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A REVIEW ON ANATOLIAN BUCKTHORN (*Rhamnus petiolaris* Boiss) AS A NATURAL DYE SOURCE

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ABSTRACT

The buckthorn plant (*Rhamnus petiolaris* Boiss) which is a dye plant has been examined in this study. The information about the plant was given. The natural dyes present in the plant were mentioned. The dyes present in the berries of the plant are mostly flavonoids, namely quercetin, rhamnetin, kaempferol, isorhamnetin, rhamnazin, and rhamnocitrin. One anthraquinone – emodin is also present in the berries. Besides, in the parts of yellow coloured of some historical textiles, the use of the buckthorn was determined. However, the yellow coloured parts were partially dyed with the buckthorn plant. Generally, in the yellow coloured parts of the historical textiles, the use of weld (*Reseda luteola* L.) plant was determined. Apart from these, nowadays there are some works concerning obtaining the lake pigments (including buckthorn lakes). The flavonoids present in the dried berries of the plant are metal chelating agent.

KEYWORDS: *Rhamnus petiolaris* Boiss, rhamnetin, quercetin, natural dye, flavonoid

1. INTRODUCTION

The buckthorn also known as altin agaci, alacehir, boyaci dikeni and akdiken is a thorny or small tree growing up to 3 meters. The plant grows at highland, hilly, rocky, sunny slopes and in sides or under rare the jungle 1000 and 1300 meters in height. The plant has twenty-two kinds in Turkey. Though some of these kinds are not defoliate, the kind of *Rhamnus petiolaris* is defoliated. The plant blossoms small yellow-green coloured in May and June months. After the seeds (berries) remain as green for a long time, they turn to brown or black colour. As the outer shell of the berries is the brown coloured, the inside of the berries is the yellow coloured. This shell is six and seven milimeters in diameter. *Rhamnus petiolaris* grows as endemic in the Central Anatolia. The buckthorn is a plant growing in the mild and hot regions in the world. The cities growing of the buckthorn in the Anatolia are as follows: Kayseri, Corum, Gaziantep, Sinop, Afyon, Usak, Yozgat, Tokat, Nevsehir, Nigde, Ankara, Maras and Konya.

2. LITERATURE REVIEW

According to the results of the dye analysis, the buckthorn dyes were determined as a dye source in the yellow coloured parts of a lot of the Anatolia carpets woven in the 15^{th} - 17^{th} centuries. Until the beginning of the 20^{th} century, the plant was exported to a lot of countries of the world from the Anatolia to dye wool and silk fibers. An important kind non-growing in Turkey of the buckthorn is *Rhamnus saxatilis*. The berries of this plant have been widely used in the dyeing of wool and silk in the Europe as a dye source for a long time. The dried *Rhamnus saxatilis* berries have been exported to Europe from Iran for many years. In the Ottoman textiles in the 16^{th} century, in the yellow and green coloured part of the textiles, the buckthorn was used. The buckthorn was an important dye plant in the 19^{th} century. The kind of *Rhamnus petiolaris* was cultivated in the 20^{th} century. In the first samples of Hereke carpets, the buckthorn was usually used in the parts of the yellow coloured [1-6].

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Figure 1.The view of Anatolian buckthorn (Rhamnus petiolaris Boiss) plant

In Figure 1, the view of Anatolian buckthorn (*Rhamnus petiolaris* Boiss) plant was given.

The buckthorn plant has been used since the period of the Hittites in Anatolia [7].

This dye plant was exported to Europe from Anatolia for a long time [8].

The culture of the plant was realized in around Ankara and Afyon [9].

The branch peels of this plant were used as purgative and antiseptic in Anatolia [10].

The berries of *Rhamnus petiolaris* Boiss contain rhamnetin, quercetin, kaempferol aglycones together with smaller quantities of isorhamnetin, rhamnazin, rhamnocitrin as flavonoids and minor amounts of anthraquinones, mainly emodin. In orchards in Turkey, the cultivation of the plant was performed [11,12].

