Dyeing Pearls with Potassium Permanganate and Aniline

Amonwan Rachanuam Student code : 640510480
Advisor : Associate Professor Dr. Apichet Boonsoong
Gemology Section, Department of Geological Science, Faculty of Science, Chiang Mai University.

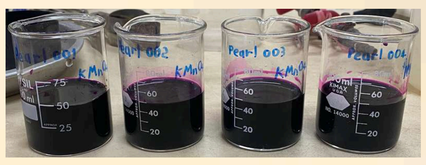
Introduction

- Pearl is an organic gemstone with the chemical formula $CaCO_3$. It is highly valued and widely popular, with its price depending on various quality factors such as shape, luster, thickness of the nacre layer, surface perfection, and color. Pearl colors include white, cream, black, golden yellow, pink, chocolate, and more. Rare colors tend to be more expensive, leading to various enhancement techniques to increase their value, such as dyeing, irradiation, and bleaching.
- This study explores the possibility of dyeing pinkish-purple pearls into chocolate-colored pearls or other market-preferred colors using potassium permanganate ($KMnO_4$) and aniline ($C_6H_5NH_2$). The aim is to enhance pearl quality while reducing production costs. Currently, chocolate-colored pearls are rare and highly valuable, and their artificial coloration is often achieved using silver (Ag), a precious metal, making the dyeing process expensive. By utilizing potassium permanganate and aniline as alternative dyeing agents, this study seeks to develop a more cost-effective method for producing desirable pearl colors.

Materials and Methods

- The study examined the gemological characteristics and dyeing process of 15 freshwater pearls with a pinkish-purple hue. These pearls were opaque and weighed between 2.73 and 3.60 grams. The dyeing process was categorized into three groups: dyeing with potassium permanganate ($KMnO_4$), dyeing with aniline ($C_6H_5NH_2$), and dyeing with a combination of both substances.

- Dyeing with Potassium Permanganate ($KMnO_4$)



A 0.2 M $KMnO_4$ solution was prepared by dissolving it in 100 ml of distilled water. 4 samples (Sample 1 to 4) 25 ml each were soaked in the solution for 5 days.

- Dyeing with Aniline ($C_6H_5NH_2$)

Aniline was mixed with distilled water in a 1:1 ratio (30 ml of each). 4 samples (Sample 5 to 8) 15 ml each were soaked in the solution for 1 day.

- Combined Dyeing Method

The same 0.2 M $KMnO_4$ solution (30 ml) was mixed with an aniline-distilled water solution 1:1 ratio (15 ml of each). 4 samples (Sample 9 to 12) 15 ml each were soaked in the solution for 1 day.

- Additional Analysis

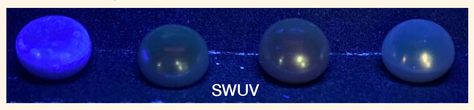
Fluorescence under UV light was examined. FTIR spectroscopy was used to analyze molecular functional groups, while SEM-EDS was employed to determine elemental composition and surface characteristics before and after dyeing, along with chemical durability testing.

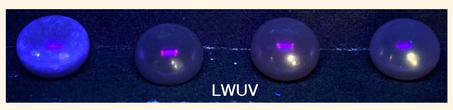
Results

Gemological properties

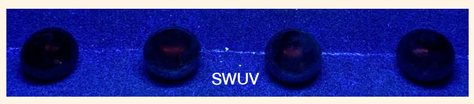
The specific gravity of the studied samples ranged from 2.63 to 2.70. The samples were opaque. Fluorescence testing under long- and short-wave ultraviolet radiation revealed blue fluorescence in two undyed samples (Sample 1 and Sample 12), while all dyed samples exhibited no fluorescence under either wavelength.

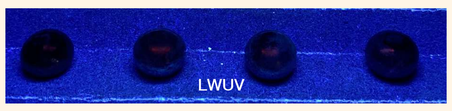
- Before dyeing (sample 1)



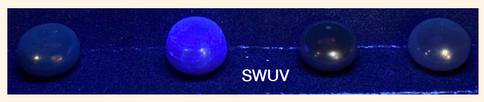


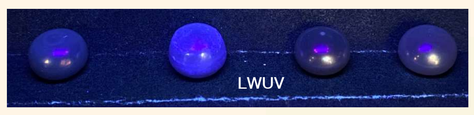
- After dyeing (sample 1)



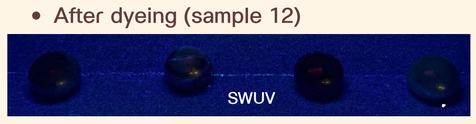


- Before dyeing (sample 12)



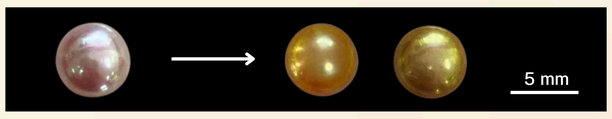


- After dyeing (sample 12)



Pearl Dyeing Experiment

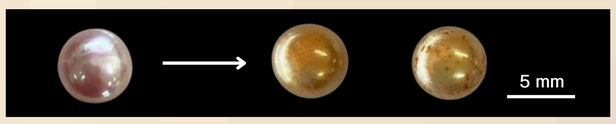
- Dyeing pearls with $KMnO_4$ for 5 days turned pinkish-purple pearls into a golden-yellow shade, matching the market preference for South Sea golden pearls.



