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STUDY ON EXTRACTION OF CEPHALOPOD'S INK FOR DYEING OF TEXTILE MATERIALS

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ABSTRACT
Squid and cuttle fish rely for defense on the ejection of dark colored ink. The cephalopod ink contains main constituent as melanin (pigment) besides proteins, lipids, Glycosaminoglycans etc, which is available in varying concentrations in variety of species. Different cephalopod species produce different color ink. Octopus, squid and cuttle fish produce black, blue-black and sepia brown colour inks. Squid and cuttlefish possess ink sac in their intestine which is non-edible and discarded as waste. The ink sac may contain about 45 to 75 grams of ink. The ink possess anti-bacterial, anti-radiation, anti-oxidant and anti-retroviral properties. Application of cephalopod's ink on cotton fabrics develops colour and imparts medicinal and protective finishes. The review of various research works reveals that there is a better scope for dyeing wool and silk material using sepia melanin.

INTRODUCTION
There are about 660 species of cephalopods in the world oceans, of which less than hundred species are of commercial importance. In the global cephalopod catch, Squids dominate by 77% followed by octopus and cuttlefish. In India, the big fin squid is high valued seafood next to the Pharaoh cuttlefish. Sepia pharaonis and is abundant in the coastal waters of the east coast of India.

Cuttlefish are cephalopod molluscs, a group which includes octopus and squid. Except the coasts of the America, there are more than 100 species that live in subtropical, tropical, and temperate waters in all seas and ocean. The name cuttlefish may be used for all species of the genus Sepia, of which Sepia officinalis is the most common in North East Atlantic waters. Squid belong to the family of Cephalopod and the South Indian species Loligo duvauceli. The cephalopods possess an ink sac which is used as predator mechanism. The Ink contains Major portions of Melanin pigments (1), enzymatic compounds, etc. The squid ink plays various primary roles in medical world of alternative medicine and has widest range of therapeutic applications (2).

MELANIN
Melanin is a dark biological pigment found throughout nature. It is a predominantly indolic macromolecule (3). Different types of melanin are there which includes eumelanin, pheomelanin, neuromelanin and allomelanin. Eumelanin and pheomelanin are both found in the skin, hair and eyes of many animal species, including humans, where they act as photoprotectants (absorbing harmful ultraviolet and visible radiation). Eumelanin is known to be a macromolecule of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA), and is black to brown in colour(4). Eumelanin forms the major component of squid ink and is responsible for the dark colouration in feathers(5).

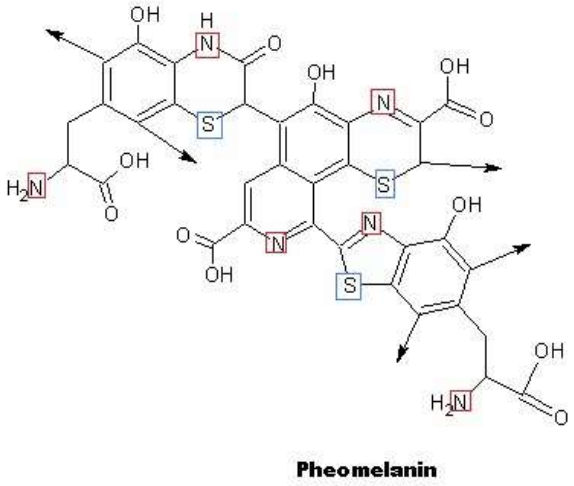

Fig. 1: Structure of Pheomelanin.

Pheomelanin is a sulphur containing macromolecule composed of 1,4-benzothiazine units(6,7), and is red to yellow in colour .Pheomelanin is responsible for the colouration of human red hair and chicken feathers.

He melanin obtained from Sepia Officinalis consists of more than 98% of Eumelanin which possess number of free radicals: melanin is a stable free radical. The chemistry of free radicals is associated with the processes of polymerization and oxidation (11, 12). Melanin is a pigment found in all realms of life in different structures and shapes and has an important role in the differentiation of species or phenotypes.

There are many hypotheses, but none is completely satisfactory (13, 14, 15, 16, 17). The pigment also has an important role in the photo-protection of human cells preventing DNA damage which could generate mutagenesis (19, 20, and 21).

