Study of Heavy metals in Natural Dyes from Lac *insect Kerria lacca.*

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ABSTRACT

The insect *Kerria lacca* is a species in the family Kerriidae, better known as the lac insects. These are in the superfamily Coccoidea, and order hemiptera commonly known as scale insects and is native to Asia. This species is the most commercially important lac insect, because it is a main source of lac, a natural resin that may be refined into shellac and different other products. *K. lacca* produces a dye and a wax as natural secretions. Larvae during the developmental stage crawl along the host plants branches and feed on the phloem. As they pierce the branches to reach the phloem, they cover the holes with their wax secretions. In this context, authors started to evaluate the environment friendliness of Lac dye, a natural colorant obtained from that insect, *Kerria lacca* which is used in India from time immemorial. In this regard authors tried to know the presence heavy metals in the dye. Results found in the experiments show the samples evaluated have no or little amount of studied heavy metals. The statistical analysis proved that it is safe for use as it was considered in different ancient texts both for food and textile.

KEY WORDS: Heavy metals, *Kerria lacca*, Lac insect, Lac Dye.

Introduction:

The movement to return to nature world over and from indiscriminate exploitation and pollution leading to health hazards and to protect the environment has become a priority. In the present day context the relevance of natural dyes in the modern world is important to understand. The harmful sometimes poisonous substances used in colouring is now coming to strict scrutiny and right thinking people have started advocating for natural dyes. Chemical dye industry which produces a rainbow of colours are not able to provide a solution to harmful waste produced during the process of manufacture also. India is endowed with a wealth of natural flora and fauna which provide the basic resources for natural dyes. The flora is widely distributed in the rural belts and therefore is in close proximity to the handloom

weavers. The availability of natural dyes primarily depends on three sources. These are Specialised plant or vegetable sources, insect or animal sources and mineral sources.

Vegetable Dyes are obtained from plant sources (Patra et al. 2001 and Siva 2007). The Survey of the available literature shows that around 500 plants are used to get the dyes. India is rich in equatorial to temperate flora. However, no systematic study has been made by the taxonomists and economic botanists towards a comprehensive survey of the flora from the view point of their potential for dyes (Hancock, 1997, Mutua, 1997, Bryan and Stella 2002 and Anonymous 2005). Lichens one of the good sources of natural dyes are also least studied (Casselman, 2001). The second types of dyes are animal dyes which are obtained from the animal sources. The secretions of insects like Cochineal, Kermes and Lucca (Lac) are commonly used as natural dyes. However, there is no study to screen the dye bearing capacity of animals. Among the large variety of insects occurring in a tropical country like India there is a scope of other sources. Among higher animals the yellow dye is extracted from the urine of cow. There might be many others like shell fish, and molluscs which need to be investigated. The last type is mineral dyes obtained from the mineral sources. The most commonly reffered and used mineral is ‘Geru (redchre) known for its characteristic shade. Antimony, Oxides of tin and iron are also used along with vegetable and insect dyes to obtain the desired shade.

The Lac Dye

India is the major Lac producing country in world. The major portion of the lac cultivation is in Chotanagpur Platue in Jharkhand. The eastern districts of Madhya Pradesh, parts of West Bengal, northern parts of Orissa, Maharashtra, Assam and some southern states produces lac. Lac is a resinous encrustation produced by an insect which sucks the juice of plants and transforms this juice into resin which completely surrounds it. This insect is known as *Kerria lacca* under the family Lacciferidae, a specialized and isolated group in the super family Coccoidea of the order Hemiptera (Khanna 1983). The lac insect, *Kerria lacca* (kerr) which thrives on a variety of trees and bushes such as kusum (*Schleichera oleosa*), Palash (*Butea monosperma*), ber (*Ziziphus mauritiana*). It also produces a very good dye which was used in ancient times. Generally it goes out as effluents from the lac producing industries (Srivastav et al. 1982). Considering the country’s annual production of sticklac as 20,000 tonnes, nearly 200 tonnes of lac dye is being lost every year. Though the process of its recovery is simple and economical. The final product that is pure lac dye can also fetch a good price by awareness generation.

Natural colouring substances such as carminic acid, kermesic acid and laccaic acid is popularly known as lac dye and derived from the insects namely, cochineal, kermes, and lac insects respectively. The lac insect produces laccaic acid and erythrolaccin, former being water soluble and the later water insoluble. The insect body alongwith its secretions which is removed from twigs and brought to the market is termed as sticklac (scrapped lac). When sticklac is crushed and washed with water, the water soluble lac dye a red coloured dye (laccaic acid) present to the extent of 1.0 per cent is dissolved out. The lac dye is fast on animal fibers like wool and silk. Different colours of this dye may be achieved by the use of suitable mordants (Rastogi et al. 1999 and Suri et al. 1999).