- Dyeing pearls with aniline for 1 day did not change their color, but it reduced their surface luster.
- Dyeing pearls with the combined substances for 1 day did not change the color, but it reduced the surface luster.

Therefore, further studies were conducted on the differences in dyed colors and chemical durability in daily life. Pearls previously soaked in aniline and the mixed solution were immersed in a 0.2 M $KMnO_4$ solution mixed with 100 ml of distilled water. The solution was then divided into four 25 ml samples and soaked for 5 days. The results showed that...

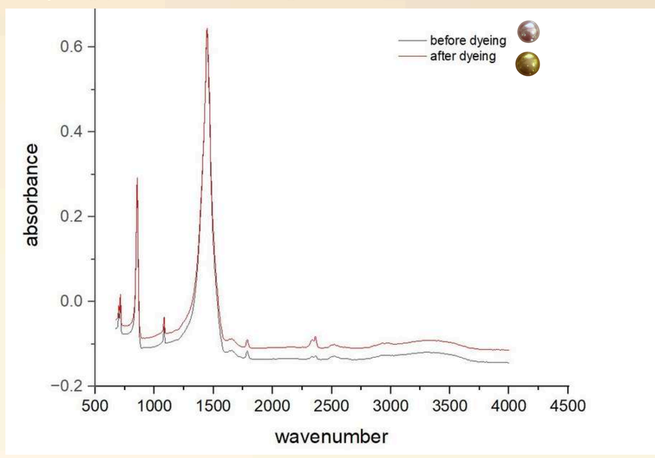
- The Pearls previously soaked in aniline turned golden, matching market demand for South Sea golden pearls. However, the color was patchy and uneven, making them less visually appealing than those dyed with only $KMnO_4$.



- The Pearls dyed with the combined substances turned brown, matching the market demand for chocolate pearls. However, the color was uneven and not uniformly distributed.

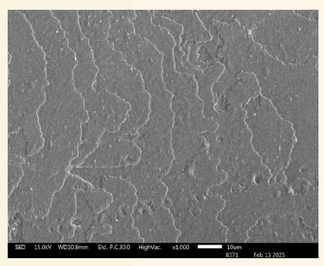
Fourier-transform infrared (FTIR) spectroscopy

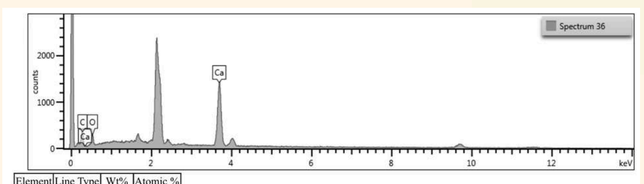
FTIR spectrometer detected peaks at 1485, 1082, and 712 cm^{-1}, which correspond to carbonate (CO_3^{2-}). The peaks remained at the same positions before and after the dyeing process, indicating that the fundamental CO_3^{2-} structure of the pearls was unchanged.



Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS)

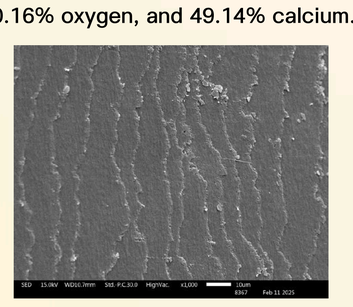
- Analysis using SEM-EDS revealed that the surface of the untreated pearl was relatively smooth and composed of 18.79% carbon, 27.82% oxygen, and 53.38% calcium.

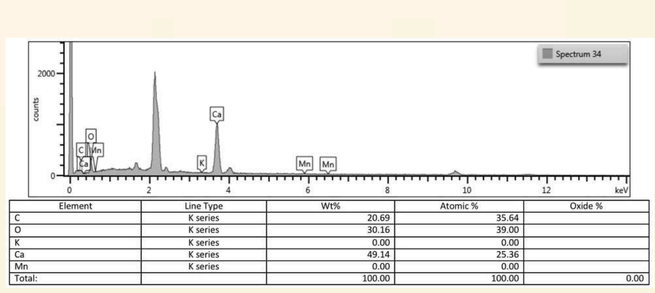




Element	Line Type	Wt%	Atomic %
C	K series	18.79	33.76
O	K series	27.82	37.51
Ca	K series	53.38	28.73
Total:		100.00	100.00

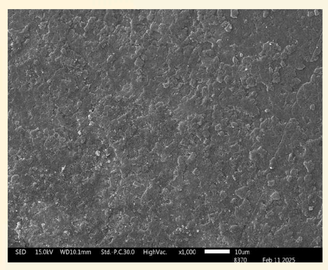
- Analysis using SEM-EDS showed that the surface of the pearl dyed with $KMnO_4$ became slightly rougher.The composition change of 20.69% carbon, 30.16% oxygen, and 49.14% calcium.

