Al-Mukhtar Journal of Sciences **37 (2): 120-126, 2022**
ISSN: online 2617-2186 print 2617-2178
Journal Homepage https://omu.edu.ly/journals/index.php/mjsc/index

Determination of Heavy Metals in Henna Leaves and Cosmetic Henna Products Available in Zliten, Libya

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Received: 06 November 2021/ Accepted: 18 May 2022
Doi: https://doi.org/10.54172/mjsc.v37i2.372

Abstract: Henna is widely used by Libyan women as a cosmetic, which may contain lead (pb), cadmium (Cd) and other toxic heavy metals. The purpose of this study was to determine heavy metal content of seven henna products, imported and locally produced in Zliten, Libya. An analytical method was performed using Atomic Absorption Spectrophotometer (AAS). In terms of heavy metal content determination, the results revealed a significant difference between henna leaves and cosmetic henna samples. The premixed henna sample H2 had the highest heavy metal concentrations with a high level of lead (6.952ppm), exceeding the WHO's maximum limit and the (ASEAN) Guidelines on Limits of Contaminants for Cosmetics Heavy metal maximum limits, Lead (Pb) is 1 ppm. Nickel (Ni) levels in (H4=5.201ppm) and (H6=2.023ppm) henna samples were found to be above the WHO's limit of 1.68ppm. The results indicated that such cosmetics expose consumers to high levels of Pb and Cu, and hence to potential health risks. Thus، investigating the sources and effects of heavy metals in such cosmetics is strongly advised.

Keywords: Heavy metal, Henna leaves, Henna Products, Toxic levels.

INTRODUCTION

Henna, scientifically known as Lawsonia inermis, is a plant in the Lythraceae family. It grows best in tropical climates across all of Africa, northern Australia, and southwest Asia (Chaudhary et al., 2010; Gevrenova, 2010), and it is well known for its cosmetic and therapeutic properties. According to ethnobotanical and historical evidence, henna was one of the first plants to be used for cosmetic purposes (Ozbek, 2018). Henna painting was done in ancient Egypt and its neighboring countries. Henna is extremely popular in Libya because it is part of the culture and traditions. The Libyan market offers a wide range of henna products in a variety of colors. Some are produced locally, while others are imported from Sudan, Yemen, Tunisia, India, and Pakistan. Unfortunately, in recent years, henna has become a potentially life-threatening substance for Libyan women, particularly in the eastern region of the country, where more than 550 cases of henna poisoning have been reported, with 57 deaths, according to the Libyan Ministry of health. Until today, scientific information about the true causes of these widespread poisoning and death cases remained unknown. Despite the seriousness of the problem, published studies on henna in Libya are rare (Kumar & Kathireswari, 2016). Therefore, it is necessary to determine the levels of heavy metals in henna leaves and henna products in order

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to identify the heavy metals ratio and protect henna users from the toxic effects of heavy metals.

Henna contains tannin product called Lawsone (2-hydroxy-1,4 naphthoquinone), which is responsible for the henna dye at concentrations ranging from 1.0 to 1.5%. Lawsone is extracted from henna leaves (Singh et al., 2005). Lawsone is a compound that imparts the characteristic red-orange pigmentation that makes the skin, nails, and hair look beautiful and appealing (DeLeo, 2006). The henna plant as a whole contains xanthones, coumarins (fraxetin and scopletin), flavanoides, luteolins, apigenin and its glycosides, and steroids (β-sitosterol). In addition to organic compounds, henna plants absorb heavy metal ions from the soil and later are accumulated in other parts such as leaves, the heavy metals that are available for plant uptake are those that are present as soluble components in soil solution or those that are easily solubilized by root exudates, however, excessive amounts of these metals can be toxic to plants. Plants' ability to accumulate essential metals also allows them to acquire nonessential metals. metals cannot be broken down, so when concentrations within the plant exceed optimal levels, they adversely affect the plant both directly and indirectly (Khattak & Khattak, 2011).

The chemical structure of the henna dye molecule places it in the class of dyes known as α-hydroxy-naphthoquinones. There are very rare reactions to the lawsone compound in henna leaves, which are mainly caused by naphthoquinone sensitivity (Kang & Lee, 2006). To make it more permanent or stronger, marketed henna is often mixed with various herbs and different chemical additives (which contain high levels of trace elements) and synthetic dyes such as para-phenylenediamine (PPD) (Aktas Sukuroglu et al., 2017). However, such additives have toxic side effects ranging from mild irritation to more severe allergic reactions exhibited through blisters, lesions, and sores on the skin, Natural henna is generally safe and well-tolerated in humans, but henna containing additives may cause side effects or even death (Fahad, 2016; Swift, 1997). Heavy metal contamination in cosmetic products is a significant environmental and health concern because the metals are toxic (Alissa & Ferns, 2011). Some of the toxic effects of lead include hematological, cardio-vascular and neurobehavioral complications such as encephalopathy, depression and malaise (Control & Prevention, 2005; Kollmeier et al., 1990). Cadmium has been linked to oestomalacia as well as respiratory effects such as pulmonary fibrosis, pneumonitis, emphysema and lung cancer. Nickel is a strong allergen and the primary cause of skin sensitivity (Bobaker et al., 2019).

