Egyptian Journal of Chemistry

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Valorization Beetroot Waste for Eco-Friendly Extraction of Natural Dye for Textile and Food Applications

Asmaa AL-Amir*, Elshimaa H.Gomaa, Ragaa E. El-Azabawy, El-Bayaa, A. A.

Faculty of Science, Al-Azhar University (for girls), Yusuf Abbas street, Nasr city, Cairo, Egypt. Postal code: 11754

Abstract

An important direction toward change refers to replacing the synthetic components, especially the synthetic dyes, currently utilized in the textile industry that is hazardous both to humans and nature. The goal of this research was to see how effective aqueous extraction of natural colour from Beetroot waste was. FTIR, UV-VIS and mass spectroscopy analysis assured the presence of the betalian and phenolic groups. Subsequently, an effort was made to develop an environmentally friendly approach for extracting betalains and phytochemicals from beetroot pomace by taking into account several experimental factors such as beetroot weight, pH, temperature, and time. The extract was utilized as a vital bio-dye to dye cotton, wool, and silk fabrics. A pseudo-second-order kinetic model (R^2 > 0.99) best describes the adsorption kinetics of textiles. The dyed fabric's colour strength (K/S) values were measured; the value has reached from 9.7 to 15.6 for treated silk fiber. All colored samples were also subjected to colour fastness tests, which included washing, perspiration, and exposure to light. In addition to their importance as colorants, betalains play indispensable role in human health because of their pharmacological activities as antioxidants and anti-carcinogens.

Keywords: Bio-dye beetroot (betalains); dyeing process; Fabrics; Thermodynamics; Food industry; Antioxidant; Anticancer.

1.Introduction

Color has always played an important part in the development of various human cultures around the world. Application of synthetic dyes can have bad affects on the health of the workers, and many dyes have been banned from use because they are possible carcinogens. Besides that, nearby rivers are really polluted that some villages, use river water as source of drinking water. The interest of using natural pigments for food coloring and also textile coloring is increasing because natural products are guaranteed with quality and health assurance whereas synthetic pigments are critically assessed and are not really favored by consumers.

Natural dye sources are eco-friendly and permanent in fabrics[1]. Natural dyes are most beneficial in comparison to the synthetic dyes. It's been attracting more of the subsequent reasons; the wide viability of natural dyes and their enormous potential. Plus, experimental evidence for allergic and toxic effects of synthetic colours, as well as non-toxic and non-allergic effects, is available. The interest of using natural pigments for food colouring and also textile colourings is increasing because natural products are guaranteed with quality and health assurance. Nature has provided us with around 500 dye-producing plant species. These plants' colouring compounds come from their roots, leaves, barks, trunks, or fruits [2]. Beetroot is the primary source of natural red dye, and the extracted colour is known as "beetroot red".

There has been a resurgence of interest in the use of natural colorants in textile dyeing applications. Since its discovery, silk has been referred to as the "queen of fibres." Silk clothing is regal, with many good attributes such as lustre, light weight, superior mechanical performance, fine and silky texture, efficient moisture transportation, and excellent draping quality [3].Cotton is a vegetable fiber hence it originated from natural source. Natural dyes are used in the dyeing of cotton, wool and silk. The chemistry of bonding of natural dyes to fibers is complex. They bind to fibers through H-bondings and hydrophobic interactions. As the H-bondings and hydrophobic interactions are weak interactions, it is necessary to use heavy metal salts named as mordant to obtain good color fastness values. In case of mordant usage, dyes are bound to the fibers through chemical bridges with the aid of mordents such as Fe, Cu, Pb, which are used

*Corresponding author e-mail: asmaamoussa.5919@azhar.edu.eg.; (Asmaa AL-Amir).
Receive Date: 11 February 2022, **Revise Date:** 12 March 2022, **Accept Date:** 20 March 2022
DOI: 10.21608/EJCHEM.2022.121319.5441

to increase the dye uptake, improve the fastness and obtain different color effects. These substances cause serious ecological problems on fabric and in wastewater [4].

Dyestuff manufacturers and textile dye houses have begun to employ harmless ingredients due to social responsibility (Abreu et al., 2012). Therefore, it is suggested in this study to use green mordant in the dyeing process. To eliminate chemical pollutants and their effluents because of chemical processes. Natural polysaccharide (chitosan) was applied to pretreatment fabrics to increase the cationic sites in the fiber polymer that results higher absorption of bio-beetroot dye and fastness compared with untreated fabrics [5].

