

Research Journal of Agriculture and Forestry Sciences \_ Vol. **10(3),** 16-23, July (**2022**)

# Review Paper Historical, economic and agricultural dimensions of madder (Rubia tinctorum L.) plant

Muge Deveoglu<sup>1</sup>, Ozan Deveoglu<sup>2</sup> and Recep Karadag<sup>3</sup>

<sup>1</sup>Department of Sociology, Faculty of Arts and Sciences, Izmir Bakircay University, Menemen/İzmir, Turkey <sup>2</sup>Department of Chemistry, Faculty of Science, Cankiri Karatekin University, Merkez/Çankırı, Turkey <sup>3</sup>Department of Fashion and Textile Design, Faculty of Fine Arts, Istanbul Aydin University, İstanbul, Turkey recepkaradag@aydin.edu.tr

> **Available online at: www.isca.in,www.isca.me** Received 18<sup>th</sup> July 2021, revised 18<sup>st</sup> February 2022, accepted 30<sup>th</sup> May 2022

#### Abstract

The madder (Rubia tinctorum L.) plant is the most well-known kinds of the Rubia genus. The plant is 1-2 meters tall, perennial and grows in fertile soils. The root shoots of the plant are natural dye source. From prehistoric times to the end of the 19<sup>th</sup> century, madder has been a dyestuff plant that has played a major role in the development of dyeing. Madder, which grows in Anatolia, Rumelia and many places and is one of the most important natural dye sources, has been a plant that is cultivated and traded. It has been the most essential of the dyeing resources that has been cultivated and traded in the historical process. It has been seen as a result of the obtained data that it is used in such as textiles, paintings and icons as a dye source. Madder, which is used in many fields, has played a significant role in its use and trade, especially in textile dyeing. The madder plant, which is the most known dye plant in natural dyeing, has been important both in dye and medical terms since it is rich in anthraquinone compounds. In this sense, in this study, the agricultural, economic and historical dimensions of the madder plant, which has a remarkable share in terms of agriculture and trade, will be examined and trade, will be examined and discussions will be carried out through various cultures where the madder plant has been used from past to present.

Keywords: Natural dyestuff, madder, agriculture, trade, dyeing.

### Introduction

Dyestuffs used in natural dyeing can be derived from biological resources such as insects, fungi (lichens and fungi), plants and mollusks<sup>1-3</sup>. Of these, plant-derived dyestuffs can be extracted from the leaves, flowers, plant wastes, fruits, stems, roots and branches of the plant<sup>4</sup>. Natural dyestuffs are used not only for coloring food, medicine and cosmetic products, but also for coloring wool, silk, leather and cotton, and in leather and fur. In addition, these dyestuffs were also used to produce inks, pigments and dyes, especially in the past<sup>5-7</sup>. In ancient times, dyestuffs were derived from plant and insect extracts. These dyes mainly include anthraquinones, flavones, flavonols, indigoids, tannins and other related colored compounds<sup>1</sup>. Until the early 1980s, the identification and analysis of natural dyestuffs were practiced by thin layer chromatography (TLC), a chromatographic technique. After the development of high performance liquid chromatography (HPLC), TLC was completely replaced by HPLC. Today, HPLC is one of the basic techniques used to analyze natural dyestuffs<sup>8</sup>. It is also one of the most effective techniques for separating colorants from natural dye extracts. These methods satisfy quantitative and qualitative analysis of natural dye components in historical textiles and natural biological resources. Extraction from textile samples containing natural dyestuffs must be performed before

HPLC analysis. The extraction method depends not only on the color of the dyestuff, but also on the textile material<sup>1</sup>. This extraction method is important for isolating organic dyestuffs from mordant metal in historical and archaeological textile samples<sup>9,10</sup>. Until the end of the 19th century, natural dyestuffs have been the main source of dyes in textile dyeing<sup>11-13</sup>. Natural dyes are more ecological, biosoluble, non-deleterious and less allergen than synthetic dyes<sup>14,15</sup>. Nonetheless, not all natural dyestuffs are environmentally friendly. This may be due to the existence of heavy metals or other toxic elements. Therefore, natural dyes require to be toxicologically examined before use<sup>5</sup>. The flavonoid dyestuff compounds obtained in yellow color have very good light resistance in protein fibers. Likewise, red anthraquinones and indigoids exhibit excellent fastness properties compared to flavonoids. On the other hand, the light resistance of anthraquinones is related to the number of hydroxyl substituent groups. There is an opposite ratio between hydroxyl number and light fastness<sup>16</sup>.

In natural dyeing, there are various sources of plant-based dyestuffs. However, it can be stated that one of the most important botanical dyestuff sources used in natural dyeing is madder. It is known that madder has been used in different fields from ancient times to the present day. In this sense, madder used in natural dyeing should be examined with different dimensions. In this study, the historical, economic and agricultural dimensions of madder will be discussed and the deficiency in the literature will be tried to be eliminated. In this respect, it is thought that this study will enrich the literature since it will examine madder with different dimensions.

