



Study the Effect of Biowaste-Based Natural Dyes on Cationic Surfactant

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Abstract

In this work, UV-Vis spectra are used to observe the absorption spectra of aqueous extraction of Beetroot peel and Henna leaves dyes, in presence and absence of cationic surfactant. The maximum absorbance in Beetroot appears to be at 535 in both cases only the intensity of the peak change after addition of surfactant. In contrast with the Beetroot, henna dye showed maximum wavelength changed from 435 nm to 347 nm after the addition of surfactant. Fourier Transform Infrared Spectroscopy (FTIR) identifies the functional groups of those dyes and the change of adding a surfactant to these dyes is also discussed. For both dyes, there is no change of the peaks, only showing intensity change in the presence of surfactant. Mass spectroscopy showed the presence of betalain as the main component in the Beetroot extract, also proved the presence of lawsone in the Henna extract. The conductance at different concentrations for the extracted dyes has been measured. Also, the effect of temperatures and pH had recorded. The results showed the highest conductance for extracted dyes were at the highest concentration (10% and 1.5%) for (2214.5 and 50.367) μScm^{-1} for Beetroot and henna respectively. The CMC of the extracted dyes at room temperature was determined by surface tension (γ) measurements in the presence and absence of the cationic surfactant. The result shows a decrease in the value in the presence of surfactant than that in its absence as it changes from (50×10^3 to 40×10^3) mg/l and (20×10^3 to 15×10^3) mg/l for Beetroot and Henna respectively.

Keywords: Beetroot, Henna, mass spectroscopy, conductivity, surface tension, CTAB.

Introduction

Dye-surfactant interactions are important in a variety of dyeing processes as well as in chemical research, such as biochemistry, analytical chemistry, and photosensitization [1-4]. Surface active agents are mainly used as wetting, dispersing, and levelling agents for improving dyeing processes by increasing the solubility, stabilizing the dispersed state, and promoting a uniform distribution of dye in a textile [5-7]. Natural dyes have gotten a lot of attention because they are inexpensive and available in nature [8]. Natural dyes are having dyeing property but also having the wide range of medicinal and high-tech applications to their non-toxic properties, fewer side effects, more medicinal values, natural dyes are used in day-to-day food products, in pharmaceutical industry and high-tech applications. [9-10]. They are generally eco-friendly and can provide a wide range of beautiful shades with acceptable levels of color fastness. Therefore, the use of natural dyes was one of

the most important means that contribute to preserving the environment [11]. One of natural dyes is betalain dye, Betalain dye (Beetroot extract) has many uses as a colorant, and natural colorants have been of interest in different fields and applications [12-13]. Henna, 2-hydroxy-1,4 naphthoquinone (lawsone), is commonly used as a dyeing agent in the cosmetic and textile industries. It is made out of the fresh or dried leaves of the Lawsonia inermis L. plant. [9]. Few attentions have been directed toward the interaction between natural dyes and surfactants. [14]. Therefore, it is important to introduce studies involving natural dyes obtained from plant residue and explain their association with surfactants. Generally, association models and thermodynamics (association constants, enthalpy of formation and Gibbs energy) and other parameters (surface tension, the surface area per surfactant molecule at the water/air interface and others) were determined for different classes of dyes [15-17]. In this study, the interaction of extracted

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Receive Date: 27 December 2021, Revise Date: 21 March 2022, Accept Date: 03 April 2022

DOI: 10.21608/ejchem.2022.113314.5149

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natural dyes from the peel of Beetroot and henna (leaves) with a cationic surfactant, cetyl tri-methyl ammonium bromide (CTAB) have been investigated for their ability to decrease surface tension and conduct metric properties. The spectral parameters of dyed samples and the dye surfactant mixture have been evaluated. A comparative study of the different parameters in presence and absence of surfactant have been made.

Experimental:

Materials:

All chemicals used during the investigation were analytical or laboratory-grade reagents. Distilled water was used for all experiments. Red Beets (*Beta vulgaris* L.) were purchased from the local market, Cairo, Egypt. The Henna leaves were collected from Saluja Reserve, Aswan, Egypt. Hydrochloric acid (0.1) N, sodium hydroxide (0.1) N. Cetyl tri-methyl ammonium bromide, 98% imported from ADVENT CHEMBIO PVT.LTD and used as received.

Preparation of Beetroot extract:

Different samples were prepared by placing a certain weight of Beetroot peel in a 100 ml Erlenmeyer flask filled with distilled water as a solvent, samples were heated at 50°C in the water bath with pH adjusted to 5 by using 0.1N HCl, and extraction time was 30 min. then filtered, the filtrate used in the conductivity and surface tension measurements.

Preparation of Henna extract:

The collected leaves washed by distilled water dried in the air then oven at 40°C, grinded in a mortar into powder, different weights placed in 100 ml Erlenmeyer flask filled with distilled water as a solvent, placed in a water bath heated to 30°C for 15 min as pH adjusted by 0.1N HCl, then filtered, the filtrate used in both conductivity and surface tension measurements.

Preparation of dye-surfactant mixture:

The stock solution of surfactant (1×10^{-2} M) by dissolving 3.644gm in a liter of distilled water. Then diluted to (5×10^{-4} M). Dye-surfactant mixture 5% (v/v) prepared as (5 ml from dye different concentration to 95ml (5×10^{-4} M) surfactant).

