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CHARACTERIZATION OF LONG-SPINED SEA URCHIN *DIADEMA SETOSUM* SHELL AND POTENTIAL USAGE AREAS

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ABSTRACT: The long-spined sea urchin *Diadema setosum* (Leske, 1778) is the most common seashore sea urchin in the tropical Indo-Pacific and also this species is distributed in the eastern Mediterranean Sea. In this study, we characterize the shell of the long-spined sea urchin *Diadema setosum* using FTIR and XRD analyses. The powdered shell of *D. setosum* was analyzed by Fourier transform infrared spectrometry. It was determined that 714 cm^{-1} and 871 cm^{-1} peaks from the formed peaks determined the amorphous and crystal structure, respectively. The results of the XRD analysis of the long spiny sea urchin shell overlap 91% with calcite with chemical formula $Ca_5MgC_6O_{18}$ and 9% with periclase chemical formula Mg_4O_4. Analysis results show that *D. setosum* shell was found to be in calcite structure, and can be used in many areas such as paper, paint, plastic, construction, food, ceramics, and pharmaceuticals. When combined with other studies as antibacterial, anti-inflammatory, antimicrobial, and antioxidant, it has been revealed to contain amorphous and crystal structures that are useful for different biomedical industries. High availability and accessibility of the long-spined sea urchin, can become a very economical product for these sectors, and in this way, an invasive species will be brought into the economy.

KEYWORDS: Long-spined sea urchin, *Diadema setosum*, calcite, crystal structures

INTRODUCTION

Sea urchin is a commercial property traded in many countries, it has a hard shell and the inside is five symmetrical. *Diadema setosum* (Leske, 1778) is the most common sea urchin in the Indo-Pacific, from Australia and Africa to Japan and the Red Sea also this species is distributed in the Mediterranean Sea (Turan *et al.*, 2011).

The sea urchin is known as beautiful seafood in many countries and is commercially grown in aquaculture activities (Salma *et al.*, 2016). The edible parts of sea urchins make up about 20% of their total weight, while the rest can be considered waste. Although these waste parts of sea urchins are used in various biomedical fields, more efficient waste recycling methods are being investigated due to their bioactive properties (Yücel *et al.*, 2016). Very fragile and poisonous spines covering 95% of the body parts are dominant on the hard shells of *D. setosum* covered with black pigments (Yusuf *et al.*, 2020).

In recent years, it has been preferred to obtain biomaterials for biomedical applications from marine organisms (Uyan *et al.*, 2020; Doğdu *et al.*, 2021). Especially, bioceramic materials are widely used in several fields such as bone tissue, biomedical applications, dentistry, and biomedicine due to their adaptability and functionality (Yücel *et al.*, 2021). Bioceramic materials obtained from nature are preferred as they are suitable for closer contact with living tissues. Up to date, many studies has carried out on *D. setosum* as an antimicrobial (Marimuthu *et al.*, 2015; Sidiqi *et al.*, 2019; El-Sayed *et al.*, 2020), anti-inflammatory (Yusuf *et al.*, 2020), and cytotoxic properties (Abdelkarem *et al.*, 2022), and bioactive compounds (Tulandi *et al.*, 2021). However, However, no studies on shell characterization have been conducted.

In this study, we characterize the shell of the long-spined sea urchin *D. setosum* using FTIR and XRD analyses. The study aimed to be revealed its usability as a bioceramic material for biomedical and other industrial purposes since it has no economic value and is very abundant in the world's marine waters.

MATERIAL AND METHODS

The specimens of *D.setosum* were collected by hand by making scuba diving on the beaches of Arsuz and Samandağ in the northeastern Mediterranean Sea and then transferred to the laboratory. After the spines on it were cleaned by hand, the inside of the shell was washed with pure water and purified from organic material. The shells, which were cleaned with pure water, were dried in the sunlight (Fig. 1). The dried samples were crushed using the ball mill (Retsch, PM100) and they were stored at room temperature until the characterization analysis.