# **About Madder**

Madder is a perennial shrub that grows throughout the summer. The upper parts of the plant die in the winter, and in the spring new twigs appear from the twig roots. The plant can grow up to about one and a half meters<sup>17</sup>. The yield obtained from the roots of a three-year-old madder plant is 3-5 tons per hectare, while the dyestuff is in the range of 150-200 kg<sup>2</sup>. Madder plant is an important dye plant. Madder has been famous with the name "Turkish red" or "Edirne red", the color with high fastness and bright, which emerged after a long and grueling natural dyeing process of botanical fiber<sup>18,19</sup>. The red anthraquinone dyes contained in the root dye plant probably contribute to the resistance of the plant against the fungus in the soil<sup>20</sup>. The old roots of the dye plant contain much more dyestuff than the young ones. Almost every region of Turkey is suitable for madder cultivation. The plant grows in shady and wet places. In particular, the plant likes creek beds and chalky-clay, clayey sandy, humus-rich soils<sup>21</sup>. Madder pertains to the "Rubiaceae" family and a herb that gives  $color^{22}$ . It can be said that numerous anthraquinones have been determined in madder so far<sup>23</sup>. The contents and amounts of anthraquinone compounds of madder vary with the age of the plant<sup>24</sup>. The roots of the plant contain approximately 1.9% dyestuff, which exists as glycosides in free form or bound<sup>5</sup>. These roots have been used for the production of red color in the dyeing of textiles since  $1500 \text{ BC}^{23}$ . The dvestuffs used for red colors in the historical process are anthraquinones<sup>25</sup>. All of the anthraquinone-based red dyestuffs fundamentally preferred to be used as mordant were dyestuffs with the carbonyl group forming the fiber-mordantdye complex and the neighbor phenolic  $group(s)^{26}$ . Madder color distilled from the madder has long been preferred as a food additive (widely in confectionery, processed meat and beverages) in Japan and Korea<sup>27</sup>. It can be said that madder plant is a part of mordant dyes which has need for pre-treatment of textile fibers with a mordant liquor (aluminum, iron, tin, chromium, cream tartar and tannins). The most commonly used metal salt is alum and is often used with cream of tartar. With the change of dyeing recipes and the use of different metal salts, a large scale of hues can be acquired, ranging from pink to purple. The dyestuffs of Rubia tinctorum are anthraquinone dyes. One of the main dyestuffs is alizarin (1,2-dihydroxyanthraquinone) and the other is purpurin (1,2,4-trihydroxyanthraquinone). However, other dyes such as xanthopurpurin, pseudopurpurin, munjistin and rubiadin are largely found in glycosidic form<sup>28</sup>. Red, orange, brown and purple tones are obtained with madder. The pigments are formed as insoluble in basic solution, insoluble in water as a metal-dyestuff complex compound<sup>29,30</sup>. The chemical compound of the pigments contingents both upon the plant types, origin, and also upon the

pigment preparation method and the methods used for extraction from plants<sup>29,31</sup>. Madder pigments in ancient paintings have been identified as aluminum cations and anthraquinone complexes<sup>31</sup>. Anthraquinone pigments (for example, derived from madder) have been used extensively by impressionist painters such as Vincent van Gogh<sup>32</sup>. The application areas of madder dyes are presented in Table-1.

Application area	References
Historical textiles	33-39
Textile dyeing	17, 40-46
Natural lake pigment	8, 31, 47-49
Food	50
Cosmetic	51, 52
Pharmaceutical	53, 54
Icons	55-58
Paintings	59-61
Medicine	62-64
Watercolour	65

Table-1: Some Application Areas of Madder Dyes

# Historical, Economic and Agricultural Dimensions of Madder

From antiquity till the exploration of unnatural dyes in the mid-19th century, mineral colorants and mostly natural dyes have had usage in the global economy. When natural dyes are mentioned, madder, which is the most important dye plant in economic terms, comes to mind.

Madder plant is known by various names. Boyacı koku, Bostan otu, Boya koku, Boya cili, Cubuk boya, Boya purcu, Kırmızı kok, Gok boya, Yumurta boyasi, Kizil kok, Kizil gok can be given as examples of these Turkish names<sup>66</sup>.

It can be said that madder is the most used dyestuff source in natural dyeing. Madder, known to be used in the production of purple color in ancient times, had an intense usage area. It has been observed that the madder plant is produced with roots, especially in the interior regions far from the sea, since it is difficult to reach the shellfish such as murex<sup>67</sup>. Madder is a source of reddish lac pigment. In this sense, it has been one of the colorants frequently used in Egyptian mummy portraits. As a pure pigment, madder is red or pink, occasionally slightly purplish in color. It has been observed that madder is mostly emphasized on the lips and face as the main coloring on purple

and red fabrics. The pink or purple fabric of the mummy portraits is strongly emphasized in the pink and purple fabrics and the face (such as the lips and cheeks). This situation makes us think that madder is widely used in these areas. In this sense, it has been seen that both the real fabrics depicted in the mummy portraits are most likely dyed with madder and the main pigment used in the pink fabrics is madder<sup>68</sup>. It has been determined that anthraquinones and their hydroxy-based compounds have had usage as red dyestuffs dated from prehistoric times. In this context, written texts exist about their utilization in Ancient Egypt. By precipitating the dyestuffs in the extract using aluminum salt, the pigments have been prepared and used in paintings<sup>69</sup>.

The roots of madder are natural basis of biological colorant and have been utilized to color textiles in most regions of the world from prehistoric times<sup>70</sup>. In this sense, it can be said that madder extract extracted from the dried roots of Rubia tinctorum has had usage for dyeing textiles from ancient times. Examples of these regions are India, the Middle East and Europe. This herb has also been utilised for the cure of kidney stones and bladder stones. In this regard, madder is also known as a traditional herbal medicine<sup>23,71</sup>.