Methods:

Ultraviolet-Visible spectra

Were carried out on both dyes' solutions with concentration 1% between 200–800 nm on Perkin Elmer, Precisely Lambda 45, UV/VIS Spectrometer.

The FT-IR spectra

For both dyes were recorded over a wavenumber range 400 – 4000 cm^{-1} on FTIR spectrometer Jasco 4100 Japan. The samples were prepared in a solution

form with a 1% concentration for both dyes.

Mass spectroscopy

Positive ion electrospray mass spectra were recorded on shimadzu Qp-2010plus Helium was used to improve trapping efficiency and as the collision gas for CID experiments. Ethanol extracted solutions of dyes with concentration 10% employed for mass spectroscopic analysis with the same condition of previous extraction parameters. Scan mode ACQ, employed electron voltage 70 eV, ionization mode EI.

Conductance measurements:

The specific conductance of double distilled water was measured before each series of measurements at room temperature. Then the specific conductivity of known concentrations of Beetroot extracts solutions (0.05,0.2,0.4,0.6,0.8,1,5,7,10%) as well as henna extract solutions of concentration (0.0625,0.125,0.25,0.5,1,2,3,4%) were measured. Then the conductivity of each solution was measured using Jenway 4510 Conductivity/TDS Meter, using a dip-type cell with a cell constant of 1.03 cm^{-1} and having an uncertainty of $\pm 0.01\%$. The measurements were carried out at room temperature $31 \pm 2^\circ\text{C}$ in all series of solvent media.

Surface tension measurement:

The surface tension of the aqueous solution of each dye extract was measured by the drop method using stalagmometry, operating on the principle of a falling drop under controlled environmental conditions ($30 \pm 1^\circ\text{C}$), operating on the principle of a falling drop under controlled environmental conditions ($30 \pm 1^\circ\text{C}$). The accuracy of the instrument was checked by frequent determination of the surface tension of water. Each experiment was repeated three or more times. Measurement of several solutions was repeated after a few days, and the results were found to be with the uncertainty limit reported. Based on Tate's law. [18]

Results and Discussion:

Spectroscopic Analysis:

Optical properties play a major role in understanding the absorption properties of the dye. Spectroscopic analysis of the aqueous extract of Beetroot and Henna leaves was made mainly to find the chromophores present in the colorant of the extract and its extent of absorbance (Visible spectrum) and presence of functional group (FT-IR spectrum), which would help in understanding the behaviour of the dye molecule.

UV-Vis Absorption Spectra:

Beetroot aqueous extract (betalain):

From Vis's spectra, Figure 1 the extract forms a broad range of absorption between 450 and 540 nm, In the visible region, the absorbance spectra of Beetroot

extracted by water, show a broad peak at around 535 nm, also at 484 nm due to presence of red violet betacyanin dye. It was reported that betalains have strong absorption between 400–600 nm range due to the color combination of yellow orange betaxanthins and red violet betacyanins [19]. By the addition of cationic surfactant to the dye solution as shown in Figure 1 illustrate that the visible spectrum shows the change in peaks intensity the intensity of peak at 535 increase while the intensity of peak at 484 as a result of complex formation.

Henna aqueous extract (lawsone):

The absorbance spectrum of aqueous extract of henna leaves Figure 2. Shows a wide band of strong absorbance from 300nm up to 550nm and reduced absorbance up to 700nm, due to lawsone pigment present in henna leaves [20]. The electronic spectrum of Lawsone dye extracted by water exhibited two prominent peaks one around 330 nm and the other at 435nm [21]. As the peak at 334 indicates that the presence of naphthoquinone in the form of hydrogen bonds with carbonyl as the attachment of functional groups such as hydroxyl (OH) at the benzene ring causes a longer wavelength peak at 334 nm [22]. The absorption band at 435 nm is due to the $n-\pi^*$ transitions of the carbonyl group in the Quinone ring [23]. The addition of CTAB solution to the lawsone aqueous extracts result in disappearance of both peaks at 334 and 435 and anew peak appear at 347nm.

Fourier-Transform Infrared Spectroscopy:

Beetroot aqueous extract (betalain): The FTIR spectra of the red Beetroot tested sample was recorded in the spectral range of 400–4000 cm^{-1} are shown in Figure 3. As the spectrum of Beetroot extract in water with different absorption bands characteristics of functional groups of betalain. From the spectra, the solution shows a strong and broadband from 3200 to 3500 cm^{-1} that belongs to the -OH group. Due to the presence of C=C aromatic ring stretching vibrations, a strong stretching vibration was also observed at 1622 cm^{-1} . The peak at 1640 cm^{-1} corresponds to the C=O stretching vibrations which represented the carbonyl group for ketone structure [24-25].

The peak absorbed at 1384 cm^{-1} is due to the presence of C-H rock in the alkanes. The peak absorbed at 642 cm^{-1} is due to the presence of $-\text{C}\equiv\text{C}-\text{H}:\text{C}-\text{H}$ in alkynes. Within the spectral region, the main vibrational characteristics associated with carbonyl compounds of the betanin molecule also were observed. Overall FTIR spectra were obtained justifying the presence of betacyanin pigment that proved by the presence of hydroxyl group and double-bound aromatic ring. [13].