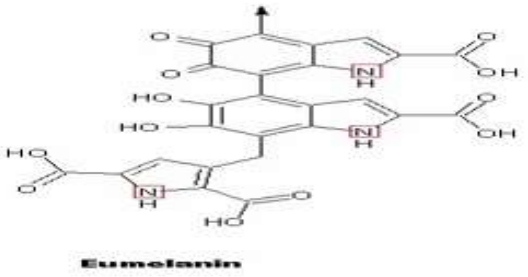

Fig 2: Structure of Eumelanin

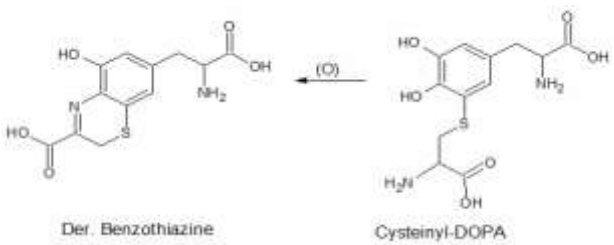

Figure 3. Pheomelanin monomers

TYPES OF NATURAL MELANINS

Melanins are classified according to their natural source:
Neuromelanin→ Neurons, gray matter and central nervous cell
Pheomelanin and Eumelanin→ Skin, hair and eyes
Allomelanin→plants and fungi

PROPERTIES OF MELANIN:

The other essential biopolymers, carbohydrates, proteins and nucleic acids, are chemically well characterized and their precursors and connectivity are well known, and the sequences of their connection can be determined with well-established methodologies. There is no available methods accurately to determinate melanin. This is largely because of the chemical properties of melanins. These pigments are insoluble in a broad range of solvents. They are difficult to purify due to heterogeneity in their structural features.

On the other hand, we still do not have a method to accurately determine the ratio of the various units present in melanin. The fact that melanin has an interesting chemical complexity has been studied for a long time and different studies have identified some of its physical and chemical properties.

Melanin is known to have the capacity to absorb a wide range of electromagnetic radiation ranging from visible light and UV radiation up to the X-ray region. On the other hand, melanin is reported to have the ability to bind different metallic ions.

Melanin can also conduct electricity and is thus considered a semiconductor material.
It is believed that melanin has a photo-protective role in animals.

Although it has been postulated to act as a cellular antioxidant, it is also known for its photo-protection. Oxidative process could produce chemical modifications on the structure of melanin and compromise its photo protective functions. All these properties of melanin make it an attractive material to use in different applications.

Nowadays, many commercial products contain melanins as active ingredient, including creams that act as filters for single-response protection against UV radiation. Finally, melanin is used in cosmetics to fade defects of the skin diseases called 'vitiligo'. The addition of melanin to plastics has enabled the production of sunglasses with a high ability to block UV radiation. Another very specialized application is its use in the coating of the internal surface of fluorescent lamps. This eliminates entirely the escape of UV light, which usually occurs at a low level in these lamps. This treatment can prevent damage to objects in museums or libraries.

In the medical field, it has been shown that melanin can be ingested by patients, functioning as a means of contrast in X-ray studies of the digestive system. Here it is noted that a controlled amount of melanin can be eaten without causing damage as it is not digested or absorbed by the body. Some of us have used melanin to enjoy a good plate of squid in its ink.

It is expected that in the near future new applications and products based on melanin may appear, which will increase the demand for this pigment. There are several natural sources and methods for obtaining them. The extraction from animal tissues or plants is a low cost option for obtaining it.

A major disadvantage of this method is that the product obtained generally has a low purity and composition may vary in each batch. This product can also be generated by chemical methods, which guarantees its purity, but at a high cost.

Eumelanin isolated from the ink sacs of Sepia officinalis is a source of melanin with cheaper cost. Sepia melanin is commonly used as a model to study the spectroscopy, photo reactivity, and morphology of this class of black pigments, because of its high purity as more than 98 % of melanosomes concentration in tissues is Eumelanin.

STUDY OF SEPIA MELANIN

Sepia officinalis is a mollusk of the class of Cephalopods; it is an invertebrate 30 to 60 cm long. The study of the excretory ink gland of Sepia officinalis has been of great interest for a long time not only for its importance on a biological level, but has also been the starting point in providing important and useful information in different studies on melanogenesis in mammals as well as on the biochemical process of melanin formation in the cell. The excretory gland is an organ specialized in the formation of melanin.

The excretory gland is anatomically simple, when compared to more complex structures, such as those present in mammals. Sepia melanin from Sepia officinalis depending on age, size and season can be obtained in large quantities of pigments and different degrees of polymerization (34).

In the study it is shown that the gland consists of cylindrical cells with a basal nucleus and an apical secretor zone containing granules of melanin. These granules are available in small packages which are filled with the pigment in the apical vacuoles and emptied into the lumen.

In Figure 31 you can observe a diagram of the formation of sepia ink in Sepia officinalis.In a second moment, it was shown that the gland is composed of two zones each having different biochemical and histological features. The apical pole of the cells is filled with particles of melanosomes, which have different types of pigments in various degrees of melanization and are contained in large vacuoles.

In mammals the pigments are contained in fibrillar melanosomes. Study of sepia melanin is done by photo degradation. The irradiation with ultraviolet radiation induced significant photochemical alterations in the sepia melanin. Melanins are highly heterogeneous polymers of pigment which give color to hair, skin, iris, and nervous cells. The structures of these biopolymers are still unknown at this time.