According to the famous historian Herodotus, Libyan women wore red-coloured dresses with madder and hairless goatskins dyed with red madder<sup>72</sup>. This situation reveals that madder was used in ancient times. Two red sacs were found in an archaeological study in India. It has been determined that these bags are made of cotton fiber and belong to 3000 BC. It is thought that these red colored sacs were painted with madder. A tablet from the 7th century BC mentions that madder was used for the red color. In addition, a sample of felt was found in the same kurgan with the Pazirik carpet that is supposed to be the oldest rug in the world, belonging to 500 BC. It can be said that madder was used in the dyestuff analysis of both of them<sup>73</sup>. Eventually, it was detected that the red part of this carpet, which was found in the Pazirik kurgan in the Altai Mountains in 1949, was dyed with madder and Polish kermes<sup>74</sup>.

It has been observed that madder is also used in silk, wool and linen fiber dyeing and cotton dyeing. This color, which is used to dye cotton red, is known in the world as Edirne red or Turkish  $red^{75}$ .

It is known that the madder plant, which is famous with the name Turkish red and was brought to Italy from the East as unground in some sources, was called Lizari or Alizari. It is thought that this word comes from Ali Zari and this person is also an Iranian. However, historical research has revealed that madder has been known by the Turks for a long time and has been also used in Central Asian dyeing<sup>76</sup>. It can be said that the homeland of madder is most likely Anatolia. However, it has also been observed that it naturally spreads to Iran, the Caucasus, the Himalayas and Central West Asia<sup>73,77,78</sup>.

It can be said that the trade and agriculture of the madder plant have been done since ancient times<sup>77</sup>. The data obtained showed that the madder was traded between the East and the West in the 1st century. Nevertheless, it is thought that the first madder trade was made between Anatolia and India. However, it is known that the madder imported in India is Rubia cordifolia. Madder was extensively cultivated in Upper Mesopotamia, around Damascus and Tripoli, in the oases of Egypt, Andalusia and Carthage. Madder has been exported to Central Asia and the Caucasus. Madder plant was used by the Ancient Greeks, Egyptians and Romans in the Roman period. In fact, it was the Romans who brought this plant to Central Europe for the first time and cultivated it. However, following the collapse of the Roman Empire in the 4th century, the cultivation and trade of madder have been declined<sup>79</sup>.

Madder is a vital dyestuff in dyeing. It is known that the culture of madder has been made in every period. Dyehouses were established in many regions of Anatolia. Besides Bursa, it is seen that it is quite common in places where weaving culture and textile trade is developed such as Istanbul, Tokat, Edirne, Konya, Kayseri, Merzifon, Corum, Sanliurfa, Adana, Kahramanmaras, Malatya, Gaziantep<sup>80</sup>.

It is known that the basis of Turkish red is madder. At the beginning of the 13th century, it can be said that the name of Ancient Philadelphia as Alasehir is related to the city's dyeing. In its early ages, the Ottomans used red a lot by making a banner from Alasehir's kizil ivlâdî. Evliya Celebi claimed that there were 70 dye houses in Aydin and Alasehir, and twenty in Izmir, around the Boyaci creek passing through Basmane<sup>81</sup>. Madder was one of the most grown plants for the manufacture of hand-knotted carpets in Turkey during the Ottoman period. In fact, it has been revealed in the Ottoman records which the world's largest request for madder was provided by Turkey<sup>82</sup>.

Turkish red, which has a great reputation in Europe, was used in silk weavings of Anatolia and Syria, in Izmir carpets and cottons from Macedonia and Thessaly. All these had a positive agricultural impact on root dye in Anatolia and Rumelia<sup>81,83</sup>.

Historically, although madder has been known by many civilizations and has been seen to be traded and produced since ancient times, the increase in the demand for cotton products after the 16th and 17th centuries and the acceleration of textile trade from the East to the West brought the Turkish Red to fame<sup>84</sup>. Madder was specially cultivated and traded in the 16th century. In the 16th century, it was seen that madder was produced in seventeen villages in Manisa, and some taxes were collected in return<sup>85</sup>. Madder was exported to Europe and provided significant income<sup>80</sup>. Madder, which grows almost all over Anatolia, has increased its importance in dyeing with alum, which is abundant in Western Anatolia. A study conducted in 2015 revealed that madder was used to give red color to Persian carpets between the 16th and 18th centuries<sup>86</sup>.