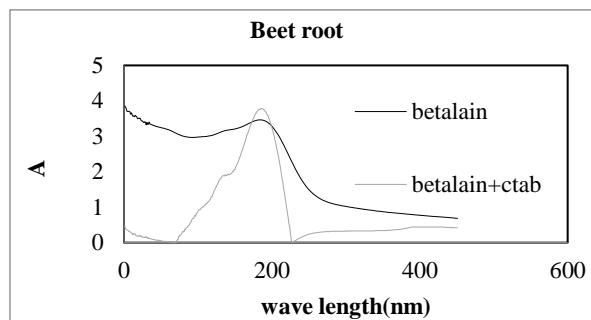


Figure 1 Visible spectra of betalain (Beetroot extract) in presence and absence of CTAB.

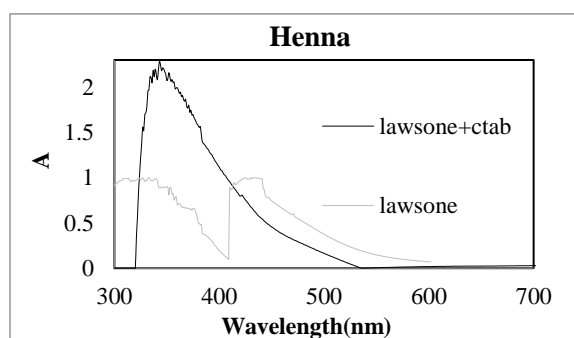


Figure 2 UV-visible spectra of henna leave aqueous extract in presence and absence of CTAB.

The results of FT-IR show that dye extracted from Beetroot contained C=O stretching vibrations at the peak of 1640 cm^{-1} and at the peak at 3412 cm^{-1} , representing the O-H stretching vibration, the CO=OH which corresponds to the carboxylic group in Betalain's pigment for Beetroot dye is observed. FTIR spectra of aqueous extract of Beetroot peel and Beet-CTAB mixture respectively were shown in Figure 3a. Due to the interaction of CTAB with the extract, the vibrations are stronger in CTAB-betalain extract FTIR spectrum when compared to Beetroot extract FTIR spectrum. It showed the presence of groups/bonds due to free O-H stretching (around 3200 to 3500 cm^{-1}), (polyols) C=N stretching vibrations, (around 2068 cm^{-1}), C=O stretching vibrations (around 1627 cm^{-1}), aromatic stretching vibrations (700 cm^{-1}).

Henna aqueous extract (lawsone): FTIR method determines the type of vibrational band presence in Lawsonia interims (Henna) is shown in Figure 4. The important peaks found in the infra-red spectrum are strong wide peak from (3650 to 3140) cm^{-1} , very weak peak at 2882 cm^{-1} weak peak at 2058 cm^{-1} , peak very weak at 1776 cm^{-1} strong sharp peak at 1623 cm^{-1} , weak sharp peak at 993 cm^{-1} , strong wide peak at 700 cm^{-1} . The vibrational frequency of the peak between (3650 - 3140) cm^{-1} was attributed to a hydroxyl group (O-H bond). Vibrational frequency due to peak around 2085 cm^{-1} results from the presence of C=N, the vibrational frequency around 1623 cm^{-1} attributed to the presence of C=O. aromatic vibrations at 700 cm^{-1} .

The groups due to the presented peaks were reported to be the presence of lawsone as the main component of the henna extract [26]. FTIR spectra of aqueous extract of Henna leaves and lawsone-CTAB mixture respectively were shown in Figure 4. Due to the interaction of CTAB with the extract, the vibrations are stronger in CTAB-Henna extract FTIR spectrum when compared to Henna extract FTIR spectrum. It showed the presence of groups/bonds due to free O-H stretching (around 3412, 3495 cm^{-1}), (polyols) C \equiv N stretching vibrations, (around 2076 cm^{-1}), C=O stretching vibrations (around 1630 cm^{-1}), aromatic stretching vibrations (670 cm^{-1}).

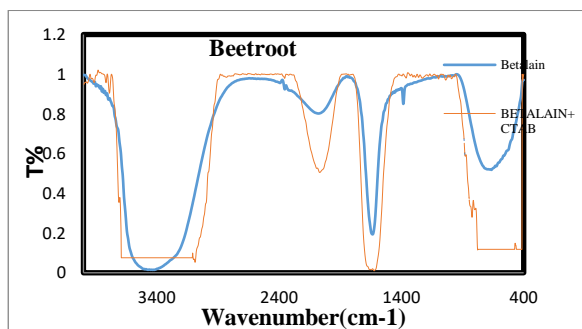


Figure 3 FT-IR spectra of Beetroot dye extract in presence and absence of CTAB

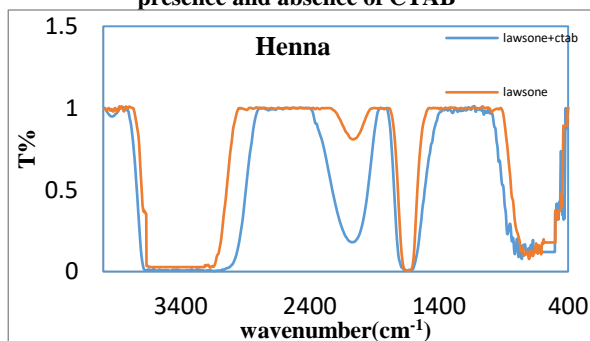


Figure 4 FT-IR spectra of henna extract in presence and absence of CTAB.