Sepia melanin is insoluble in organic solvents, acids, aqueous solutions, and only partially dissolves in alkaline solutions. Sepia ink from Sepia officinalis contains CaCO3, MgCO3, NaCl and Na2SO4, enzymes and other substances. The pigment can be found in it two different forms: a salt form with Na, K, Ca, Mg and Fe and an acid form obtained following reaction in a dilute acid medium(33).

Purified sepia melanin is a black powder, hygroscopic that should be refrigerated at -20 ° C to avoid decomposition. Sepia melanin is also sensitive to oxygen, pressure and pulses of radiation which produce a fragmentation of melanosomes similar to what happens in the skin.

The studies on the extraction and purification of sepia melanin by acid treatment using different concentrations of HCL acid, under ultrasonic or mechanic agitation. A first modification of sepia melanin using hydrochloric acid afforded the hydrolysis of the sepia melanin while a second modification, is obtained by adding different salts, the melanin obtained as salt..

Among biopolymers, melanins are unique in many aspects. Some essential biopolymers are chemically well characterized and can be determined using well established analytical methodologies.

On the contrary,melanin cannot be accurately determined due to its intristic chemical properties. Mammalian melanins exist in two chemically distinct forms: the brown to black Eumelanin and the yellow to reddish-brown Pheomelanin.

Considerably less expensive sepia melanin can be obtained, which could prove important as a standard in future determinations of eumelanin and pheomelanin as well as in a vast field of scientific and industrial applications in such fields as human and veterinary medicine, pharmacology and cosmetics.

SEPARATION OF INK SAC FROM CUTTLE FISH

Ink can be collected from the ink sac which is present in the body and behind the eyes of the organism.
The body of the cuttle fish is cut open to extract a small silvery ink gland of nearly two inches length.

The sac is punctured gently to extract the ink.

PURIFICATION

The extraction and purification is performed in an acid medium which results in a smaller structural change. 50 g of commercial cuttlefish ink is added to 100.0 ml of hydrochloric acid (1M) in a dark recipient. The slurry is stirred for 30 min (mechanical stirring) and then kept for 24 hr at 10 °C. Solid is separated from the supernatant fluid by centrifugation (10000 rpm at 5 °C for 15 min), washed three times with 1 M HCl solution, water, acetone and finally water. Following a 24 hour lyophilization to remove all solvent, a very thin black product was obtained at the end of the procedure.

LYOPHILIZATION

Freeze-drying, also known as lyophilization, or cryodesiccation, is a dehydration process typically used to preserve a perishable material or make the material more convenient for transport. Freeze-drying works by freezing the material and then reducing the surrounding pressure to allow the frozen water in the material to sublimate directly from the solid phase to the gas phase.

There are four stages in the complete drying process: pretreatment, freezing, primary drying, and secondary drying.

Methods of pretreatment include: Freeze concentration, Solution phase concentration, Formulation to Preserve Product Appearance, Formulation to Stabilize Reactive Products, Formulation to Increase the Surface Area, and Decreasing High Vapor Pressure Solvents.[2]In this step, it is important to cool the material below its triple point, the lowest temperature at which the solid and liquid phases of the material can coexist. This ensures that sublimation rather than melting will occur in the following steps. The freezing temperatures are between −50 °C and −80 °C. The freezing phase is the most critical in the whole freeze-drying process, because the product can be spoiled if badly done.

Primary Drying

The pressure is lowered (to the range of a few milli bars), and enough heat is supplied to the material for the water to sublime. This phase may be slow (can be several days in the industry), because, if too much heat is added, the material's structure could be altered.

In this phase, pressure is controlled through the application of partial vacuum. The vacuum speeds up the sublimation. It is important to note that, in this range of pressure, the heat is brought mainly by conduction or radiation; the convection effect is negligible, due to the low air density.

Secondary Drying

The secondary drying phase aims to remove unfrozen water molecules. In this phase, the temperature is raised higher than in the primary drying phase, and can even be above 0 °C. At the end of the operation, the final residual water content in the product is extremely low, around 1% to 4%.

DYEING

The purified sepia dye was combined with a wetting agent to form the dye liquor with material liquor ratio as 1:30. Then the fabric is immersed in the above liquor at room temperature and stirred. After 10 minutes Acetic acid is added stirred and dyeing is done for 45 minutes.

After dyeing, the samples are rinsed, squeezed and soaped with soap oil at room temperature for 20 min. Finally the samples are thoroughly washed and air-dried.

CONCLUSION

The review of various literatures gives the information that dyeing of Protein fibers is highly possible by Sepia melanin. The sepia melanin pigments are UV protective, IR protective, anti-bacterial etc. Thus the dyed fabric will show noticeable impact of the above properties.

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