Atharva veda gives a brief account of lac, the lac insect and its medicinal use. The Vinaya texts of Buddhists also describe the extraction method of lac dye and its application in dyeing. Age-old uses of lac dye include dyeing of silken saries, and in 'alta' used in religious ceremonies for colouring the feet and hands of the ladies (Bose et al. 1963). There are references that foreign writers had a good knowledge of lac dye. Garcia de Orta was the first European who critically examined and published about lac and lac dye in his volume Colloquies at Goa in 1553. Spanirads brought it from India to use as dye and also in the medicinal preparation, '*Dia lacca'*. The use of lac dye seems to have been known to Chinese some 4000 years ago as they extensively used lac dye for dyeing silk to impart very attractive and lustrous red colour. Similarly dyeing of leather was another ancient chinese craft in which lac dye was widely used. In India, lac dye assumed commercial importance from 17th century as an export item for Europe where the high prices of cochineal stimulated interest in lac dye as a cheaper substitute. The lac dye industry flourished till 1871-72 and thereafter the export of dye registered a sharp decline because it could not withstand the competition from synthetic dyes. The lac dye was thus nearly ousted from dyeing industry (Singh, 2002).

The lac dye which has anthraquinode type structure resembling to Alizarin, Indathrene Golden Yellow and Indathrone. It is a mixture of some five closely associated compounds, all being anthraquinone derivatives. They are known as laccaic acids A, B, C, D and E. The lac dye is acidic in nature and is generally present as its sodium or potassium salts which are completely soluble in cold water but highly soluble in boiling water. The dye is also soluble in methyle alcohol, amyl alcohol, acetone, acetic acid and formic acid but insoluble in ether, chloroform and benzene. It dissolves slowly in ethyl alcohol. It turns to orange or red in aqueous acid solution and reddish violet in alkaline solution but the alkaline solution of laccaic acid is unstable and decomposes rapidly. It also dissolves in concentrated sulphuric acid with beautiful carmine red colour (Bose et al. 1963).

Materials and Methods:

The Lac insect grow on trees in forest areas so there was no evidence of pesticides. But the presence of heavy metals can not be ruled out due to its natural origin. It was tested for major heavy metals that may be present and harmful. The detection was done through Atomic Absorption Spectroscopy (AAS) at chemistry laboratory in Ranchi Agriculture College, Birsa Agricultural University, Ranchi, Jharkhand. The AAS instrument looks for a particular metal by focusing a beam of uv light at a specific wavelength through a flame and into a detector. The sample prepared is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As concentration goes up, absorbance goes up. The calibration curve was constructed by running standards of various concentrations on the AAS and observing the absorbances. In this lab, the computer data system draw the curve after that the prepared samples were tested and measured against this curve. All sample were prepared from chemicals of analytical grade with double distill water. 1gm of metal cadmium, cobalt, nickel and zinc dissolve in aqua regia (1:3) HCl & HNO3, made up to 1 liter in volumetric flask. Thus with the help of Atomic absorption spectroscopy (AAS) the presence of metals in liquid samples were determined (Padma 2000, Bhagi and Chatwal 2005). The Metals studied included Fe, Cu, Zn, Co, Pb, Ca, Ni, Mn, Cr, Cd by the method. It measures the concentrations of metals in the samples. Typical concentrations range was studied in the mg/L range.

Results and Discussion

The experimental results of concentration of different heavy metals are given below in Table-1. The concentration of copper in different samples was estimated and the result was found between 0.02 to 0.14. The concentration of Zinc in different samples was found between 0.00 to 0.02. The concentration of Cobalt in different samples was found between 0.00 to 0.10. The concentration of Lead in different samples was was found between 0.00 to 0.90. The concentration of Iron which is also common impurity was estimated and was found between 0.00 to 0.01. The concentration of Manganese in studied samples was found between 0.00 to 0.01. The concentration of Chromium in different samples was found between 0.01 to 0.09. No traces of Mercury, Cadmium and Nickel was found in the different samples studied (Table-1). The different concentrations of different heavy metals, which are present also varies greatly.

Khanna et. al 1992, has shown the importance of testing the dyes for its environment friendliness. The different metals are needed as nutrients but it is also toxic and causes