Mass spectroscopy

Beetroot extract (betalain) mass spectra:

Figure 5 illustrate, Mass spectrum for betalain: $m/z = 551$ [M], 388, 355, 214, 163 and 149. The mass spectrum gives the molecular ion peak at 551 m/z , and base peak at 149 pointing to the stable part of this compound. The loss of the glucose moiety leads to the ion with $m/z = 388$ betanidin. The ion with $m/z = 355$ result form the betanidin by losing O_2 . Which finally loses C and give the derivative of betalamic acid and cyclo dopa moiety with $m/z = 214, 149$. The presence of the betalain was confirmed by its protonated molecular ions $[\text{M}+\text{H}]^+$ with $m/z = 551$, and the presence of protonated aglycones $[\text{betanidin}+\text{H}]^+$ [32]

Henna leaves extract (lawsone) mass spectra:

Figure 6 illustrate, Mass spectrum for lawsone:

$m/z = 174$ [M]⁺, 146.9, 133, 118, 103, 85 and 77. The mass spectrum gives the molecular ion at 174 m/z , and base peak at 103 pointing to the stable part of this naphthoquinone. The loss of CO leads to the ion with $m/z = 146$. The ion with $m/z = 146$ can form the benzoyl ion with $m/z = 103$, which finally loses CO to give the phenyl ion with $m/z = 77$ [33].

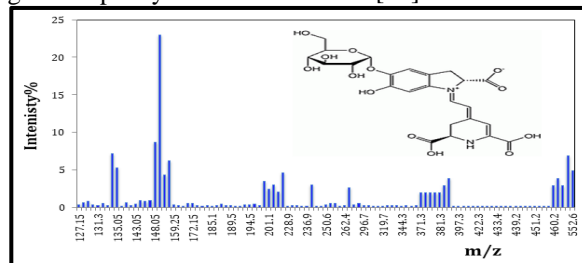


Figure 5 Representative chromatogram and corresponding mass spectra of Beetroot extract.

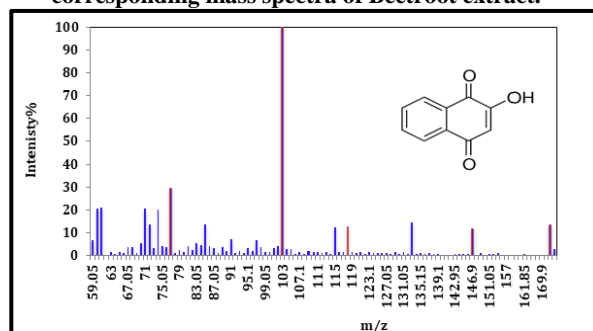


Figure 6 Representative chromatogram and corresponding mass spectra of Henna extract.

Physical properties for extracted dyes:

A-Conductmetric measurements

For Beetroot extract:

1- Effect of dye concentration

The specific conductance of the Beetroot peel extract (κ_b) was measured as a function of the dye concentration at room temperature (32 $^{\circ}\text{C}$). Measured values of the specific conductance in μscm^{-1} were illustrated in Figure 7. There was a significant increase in the specific conductance of the dye with the increase of concentration as shown. The maximum value was observed at 10% of the dye concentration. The specific conductivity of a series of solutions of dye in the absence and presence of surfactant in the solution mixture has been measured at a constant temperature, Figure 7 illustrates that the specific conductance values of the dye-surfactant mixtures decreased than the pure dye solutions, as the conductance decreased from 2214.5 μscm^{-1} to 1780.02 μscm^{-1} for pure dye 10% concentration compared with the same concentration after addition of surfactant. The decrease in the measured values can be explained by the formation of a non-conducting or a less-conducting species in the solution. This behaviour is due to interionic attraction. At a low proportion of the dye in the surfactant solutions, the ions are relatively far apart. So, they exert little influence upon one another.

As the proportion of the dye in the surfactant solutions is increased, the ions come closer to each other. The attraction between ions results in a decrease in their speeds and consequently in the specific conductance of the solution. [27]

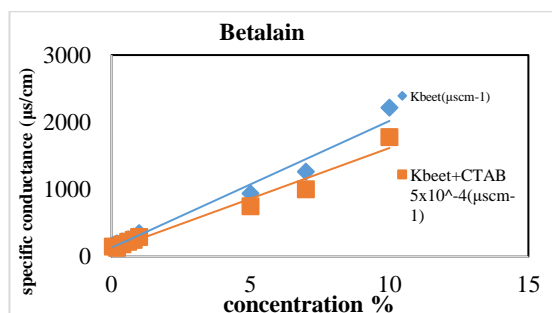


Figure 7 Concentration effect on the specific conductance of betalain also the surfactant of 5×10^{-4} M effect on dye conductivity at room temperature.

