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Saffron Petals, a By-Product for Dyeing of Wool Fibers

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ABSTRACT

Nowadays, natural dyes obtained from bioresources are significantly used in many applications such as textile and carpet industry. As a natural dye, saffron petals are used in this study for dyeing wool fibers. A series of dyeing formulations were prepared with saffron petals and different mordants. The mordant effect on hue, light and wash fastness of dyed fibers was investigated. The results showed that varied hues from light yellow to light brown were obtained. It was found that the best mordants in this study to improve wash and light fastness of dyed fibers were $FeSO_4$ and $Na_2Cr_2O_7$. Prog. Color Colorants Coat. 5(2012), 75-84. © Institute for Color Science and Technology.

1. Introduction

Recently, many articles on natural dyes in textile coloration have been published. Natural dyes are environmental friendly, biodegradable, and non-toxic. Dyes and pigments derived from natural sources such plants (leaves, stems, fruits, seeds, flower heads, bark, root, etc) animal (Lac, Cochineal and kermes) and mineral (prussion blue, red ochre and ultramarine blue) for coloring materials have been used for centuries [1-7].

Dyes are substantive or adjective. Substantive dyes are absorbed and fixed by chemical bonds within the fibers without further chemical treatment. However, most natural dyes are adjective dyes and need the use of mordants to help their absorption and fixing on fibers.

Metal salts act as chemical bonds between the dye molecules and the functional groups of the fibers, and generally change the color produced by the dye. In wool fibers, there are numerous ways in which a mordant can bind to the fiber. It may make chemical links either to the terminal -NH_2 or -COOH groups of the polypeptide chain or to the functional groups present in the side chains of the component amino acids. Mordants are most commonly used on the fiber before dyeing (pre-mordanting) but they can also be used during (simultaneous mordanting) and after dyeing (after-mordanting). Assistant materials such as cream of tartar (potassium hydrogen tartarate), oxalic acid, acetic acid,

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formic acid etc. may be used in addition to dyes and mordants to change the pH in order to brighten colors, and to help the absorption of the mordant metal [8-15].

Historically, saffron was particularly important as a dye plant. Crocus sativus L., commonly known as Saffron, is a perennial meadow grass belonging to Iridaceae family. Saffron is considered to be the most precious and expensive spice in the world. Today, the greatest saffron producing countries are Iran, Greece, Spain, Turkey, India, and Morocco. Iran has 50000 hectares area (90% of the total world harvest areas) of saffron. Saffron flower is divided into three main parts; namely, stigma, petal and anther. The flower has 3 petals and 3 sepals as shown in Figure 1.

According to statistics, in each kg of harvested fresh flower, there are 2,170 flowers, and therefore 13,020 petals and sepals. The processing of every 78 kg of fresh flowers results in 1 kg of dried saffron (stigma). So, considering the production of about 170 tones of dried saffron in Iran, there are approximately 173 trillion petals and sepals. Thus, Saffron petal is one of the by-products of fields great amount of which is thrown away after harvesting while they can possibly be used. As saffron petal is cheaper than its stigma, there will be economical interests for further studies by carpet industry. Saffron petals contain Phenolic compounds, and flavonoides and anthocyanins are among phenolic compounds. So, saffron petals are a bioresource rich in flavonoids and can be used as a potential source of dietary flavonoids. Flavonoids are naturally occurring polyphenolic compounds used as food supplements. Nowadays, most usage of saffron petals is as a source of an organic matter in soil. Hence, researchers use saffron petals for the germination and growth of cotton and wheat. Folk and traditional medicine also used saffron petals as antispasmodic, stomachic, curative of anxiety, antitumor and antidepressant. Hosseini et al had reported that anthocyanidins of petals (e.g. pelargonidin) is responsible for saffron purple color which is oxidized to flavonol (yellow color) (see Figure 2) [16-22]. In fact, flavanoids include flavonoe and flavol (Figure 3), which are yellow and anthocyanines are may be red, blue, or purple, depending on pH (Figure 4) [24]. The general aim of this research was the optimum use of saffron petals, which are repulsed as cultch today.

Figure 1: Saffron flower and its main parts.