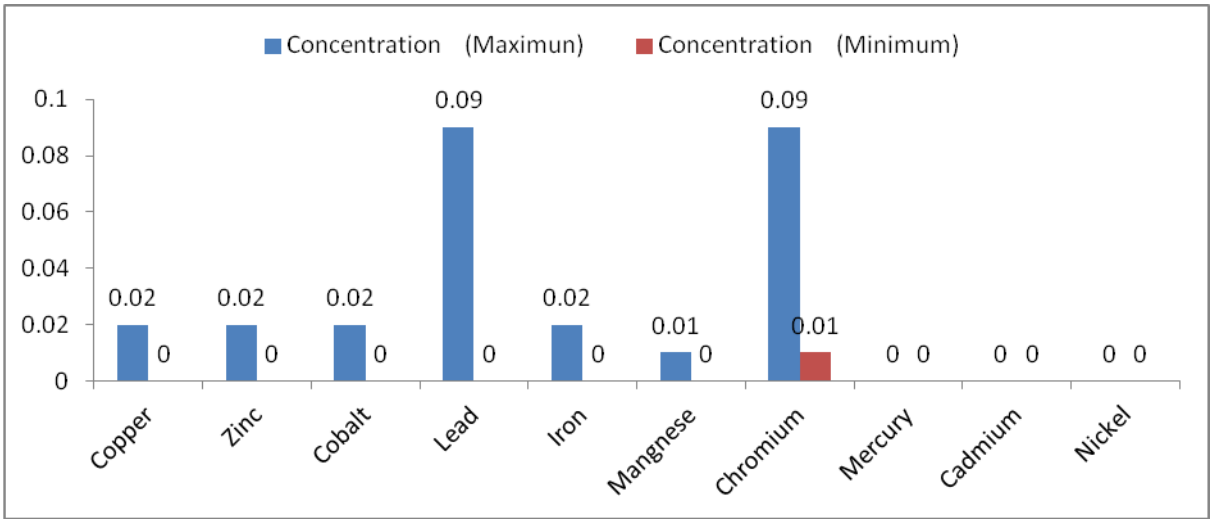
diseases and even death to human being and other organisms (Forstner and Wittmann, 1981). Das and Mishra (2001) has also described important effects of heavy metals in his monumental work Man and Environment. There is no study available on presence of heavy metals in Lac Dye, so it was not possible to compare the values.

Table -1 Maximum and Minimum concentration of heavy metals in different samples of Lac Dye

Sr No.	Name of the Heavy Metal	Concentration (mg/L) (Maximun)	Concentration (mg/L) (Minimum)
1.	Copper	0.02	0.00
2.	Zinc	0.02	0.00
3.	Cobalt	0.02	0.00
4.	Lead	0.09	0.00
5.	Iron	0.02	0.00
6.	Mangnese	0.01	0.00
7.	Chromium	0.09	0.01
8.	Mercury	0.00	0.00
9.	Cadmium	0.00	0.00
10.	Nickel	0.00	0.00

After the statistical analysis of the available data through test of significance, it was concluded that the levels of metals present in studied lac dye samples are not significant as shown in the table (Table-2). Some of the harmful metals which are not at all present in the sample of lac dye were cadmium (Cd), Nickel (Ni), and Mercury (Hg) (Graph-1).

There is little research work available on the chemistry of Lac dye. Till now the work done on the environment friendliness of lac dye is fragmentary and does not allow us to draw any conclusion. In the present study first time, a systematical attempt has been made to study the presence of heavy metals in lac dye. With this information on lac dye, it is possible to draw certain sound conclusions on the environment friendliness of lac dye. For the proper understanding the information available can be seen as a beginning towards establishing the traditional notion of environment friendliness of lac dye. As these are collected from the wild trees where there is no possibility of any contamination from pesticides or herbicides and the presence of heavy metal tested may be due to the terrain that may have heavy metal contamination of natural origin.



Graph- 1. Graphical representation of presence of heavy metals in Lac Dye.

Table-2 : Mean (m) and standard deviation (sd) of different metals present in lac dye (n=20) and test of significance.

SL NO.	Metals	M	Sd.	Non Harmful Level	T	P
1	Copper (Cu)	0.0085	0.088	0.05	21.09	<0.001
2	Zinc (Zn)	0.086	0.041	5.0	536.00	<0.001
3	Cobalt (Co)	0.0055	0.0069	0.5	320.00	<0.001
4	Lead (Pb)	0.0345	0.306	0.05	2.27	<0.05
5	Iron (Fe)	0.003	0.0057	0.3	233.02	<0.001
6	Manganese (Mg)	0.001	0.0031	0.1	142.82	<0.001
7	Chromium (Cr)	0.034	0.0235	0.05	3.04	<0.01

Conclusion

With the worldwide ban on azo dyes (Lokhpande and Naik, 1997), the revival of lac dye, which had been earlier sidelined due to the emergence of aniline dyes, is now staging a comeback, for the dyeing of wool, silk, jute with various mordants. It has also found use as a colourant in the food and beverages industry. The use of lac resin and lac dye in traditional medicinal systems. e.g. ayurveda and unani continues even today (Singh, 2002).

Specification for lac dye ISS 12921-1990 has already been approved by the Bureau of Indian Standards, New Delhi as guide information for the consumer industries. Japan is importing lac dyes from China and Thailand. The dye is being used mainly for colouring beverages and food products like ham, sausages, bean, jam etc. The present consumption of lac dye in Japan is reported to the tune of 5-6 tonnes. According to estimates of Indian Institute of Natural Resin and gum, Namkum, Ranchi, Jharkhand (Formerly Indian Lac Research Institute, Ranchi, Jharkhand), India can produce 50 to 100 metric tonnes of lac dye annually because India has a premier country in the world production of sticklac.

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