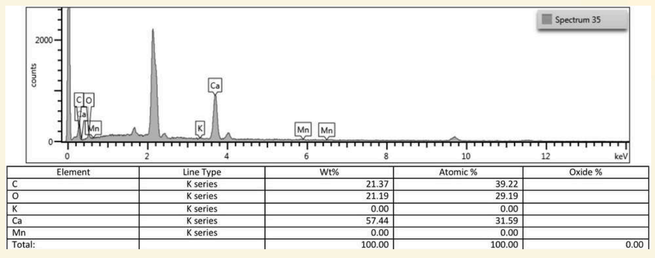




Element	Line Type	Wt%	Atomic %	Oxide %
C	K series	20.69	35.64	
O	K series	30.16	39.00	
K	K series	0.00	0.00	
Ca	K series	49.14	25.36	
Mn	K series	0.00	0.00	
Total:		100.00	100.00	0.00

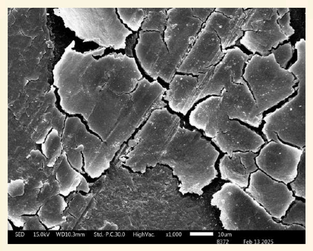
- Analysis using SEM-EDS showed that the surface of the pearl, after being dyed with aniline and further dyed with $KMnO_4$ for an additional 5 days, became slightly rougher. The elemental composition was 21.37% carbon, 21.19% oxygen, and 57.44% calcium.

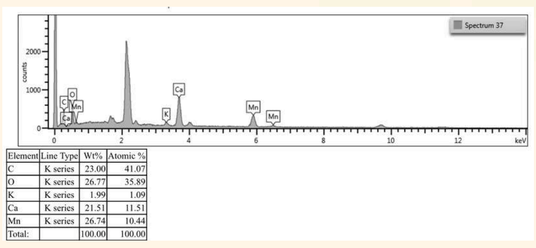




Element	Line Type	Wt%	Atomic %	Oxide %
C	K series	21.37	39.22	
O	K series	21.19	29.19	
K	K series	0.00	0.00	
Ca	K series	57.44	31.59	
Mn	K series	0.00	0.00	
Total:		100.00	100.00	0.00

- Analysis using SEM-EDS showed that the surface of the pearl, after being dyed with aniline and then further dyed with a mixture of $KMnO_4$ and aniline for an additional 5 days, became rougher. The elemental composition changed to 23% carbon, 26.77% oxygen, 21.51% calcium, 1.99% potassium, and 26.74% manganese.





Element	Line Type	Wt%	Atomic %
C	K series	23.00	41.07
O	K series	26.77	35.89
K	K series	1.99	1.09
Ca	K series	21.51	11.51
Mn	K series	26.74	10.44
Total:		100.00	100.00

Chemical durability testing

The color fastness test against chemicals revealed that acetone and detergent did not cause any color changes, whereas dishwashing liquid caused the color to fade.

Conclusion

- Dyeing freshwater pearls with a pinkish-purple hue using potassium permanganate ($KMnO_4$) and aniline ($C_6H_5NH_2$) successfully altered their color to meet the demands of the gemstone market. The resulting colors included golden yellow (South Sea pearl) and chocolate pearl, aligning with the objectives of this project.
- The dyed pearls did not exhibit fluorescence under a UV lamp.
- FTIR spectroscopy showed no significant differences in peaks before and after dyeing.
- Elemental analysis revealed increased levels of potassium (K) and manganese (Mn) in pearls dyed with aniline and those subjected to additional dyeing with a $KMnO_4$ and aniline mixture for five more days, indicating absorption of these elements from the dyeing solution.
- Chemical durability tests showed that nail polish remover and bleach did not affect the pearl's color, but dishwashing liquid caused noticeable fading. This is likely due to its surfactant properties, which may have altered the pearl's surface after dyeing.

References

- Burapha University. (Year). *Gemological technology*. CDG, Burapha University.
- Changcharoen, T. (n.d.). *Dyeing freshwater pearls with inorganic dyes to achieve a chocolate color*. Burapha University.
- Gemological Institute of America. (2000). *GIA pearl grading color reference charts*. Carlsbad, CA: Author.