Hence the treatment of cotton with chitosan provides ample scope for further investigations to suit today's environmentally friendly dyeing needs. Food industry, the developing hobby of clients in the aesthetic, nutritional and protection components of food has elevated the demand for natural pigments including betalains to be used as alternative synthetic colorants, which may additionally trigger adverse effects in human beings in food outputs **[**6]. Although betalains from Beetrootroot are one of the most widely used food colorant, betalains are not as well studied as compared to other natural pigments such as anthocyanin, carotenoids, or chlorophylls. The pharmacological properties, which include antioxidant and anti-cancer of betalains derived from source for potential application as functional foods. The process of dyeing fabric with natural colors can be done several times to obtain the desired shade color intensity. There are several factors that influence the dye absorption into the cotton fabric, coloring process temperature, concentration of dyes, and pH . This article is intended to extract of bio-colorants derived from bio-resources, and for textile dyeing, adsorption, and chemical kinetics and for eco-friendly extraction of natural dye from Beetroot waste and food applications.

2.Materials and methods

2.1Materials

All chemicals used during the investigation were analytical or laboratory-grade reagents. Distilled water was used for all experiments**.** Beetroots (Beta vulgaris L.) were purchased from the local market, Cairo, Egypt. Hydrochloric acid (0.1) N, sodium hydroxide (0.1) N and Chitosan were imported from sigma Aldrich and used as received. Fabrics (wool and silk provided from the textile factory, tenth of Ramadan),Cotton fabrics provided from (Misr Helwan Company) were scoured in aqueous solution containing 5% of sodium dodecyl sulfate at 50°C for an hour to remove waxes and impurities, then rinsed thoroughly in distilled water and dried at room temperature**.**

2.2. Methods

2.2.1 Extraction of bio- dye beetroot (betalains)

The extraction of natural dyes samples was undergoing various trials so as to obtain the optimum conditions of extraction natural dyes for weight, pH, temperature, solvents and time. The data of absorbance for all samples were measured using UV-VIS Spectrophotometer and recorded. The content of betalain in the extracts spectrophotometrically determined at 535 nm with a UV–Vis spectrometer; the absorbance reading obtained was used to calculate the betalain by applying the Equation (1), [7].

Betalain Content (mg L-1) **=** [(A × DF × MW × 1000) / (e × l)] **(1)**

Where,

A = Absorbance of samples

MW = Molecular weight of pigment (betalain = 550 g/mol)

DF = Dilution factor

ε = Absorptivity coefficient of betalain (60.000 L M^{-1} cm^{-1})

l = Path length (1 cm).

2.2.2 Characterization of bio-dye beetroot (betalains)

The structural of extracted betalains was characterized using Fourier-transform infrared spectroscopy (FTIR), UV/VIS spectroscopy and Mass spectroscopy. The existence of functional groups or identification of chemical bonding in betalains was evaluated using FTIR analysis (FTIR spectrometer Jasco 4100 Japan). Optical properties of betalains was analyzed using UV/V is absorption double beam spectrophotometer (Perkin Elmer, Precisely Lambada 45,UV/VIS Spectrometer) within 200–800 nm wavelength range. Mass spectroscopy, the 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.

2.2.3 Dyeing procedures

Dyeing wool and silk

Wool and silk fabrics were dyed with betalain dye. As dye concentrations for betalain were (5,10,15,20,30,50,100,150) g/l with liquor ratio of 50:1. The dried scoured fabrics were introduced into the dye bath and dyed at duration of (120 min) and temperatures of (50,70,90ºC). The dye bath was monitored and controlled at pH =2.2 with a pH meter, using 1g of citric acid. The dyed samples were rinsed with cold water and finally dried

Dyeing of cotton

Cotton fabrics dyed with betalain with same concentrations as in silk and wool. The cotton fabrics washed by water and placed in solution of sodium chloride (6.25) % at temperature 60ºC in water path for 1hour then removed and placed on dyeing path with liquor ratio of (1:40) for a duration time of (120) minute at temperatures of (50,70,90) ºC. The dyed fabric washed with cold water and finally dried [8].

2.2.3.1 Pre-treatment of fabrics by chitosan

Chitosan solution 1% freshly prepared by dissolving 1g in 100 ml 1% aqueous acetic acid solution. The fabric immersed directly into the chitosan solution with liquor ratio of (1:50) for 1 hour at room temperature. The fabric after treatment with chitosan rinsed with distilled water 40ºC and allowed to dry in open air. The dyeing process conducted by the same mentioned method [9].