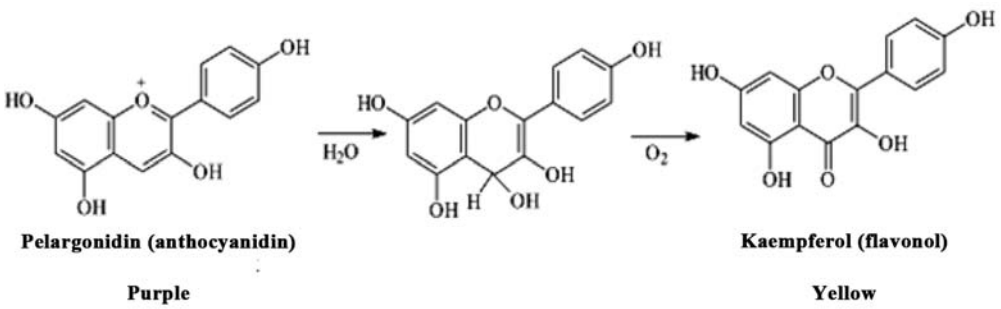

Figure 2: Main structure of petal: oxidizing of anthocyanidin to flavonol.

Therefore, in this study the possibility of dyeing wool fibers using saffron petals as a natural dye was investigated. Also, by using of some mordants, the range of hue that wool fiber can get is studied. Color depth and fastness properties (light and wash fastness) as key properties for technical and commercial success were measured.

2. Experimental

2. 1. Materials and Methods

Dyeing wool fibers with saffron petals (collected from north Khorasan, Iran) and tin (IV) chloride, copper sulfate, aluminum sulfate, iron (II) sulfate, iron (III) sulfate and sodium dichromate as mordants has been applied.

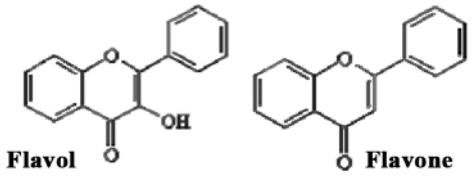

Figure 3: Two structure of flavanoids: flavone and flavol.

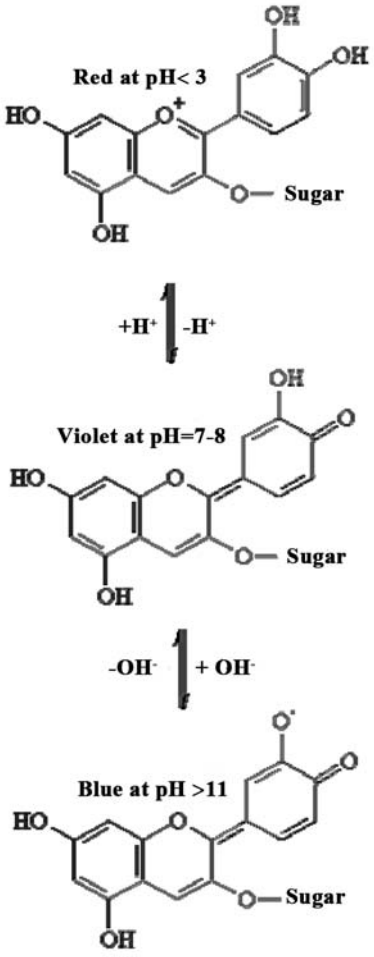

Figure 4: Color changes of anthocyanins with pH.

Also, to regulate the pH, assistants such as oxalic acid and cream of tartar were used (Merck, German). The non ionic detergent (Nekanil LN-BASF) was used for washing. There are a number of methods of dyeing textiles. The simplest form of dyeing a textile material is to immerse it in a dye and gradually boil it. In this method, the fibers are allowed to soak for several hours with agitation. Firstly, the raw wool should be scoured to remove the oil from the fiber, thus, the samples (5 g) are washed for 20 min in an aqueous solution containing 1 gL^{-1} of detergent with a liquor ratio of 40:1 at 45-50°C and then the yarn rinsed in cold water.