The most important dye plants in terms of dyeing with the buckthorn are as follows: *Rhamnus petiolaris, Rhamnus saxatilis, Rhamnus cathartica, Rhamnus tinctoria* and *Rhamnus infectoria*. The buckthorn berries have been also used as colourant in the foodstuffs in the past and in the production of the medicine also at the present time. Because of anthracene substances present in the plant, the use of it was not forbidden in food matters in the some Europe countries in the late years [13,14].

In 1999, Karadag analysed some 16th century Ottoman silk brocades by thin layer chromatography (TLC) and spectrophotometric methods. According to the results, the yellow coloured part alone was not dyed (together with *Reseda luteola* L.) with the buckthorn (*Rhamnus petiolaris* Boiss) plant in art object number 13/1631. In this yellow coloured sample, quercetin, rhamnetin and emodin were determined [15].

In 2009, Deveoglu et al. produced the natural pigments from the buckthorn berries via metal salts such as Al^{3+}, Fe^{2+} and Sn^{2+} in the solid state. These pigments were hydrolysed with hydrochloric acid / methanol / water (2:1:1; v/v/v). According to the hydrolysates, in the aluminium buckthorn pigment, rhamnetin and emodin were identified. Whereas, emodin was determined in the iron-buckthorn and the tin-buckthorn pigments. In the non-hydrolysed buckthorn extract, quercetin, rhamnetin and emodin were identified. Rhamnetin and emodin were determined in the acid hydrolysed buckthorn extract [16].

According to the work published in 2012, Deveoglu et al. determined quercetin-3-arabinosid and possible quercetin glucosides in the non-hydrolysed *Rhamnus petiolaris* extract. In the acid hydrolysed extract, rhamnetin, isorhamnetin (flavonoids) and emodin (anthraquinone) were identified. In the acid hydrolysed alum-mordanted buckthorn dyed wool extract, rhamnetin and isorhamnetin were determined [17].

In 2013, the according to the work realizing on dyeing silk with buckthorn and walloon oak, Deveoglu et al. identified quercetin, kaempferol or isorhamnetin, rhamnetin, rhamnazin (dimetylquercetin) and emodin in the acid hydrolysed buckthorn extract [18]

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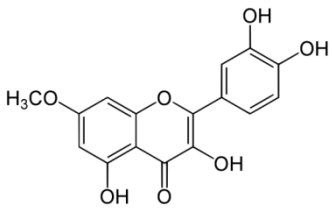
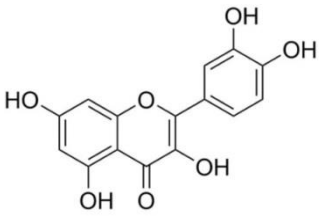
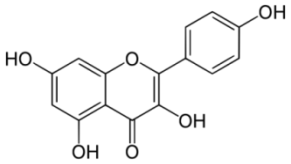


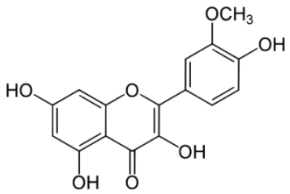
Rhamnetin



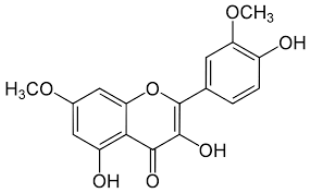
Quercetin



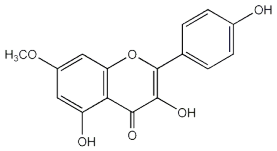
Kaempferol



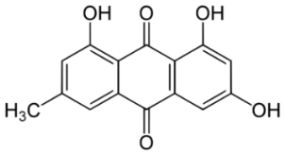
Isorhamnetin



Rhamnazin



Rhamnocitrin



Emodin

Figure 2. The natural dyes present in Rhamnus petiolaris Boiss [11,19]

In Figure 2, the natural dyes present in *Rhamnus petiolaris* Boiss plant were given.

The berries of the buckthorn plant are an old Turkish dye source. The natural dyes (such as flavonoids and anthraquinones) are effective metal ion chelators. These dyes can form chelate with metal ions such as aluminium (III), iron (II), tin (II) ions [16, 20, 21].

From the dyes present in the berries of the buckthorn, yellow, green, beige and khaki colours can be obtained with using of various mordants such as alum, bluestone, sulfric acid, common salt, bichromate, lime and tin salts. The buckthorn has been used in Yahyalı carpets in Kayseri city of Turkey at the present time. Kayseri in Anatolia in the 19th century was an optimum place in terms of the most and the best superior quality growing product [7].

