traced out in reflectance spectroscopy. MWCP species used in this experiment i.e. *P. Fucata* and their MOPs is analyzed with surface diffuse reflectance mode in UV-VIS absorption spectroscopy showed in figure 5. Spectral curves observed with all *P. Fucata* pearls are identical to the UV-VIS graph of their respective MOPs. As explained in ED-XRF results, we have shown here the spectra of MWCP-1, 2 and 6. The figure 5 showed the absorption peak recorded in the UV region in the region of 280-290 nm, followed by broad absorptions in some pearls in visible region area ranging from 500 to 700 nm. Figure 6 showed UV-VIS spectra of rice-crispie shaped pearls and nucleus bead from the same batch of MWCP used during culturing. We also found the similar absorption in the region of 260-270 nm for both nucleus bead and rice-crispie shaped pearls. We had also obtained the same results for FWCIP for the UV region. We have mentioned this in our earlier studies [14].





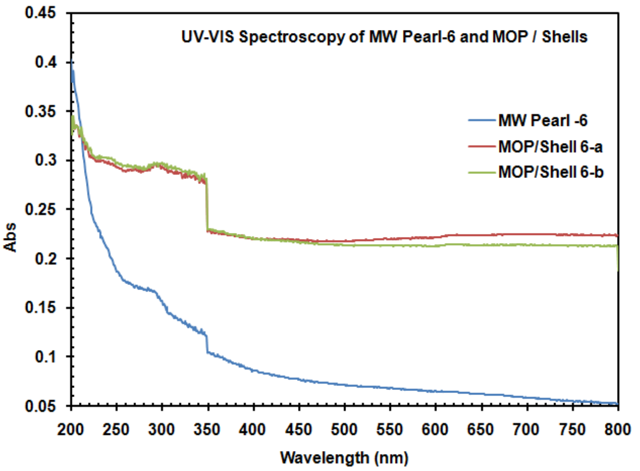
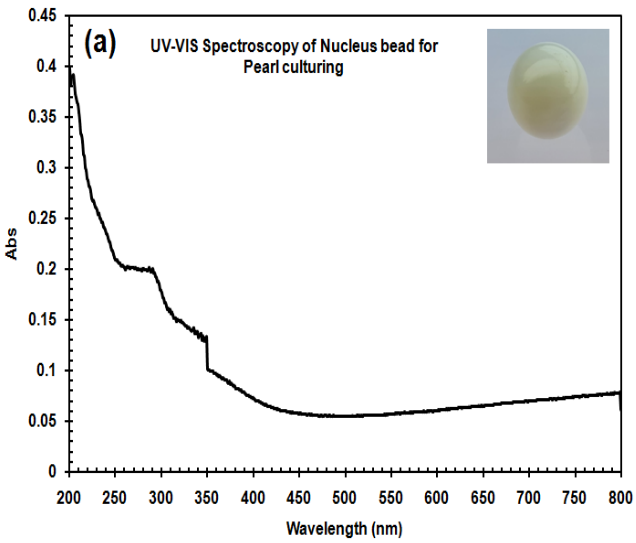


Figure 5: UV-VIS Absorption spectroscopy of MW-pearl and their MOP/shells a and b of Pinctada fucata

The absorption in the UV region around 260-290 nm is common to all the spectra for these MWCP and FWCIP pearls and their respective MOPs and nucleus bead. As we obtained similar absorption in the UV region for the nucleus bead, MWCP and MOPs, FWCIP and their shells and rice-crispie shaped pearls may indicate organic matrix present in the material. As per visual observation with naked eyes, we have chosen MWCP-1, 2 and 6 but all MWCP showed similar absorption spectra throughout the visible region. The absorption obtained in the UV region may be because of nacreous part of pearls. As mentioned in earlier study, organic matrix plays a key role for absorption in the UV region spectroscopy [13]. As per our earlier study of FWCIP and their MOPs / shells, lord Ganesha and lord Tirupati image pearl shell spectrum showed intense broad absorption obtained in the violet-blue region, as the nacre is from cream to yellow color with pink hue. The color of nacre of goddess Lakshmi is very weak cream to yellow compared to rest of the two shells. UV-VIS spectroscopy analysis showed very weak / no absorption in violet-blue region [14]. These results can be co-related to complementary color ideology as opposite colors are diametrically opposite to each other.



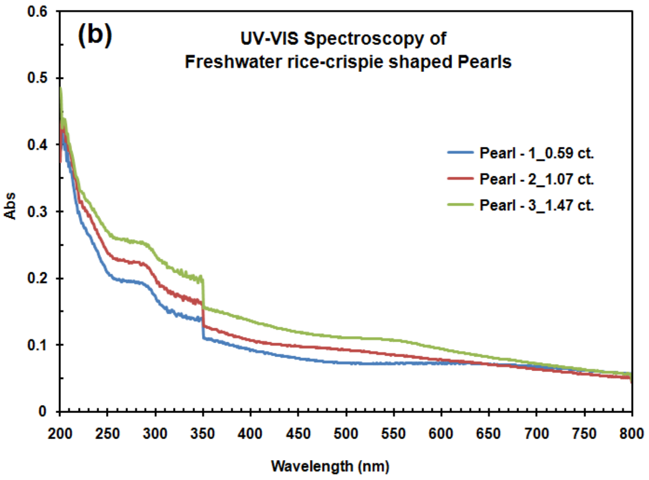


Figure 6: UV-VIS Absorption spectroscopy of (a) Nucleus Bead and (b) freshwater rice-crispie shaped Pearls