2. 2. Pre-mordanting

The wool fibers were treated with mordant and then dyed under different conditions using petals. The metal salts and the assistants were dissolved in hot water and then this solution was added to cool water in the mordant pan. The fibers were treated with a mordant concentration of 1-20% on weight of fibers (owf) (see Table 1). The fiber to liquid ratio (F:L) used for mordanting was 1:20. The heat was increased slowly over thirty minutes to boil and then was kept there for one hour. The mordanted fibers were then cooled and rinsed well. Then the mordanted wool fiber was dyed under optimized conditions.

Table 1: CIE Lab of mordanted wool fibers dyed with saffron petals.

Sample	Mordant (%)	Oxalic acid (%)	Cream of tartar (%)	Mordants																			
				$FeSO_4$				$Fe_2(SO_4)_3$				$SnCl_4$				$CuSO_4$				$Na_2Cr_2O_7$				$Al_2(SO_4)_3$			
				L*	a*	b*	C*	L*	a*	b*	C*	L*	a*	b*	C*	L*	a*	b*	C*	L*	a*	b*	C*	L*	a*	b*	C*
1	1	3	-	42.4	3.5	16.4	16.5	47.2	2.5	15.6	15.8	57.7	-5.6	17.2	18.1	59.1	-0.2	18.2	18.2	61.1	-0.83	22.1	22.1	70.1	-2.6	23.6	23.8
2	2	3	-	45.4	3.9	17.2	17.6	45.5	3.1	17.7	17.9	56.9	-9.9	13.7	16.9	65.8	-1.1	15.9	15.9	60.6	1.5	29.3	29.3	68.3	-0.67	22.5	22.5
3	3	3	-	43.9	4.1	16.7	17	46.8	3.1	16.1	16.4	58.3	-8.9	14.6	17.1	63.4	-1.7	17.5	17.6	60.8	2.4	26.5	26.6	69.6	-2.2	25.2	25.3
4	4	3	-	44.2	4.5	17.2	17.7	50.4	2.3	16.3	16.5	55.9	-8.3	11.6	14.3	62.6	-0.67	16.2	16.2	62.8	1.1	26.1	26.1	72.1	-0.6	20.5	20.5
5	5	3	-	39.8	5.1	18.2	18.9	45.2	3.9	17.1	17.5	51.6	-11.5	8.6	14.4	60.4	-1.9	20.1	20.1	59.1	1.5	29.5	29.6	66.7	-2.2	21.1	21.2
6	10	3	-	46.1	6.15	21.1	21.9	45.7	4.1	16.0	16.5	48.7	-12.2	13.7	18.4	60.5	-1.4	20.5	20.5	60.5	0.62	28.3	28.3	71.9	-2.68	21.99	22.15
7	15	3	-	42.6	6.6	20.3	21.3	46.2	3.3	16.9	17.2	46.6	-14.2	16.1	21.5	61.5	-0.88	21.8	21.9	52.5	3.1	21.1	21.2	65.2	-5.9	21.7	22.5
8	20	3	-	42.1	6.7	20.6	21.7	47.9	3.4	17.5	17.8	44.5	-9.2	19.8	21.9	57.8	-3.3	22.3	22.5	54.2	2.3	20.5	50.6	61.8	-1.9	29.61	29.7
9	5	-	3	61.8	3.2	18.2	18.5	42.9	4.9	20.2	20.7	59.4	-6.8	14.5	16.1	55	-5.2	21.2	21.8	61.2	0.07	25.1	25.1	67.3	-0.08	17.4	17.4
10	10	-	3	54.1	3.6	16.9	17.3	53.3	2.9	18.6	18.8	44.1	-9.5	10.3	14.1	60.7	-4.5	21.5	21.9	53.5	2.9	36.9	37.1	69.6	-3.7	22.7	23.1

2.3. Dyeing process

Dyeing process was performed in a dye bath with an L:R= 20:1 by exhaustion method. The saffron petals were powdered with a mortar and 20 g of this powder dipped in 400 ml distilled water for 30 min and allowed to boil for 1 hour. The dye solution was cooled and filtrated. For 5 g wool fibers, 30 ml of dye solution was used (30 % owf). The bath temperature was increased over 20 minutes to boiling point, and wool dyeing was carried out for one hour. Then, the dyed wool was rinsed in cold water and washed in a bath of liquor ratio 20:1 using 1 g/l of non-ionic detergent (Nekanil LN) at 60 °C for 15 min, then rinsed and dried at ambient temperature.

