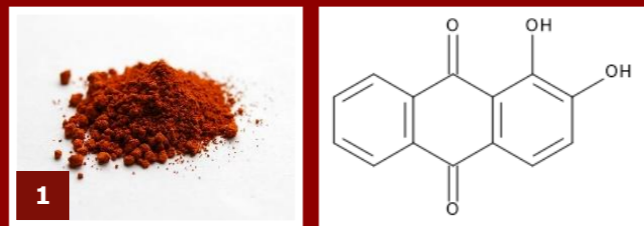


ALIZARIN

Molar Mass : 240.214 g mol⁻¹

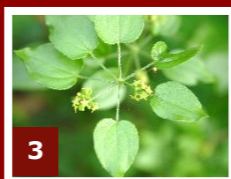
Melting point : 277-278 °C



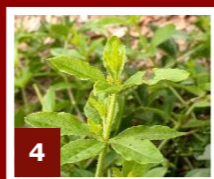
Alizarin Red



M. citrifolia



R. cordifolia



R. tinctorum

For thousands of years, several plants belonging to the *Rubiaceae* (*Ruber* means red in Latin) family have been used for dyeing. *Aal* (*Morinda citrifolia*) and *madder* (*Manjistha- Rubia cordifolia* and *Rubia tinctorum*) being the most commonly used species in India for the red dyes obtained from the root barks of these plants.

In 1826, French chemists Pierre-Jean Robiquet & Jean-Jacques Colin isolated two anthraquinone dyes Alizarin and Purpurin from the madder roots. More dye compounds were discovered from madder in the following years.

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Isolation of the natural dye



Roots harvested from 3 to 5 year old aal or madder plants are washed, cut, sundried and stored. The stored roots are also allowed to age for a few months, for better result.



Dried root pieces/ powder are simmered in hard water, at medium temperature (60-70°C), till the red dye is released into the dye bath. Calcium carbonate can be added to make pH alkaline.

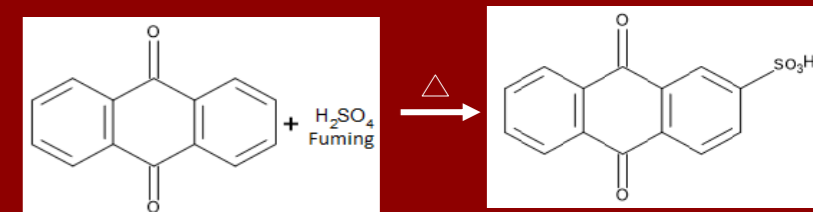
Excess heat can give rise to undesirable changes in the dye colour. Some dyers therefore, prefer soaking the madder root pieces/powder in hard water for 4-7 days at room temperature over use of heat to obtain the red dye.

Do you know?

In 1826, Alizarin became the first natural dye to be synthesized. German chemists, Carl Graebe and Carl Liebermann from BASF, German chemical company, are given the credit for the method of synthesis of Alizarin from anthracene. During the same period, British chemist William Perkin also developed the same procedure independently. Interestingly, BASF filed the patent for the dye one day before Perkin. Both patents were granted and their markets were divided.

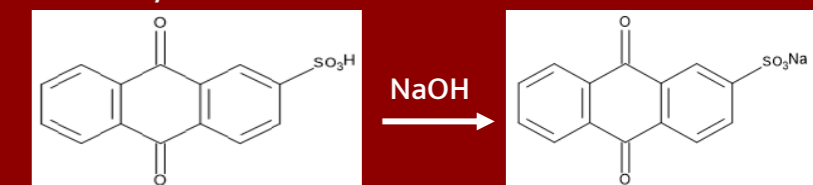
Laboratory synthesis of Alizarin

Anthraquinone when heated with fuming sulphuric acid at 180°C produces anthraquinone-2-sulphonic acid. The reaction of this compound with sodium hydroxide results in the formation of its sodium salt.

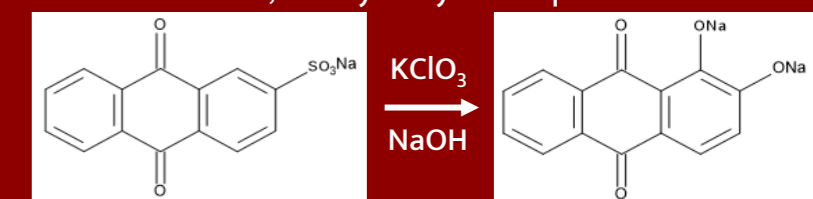


Anthraquinone

Anthraquinone-2-sulphonic acid



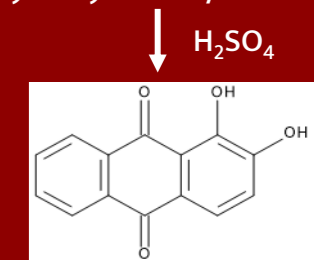
This sodium salt on heating with sodium hydroxide and potassium chlorate at 200°C under pressure gives sodium salt of 1, 2- dihydroxyanthraquinone.