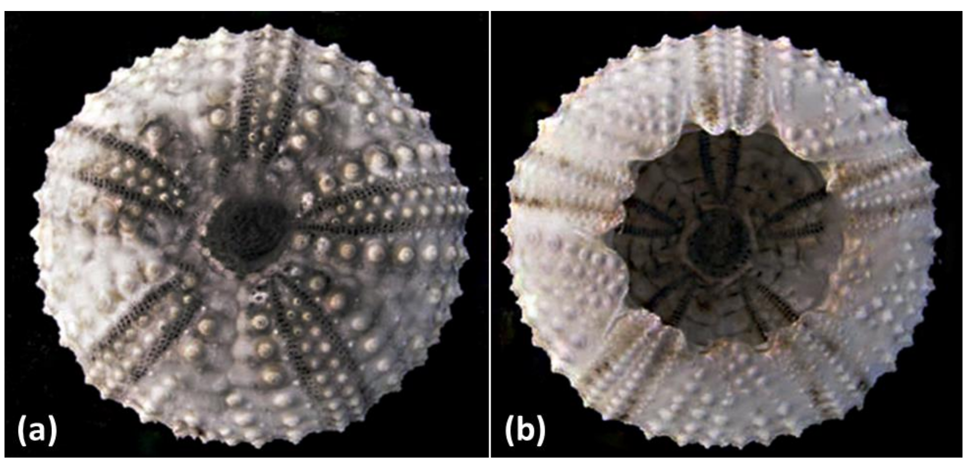

Fig. 1. a, top view; b, bottom view of dried *D. setosum*.

FTIR analysis: Fourier Transform Infrared Spectroscopy is based on the principle of measuring the frequencies of chemical components by absorption of infrared radiation. With the FTIR analysis, the change in the frequencies of the chemical bonds and the absorption properties provide the formation of the peaks. Analyzes were performed directly on the powdered bark of *D. setosum*. Samples were prepared in potassium bromide pellets at a 5% concentration. Samples were placed in the crystal cell and clamped to the assembly of the cell FTIR spectrometer and scanned in the spectrum wavelength range of 400–4000 cm^{-1}. FTIR analyses were carried out at Iskenderun Technical University, Science and Technology Application and Research Center (ISTE-BTM).

XRD analysis: Within the scope of the study, the structure of the powdered bark of *D. setosum* was determined by XRD analysis. XRD patterns were recorded with a Rigaku Miniflex 600 Diffractometer with Cu Ka (40 kV, 15 mA, λ=1,54050 Å) radiation. Scanning was performed between 10 degrees < 2θ < 70 degrees (0.01 degrees and 0.05 degrees steps and 1 degree/min speed). XRD analyses were carried out at Iskenderun Technical University, Science and Technology Application and Research Center (ISTE-BTM).

RESULTS AND DISCUSSION

The powdered shell of *D. setosum* was analyzed by Fourier transform infrared spectrometry (FTIR) (Fig. 2). It was determined that 714 cm^{-1} and 871 cm^{-1} peaks from the formed peaks determined the amorphous and crystal structure, respectively. Another peak formed, 1078 cm^{-1}, characterizes sodium sulfate in the structure of the analyzed shell, 1402 cm^{-1} peak characterizes sodium carbonate and 1638 cm^{-1} peak characterizes calcium sulfate.

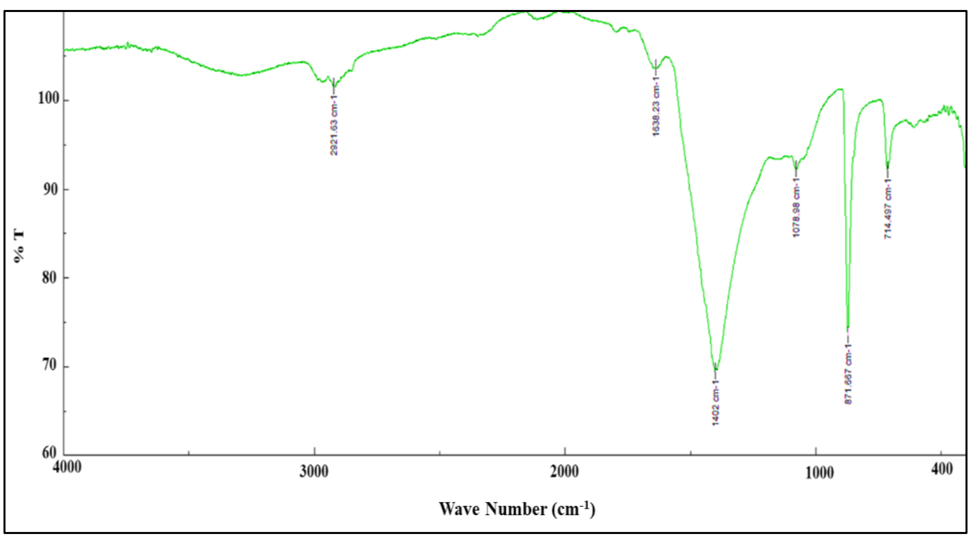

Fig. 2. FTIR image of *D. setosum* shell in the spectrum range of 4000-400 cm^{-1}