2.2.4 Determination of sample Fabric Properties

Color Fastness residences for the untreated and pre-treated dyed samples at dyeing recipe were tested for various fastness features such washing, light and perspiration according to ISO standard test methods **[**10].

2.2.5 Health benefits of betalains

Betalains are plant derived natural pigments that are presently gaining popularity to be used as herbal colorants with in the food industry because of their pharmacological activities like antioxidant and anti-cancer betalains play a crucial role in human health [6].

3.Results and Discussion

3.1. Extraction of bio-based dye beetroot

Green chemistry in the extraction of natural colorant from Beetroot waste involved the use of water as a solvent, without other additives. Beetroots are the chief sources of betalains, which may be a water-soluble nitrogen pigment with heterocycle, which may be further subdivided into two classes containing on chemical structure. Betalains (betacyanins and betaxanthins) is that the main component of the red colorant extracted from Beetroot. The aqueous technique was used to extraction of natural dye from Beetroot waste.

3.1.1 Determination of optimal weight for the extraction process.

The effect of beetroot weight rang from (0.005, 0.02, 0.04, 0.06, 0.08, 0.1, 0.25, 0.5) g/10 ml water on extraction content were shown in Figure 1. A significant raise in the yield of betalain (betacyanin and betaxanthin) with increasing beetroot weight was observed which might be due to the concentration of the solute. The maximum extraction content was observed at (0.5) g /10 ml and was found to be 55 mg L^{-1} **[**11].

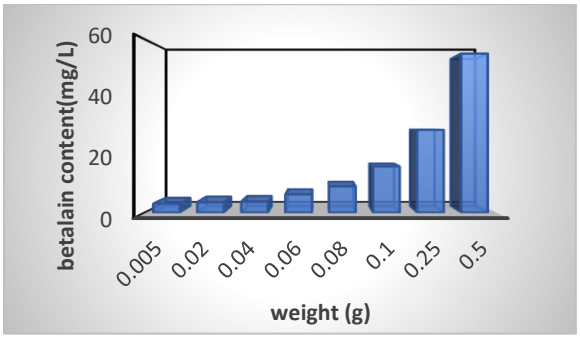

Fig. (1) The of betalain content as a function of weight

3.1.2 Determination of optimal temperature for the extraction process

Temperature is one of the vital factors controlling the extraction content. Different temperature effects to extraction betalain from (0.1g /10 ml) are presented in Figure 2. The graph showed extraction increased gradually by increasing the temperature degree from 20°C to 50°C [12]. However, maximum yield of betacyanin and betaxanthin was result at 50°C which could be due to the softening of the tissue, accelerating the diffusibility of the molecules and penetration of the solvent into the solid and thus enhancing the solubility and diffusibility of the pigment in solvent and finally increasing the yield . The total betalain content reaches the highest value at a temperature of 50°C with a yield of 30.36 mg L^{-1}. It was observed that the red color of betacyanin changed to light brown at 100 °C. Owing to the increase in the betacyanin degradation rates as the temperature of extraction increased **[**13].

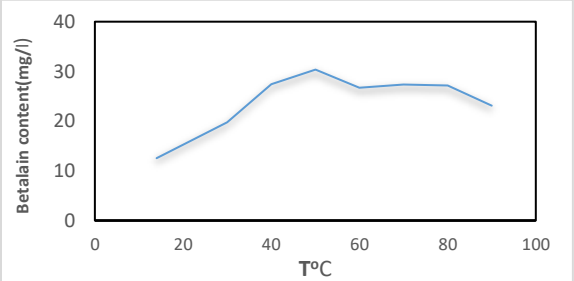

Fig. (2) The temperature affect on the extraction process.

3.1.3 Determination of the optimal pH for the extraction process

The pH of the extraction is an important influencing factor controlling the extraction content. In this study, the pH range was varied from (1-12). As shown in Figure 3 the best highest yields of betalain content were observed at pH 5 and were found to be 30.29 mg L^{-1}. Previous studies, shows that betalain dye favors pH ranging from pH 4 to pH 6 [12]. A slight decrease in extraction yield was observed with increase in pH of the extraction media increase from pH 5 to pH 7, this may be attributed to the effect of

high pH on the stability of these compounds [14]. The shade of betalain was variable under the alkaline condition as the concentration reduced above pH 6 as a result of degradation of betalain [15].