Madder is the most widely used botanical dyestuff in Turkey. Madder has gained a commercial value in exports during the Ottoman period<sup>79</sup>. It has been seen that the red coats of British soldiers and the red trousers of Napoleon's soldiers were dyed with madder in the 18<sup>th</sup> and 19<sup>th</sup> centuries<sup>71</sup>. Turkey, which is seen as the homeland of madder, supplied madder to the world with a high rate of almost 70% in the 18th century<sup>79, 87, 88</sup>. This ratio reveals that madder is in a leading position in exports. That is to say, in the 18<sup>th</sup> century, the concentration of madder on raw materials and the red coloration of cotton fabrics enabled Europeans to demand madder. In this way, madder showed a development towards export-oriented production<sup>84</sup>. It is believed that in the midst of the 19th century, madder came after grain and silk in the Ottoman foreign trade<sup>81</sup>. In the 19th century, it was seen that madder was grown in Plovdiv and its surrounding regions<sup>89</sup>. At the same time, in the 19th century, it was seen that there were tithe records of madder in Temettuat notebooks in Anatolia<sup>90</sup>. After 1850s, experts were brought from Kayseri and Tokat for the production of madder<sup>91</sup>. At this point, the most important buyer of madder was England. In 1860, madder took the second place in the exports of the Ottoman Empire to England with 7.8%, after cereals. 90% of the madder exported from Izmir went to England, 3% to Austria, France and America, and 1% to Rumelia. However, these amounts may vary from year to year. For example, in 1857, 94% of exports went to England, 2.2% to Russia, 1.1% to Austria, and the rest to various countries. Considering, it was seen that 90% of the export of madder in the Ottoman Empire was made from Izmir port<sup>81</sup>. Considering only the madder that came out of Izmir port until 1875, it is seen that the income it provided to the country exceeded 500,000 gold liras. In this sense, it can be said that madder has an important economic place for Turkey.

The necessity of using alum in order to obtain Turkish red from root dye and the existence of alum only in Tashkent in Central Asia reveals that Turkish red dyeing was developed here by the Turks and spread to India from there. This red, which came to Anatolia with migrations and was used by the Turks in Anatolia and then spread to Europe, maintained its value until the beginning of the 20th century<sup>76</sup>.

However, when we look at it, it has been seen that madder, which is one of the main sources of the red dyestuff, is one of the main colors in Persian carpets. Madder has maintained its importance in the 20th century, which was a golden period for the Iranian carpet manufacture and exportation industry<sup>92</sup>.

Madder grows wild in Turkey in provinces such as Demirci, Adiyaman, Konya, Ankara, Gordes, Nigde, Kirsehir, Kayseri, Yozgat, Kahramanmaras, Elazig, Aksaray, Malatya, Amasya, Manisa, Tokat, Canakkale, Corum and Mugla. However, in some regions, madder can also be engaged in agriculture<sup>73</sup>. In this sense, it can be stated that madder is a significant dye plant for our country. It is known that madder lacquer is widely used in handwritten illuminations and paintings, as well as being used as an artistic material today<sup>69</sup>.

# Conclusion

Madder, which is one of the most significant resources of coloring agent in natural dyeing, has had usage in multiple areas such as pigment, fabric dyeing, cosmetics, medicine from antique times. When madder is used in textile dyeing, the textile industry has shown great improvement. Textile trade has developed. Accordingly, economic growth has taken place in places where dyeing is present. This economic growth has had an impact on art and culture. It has provided economic inputs to the countries with the madder trade. In this respect, madder has deeply affected societies and cultures. In the historical process, the use of madder in various fields has had a favourable influence on the economy of societies.

In this study, historical, economic and agricultural dimensions of madder, which is a valuable source of dyestuff, are emphasized. Since this study is a multidisciplinary study, it has approached the subject from different angles. The fact that a multidisciplinary study has not supposably been conducted on this subject before makes this study valuable. It is thought that this study will contribute to the researchers especially studying in this field in terms of examining madder historically, economically and agriculturally. In addition, we think that madder will increase its importance in recent years in terms of being one of the leading re-sustainable dyeings as non-toxic and non-carcinogenic, non-polluting and zero chemical waste. Many textile sectors have already started to use natural dyes again.

### References

- Surowiec, I., Orska-Gawryś, J., Biesaga, M., Trojanowicz, M., Hutta, M., Halko, R., & Urbaniak-Walczak, K. (2003). Identification of natural dyestuff in archeological coptic textiles by HPLC with fluorescence detection. *Analytical Letters*, 36(6), 1211-1229.
- 2. Saxena, S., & Raja, A. S. M. (2014). Natural dyes: sources, chemistry, application and sustainability issues. In S. S. Muthu (Eds.), Roadmap to sustainable textiles and clothing (pp. 37-80). Springer, Singapore.
- **3.** Bukhari, M. N., Shahid-ul-Islam, Shabbir, M., Rather, L. J., Shahid, M., Khan, M. A., & Mohammad, F. (2017). Effect of binary and ternary combination of metal salt mordants on dyeing and fastness properties of natural protein fibre with Juglans regia L. Dye. *Journal of Natural Fibers*, 14(4), 519-529.
- **4.** Aydin, A. H., Guzel, F., & Tez, Z. (1996). Investigation of adsorption isotherms used for wool dyeing by aqueous extraction of cehri fruit (fructus rhamni petiolari) and dyeing of wool and silk accompanied by various mordants. *Turkish Journal of Chemistry*, 20(4), 283-288.
- 5. Samanta, A. K., & Agarwal, P. (2009). Application of natural dyes on textiles. *Indian Journal of Fibre & Textile Research*, 34(4), 384-399.