Figure: (1). shows the Adverse effects of premixed Henna products

The current study is primarily motivated by the urge to determine the heavy metal concentrations in the henna merchandise in the city of Zliten, Libya.

MATERIALS AND METHODS

Sample collection: In this study, two types of natural henna were used; the first was collected from a henna tree on one of Zliten's farms, and the second was prepared by drying and grinding the leaves. The other sample was a pre-prepared natural henna from an herbalist shop. And five types of commercial henna traded on the market were used. However, all henna products are sold without information about their chemical contents. and placed in bags weighing approximately 100 grams.

Table: (1). shows the names of henna samples and their symbols

Code	Sample
H1	Natural henna from the henna tree
H2	Natural henna from an aromatic store
H3	Premium Crown Henna
H4	Bride's henna
H5	Henna Gulf Cup
H6	Royal Al Haramain Henna
H7	Herbal henna

Sample Digestion: Using the dry burning method by weighting 5 grams per natural henna leaf and sold henna and placing it in an incineration oven at 450-500 ºC for 4-6 hours. The ashes were then washed with 5.1% nitric acid and the volume was completed up to 50 ml. The extract was ready to determine the concentration of heavy elements in samples studied using an Atomic Absorption Spectrophotometer,(AAS) Perkin Elmer Model 2380.

Figure: (2) The Atomic Absorption Spectrophotometer (AAS)

The pH values were measured by taking 0.5g of each henna sample and adding 70ml of distilled water into a 250ml flask with stirring until the henna is well combined with the water. A pH test was then performed using a pH meter (Fig.3).

Figure: (3). The PH device used to measure acidity in the Henna samples.

RESULTS

pH measurement: As shown in figure (4) below, the pH values of Henna samples were acidic in the range between 3.6 and 5.3.

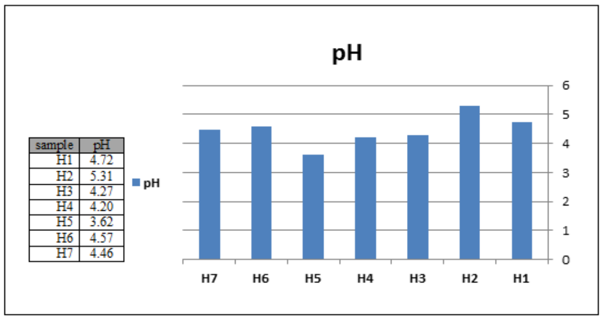

Figure: (4). pH values of Henna samples

Low pH (acidic) mixes are rich in hydrogens, which keep aglycones relatively stable until it is time to use the dye. This hydrogen-rich environment provided by the acid liquid allows for a longer and fuller dye-release as well as a more stable bond to keratin aglycones to bond to the keratin of the hair through a Michael Addition.

The low pH level of an acidic henna paste allows the aglycones to remain stable for a longer period of time. This allows for a slow, steady dye-release for the optimal amount of available aglyones. Mixing henna without an acid (such as using only water) will cause the paste to have a weaker dye release which demises faster. The optimal pH level for a henna mix is right around 5.5, which can be achieved with a number of fruit juices, or the use of a fruit acid powder and distilled water.

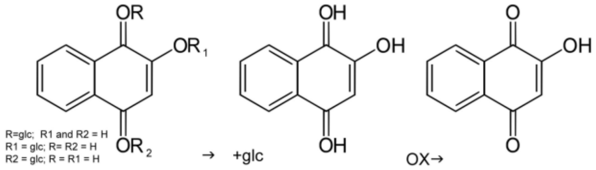

Figure (5). Hennocide precursors convert into an aglycone state in a low pH medium, and eventually oxidize to a stable molecule.

Heavy metals determination: Table (2) shows the results of AAS analysis of ten heavy metals in Henna samples, including Aluminum, Arsenic, Silver ,cadmium, chromium, copper, cobalt, lead, Nickel, and zinc. . The prepared standards of each metal and their corresponding absorbencies were used to plot calibration curves. The product-moment correlation coefficient factor and the equation for the line of regression were derived from calibration curve of each metal.

$$\text{Actual concentration} = \frac{Concentration\left(\frac{\mu g}{ml}\right) X\ Volume\ digested\ (ml)}{Weight\ of\ sample\ (g)} \ldots Eq\ (1)$$

The actual concentration of heavy metals in henna leaf samples obtained from AAS was derived using Equation (1) For dilutions, the actual weight was obtained by multiplying the readout results from AAS with the dilution factor.