The buckthorn dye plant was especially used to dye fibre and fabric in the period of the Ottoman [22].

Dye extraction from historical textiles was realized according to the previously described methods [23,24]

Erkan et al. analysed the silk fabrics dyed with the buckthorn (*Rhamnus petiolaris* Boiss) as chromatographic and colorimetric in 2014. In this study, the dyeings were performed in a dye-bath ratio of 33:1 at 65°C for 60 min. According to the HPLC analysis results in the study, in the unmordanted silk fabric extract (directly

buckthorn-dyed silk), rhamnetin, isorhamnetin, and emodin were identified. Whereas, in the buckthorn-dyed silk fabric extract (1 % mordant), quercetin, rhamnetin, isorhamnetin and emodin were determined. In addition, in the buckthorn-dyed silk fabric extract (4 % mordant), quercetin, kaempferol, isorhamnetin, rhamnetin and emodin were identified [25].

According to the study published in 2015, in the one post-Byzantine and two Ottoman textiles, yellow dyes were determined. For the colouring of textiles, one of the used dye plants was buckthorn plant [26].

Kahraman and Karadag analysed some 16th-19th century Ottoman silk brocades (belonging to the Topkapi Museum) to identify natural dyes by HPLC-DAD in 2017. The yellow coloured part in art object number 13/574 could be dyed with *Rhamnus petiolaris* Boiss plant. Besides, the HPLC analysis results showed that rhamnetin, isorhamnetin and emodin were identified in the extract which includes the colouring dyes [27].

In 2018, Zhao et al. characterized glycosylated flavonols in the extract of *Rhamnus petiolaris* by HPLC-PDA-MS. The main dye compound is rhamnetin-3-*O*-rhamninoside for *R. petiolaris*. The natural yellow dye used in the wall cloth in the Palace Museum can be determined as *R. petiolaris* or a closely related species [28].

To the buckthorn in the notes of the voyagers passing from Anatolia was encountered. In the work written by Vitale Cuinet (a French diplomat), the information about the buckthorn was mentioned [29].

Rhamnus berries were mentioned in German manuals to be used in the dyeing of textiles and the preparation of the coloured lake pigments during the Middle Ages [30].

The buckthorn together with other dye plants (madder or saffron) was taken an important place throughout the world up to the last of 19th century [31].

The past of the buckthorn in the Anatolia goes back rather. The buckthorn is an important dye plant. It is not coincidence that its growing regions are usually places improving the carpet industry and the weaving. During the dyeing, the berries approximately lose the half of their weight. The product being given by the plant changes according to the place, year and tree [32].

The berries of the buckthorn give a greenish-yellow colour with alum. The juice obtaining from the buckthorn berries was also used as a water colour pigment in miniature paintings and illuminated manuscripts. We can see over 100 species of shrubs or trees concerning to the genus *Rhamnus*, family Rhamnaceae [33].

The berries of the buckthorn plant were commonly used in the dyeings in the past and cultivated in Turkey. Böhmer defined this dye in his work and analyses of Turkish carpets. We can see the sample of 15th century prayer rug in the Türk ve Islam Eserleri Müzesi in Istanbul. In order to get the different tonnes of green, this dye is mostly used with woad or indigo blues in Turkish carpets [34].

3. CONCLUSION

The dried buckthorn berries are natural dye source to obtain yellow colour. Flavonoids (flavones and flavonols) are main chromophores in the most commonly used yellow dyes. If these dye plants (for example, buckthorn) which are annual or bi-annual are not collected, they return to soil.The plants using in the natural dyeing are naturally growing plants in that region. After the dyeings with dye plants, the used plant residues mix soil again as natural manure at the time under one year. The berries of this plant contain mostly flavonoid dyes except emodin – an anthraquinone. These dye molecules are metal chelating agents. The dyeings with this dye plant are realized in the literature. Besides, the natural pigments (lake pigments) with using mordant metal salts (Al, Fe, Sn, *etc*.) with the extract of this plant were obtained. These pigments can especially be used for wall paintings and historical manuscripts.

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