Research Journal of Agriculture and Forestry Sciences\_ Vol. 10(3), 16-23, July (2022)

- 6. Gulrajani, M. L. (2001). Present status of natural dyes. Indian Journal of Fibre & Textile Research, 26(1-2), 191-201.
- Acquaviva, S., D'Anna, E., De Giorgi, M. L., Della Patria, A., & Baraldi, P. (2010). Physical and chemical investigations on natural dyes. *Applied Physics A*, 100(3), 823-828.
- Clementi, C., Doherty, B., Gentili, P. L., Miliani, C., Romani, A., Brunetti, B. G., & Sgamellotti, A. (2008). Vibrational and electronic properties of painting lakes. *Applied Physics A*, 92(1), 25-33.
- **9.** Zarkogianni, M., Papliaka, Z. E., & Tsatsaroni, E. (2009). Identification and quantitative determination of madder by high performance liquid chromatography: Application to historical textiles. *Journal of Liquid Chromatography & Related Technologies*, 32(16), 2334-2345.
- **10.** Karadag, R. (2014). Some non-destructive and microanalytical methods for the conservation on textiles from cultural heritage. In Proceedings of the 19th International Conference on Cultural Heritage and New Technologies, Vienna, 1-12.
- Peggie, D. A., Hulme, A. N., McNab, H., & Quye, A. (2008). Towards the identification of characteristic minor components from textiles dyed with weld (Reseda luteola L.) and those dyed with Mexican cochineal (Dactylopius coccus Costa). *Microchimica Acta*, 162(3), 371-380.
- Kumaresan, M., Palanisamy, P. N., & Kumar, P. E. (2012). Dyeing of cotton fabric with eco-friendly natural dyes using single mordants: Comparison of fastness properties and colour strength. Universal Journal of Environmental Research & Technology, 2(4), 280-285.
- **13.** Colombini, M. P., Andreotti, A., Baraldi, C., Degano, I., & Łucejko, J. J. (2007). Colour fading in textiles: A model study on the decomposition of natural dyes. *Microchemical Journal*, 85(1), 174-182.
- 14. Ali, S., Nisar, N., & Hussain, T. (2007). Dyeing properties of natural dyes extracted from eucalyptus. Journal of the Textile Institute, 98(6), 559-562.
- **15.** Kamel, M. M., Abdelghaffar, F., & El-Zawahry, M. M. (2011). Eco-friendly dyeing of wool with a mixture of natural dyes. *Journal of Natural Fibers*, 8(4), 289-307.
- **16.** Crews, P. C. (1987). The fading rates of some natural dyes. *Studies in Conservation*, 32(2), 65-72.
- 17. Karadag, R., & Dolen, E. (2007). Reexamination of Turkey red. *Annali di Chimica*, 97(7), 583-589.
- **18.** Onal, A. (1996). Extraction of dyestuff from madder plant (Rubia tinctorum L.) and dyeing of wool, feathered-leather and cotton. *Turkish Journal of Chemistry*, 20(3), 204-213.
- **19.** Dolen, E. (1992). Tekstil tarihi: Dünyada ve Türkiye'de tekstil teknolojisinin ve sanayiinin tarihsel gelişimi.

Marmara Üniversitesi Teknik Eğitim Fakültesi Yayınları No: 92/1, Istanbul.

- 20. Derksen, G. C. H., & Van Beek, T. A. (2002). Rubia tinctorum L. *Studies in Natural Products Chemistry*, 26, 629-684.
- **21.** Kayabasi, N., & Dellal, G. (2004). Koyun ırklarından elde edilen yünlerin kökboya (Rubia tinctorum L.) ile verdikleri renklerin ışık haslık değerleri üzerine bir araştırma. *Yüzüncü Yıl Üniversitesi Ziraat Fakültesi Tarım Bilimleri Dergisi*, 14(2), 79-83.
- **22.** Cuoco, G., Mathe, C., Archier, P., Chemat, F., & Vieillescazes, C. (2009). A multivariate study of the performance of an ultrasound-assisted madder dyes extraction and characterization by liquid chromatographyphotodiode array detection. *Ultrasonics Sonochemistry*, 16(1), 75-82.
- **23.** Baghalian, K., Maghsodi, M., & Naghavi, M. R. (2010). Genetic diversity of Iranian madder (Rubia tinctorum) populations based on agro-morphological traits, phytochemical content and RAPD markers. *Industrial Crops and Products*, 31(3), 557-562.
- 24. Ferreira, E. S., Hulme, A. N., McNab, H., & Quye, A. (2004). The natural constituents of historical textile dyes. *Chemical Society Reviews*, 33(6), 329-336.
- **25.** Berrie, B. H. (2009). An improved method for identifying red lakes on art and historical artifacts. Proceedings of the National Academy of Sciences of the United States of America, 106(36), 15095-15096.
- **26.** Rosenberg, E. (2008). Characterisation of historical organic dyestuffs by liquid chromatography–mass spectrometry. *Analytical and Bioanalytical Chemistry*, 391(1), 33-57.
- 27. Inoue, K., Yoshida, M., Takahashi, M., Fujimoto, H., Ohnishi, K., Nakashima, K.,... & Nishikawa, A. (2009). Possible contribution of rubiadin, a metabolite of madder color, to renal carcinogenesis in rats. *Food and Chemical Toxicology*, 47(4), 752-759.
- **28.** Clementi, C., Nowik, W., Romani, A., Cibin, F., & Favaro, G. (2007). A spectrometric and chromatographic approach to the study of ageing of madder (Rubia tinctorum L.) dyestuff on wool. *Analytica Chimica Acta*, 596(1), 46-54.
- **29.** Yildiz, Y., Gunes, A., Yalcin, B., & Karadag, R. (2013). Natural pigments from the gall oak (Quercus infectoria Olivier) shellac. *Asian Journal of Chemistry*, 25(12), 6881-6884.
- **30.** Deveoglu, O., Karadag, R., & Yurdun, T. (2009). Preparation and HPLC analysis of the natural pigments obtained from Buckthorn (Rhamnus petiolaris Boiss) dye plants. *Jordan Journal of Chemistry*, 4(4), 377-385.
- **31.** Sanyova, J., & Reisse, J. (2006). Development of a mild method for the extraction of anthraquinones from their

aluminum complexes in madder lakes prior to HPLC analysis. *Journal of Cultural Heritage*, 7(4), 229-235.