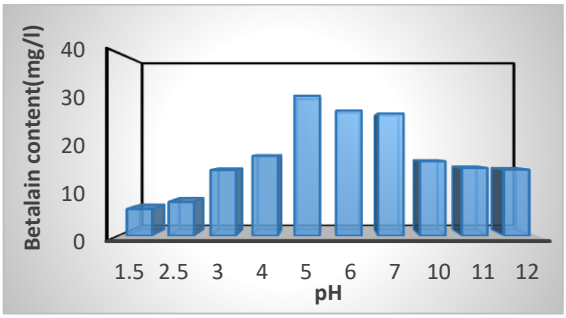

Fig. (3) The betalain content at different pH.

3.1.4 Determination of optimal time for the extraction process

The effect of reaction time is another vital parameter that must be considered during the extraction process. In this study, different time durations extending from (5 to 60) min for betalain, has been considered. The effect of extraction time on extracted content of natural pigment was shown in Figure 4. The extraction rate is fast at the beginning of the process and reduces as it approaches the saturation level or equilibrium point. The effect of time on extraction is related to the mass transfer rate which was highest initially and decreased laterally [16]. The optimum time for betalain extraction was 30 min., above this time there is slight stability noticed.

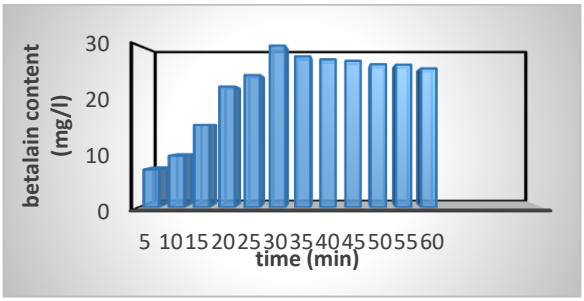

Fig. (4) The change of time influences the betalain content.

3.2. Characterization of the Extract

3.2.1 UV-VIS analysis

To dye the textile materials with aqueous extracts of some natural dyes, it is necessary to know the behavior in the UV-VIS field. For the raw extract, a calibration curve was made which highlights the dependence of the absorption on the concentration of beetroot extract. This calibration curve allows determining the concentrations of dye from the extracts. The UV-VIS spectra of beetroot extracted in aquatic media were depicted in Figure 5.

It has been recorded that the wavelength of the maximum of absorption of betalains (betacyanins and betaxanthins) is in the wavelength range from 450 and 540 nm because of the coloration combination of yellow orange betaxanthins and red violet betacyanins [17]. In this study, the maximum wavelength of absorption for Betacyanins generally present as red-to-red violet in color they absorb in the 535nm range. Also small hump of Betaxanthins generally appear yellow in color absorb in the 484 nm range.

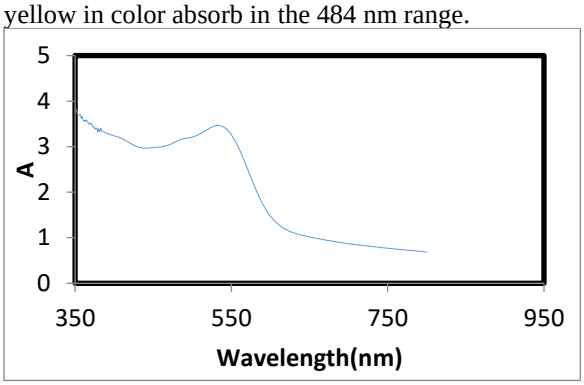

Fig. (5) Visible light spectrum for betalain.