2-Effect of pH

Figure 8 show the pH measurements applied on the betalain dye conductance at room temperature with a concentration of 10% showed that the best pH was in range (3-5) as the conductance reach maximum at pH 4 with the conductance of $3790 \mu\text{scm}^{-1}$ start decrease over that range and reach the value of $1473 \mu\text{scm}^{-1}$ at pH 12.

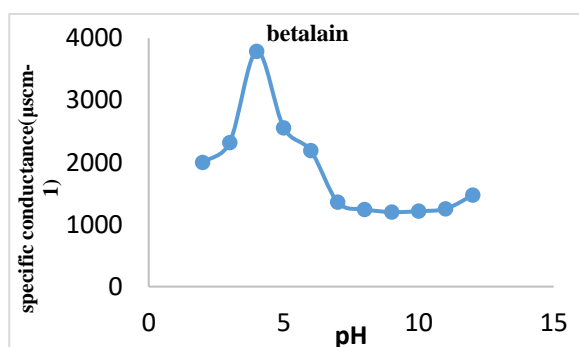


Figure 8 The influence of pH change on the specific conductivity of betalain 10% at room temperature.

3- Effect of Temperature

The electrical conductivity of Beetroot dye extract was measured to determine the effect of the heating process on the quality of pigments produced from red Beet peel. The conductivity measurement of the betalain dye was obtained as shown in Figure 9.

Figure 9. Shows that the addition of temperature treatment greatly affects the electrical conductivity of betalain dye. At 32°C , the betalain pigment has an electrical conductivity of $2450 \mu\text{Scm}^{-1}$, at a temperature of 60°C the conductance becomes $2210 \mu\text{Scm}^{-1}$ for dye measured. It shows that there is a decrease in conductivity of 90%. So that, the electrical conductivity of betalain is strongly influenced by changes in temperature, and it is stable at room

temperature. [28]. The values decrease with an increase in temperature, which may be due to the enhanced molecular thermal agitation at the higher temperature. Such behaviors were also observed in the previous study [29]

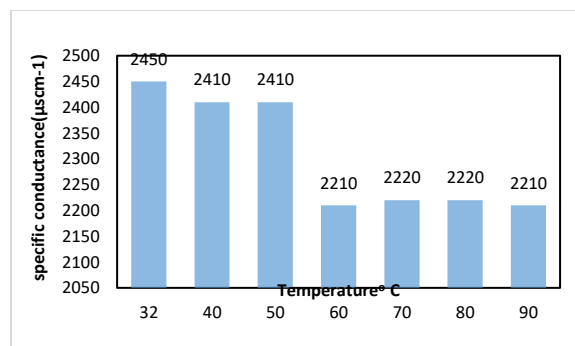


Figure 9: The temperature effect on the specific conductivity of Beetroot dye.

For Henna aqueous extract (lawsone):

1- Effect of dye concentration

The specific conductance of the henna aqueous extract (κ_h) was measured as a function of the dye concentration at room temperature (32°C). Measured values of the specific conductance in μscm^{-1} were illustrated in Figure 10. There was a significant increase in the specific conductance of the dye with the increase of concentration as shown. The maximum value observed at 1.5% of the dye concentration was $50.367 \mu\text{scm}^{-1}$. The addition of surfactant to the dye solution result in a decrease in the conductivity as it decreased from 50.376 to $23.39 \mu\text{scm}^{-1}$ for the same concentration of 1.5%. The decrease was found because of the formation of fewer conducting species as mentioned before in betalain dye.

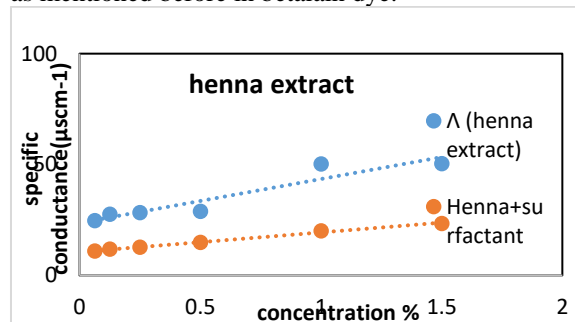


Figure 10 The conductivity changes with concentration for henna extract at 30°C in the presence and absence of CTAB (5×10^{-4}).

2-Effect of pH

The pH measurements Figure 11, applied on the lawsone dye conductance at room temperature with the concentration of 1.5% showed the raise of the conductance up to pH 6 as it start declines over that range and rise again at pH 9, the maximum conductance appear at pH 10 for $85.00 \mu\text{scm}^{-1}$.

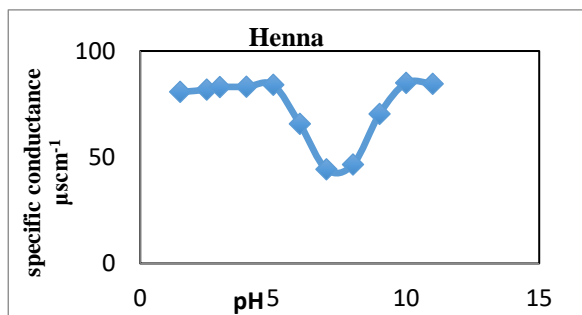


Figure 11 Conductance change vs. pH measurements for 1.5% henna extract at 32°C

3- Effect of Temperature

Figure 12 show that the addition of temperature treatment affects the electrical conductivity of lawsone dye. As the temperature increases the pigment conductivity increase from 9.4 μScm^{-1} , at a temperature of 30°C to 23.5 μScm^{-1} at 100°C for the measured dye. It shows that there is an increase in conductivity of 40%. So that, the electrical conductivity of lawsone is strongly influenced by changes in temperature, and it is stable at 100°C.