- **32.** Melo, M. J. (2009). History of natural dyes in the ancient mediterranean world. In T. Bechtold, & Mussak, R. (Eds.), Handbook of Natural Colorants (pp. 3-20). Wiley, United Kingdom.
- **33.** Karadag, R., & Yurdun, T. (2010). Dyestuff and colour analyses of the Seljuk carpets in Konya Ethnography Museum. *Studies in Conservation*, 55(sup2), 178-183.
- 34. Karadag, R., Yurdun, T., & Dolen, E. (2010). Identification of natural red dyes in 15-17th centuries Ottoman silk textiles (kaftans, brocades, velvets and skullcaps) by HPLC with diode array detection. *Asian Journal of Chemistry*, 22(9), 7043-7056.
- **35.** Liu, J., Mouri, C., Laursen, R., Zhao, F., Zhou, Y., & Li, W. (2013). Characterization of dyes in ancient textiles from Yingpan, Xinjiang. *Journal of Archaeological Science*, 40(12), 4444-4449.
- **36.** Karadag, R., Torgan, E., Taskopru, T., & Yildiz, Y. (2015). Characterization of dyestuffs and metals from selected 16– 17th-century Ottoman silk brocades by RP-HPLC-DAD and FESEM-EDX. *Journal of Liquid Chromatography & Related Technologies*, 38(5), 591-599.
- **37.** Ahmed, H. E., Tahoun, I. F., Elkholy, I., Shehata, A. B., & Ziddan, Y. (2017). Identification of natural dyes in rare Coptic textile using HPLC-DAD and mass spectroscopy in museum of Faculty of Arts, Alexandria University, Egypt. *Dyes and Pigments*, 145, 486-492.
- Ding, L., Gong, T., Wang, B., Yang, Q., Liu, W., Pemo, R., & Metok, T. (2021). Non-invasive study of natural dyes in textiles of the Qing Dynasty using fiber optic reflectance spectroscopy. *Journal of Cultural Heritage*, 47, 69-78.
- **39.** Liu, J., Li, W., Kang, X., Zhao, F., He, M., She, Y., & Zhou, Y. (2021). Profiling by HPLC-DAD-MSD reveals a 2500-year history of the use of natural dyes in Northwest China. *Dyes and Pigments*, 187, 109143.
- Deveoglu, O., Sahinbaskan, B. Y., Torgan, E., & Karadag, R. (2012). Investigation on colour, fastness properties and HPLC- DAD analysis of silk fibres dyed with Rubia tinctorium L. and Quercus ithaburensis Decaisne. *Coloration Technology*, 128(5), 364-370.
- **41.** Karadag, R., Torgan, E., & Erkan, G. (2014). Dyeing properties and analysis by RP-HPLC-DAD of silk fabrics dyed with madder (Rubia tinctorum L.). *Journal of Textile Science and Engineering*, 4(2), 1-5.
- **42.** Sadeghi-Kiakhani, M. (2015). Eco-friendly dyeing of wool and nylon using madder as a natural dye: Kinetic and adsorption isotherm studies. *International Journal of Environmental Science and Technology*, 12(7), 2363-2370.
- **43.** Ozer, L. M., Karadag, R., & Torgan, E. (2016). Investigation of the effect of Turkey red oil on colour,

fastness properties and HPLC-DAD analysis of silk fabrics dyed with madder (Rubia tinctorium L.) and gall oak. *Tekstil ve Mühendis*, 23(103), 197-204.