Conclusion

Water quality, environmental conditions and temperature are accountable for pearl quality, their metabolic and mortality rate. During implantation for pearl culturing; human skill, types of nucleus bead and place of operation plays a vital role. As per the results obtained in the present study it was shown that all types of pearls; FWCP, fresh water pearls (Rice-crispie shaped tissue cultured pearl) and FWCIP are made up of aragonite phase of $CaCO_3$. As per visual observation, all samples under test were showing pearly lustre and cream-yellow to pinkish color as an external appearance. To identify the actual material, Raman spectroscopy showed 1086cm^{-1} and 704.2 cm^{-1} characteristic peaks of aragonite phase of $CaCO_3$. Thus the material has been identified as Pearl due to pearly luster and $CaCO_3$ peak. X-ray fluorescence method helped to determine the presence of Mn, Sr and Fe in the various types of pearls. It was found that MWCP has a significant amount of Fe and very negligible amount of Mn. This quantitative investigation of MWCP, Sr is the main element present subsequent to Ca as a trace element in both MOP and pearl. Due to Fe $\geq$ Mn the bluish hue has been observed for MWCP. However, in freshwater pearls analysis; more Mn is found as compared to marine water pearls. Pearly lustre has been observed with cream-yellow color with pinkish hue may be caused by Fe $\leq$ Mn. With quantitative analysis of ED-XRF, MWCP and FWCP can be distinguished from each other based on their atomic mass % concentration ratio of Mn and Sr. For rice-crispie shaped pearls, according to ED-XRF data was confirmed that they have originated from the freshwater origin. Signal to noise ratio of diffused reflectance spectra is always dependent on the type of the surface (smooth / rough) of the sample. As the surface of FWCIP is rough as compare to MWCP and all MOPs inner surface the behavior of incident rays and reflected rays were different which we have explained in our earlier study. We obtained broad absorption roughly 600 to 700 nm in that study, which may be recognized to Mn^{2+} and Fe^{2+}. Those can act as chromophores / coloring elements in pearls. The absorption peak observed in UV- region around 260-290 nm for Nucleus bead, MWCP, FWCIP, all MOPs and rice-crispie shaped pearls. This absorption behavior may indicate a trace of organic matrix. As per complementary color ideology, UV-VIS spectroscopy is a non-destructive technique to determine color of pearl samples. With the above results, we can differentiate nature and type of origin of the pearl. Though it has identical properties for further detailed study, one can destruct shell rather than the gem value pearl. Thus, this instrumentation can help us to increase the trade economy as it will help in determining the commercial value of the sample.

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REFERENCES

[1] Farn Alexander E. (1986): Pearl: Natural, Cultured and Imitation: pp 7-15
[2] Strack E. (2006): Pearls. Ruhle-Diebener Verlag, Stuttgart, Germany, pp 107-225.
[3] Dakin W.J. (1913): Pearls: Cambridge University Press Cambridge.
[4] Kunz, G. and Stevenson, C.H. (1908): The Book of the Pearl. The Century Co: New York.

[5] Kiran Dubey, manual on skill development programme Fresh Water Pearl Culture, page no. 1, Year2019.
[6] Joseph M. M., Kripa V. "Status of Marine Pearl Culture in India" Fishing Chimes, Vol. 21-4, July 2001, pp.13-
19.
[7] Bondad-Reantaso M. G., McGladdery S. E., Berthe F. C.J., Pearl oyster health management, A manual, Food and Agriculture Organization of the United Nations, Rome, 2007.
[8] Zhu C., SouthgateTing P. C., Li T. Chapter - Production of Pearls, Goods and Services of Marine Bivalves pp 73-93, 2018.
[9] Athavale S. A., Hambarde M. S., Parab S.S. (2020) “Water Quality and Chemical Analysis of Marine Cultured Pearl and its Oyster Shell”, Int. Res. J. Eng. Tech., 2020, Vol. 7, No.3, pp. 4989-4994.
[10] Bureau of Indian Standards (BIS) (2012) Indian standard drinking water specification (second revision) BIS 10500:2012, New Delhi.
[11] Balakrishnan A., Ramu A., “Seasonal Variations of Ground Water Quality in and around Gulf of Mannar
Coastal Aquifers”, J. Environ. Sci. Pollut. Res. 2012, Vol. 3-2, pp. 186–188.
[12] Jeyageetha J.C., Kumar S.P., “Study of physico-chemical parameters of sea water in Tuticorin Coastal area and assessing their Quality, Tamil Nadu, India”, J. Chem. and Pharma. Res., 2015, Vol. 7-5, pp. 1298-1304.
[13] Mamangkey N.G.F, Agatonovic S., Southgate P.C., Assessing Pearl Quality Using Reflectance UV-Vis
Spectroscopy: Does the Same Donor Produce Consistent Pearl Quality? Mar. Drugs 2010, Vol. 8, pp. 2517-2525.[14] Hambarde M. S., Athavale S. A., Parab S.S. (2020) “Spectroscopic and water quality Analysis of Lamillidens
Marginalis Image Pearls”, Pramana Research Journal, Vol. 10, Issue 12, pp. 1-15.