3.2.2 FTIR spectroscopy

FTIR spectral analysis of dried beetroot pomace was done to identify the existence of major functional groups according to libraries and bibliography. The FTIR spectra of the tested sample was registered in the spectral range of 400–4000 cm^{-1} are shown in Figure 6. The spectrums of aqueous extract of Beetroot waste have different absorption bands characteristics of functional groups of betalain. From the spectra, the solution shows a strong and broad band from 3200 to 3500 cm^{-1} that belongs to the -OH bond stretching vibration group**.** On the other hand, the absorption band around 1624 cm^{-1} was ascribed to the C **=** N bond stretching vibration. The peak at 1640 cm^{-1} corresponds to the C=O stretching vibrations which represented the carbonyl group for ketone structure. The peak absorbed at 1384 cm^{-1} was assigned to the extension stretching vibration of the C–H bond, while the absorption band at 1243 cm^{-1} was ascribed to the C–O bond of the carboxylic acid stretching vibration. The peak absorbed at 642 cm^{-1} is due to the presence of -C≡C-H:C-H in alkynes[18-19]. Within the spectral region, the main vibrational characteristics related 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 [20]. 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 for Beetroot dye is observed. The presence of polar groups such as COOH, OH, and NH_2 gives them an affinity for water and certain solubility, which is why the components of betalains cannot be called pigments but dyes.

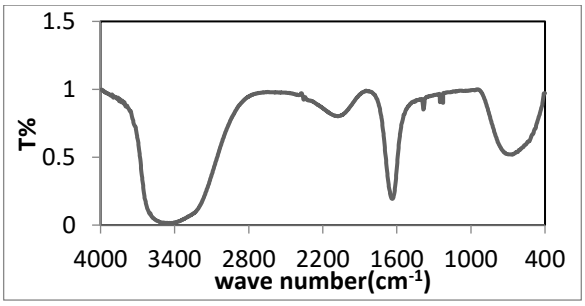

Fig.(6) FT-IR spectra of Beetroot dye.

3.2.3 Mass spectrum analysis

Figure 7 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 from the betanidin by losing O_2. Which finally loses C and give the derivative of betalamic acid and cyclodopa moiety with m/z = 214, 149. The presence of the betalain was confirmed by its protonated molecular ions $[M^+H]^+$with m/z=551, and the presence of protonated a glycones $[betanidin+H]^+$ [21].

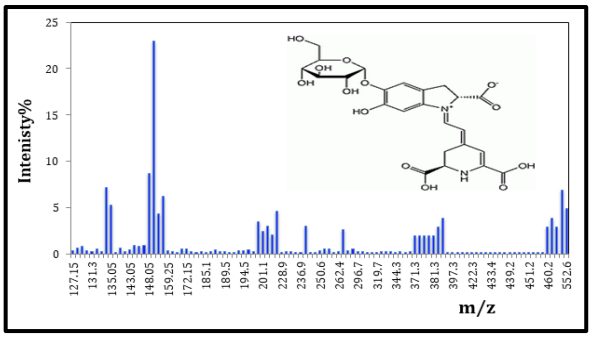

Fig.(7) Repreentative chromatogram and corresponding mass spectra of Beetroot extract

3.3 Dyeing kinetics

3.3.1 Dyeing of fabrics by bio-dye beetroot

Cotton, wool, and silk fabrics were dyed with bio-dye beetroot **(betalain)**. The reaction mechanisms are further presented in detail as below [22]. Citric acid is added to the colored extract until a pH = 2.2 is reached; Citric acid is a weaker acid than betalains, the latter will release protons from the COOH groups. The protonation of wool in acidic medium is predicated dissociation reactions (of the acid and amino acids in wool), activation of wool, and double change response among activated wool and betalains reactions (1- 4), thus:

$$HX \rightarrow H^+ + X \qquad \textbf{(1)}$$

Acid

$$HOOC\text{-}Wool\text{-}NH_2 \rightarrow {}^-OOC\text{-}Wool\text{-}{}^+NH_3 \qquad \textbf{(2)}$$

Wool

Wool is an amphoteric compound; therefore, in the acid environment, it interacts with the acid, accepting protons, thus resulting in activated/protonated wool.

$$^-OOC\text{-}Wool\text{-}{}^+NH_3 + H^+ + {}^-X \rightarrow H^+ {}^-OOC\text{-}Wool\text{-}{}^+NH_3\,{}^-X \qquad \textbf{(3)}$$

Activated wool

This intermediate phase means an activation of the amino groups of the wool, which thus become binding centers for the anions of the dye in the solution

$$H^{+-}OOC\text{-}Wool\text{-}{}^+NH_3\,{}^-X + Dye\text{-}COO^-\,H^+$$

Activated wool **+** **Betalains**

$$\rightarrow H^+ {}^-OOC\text{-}Wool\text{-}{}^+NH_3\text{-}OOC - Dye + {}^+H\,{}^-X \qquad \textbf{(4)}$$

Dyed wool

The E% values of cotton, wool and silk fabrics are (51.22%, 76.32 %, 91.6 %) respectively it is showed in Figure 8. When the dyeing temperature was raised the dye exhaustion increased. This may be attributed to various factors on top of which is that the increase of temperature increases the kinetic energy of the dye molecules and the molecular vibrations of both the fabrics and the dye, there by enhances the rate of penetration of the dye into the vicinity of the substrate, which induces favorable fixation kinetics [23].