- **44.** Alkan, R., Torgan, E., & Karadag, R. (2017). The investigation of antifungal activity and durability of natural silk fabrics dyed with madder and gallnut. *Journal of Natural Fibers*, 14(6), 769-780.
- **45.** Jahangiri, A., Ghoreishian, S. M., Akbari, A., Norouzi, M., Ghasemi, M., Ghoreishian, M., & Shafiabadi, E. (2018). Natural dyeing of wool by madder (Rubia tinctorum L.) root extract using tannin-based biomordants: Colorimetric, fastness and tensile assay. *Fibers and Polymers*, 19(10), 2139-2148.
- **46.** Guzel, E. T., Karadag, R., & Alkan, R. (2020). Durability, antimicrobial activity and HPLC analysis of dyed silk fabrics using madder and gall oak. *Journal of Natural Fibers*, 17(11), 1654-1667.
- **47.** Karadag, R., Torgan, E., & Yurdun, T. (2010). Formation and HPLC analysis of the natural lake pigment obtained from madder (Rubia tinctorum L.). *Reviews in Analytical Chemistry*, 29(1), 1-12.
- **48.** Campanella, B., Grifoni, E., Hidalgo, M., Legnaioli, S., Lorenzetti, G., Pagnotta, S., ... & Palleschi, V. (2018). Multi-technique characterization of madder lakes: A comparison between non-and micro-destructive methods. *Journal of Cultural Heritage*, 33, 208-212.
- **49.** Mazzitelli, J. B., Mathe, C., & Vieillescazes, C. (2019). Decomplexing madder lakes using oxalic acid: A novel method coupled with microwave or ultrasound processes. *Comptes Rendus Chimie*, 22(5), 428-434.
- **50.** Inoue, K., Yoshida, M., Takahashi, M., Shibutani, M., Takagi, H., Hirose, M., & Nishikawa, A. (2009). Induction of kidney and liver cancers by the natural food additive madder color in a two-year rat carcinogenicity study. *Food and Chemical Toxicology*, 47(1), 184-191.
- **51.** Shahi, Z., Mehrizi, M. K., & Hadizadeh, M. (2017). A review of the natural resources used to hair color and hair care products. *Journal of Pharmaceutical Sciences and Research*, 9(7), 1026-1030.
- **52.** Yusuf, M., Shabbir, M., & Mohammad, F. (2017). Natural colorants: Historical, processing and sustainable prospects. *Natural Products and Bioprospecting*, 7(1), 123-145.
- **53.** Nejad, H. E., & Nejad, A. E. (2013). Rubia tinctorum L.(Rubiaceae) or madder as one of the living color to dyeing wool. *International Journal of Advanced Biological Biomedical Research*, 1(11), 1315-1319.
- Sanli, H. S., & Gok, E. C. (2017). Bitkisel boyacılıkta kökboyanın (Rubia tinctorum L.) önemi. Uluslararası Sosyal Araştırmalar Dergisi, 10(48), 772-778.
- **55.** Burgio, L., Clark, R. J. H., & Theodoraki, K. (2003). Raman microscopy of Greek icons: Identification of

unusual pigments. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59(10), 2371-2389.

- 56. Karapanagiotis, I., Valianou, L., Daniilia, S., & Chryssoulakis, Y. (2007). Organic dyes in Byzantine and post-Byzantine icons from Chalkidiki (Greece). *Journal of Cultural Heritage*, 8(3), 294-298.
- 57. Karapanagiotis, I., Minopoulou, E., Valianou, L., Daniilia, S., & Chryssoulakis, Y. (2009). Investigation of the colourants used in icons of the Cretan School of iconography. *Analytica Chimica Acta*, 647(2), 231-242.
- Valianou, L., Wei, S., Mubarak, M. S., Farmakalidis, H., Rosenberg, E., Stassinopoulos, S., & Karapanagiotis, I. (2011). Identification of organic materials in icons of the Cretan School of iconography. *Journal of Archaeological Science*, 38(2), 246-254.
- **59.** Pinto, M., Gill, M. S., Georgakopoulou, M., & Menon, S. (2018). Examination of 14–15<sup>th</sup> century Buddhist wall paintings from a cave complex in Saspol, Ladakh. *Journal of Archaeological Science: Reports*, 21, 259-267.
- Holakooei, P., Karimy, A. H., Saeidi-Anaraki, F., Vaccaro, C., Sabatini, F., Degano, I., & Colombini, M. P. (2020). Colourants on the wall paintings of a mediæval fortress at the mount Sofeh in Isfahan, central Iran. *Journal of Archaeological Science: Reports*, 29, 102065.
- **61.** Cakmak, Y., Karadag, R., Apohan, N., Aral, Ö. Y., & Cakmakci, E. (2021). Characterization of the alphabet reform painting. *Journal of the Turkish Chemical Society Section A: Chemistry*, 8(1), 249-262.
- **62.** Altenhofer, P., & Vankar, P. S. (2017). Identification of natural madder and indigo dyes by novel HPTLC method. *Chromatography and Separation Techniques Journal*, 1(1), 113.
- **63.** Nartop, P. (2018). Green sterilization of Rosmarinus officinalis L. stem surfaces with silver nanoparticles synthesized using Rubia tinctorum L. cell culture extracts. *Iranian Journal of Science and Technology, Transactions A: Science*, 42(6), 411-414.
- **64.** Marhoume, F. Z., Aboufatima, R., Zaid, Y., Limami, Y., Duval, R. E., Laadraoui, J., ... & Bagri, A. (2021). Antioxidant and polyphenol-rich ethanolic extract of Rubia tinctorum L. prevents urolithiasis in an ethylene glycol experimental model in rats. *Molecules*, 26(4), 1005.
- **65.** Wang, B., Hui, Y., Bovyn, G., & Caen, J. M. A. (2018). In situ investigation of Chinese export watercolours in the nineteenth century: Pigments and dyes. *Journal of the Institute of Conservation*, 41(3), 218-234.
- **66.** Canatar, M. (1998). Osmanlılarda bitkisel boya sanayii ve boyahaneler üzerine. *Osmanlı Araştırmaları*, 18(18).
- **67.** Adiguzel, G., & Kolancı, B. Y. (2017). Antikçağda statünün rengi: Mor. Cedrus. 5, 261-285.