According to the results of the FTIR analysis, the 714 cm^{-1} peak represents an amorphous structure and the 871 cm^{-1} peak represents a crystal structure (Yuniarto *et al.*, 2016). Among the other peaks, it was determined that the 1078 cm^{-1} peak characterizes sodium sulfate in the structure of the analyzed crust, the 1402 cm^{-1} peak characterizes sodium carbonate and the 1638 cm^{-1} peak characterizes calcium sulfate (Kiefer *et al.*, 2018).

The structure of the powdered shell of *D. setosum* was determined by XRD analysis (Fig. 3). The results of the XRD analysis of the long spiny sea urchin shell given in Figure 3 shows that the reflections in the results of the XRD analysis overlap 91% with calcite (crystalline structure as calcium carbonate) with chemical formula $Ca_5MgC_6O_{18}$ and 9% with periclase chemical formula Mg_4O_4. These reflections match perfectly with the calcite data presented on ICDD Card No: 96-900-1299 and periclase presented on ICDD Card No: 96-901-3253 (Paquette and Reeder, 1990; Jacobsen *et al.*, 2008). The cell parameters of *D. setosum* shell were found as a = 4.9380, b = 4.9380, and c = 16,8320. Obtained XRD results support FTIR analysis results.

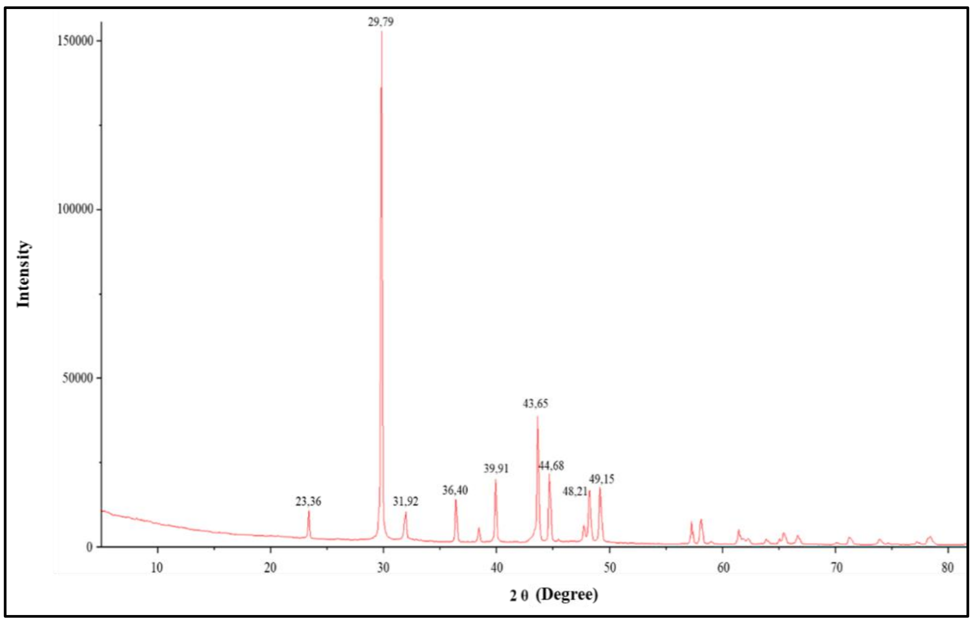

Fig. 3. X-ray diffraction patterns of *D. setosum* shell.

CONCLUSIONS

In conclusion, this study showing in the characterization of long-spined sea urchin shells. Obtained XRD and FTIR data support that the *D. setosum* shell has a calcite structure. *D. setosum* shell, which was found to be in a calcite structure, can be used in many areas such as paper, paint, plastic, construction, food, ceramics, and pharmaceuticals. When combined with other studies as antibacterial, anti-inflammatory, antimicrobial, and antioxidant, it has been revealed to contain amorphous and crystal structures that are useful for different biomedical industries. Because of the high availability and accessibility of the long-spined sea urchin, it can become a very economical product for these sectors, and in this way, an invasive species will be brought into the economy.

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REFERENCES

Abdelkarem, F.M., E.E.K. Desoky, A.M. Nafady, A.E. Allam, A. Mahdy, A. Ashour and K. Shimizu, 2022. *Diadema setosum*: isolation of bioactive secondary metabolites with cytotoxic activity toward human cervical cancer. *Nat. Prod. Res*. 36(4): 1118-1122.