The dyeing and fastness properties of the colorants extracted from saffron petals on wool fibers were investigated.

2.4. Effect of mordanting on properties

Effects of mordanting, evaluated in terms of dye uptake (K/S value), were calculated from the reflectance data (R) of dyed sample and CIELAB color (Spectra Flash 60, Datacolor International, reflectance spectrophotometer). The effect of mordanting on light fastness was assessed according to ISO 105-B02. Also, ISO 105- C01 was used to measure the wash fastness. The FTIR spectroscopy (Bomem-MB 100 series, Canada) using KBr disc technique was used to show the types of chemical functionality and bonds present in the main color components of saffron petals powder.

3. Result and discussion

3.1. Color strength

The effect of mordant concentration on the color strength (K/S value) of wool fibers is shown in Figure 5.

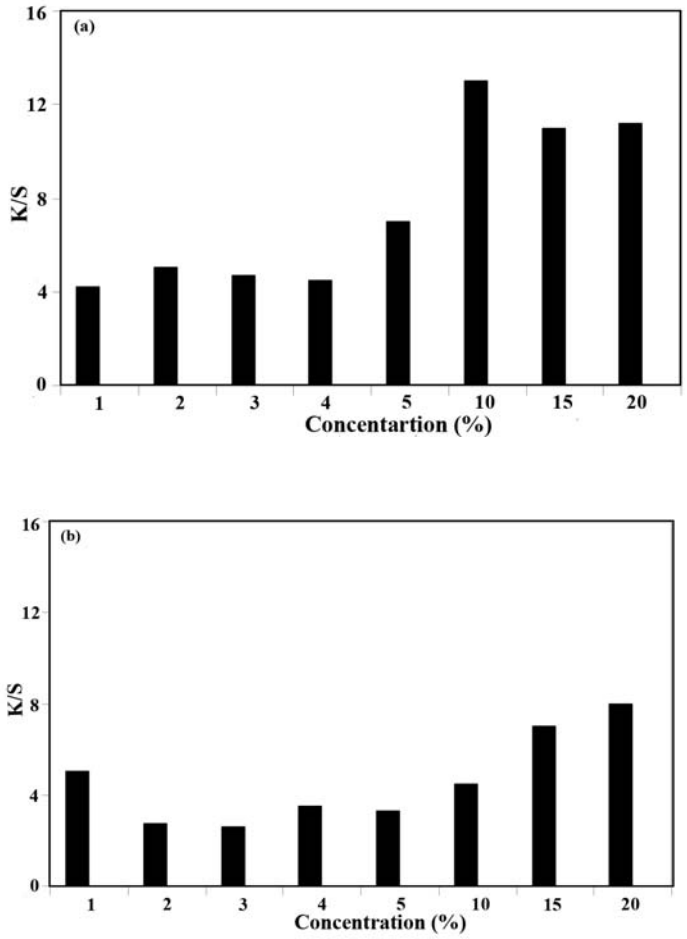

Figure 5: K/S value versus (a) Tin (iv) chloride, (b) Copper sulfate, (c) Aluminium sulfate, (d) Iron (III) sulfate, (e) Iron (II) sulfate and (f) Sodium Dichromate concentrations.