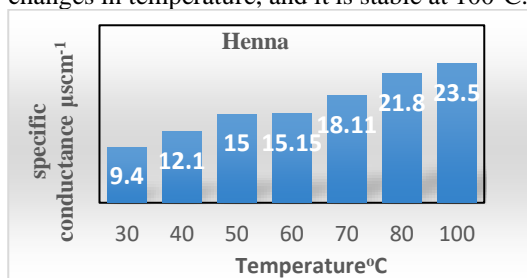


Figure 12 Temperature change effect on the conductance of henna extract (lawsone)

B-Surface active properties:

Beetroot extract:

The surface tension (γ) of natural dyes' aqueous solution is measured to investigate the effects of those dyes' structures on the (γ). Surface activity is the ability of a material at a low concentration to lower the (γ or interfacial tension) between two liquids, a gas and a liquid, or a liquid and a solid [30]. Surfactant molecules contain hydrophilic and hydrophobic parts. The hydrophilic part is directed to the water phase and the hydrophobic part is located at the air-water interface. It was found that the adsorption of surfactant molecules in the air-water interface decreases the (γ) of the solution. Since this dye has about the highest ratio of ionic groups to hydrophobic residue possible in a normal dye, it is safe to assume that all ionized dyes are surface-active and therefore will tend to concentrate at the air-water interface [31]. The (γ) value of the distilled water at 30°C was found to be 71.12 mN/m, which is attributed to the attraction forces between water molecules at the water surface due to the hydrogen bonds. Figure 13, Table 1 shows that the surface tension of the betalain dye decreases

with concentration until it reaches the concentration where the dye excess doesn't affect the surface tension anymore. Figure 13 shows a comparison between the change of dye concentration with surface tension in the presence and absence of cationic surfactant (CTAB). The decrease in the surface tension in the case of surfactant present than that of pure dye solution may be attributed to the higher hydrophobicity of the dye-surfactant complexes, which shaped rapidly under ionic and electrostatic interactions. The hydrophobic species performed as a nonionic surfactant and decreased the surface tension relative to the pure dye solution because no electrostatic repulsion was present at the surface. [27]

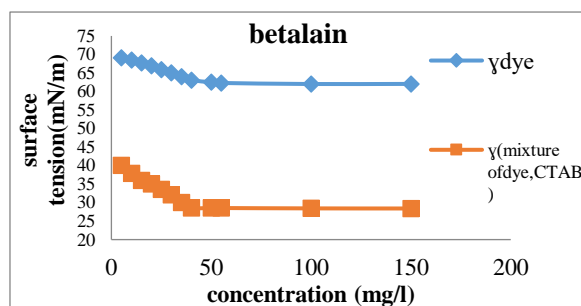


Figure 13 Comparison between the surface tension of dye and the mixture of dye -surfactant at room temperature.

Surface tension (γ) and critical micelle concentration (CMC):

The measured surface tension (γ) of a solution was plotted against the log (C) of betalain dye Figure 14. The plot showed two straight lines with different slopes. These two lines are characterized by two regions, one at a lower concentration at which surface tension is greatly sensitive towards concentration reaction, the other at which the surface tension is almost constant up on variation of betalain concentration. The critical micelle concentration (CMC) of the solution is determined from the point of intersection of two straight lines. The critical micelle concentration is found to be 5×10^4 mg/l.

Surface parameters

The adsorption of the dye at the liquid/air interface can be described by the Gibbs adsorption Equation (surface excess).

$$\Gamma = -\frac{c}{2RT} \frac{d\gamma}{dc} = -\frac{1}{2RT} \frac{d\gamma}{d \ln c} \quad (1)$$

Where Γ is the surface excess concentration, C is the bulk surfactant concentration, R is the gas constant, and T is the absolute temperature and γ is the surface tension. Applying of the result data to Equation (1) yields the surface excess concentration; Γ . Figure 15 shows the dependence of Γ on the surfactant concentration, C. As C increases, Γ increases towards a limiting value known as the maximum surface excess

concentration, Γ_{\max} [31] which result of value equal 9.77×10^3 mol/m². Figure 15, Table 1. The values of surface excess concentration, Γ were used to calculate the surface area (A), in nm² molecule⁻¹ at the liquid/air interface using the Equation:

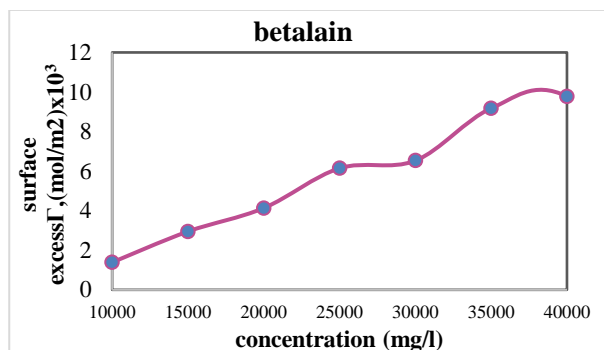


Figure 14 Surface tension of betalain dye as a function of log c at 30°C

$$A = 10^{16} / N\Gamma \quad (2)$$

where N is the Avogadro's number. The surface area per molecule was found to be decreased with an increase in concentration until reach a minimum area at the value of 1.7 nm², Table 1. The decrease in the surface area occupied by an adsorbed molecule with concentration is the result of the solute being enriched at the interface and the surface tension decreasing upon the addition of a solute.