Another factor is that raising the temperature causes the capillaries inside the fabric to be more accessible and the mobility of the dye ions become higher resulting in a swelling effect within the internal structure of the fabrics, thus enabling the large dye molecules to penetrate further [24]. Causing rapid increase in E%. The optimum temperature was recommended to be 90^0C.

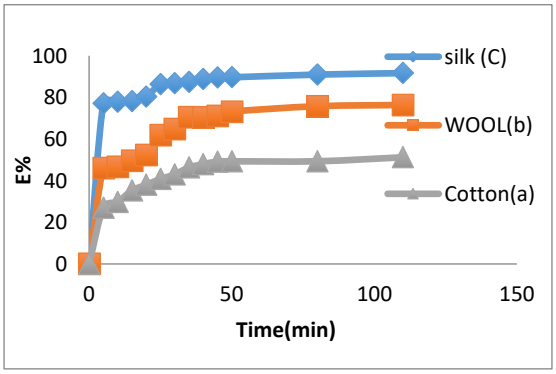

Fig. (8) Time-Exhaustion isotherms of bio-dye *beetroot* adsorbed into (a) cotton (b) wool (c) silk fabrics [dyeing recipe: LR 1:50, 50 g/l, 90^0C].

3.3.2 Pretreatment of fabrics by chitosan and their dyeing

To reduce or eliminate use the electrolyte concentration in the liquid dye. The introduction of cationic sites within cellulose is the most anticipated technique to increase dye uptake.Positive sites can be introduced by either ammonization or cationization. Chitosan treatment of cotton is an aminization technique for introducing the cationic site within the polymer fibrous structure.

Chitosan is a natural polysaccharide-based cationic biopolymer, is derived from the chitin component of the shells of crustaceans. The advantageous properties of chitosan are nontoxicity, biocompatibility, biodegradability, antimicrobial activity and chemical reactivity. Cotton fibres create cross-links with chitosan, resulting in positive dye sites on the fibres' surface **[9]**. As a result of the cationic character of the fibres' surface, anionic dyes are easily absorbed by electrostatic attraction. The application of chitosan to cotton fibres leads to the possibility of dyeing without electrolytes while maintaining the required level of fatigue, as shown in the preceding discussion. In addition, the introduction of more hydroxyl groups into the cellulose due to the cross-linking of chitosan with the polymer fibers can enhance the depletion of the dye by the fibers. As well as examining the dye-ability and chromaticity performance of chitosan-treated cotton fabric treated with chitosan dyed without salt and compared the results with salt-dyed fabric. The values of color strength (K/S) were found to increase from 5.2 to 7.5 for untreated cotton and pretreated cotton fabric with chitosan respectively, listed in Table (1)

Wool and silk fibers pretreated with chitosan and dyed with bio-dye beetroot (betalains) as natural dye. The effect of chitosan on color strength (K/S) was measured as shown in Table (1). Pretreated wool and silk fibers with chitosan gave higher K/S values than that of untreated fibers. The insertion of primary amino groups to the fiber structure is linked to the improvement in color strength (K/S) values of chitosan prepared wool and silk fibers. The electrostatic attraction of cationized amino groups can adsorb anionic dye molecules (betalains) in acidic media. Ionic interactions are also thought to be involved in the binding of chitosan to wool fibers [25].

Table (1):Color strength of untreated and treated fabrics dyed with betalains at 90^{0}C.

Type of fabrics	K/S	
	Untreated	Treated
Cotton	5.2	7.5
Wool	7.42	11.03
Silk	9.7	15.6

3.4 kinetic of adsorption

In order to examine the mechanism and rate controlling step in the overall adsorption process, four kinetic models, Pseudo-first-order, Pseudo-second-order, Intra-particle diffusion and Elovich-diffusion model, are adopted to investigate the dyeing kinetics of cotton, wool and silk fabrics with betalains are expressed, respectively, as follows :

A simple kinetic analysis of adsorption is the Lagergren Equation [26-27].