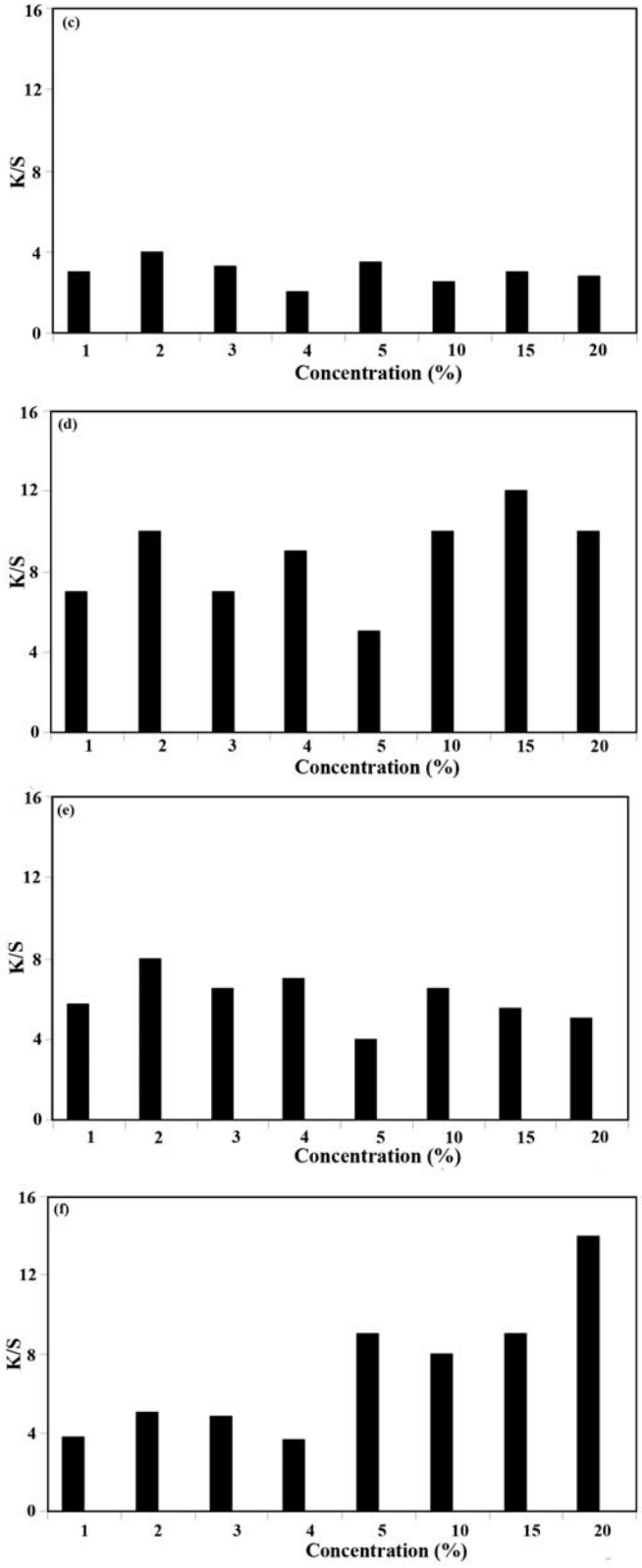

Figure 5: Continued.

The color strength (K/S value) was determined using the Kubelka- Munk equation: $K/S=(1-R)^2/2R$, where R is the decimal fraction of the reflectance of dyed fiber. The results showed that most of the metal salts have high color strength, K/S, due to their ability to form coordination complexes with the dye molecules. The figure showed that Aluminum sulfate has a less K/S value. It seems that Aluminum sulfate is one of the metals forming a weak coordination complex with the dye which has a tendency to form stronger bonds with the dye than with the fiber. Thus, it blocks the dye and reduces its interaction with the fiber. Bhattacharya et al obtained the same results[10]. As evident, the higher K/S value was obtained at 10% (owf) of Tin (IV), 20% (owf) Copper sulfate, 2% (owf) Aluminum sulfate, 15% (owf) Iron (III), 2% (owf) Iron (II) and 20% (owf) sodium dichromate.

3.2. CIE LAB

To evaluate the color parameter, CIE L^* a^* b^* system is used, where L^*refers to lightness-darkness values from 100 to 0 representing white to black, a^* values run from negative (green) to positive (red) and b^* values run from negative (blue) to positive (yellow).

Lower L^* values indicate that the sample becomes darker than that of control sample. The CIE lab of wool fibers is represented in Table 2. As shown in the Table, varied hues (ranges from light yellow-dark green to light brown) were obtained from mordanted wool fiber with metal salts when dyed by aqueous extract of saffron petals. In spite of tin and aluminum salts are white, but tin salt yielded yellowish green and aluminum salt caused cream to light yellow color. The copper sulfate is blue and provided dark cream to green color. Dyed wool fibers with saffron petals possessed greenish yellow color with Sodium dichromate. Moreover, ferrous sulfate yielded brownish, whereas Fe (II) caused darker color than Fe (III). So, a various color can be obtained by changing the mordants.