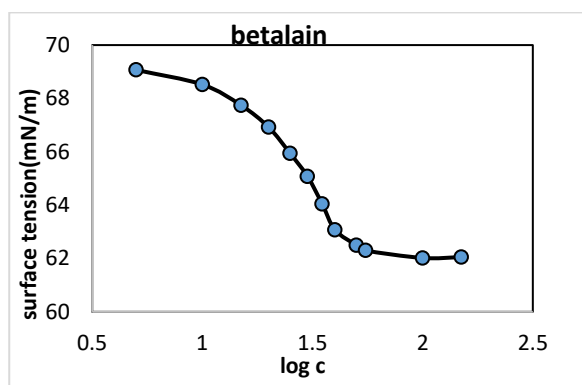


Figure 15 Surface excess as a function of the concentration of betalain dye at 30°C.

The molecular diameter:

The molecular diameters of Dye molecules estimated from the measurement of surface area (S_m) according to the following relation:

$$d_m = \frac{\sqrt{8S_m}}{3\sqrt{3}} \quad (3)$$

The molecular diameter was found to decrease with increase concentration of dye and reach minimum value at a concentration of 4×10^4 mg/l for 5.1×10^{-5} nm. Table 1.

Diffusion coefficient:

The diffusion coefficient (diffusion constant, diffusivity) is a measure of the rate of material transport because of the random thermal movement of particles (diffusion). Using the calculated diameters, it is possible to estimate the equilibrium diffusion coefficients of the dye by the Stokes-Einstein Equation (4) Table 1:

$$D = \frac{kT}{6\pi\eta r_m} = \frac{kT}{3\pi\eta d_m} \quad (4)$$

Where (d_m) the molecular diameters, D is the diffusion coefficient, r_m is the molecular radius, k is the Boltzmann constant, T is the temperature, and η is the dynamic viscosity of medium (water). The data shows that the diffusion of dye particles decrease from (5.9×10^{-24} to 2.2×10^{-24}) m²/sec, Table 1.

Surface pressure :(surface effectiveness)

The effectiveness if defined as the difference between the surface tension of the distilled water (γ°) and that of the surfactant solution (γ) at room temperature is as follows:

$$\pi = \gamma^\circ - \gamma \quad (5)$$

Where γ and γ° are the surface tension of solution and solvent, respectively. As the surface tension decrease with concentration the surface pressure increases as illustrated in Table 1.

Henna aqueous extract:

Figure 16, Table 2 shows that the surface tension of the lawsone dye decreases with concentration until raised to the concentration where the dye excess doesn't affect the surface tension anymore. The addition of the surfactant results in a decrease of surface tension from 50.023 mN/m to 27mN/m for the same dye concentration. That decrease may attribute the hydrophobic species as mentioned above for betalain dye.[27]

Surface tension (γ) and critical micelle concentration (CMC):

The measured surface tension (γ) of a solution was plotted against the log (C) of lawsone dye Figure 15, the CMC found to be at 10×10^3 mg/l for 54.3 mN/m as shown in Figure 17 and Table 2.

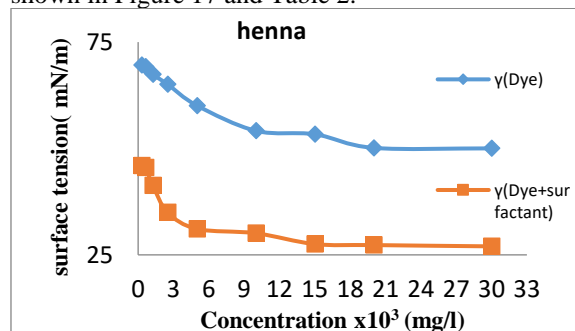


Figure 16 The surface tension of Henna extract change with concentration in presence and absence of CTAB (5×10^{-4} M) at room temperature.

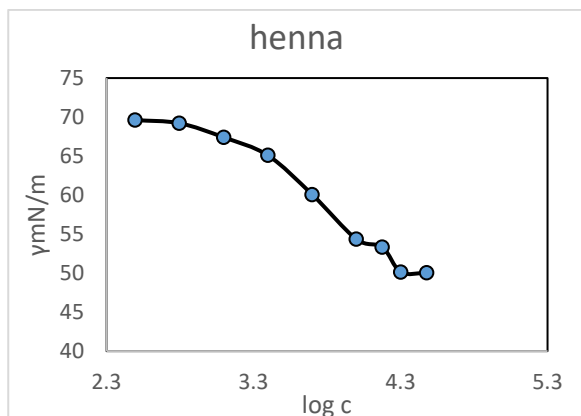


Figure 17 Surface tension of lawsone dye as a function of log c at 30°C.