Sodium salt of Anthraquinone-2-sulphonic acid

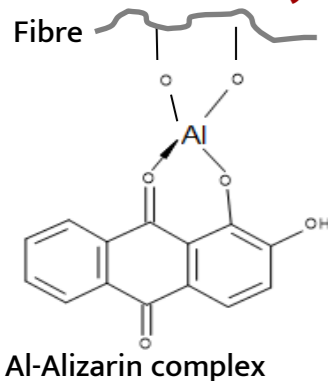
Sodium salt of 1, 2-dihydroxyanthraquinone

The sodium salt when treated with sulphuric acid, produces Alizarin red.



Alizarin red

Mordant dyeing with Alizarin



Alizarin is a polygenetic dye which produces different colours when combined with various mordants. Metal ions in these mordants also form metal-dye complexes and bind the dyes to the fabric fibres.

Mordant	Ions	Colour
Alum/Aluminium sulphate	Al ³⁺	Red
Ferrous sulphate	Fe ²⁺	Deep violet
Ferric sulphate	Fe ³⁺	Brownish black
Stannous chloride	Sn ²⁺	Reddish violet

For dyeing wool, the yarn/fabric is first soaked in alum solution for mordanting. The mordanted fibres are squeezed to remove excess alum solution and is then transferred to the dye bath. The fabric can be soaked for a few hours at room temperature or in a warm dye bath. Then the yarn/ fabric is taken out of the dye bath, washed gently and dried. Dyeing plant-based fabrics like cotton involve additional steps like scouring, bleaching etc.



In India, age-old textile weaving, dyeing and block printing techniques like *Bagru* and *Leheriya* (Rajasthan), *Ajrak* (Kutch), *Kalamkari* (Andra Pradesh), *Kotpad* (Odisha) etc. have been using natural Alizarin. The Valsang village in Solapur, Maharashtra also has a history of dyeing with Indigo and Surangi (Aal) dyes.



10 *Kalamkari*

11 *Ajrak*

12 *Kotpad weave*

Chemistry of the Kotpad weaves

For dyeing cotton yarn with natural Alizarin, the tribal community in Kotpad practices an elaborate pre-dyeing treatment of yarn. This involves repetitive application of castor oil, cow dung and supernatant of wood ash suspension on the yarn, for 15 days. The yarn is trampled with feet and sundried between each of these steps. Since, water soluble metallic mordants like alum have less affinity to cotton fibres, they use castor oil and tannins as mordants in the Kotpad weaves. The supernatant of wood ash creates an alkaline pH. The cow dung also helps in bleaching the yarn and binding the mordants to the fibres. For preparing maroon colour, the yarn is dyed with aqueous extract of *aal*/root powder which is the source of Alizarin. The brown colour is produced by adding ferrous sulphate and *harda* powder to the *aal* dye. Here, *harda* (*Terminalia chebula*) powder is the natural source of tannins.

Art and Alizarin



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A red lake pigment, called rose madder can be precipitated from the aqueous extract of madder root powder, using metal salts (eg. Alum) and strong alkali like sodium carbonate. Rose madder and it's cheaper, synthetic and more lightfast version called Alizarin crimson are used by artists for painting.



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Madder red pigments were also used in the Madhubani paintings, traditionally painted in north Bihar, by women on the interior walls of their houses. These paintings gained British officers' attention after the 1934 Bihar earthquake exposed the inner walls of houses.

Did you know???

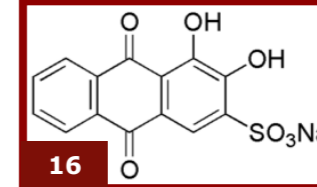
To promote the madder dyeing culture, King Charles X, in the year 1829, ordered the French army uniform pants and kepi (cap) to be dyed red. By the end of the 19th century, natural madder dye was replaced with the synthetic dye produced by BASF.

The French were emotionally attached to the bright red colour in their uniforms. However, inspite of their resentment, during World War I, the French army had to adopt a new subtle coloured uniform so that they attract less attention from their enemies.



15

Other applications of Alizarin



16

Alizarin Red S (image 16) stains calcium compounds. So, it is used in biology and geology, for studies related to calcium in minerals, bones and tissues. Alizarin is also used as a pH indicator.



17

References and Further Reading-

- Vankar, P. S. (2017). *Natural Dyes for Textiles: Sources, Chemistry and Applications (The Textile Institute Book Series)* (1st ed.). <https://doi.org/10.1016/B978-0-08-101274-1.00003-3>
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Image sources

See the supplementary document.

Now, can you find?

- What are the pros and cons of using madder for textile dyeing?
- Which Indian brands use natural madder dye at present?
- What are the pros and cons of using tin and chrome mordants?