Doğdu, S.A., C. Turan, T. Depci and D. Ayas, 2021. Natural hydroxyapatite obtained from pufferfish teeth for potential dental application. *J. Cera. Proc. Res*. 22(3): 356-361.

El-Sayed, W.M.M., M.M. Elshaer, H.A.H. Ibrahim and M.E.A. El-Metwaly, 2020. Antimicrobial agents from sea urchin (*Diadema setosum*) collected from the Red Sea, Egypt. *Egypt. J. Aquat. Biol. Fisher*. 24(5): 33-51.

Jacobsen, S.D., C.M. Holl, K.A. Adams, R.A. Fischer, E.S. Martin, C.R. Bina, J.F. Lin, V.B. Prakapenka, A. Kubo and P. Dera, 2008. Compression of single-crystal magnesium oxide to 118 GPa and a ruby pressure gauge for helium pressure media. *Amer. Mineral*. 93(11-12): 1823-1828.

Kiefer, J., A. Stärk, A.L. Kiefer and H. Glade, 2018. Infrared spectroscopic analysis of the inorganic deposits from water in domestic and technical heat exchangers. *Energ.* 11(4): 798.

Marimuthu, K., P. Gunaselvam, M.A. Rahman, R. Xavier, J. Arockiaraj, S. Subramanian, F.M. Yusoff and A. Arshad, 2015. Antibacterial activity of ovary extract from sea urchin *Diademasetosum*. *Euro. Rev. Med. Pharmacol. Sci.* 19(10): 1895-1899.

Paquette, J. and R.J. Reeder, 1990. Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals. *Amer. Mineral*. 75(9-10): 1151-1158.

Salma, W.D., I. Hafizah, T. Nurtamin, L.O.M.Y. Haya and S. As'ad, 2016. The potential gonad of *Diadema setosum* as a healthy food to improve the nutritional status of coastal children. *Int. J. Sci.: Basic Appl. Res*. 27(2): 189-195.

Sidiqi, F.M., D. Pringgenies and W.A. Setyati, 2019. Antibacterial activity of gonad methanol extract of the sea urchin *Diadema setosum* against methicillin-resistant Staphylococcus aureus and Escherichia coli. In IOP Conference Series: *Earth Environ. Sci*. 246(1): 012040. IOP Publishing.

Tulandi, S.M., L. Tanzil and D.M. Ulfa, 2021. Analysis of Bioactive compounds from methanol extract of *Diadema setosum* sea urchin gonads using gas Chromatography-mass spectrometry. *Res. J. Pharma. Technol.* 14(3): 1629-1634.

Turan, C., D. Erguden and N. Uygur, 2011. On the occurrence of *Diadema setosum* (Leske, 1778) in Antakya Bay, Eastern Mediterranean Sea. *J. Bl. Sea/Mediterran. Environ*. 17(1): 4-8.

Uyan, A., C. Turan, E.A. Erdoğan-Eliuz and M.K. Sangun, 2020. Antimicrobial properties of bioactive compounds isolated from epidermal mucus in two Ray species (*Dasyatis marmorata* and *Gymnura altavela*). *Trop. J. Pharma. Res*. 19(10): 2115-2121.

Yücel, A., K. Onar, C.C. Turan, T. Depci and M.E. Yakıncı, 2016. Synthesis of nano-size whitlockite bioceramic precursor from Sea Urchin skeleton. *TIP TEK.*16: 348-350.

Yücel, A., S. Sezer, E. Birhanlı, T. Ekinci, E. Yalman and T. Depci, 2021. Synthesis and characterization of whitlockite from sea urchin skeleton and investigation of antibacterial activity. *Cera. Int*. 47(1): 626-633.

Yuniarto, K., Y.A. Purwanto, S. Purwanto, B.A. Welt, H.K. Purwadaria, T.C. ve Sunarti, 2016. Infrared and Raman studies on polylactide acid and polyethylene glycol-400 blend. *In*: AIP Conference Proceedings. 1725(1): 1-6.

Yusuf, M., N.F.U. Atthamid, S. Indriati, R. Saleh, M. Latief and A. Rifai, 2020. Optimization ultrasonic assisted extraction (UAE) of bioactive compound and antibacterial potential from sea urchin (*Diadema setosum*). *Curr. Res. Nutrit. Food Sci. J.* 8(2): 556-569.