- **68.** Newman, R., & Gates, G. A. (2020). The Matter of madder in the ancient world. M. Svoboda, & Cartwright, C. R. (Eds.), Mummy Portraits of Roman Egypt: Emerging Research from the APPEAR Project. Getty Publications, Los Angeles. pp. 24-33.
- **69.** Claro, A., Melo, M. J., Schäfer, S., de Melo, J. S. S., Pina, F., van den Berg, K. J., & Burnstock, A. (2008). The use of microspectrofluorimetry for the characterization of lake pigments. *Talanta*, 74(4), 922-929.
- **70.** Derksen, G. C. H., Lelyveld, G. P., van Beek, T. A., Capelle, A., & de Groot, Æ. (2004). Two validated HPLC methods for the quantification of alizarin and other anthraquinones in Rubia tinctorum cultivars. *Phytochemical Analysis*, 15(6), 397-406.
- **71.** Jäger, I., Hafner, C., Welsch, C., Schneider, K., Iznaguen, H., & Westendorf, J. (2006). The mutagenic potential of madder root in dyeing processes in the textile industry. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, 605(1-2), 22-29.
- **72.** Yildiz, N. (1993). Eski Çağda Deri Kullanımı ve Teknolojisi, Marmara Üniversitesi Fen Edebiyat Fakültesi Yayınları, İstanbul.
- 73. Karadag, R. (2007). Doğal Boyamacılık, Dösim, Ankara.
- **74.** Etikan, S. (2011). Doğal boya geleneğinin Türk halı sanatında yeri ve önemi üzerine bir değerlendirme, Türk Sanatları Araştırmaları Dergisi. 1(1), 11-16.
- **75.** Karadag, R. (1997). Türk halı ve kumaşlarında kullanılan doğal boyarmaddeler. *Arış Dergisi*, 1(2), 38-51.
- **76.** Imer, Z. (1999). Türklerin dokuma sanatında boyacılık. *Erdem*, 10(29), 331-354.
- 77. Erkan, G., Sengul, K., & Kaya, S. (2010). Denim kumaşların Rubia tinctorum L. (kökboya) ile boyanması üzerine bir araştırma. *Tekstil ve Mühendis*, 17(80), 1-10.
- 78. Yeniocak, M., Goktas, O., Ozen, E., Colak, M., Ugurlu, M., & Yeniocak, S. (2015). Kökboya ile renklendirilen ağaç malzemenin yıkanma performanslarının incelenmesi. *Selçuk Üniversitesi Teknik Online Dergisi*, 14(2), 304-323.
- **79.** Genc, M. (2014). Başbakanlık Osmanlı arşiv belgelerinde kökboya ve cehri ile ilgili bazı kayıtlar. Art-e Sanat Dergisi, 7(13), 174-212.
- **80.** Okca, A. K., & Genc, M. (2015). Anadolu halı ve kilimlerinde renk. *Sosyal Bilimler Dergisi*, 2(4), 235-246.
- 81. Baykara, T. (1998). Kökboya. Arış Dergisi, (4), 64-71.
- **82.** Baydar, H., & Karadogan, T. (2006). Agronomic potential and industrial value of madder (Rubia tinctorum L.) as a dye crop. *Turkish Journal of Agriculture and Forestry*, 30(4), 287-293.

- **83.** Dogan, Y., Baslar, S., Mert, H. H., & Ay, G. (2003). Plants used as natural dye sources in Turkey. Economic Botany, 57(4), 442-453.
- **84.** Yildirim, L. (2014). Avrupa tekstil baskıcılığının gelişiminde Türk Kırmızısı' nın rolü. Yedi: Sanat, Tasarım ve Bilim Dergisi, (12), 11-22.
- 85. Kaya, M. K., & Basol, S. (2017). Osmanlı Bursa'sında Ermeni kökçü esnafi Hirfet Vakfı. Vakıflar Dergisi, (47), 25-44.
- **86.** Shibayama, N., Wypyski, M., & Gagliardi-Mangilli, E. (2015). Analysis of natural dyes and metal threads used in 16th-18th century Persian/Safavid and Indian/Mughal velvets by HPLC-PDA and SEM-EDS to investigate the system to differentiate velvets of these two cultures. Heritage Science, 3(1), 1-20.
- **87.** Demir, M., Celik, S., & Noyan, O. F. (2010). Türkiye'de yetişen bazı önemli boya bitkilerinin üretim teknikleri ve elde edilen renklerin haslık dereceleri. III. Ulusal Karadeniz Ormancılık Kongresi, III, 1187-1196.

- **88.** Cebeci, D. T. (2020). Dokumacılık sanatında kullanılan bazı doğal boyarmaddeler ve özellikleri. İdil Sanat ve Dil Dergisi, 9(68), 657-674.
- 89. Tekdemir, A. (2015). 19. yüzyılın ikinci yarısında Meriç Nehri'nde vapur işletme imtiyazı. In S. Batmaz & Tok, O. (Eds.), Osmanlı Devleti' nde Nehirler ve Göller 1 (pp. 643-659). Not Yayınları, Kayseri.
- **90.** Yigit, I., & Yucedag, C. (2020). XIX. yüzyıl Anadolu'sunda tarımsal ürün çeşitliliği. Doğu Coğrafya Dergisi, 25(43), 209-236.
- **91.** Yazici, O. K. (2019). 19. yüzyılda Osmanlı Devleti'nde cehri üretimi. Asia Minor Studies, 7(1), 24-33.
- **92.** Chahardoli, Z., Berghe, I. V., & Mazzeo, R. (2019). Twentieth century Iranian carpets: Investigation of red dye molecules and study of traditional madder dyeing techniques. Heritage Science, 7(1), 1-17.