The results show that mordant has the most influence on L*. As evident from Table 2, the lightness value of fibers is reduced in order of mordanting using Al> Cr> Cu> Sn> Fe (III)> Fe (II). The Table shows that the chroma or brilliance (C* values) of fiber increases with mordant concentration. Also, the use of assistant materials such as oxalic acid and cream of tartar caused varied hues of color. The results also showed that the cream of tartar led to little change in lightness, chroma and hue in fibers mordanted with metal salts, especially with Copper and Iron sulfate.

Table 2: Mordanting conditions of the wool fibers and the results of color fastness to washing and light.

Sample	Mordant (%)	Oxalic acid (%)	Cream of tartar (%)	Mordants											
				$FeSO_4$		$Fe_2(SO_4)_3$		$SnCl_4$		$CuSO_4$		$Na_2Cr_2O_7$		$Al_2(SO_4)_3$	
				L	W	L	W	L	W	L	W	L	W	L	W
1	1	3	-	7	3-4	6	2-3	2	3-4	6	2	5	4	5	3
2	2	3	-	7	4	7	3	3	2-3	4	2-3	5	4-5	3	2
3	3	3	-	7	4	6	2	2	3-4	3	3	6	4-5	4	2
4	4	3	-	7	4	7	2	2	3	6	2-3	7	4-5	4	2
5	5	3	-	5	4	7	2	3	2-3	4	3	7	4-5	4	2
6	10	3	-	7	4-5	7	2	6	3	6	3	7	4-5	4	2
7	15	3	-	5	4-5	7	4	4	2-3	6	2-3	6	4-5	6	2-3
8	20	3	-	6	4	7	3-4	4	2	7	3-4	6	4-5	6	3-4
9	5	-	3	7	4-5	7	3-4	2	3-4	6	3-4	6	4	6	2
10	10	-	3	7	4-5	7	2-3	4	2	7	3	6	4-5	4	2-3

The effect of auxiliaries in dye bath may be related to pH, hence to the correlation between dye structure and wool fibers. For example, the wool fibers mordanted with copper sulfate in presence of cream of tartar have greener color than the same fibers dyed in oxalic acid bath.

3.3 Fastness properties

Most natural dyes have poor to moderate light fastness. Poor light fastness of some natural dyes is attributable to photo oxidation of the chromosphere. Since the Mordants have substantivity for both the fiber and the colorants, they play an important role in natural dyeing and form coordination bonds with fiber which lead to a change in the light fastness and to improve the washing fastness. The light fastness is influenced by many factors such as the nature of the fibers, the mordant type, the dye chemical and concentration and its physical state, and is rated from 1 to 8, in which 1 is the worst and 8 is the best. It is a general rule that dyes show a greater resistance to fading when heavily applied to textile than lightly applied to give pale tints. The wash fastness is the ability to retain color after washing. The wash fastness is rated from 1 (the worst) to 5 (the best). In some natural dyes, washing the dyed sample with alkali causes a complete change in the color of the sample instead of fading. So, the wash fastness rating measurement using grey scale was a little difficult as the sample look completely different in color before and after washing. The results of light and wash fastness are summerized in Table 2. The results of fastness properties of the dyed fibers were fair to good. From these results, it was concluded that mordants $Na_2Cr_2O_7$ and $FeSO_4$ were the best mordant to improve the wash fastness (4-5), while the samples mordanted with Aluminum sulfate had poor fastness to washing (2-3). The best mordants were found to be Iron sulfate and sodium dichromate for improving the light fastness of dyed wool fibers, whereas the Aluminum sulfate and $SnCl_4$ had poor fastness. The table showed that (10%) $FeSO_4$, (15%) Fe $(SO_4)_2$, (10%) $SnCl_4$, (20%) $CuSO_4$, $Na_2Cr_2O_7$ at (4%) and Aluminum sulfate at 20% had better properties. These results are compatible with the study of Cox-Crews on 18 yellow natural dyes which concluded that the use of tin and Aluminum sulfate mordant results in significantly more fading than when chrome, iron or copper mordants were used [23].