Surface parameters:

Surface excess: by using Equation 3 the surface excess determined shows the dependence of Γ on the surfactant concentration, C. As C increases, Γ increases towards a limiting value known as the maximum surface excess concentration, Γ_{\max} which result of value equal $113.7 \times 10^{-5} \text{ mol/m}^2$. Figure 18, Table 2. The values of surface excess are used for the determination of the surface area (A) according to Equation (2).

The surface area per molecule was found to be decreased with an increase in concentration until reach a minimum area at the value of $1.45 \times 10^{-4} \text{ nm}^2$, Table 2.

The molecular diameter:

The molecular diameter was calculated according to Equation (3) and was found to decrease with increase concentration of dye and reach minimum value at a concentration of $1 \times 10^4 \text{ mg/l}$ for $1.4 \times 10^{-2} \text{ nm}$, Table 2.

Diffusion coefficient: using the data result of molecular diameter and Equation (4) the diffusion

coefficient can be determined and found to increase from $0.78 \times 10^{-9} \text{ m}^2/\text{sec}$ and become the highest at $2.9 \times 10^{-9} \text{ m}^2/\text{sec}$ as recorded in Table 2.

Surface pressure: by applying Equation (5) surface pressure was calculated and showed arise with a decrease in surface tension as shown in Table 2.

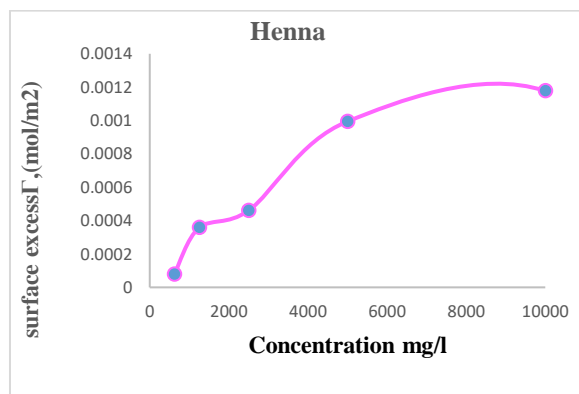


Figure 18 surface excess as a function of concentration for henna aqueous extract

Conclusion:

The present study leads to the following conclusions: The UV-Visible spectra and the FTIR spectra proved the presence of lawsone and betalain as the main component for Henna and Beetroot aqueous extract respectively. The measurement of conductivity and surface tension leads to the belief of the ability of natural dyes to work as conducting medium also their surface activity for both henna and Beetroot pigments, the difference in values between both dyes attributed to their difference in the structure. Ability of the complex mixture (Dye-Surfactant) to affect surface tension and conductivity proved that is more effective than the dye alone. As the critical micelle concentration for dyes decreases in presence of CTAB.

Table 1 Surface parameters of betalain dye.

Concentration (mg/l) $\times 10^3$	γ (mN/m)	γ^l (mixture of dye-surfactant) mN/m	Γ (mol/m ²) $\times 10^3$	A (nm ²) $\times 10^{-9}$	dm (nm) $\times 10^{-5}$	D (m ² /sec) $\times 10^{-24}$	Surface pressure (π) mN/m
10	68.52	37.92	1.38	12.0	13.59	5.92	2.60
15	67.74	36.03	2.95	5.63	9.32	4.06	3.38
20	66.92	35.02	4.13	4.02	7.86	3.43	4.20
25	65.94	33.6	6.15	2.70	6.45	2.81	5.176
30	65.08	32.06	6.53	2.54	6.26	2.73	6.04
35	64.04	30.06	9.17	1.81	5.28	2.30	7.08
40	63.07	28.55	9.77	1.70	5.12	2.23	8.05
50	62.50	28.55	3.58	4.62	8.44	3.68	8.62
55	62.30	28.52	2.77	5.99	9.61	4.19	8.82
100	62.02	28.43	0.78	0.21	18.07	7.88	9.10
150	62.05	28.40	-0.11	-0.01	-	-	-

Table 2 Surface parameters of henna extract

Concentration (mg/l) $\times 10^3$	γ (mN/m)	γ^1 (mixture of dye- surfactant) mN/m	Γ (mol/m ²) x - 10 ⁵	A(nm ²) x -10 ⁴	dm(nm) -x10 ²	D(m ² /sec) -x 10 ⁹	Surface pressure (π) mN/m
0.625	69.20	45.501	7.90	20.88	5.60	0.78	1.91
1.25	67.40	41.32	35.80	4.62	2.60	1.66	3.71
2.5	65.10	35.00	46.04	3.60	2.30	1.80	6.03
5	60.10	31.09	99.40	1.66	1.60	2.70	11.04
10	54.30	30.09	113.70	1.45	1.40	2.90	16.97
15	53.30	27.54	26.40	6.27	3.10	1.40	17.77
20	50.10	27.30	95.20	1.74	1.60	2.70	20.97
30	50.02	27.00	9.50	5.20	8.90	4.90	21.09

Conflicts of interest

There are no conflicts to declare.

Formatting of funding sources

No funding sources.

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