Table:(2). Concentration of Heavy Metals in Henna Samples

Metal	Sample (Concentration ppm)						
	H1	H2	H3	H4	H5	H6	H7
Al	496.9	53.8	81.52	737.8	285.1	754.8	754.8
As	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ag	2.210	1.064	1.708	<0.002	<0.002	<0.002	<0.002
Cd	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Cr	0.562	<0.002	<0.002	0.678	0.063	3.69	0.193
Cu	4.273	7.570	6.628	5.96	5.014	5.078	5.208
Co	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pb	< 0.03	6.952	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Ni	0.669	1.642	< 0.01	5.201	0.874	2.023	0.395
Zn	10.219	4.736	21.72	-	-	-	10.99

DISCUSSION

Seven different cosmetic henna products were tested in this study to determine the concentration of some heavy metals. Aluminum and copper metals were detected in all samples, while zinc was detected in four. Although some metals, such as chromium, copper, aluminum, and zinc, play important biochemical roles in many organisms at low concentrations, their toxic effects are observed at high concentrations. All of these metals can damage or impair central nervous system functions, as well as blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may cause slow-progressive physical, muscular, and neurological degeneration processes such as Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Despite the fact that EU regulation suggests that the concentration of some heavy metals, such as chromium, in color additive cosmetics should be 1.0 mg/kg (Borowska & Brzóska, 2015), one sample [H6=3.69ppm] had a chromium concentration higher than the EU standard in cosmetic products. The presence of chromium in the body facilitates glucose entry into cells (Krejpcio, 2001). On the other hand, exposure to high levels of chromium, on the other hand, has been linked to kidney and lung damage, as well as other cancers. Chromium has also been linked to skin effects such as eczema and other skin inflammations (Umar & Caleb, 2013).

Table 2 shows that the lead content of one sample exceeded the WHO's recommended maximum limit for cadmium in cosmetics. Zinc was detected in four samples. According to (Zafar Alam et al., 2009), zinc oxide was probably used in cosmetics due to its powerful natural sunblock property. Furthermore, zinc is also required for oxygen metabolism and mitochondrial function (Popoola et al., 2013). These toxic metals may enter the products when low-quality raw materials are used.

CONCLUSION

According to the findings of this study, henna leaves from Zliten are a good raw material for henna products due to their low levels of lead, cadmium and nickel in comparison to WHO standard limits. Henna leaves had lower significant levels of Pb, Cd and Ni as raw materials than henna products, but more of these metals were added during the manufacturing process. the concentrations of Lead and copper in the H2 premixed henna sample exceeded the WHO's maximum allowable limits. Therefore it conceder dangerous product. As a result, the general public should be educated about the dangers of long-term use of toxic cosmetic products. Extensive and continuous use of these cosmetic products may cause the slow release of heavy metals and endangering consumers. National standard legislations for cosmetic products should be available to monitor the safety of these products before they are imported and reach consumers. However, more research is needed to assess the metals concentrations in various types of cosmetics and body care products in order to protect consumer health.

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تقدير العناصر الثقيلة في أوراق الحناء ومنتجات الحناء التجميلية في مدينة زليتن، ليبيا

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تاريخ الاستلام: 06 نوفمبر 2021 / تاريخ القبول: 18 مايو 2022

Doi: https://doi.org/10.54172/mjsc.v37i2.372

المستخلص : تستخدم النساء الليبيات الحناء على نطاق واسع مستحضرا تجميلا، والتي قد تحتوي على الرصاص(Pb)، والكادميوم (Cd)، والعناصر الثقيلة السامة الأخرى. والغرض من هذه الدراسة تحديد محتوى العناصر الثقيلة من سبع عينات لمنتجات الحناء المستوردة، والمنتجة محليا المتداولة في مدينة زليتن، ليبيا. تم إجراء التحاليل باستخدام مطياف الامتصاص الذري (AAS). و كشفت النتائج عن وجود فرق كبير بين أوراق الحناء، وعينات الحناء التجميلية. عينة الحناء المصنّعة H2 أظهرت أعلى تركيزات المعادن الثقيلة؛ نتيجة تلوثها بمستوى عال من الرصاص (6.952ppm)، متجاوزة الحد الأقصى لمنظمة الصحة العالمية وهو ppm 2، و كذلك متجاوزة معايير المنظمة الأسيوية (ASEAN)، وبشأن حدود الملوثات لمستحضرات التجميل الحد الأقصى للمعادن الثقيلة الرصاص هو ppm 1. ومستويات النيكل (Ni) في عينات الحناء التجميلية (H4 = 5.201ppm)، و (H6 = 2.023ppm) لتكون فوق الحد الأقصى المسموح به لمنظمة الصحة العالمية، وهو 1.68 ppm. تركيزات كل من As , Co, Cu و Cd كانت في جميع العينات أقل من الحد المسموح به. وأشارت النتائج إلى أن مثل هذه المستحضرات التجميلية تعرض المستهلكين لمستويات عالية من العناصر الثقيلة السامة، وبالتالي إلى مخاطر صحية محتملة. لذا نوصي بشدة بضرورة إجراء المزيد من الدراسات لتحديد مصادر العناصر الثقيلة السامة في منتجات الحناء، والمستحضرات التجميلية المصنعة منها.

الكلمات المفتاحية : العناصر الثقيلة، أوراق نبات الحناء، منتجات الحناء، معدلات التسمم.

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