Comparing the role of oxalic acid and cream of tartar, it was clear that the cream of tartar improves the fastness (see sample 5 and 9). In fact, cream of tartar improved dyeing fastness when Fe, Cu and Aluminum mordants were used, whereas oxalic acid was better when $SnCl_4$ and $Na_2Cr_2O_7$ were applied.

3.4. FT-IR analysis of colorants

The functional groups of saffron petals powder were studied by the FTIR spectroscopy. Figure 6 shows distinct peaks at 3400, 2922, 1763, 1615, 1370, 1087 and 642 cm^{-1}, respectively.

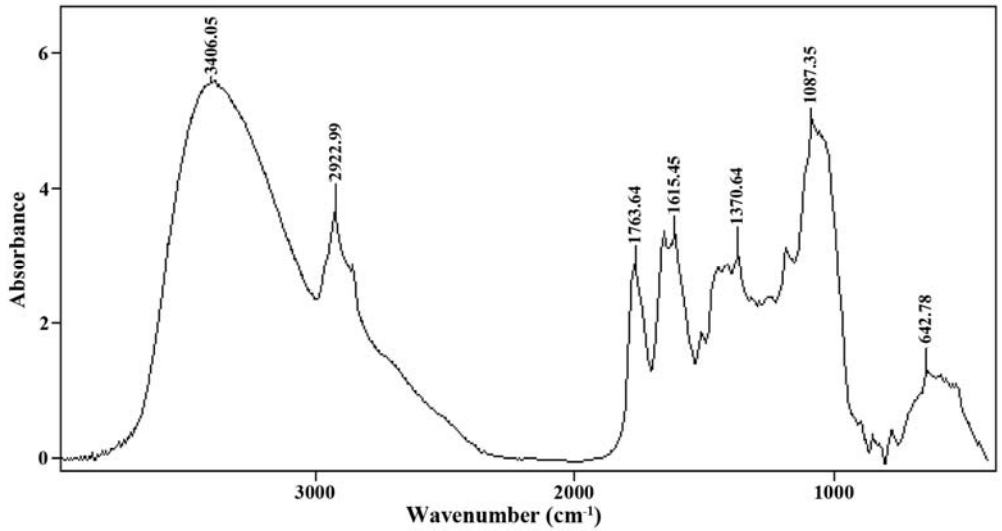

Figure 6: FT-IR spectra of saffron petals.

The peak at 642 is CH=CH stretching vibration. The FTIR spectral analysis shows the absorption peak at 1087 cm^{-1} which refers to C-O stretching. The CH_2 scissors vibration at 1370 cm^{-1} and the C=C stretch at 1615 cm^{-1}. The absorption band at 1763 cm^{-1} is characteristic of C=O stretching, CH asymmetric and symmetric stretch at 2922 and 2887 cm^{-1}. It was seen that there were no C-H stretching absorptions above 3000 cm^{-1} and the sharp peak at 3406 cm^{-1} represented the stretching of –OH [22]. These results confirmed that saffron petals contain phenolic and flavonoide components.

4. Conclusions

Dyeing wool fibers with saffron petals has been used. Saffron petals were chosen as natural dyes because it is one of the by-products of field where a great amount of them was thrown away after harvesting, while they can possibly be used for dyeing. The petal and sepals of saffron are a light purple, but the wool dyed with saffron petals and different mordants have a varied hue in a color range from yellow to brown. The results showed that Iron sulfate ($FeSO_4$) and sodium dichromate ($Na_2Cr_2O_7$) were the best mordant to improve the wash and light fastness. In this study, the amounts of 10% (owf) iron and copper sulfate in the presence of cream tartar, 5-10% (owf) sodium dichromate in the presence of oxalic acid, 15-20% (owf) Aluminum sulfate in the presence of oxalic acid proved to have the best values of light-fastness and washing-durability; moreover, the use of these concentrations is cost-effective. In wool dyeing with saffron petals, the Tin (IV) chloride as a mordant is not recommended due to poor fastness properties. Cream of tartar led to an increase in lightness and chroma compared to oxalic acid. The results showed that saffron petal can be a good natural dyestuff for wool dyeing, but need more experiments and study.

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