A pseudo-first-order type, written as follows:

$$\mathbf{Log\ (q_e\text{-}q_t)=log\ q_e\text{-}\ kt/2.303} \qquad \mathbf{(2)}$$

Where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_t is the amount of adsorbate adsorbed at contact time t (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}). A plot of log (q_e-q_t) versus t gives a linear line relationship from which the values of k_1 and q_e were determined from the slopes and intercepts respectively, as presented in Table ٢.

The pseudo-second-order kinetic model is another important model to investigate the kinetic of adsorption of dyes on textile fabrics [28-29]. The pseudo-second order kinetic model can be expressed in linear form as follows:

$$\mathbf{t/q_t=1/k_2q_e^2+t/q_e} \qquad \mathbf{(3)}$$

Where k_2 is the rate constant of pseudo-second order adsorption (g/mg min). A plot of t/q_t versus t gives a linear relationship Figure 9 (a, b, c), from which qe and k_2 were determined from the slope and intercept of the plot respectively and presented in Table 2. The correlation coefficients R^2 higher than 0.99 suggest that adsorption of betalains onto cotton, wool and silk fabrics predominantly follows the pseudo-second order kinetic model. The pseudo-second order rate constants for adsorption of betalains onto cotton, wool and silk fabrics show a steady increase with an increase in the solution temperature from 323 to 363 ^{0}K as shown in Table (2) In conventional physisorption systems, increasing the temperature usually increases the rate of approach to equilibrium.

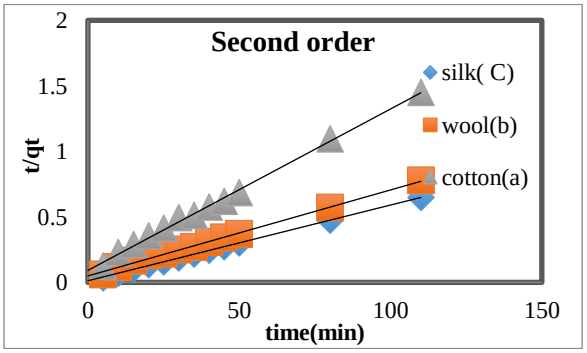

Fig. (9) Pseudo-second order Kinetic plots for the adsorption of betalains into (a) cotton, (b) wool and (c) silk fabrics at 90 ^{0}C.

3.5 Diffusion mechanism

The two models above cannot identify the diffusion mechanism during the adsorption process, so the Intra-particle and Elovich diffusion models test the experimental data.

3.5.1 Intra-particles diffusion

Intra-particle diffusion can be expressed by following Equation (4):

$$\mathbf{q_t = K_P\ t^{1/2} + C} \qquad \mathbf{(4)}$$

Where q_t (mg/g) is the amount of betalains adsorbed at time t, K_P (mg/g $min^{1/2}$) is the Intra-particle diffusion rate constant obtained from the slope, of the plot q_t versus $t^{½}$. The plots were linear

over a detectable time range but with marked deviation from the origin; this indicates that the Intra-particle diffusion is not only the rate controlling step, but also some other processes may control the rate of dye adsorption [30].

The Intra-particle diffusion rate constant k_p and C are given in Table 2. The Intra-particle diffusion rate constants k_p increase with rising temperature because increasing temperature results in an increase of the driving force, which will increase the diffusion rate of betalains [31]. While the C value gives an indication of the thickness of the boundary layer. The larger C shows greater boundary layer effect that account greater contribution of the surface sorption in the rat-limiting step [32].

3.5.2 Elovich diffusion

The Elovich equation was first applied to the chemisorption's kinetics of gases on solid [33]. It has also been successfully used in recent years to describe the adsorption of the solutes from a liquid solution.

The linear form of the Elovich Equation (5) is given as

$$\mathbf{qt = 1/\beta ln (\alpha\beta) + 1/\beta Lnt} \qquad \mathbf{(5)}$$

Where α is the initial adsorption rate constant (mg/(g min) and the parameter β is the desorption constant (g / mg). The constant can be obtained from the slope and the intercept of the plot of q_t versus ln(t) at different temperature. The value of β decreases while that of α increases as the concentration rises as shown in Table 2.

Adsorption isotherm models are widely used to describe and investigate mechanisms of adsorption.

3.6 Adsorption isotherm

Adsorption isotherm models are widely used to describe and investigate mechanisms of adsorption. The Langmuir and Freundlich isotherm model analyzed the equilibrium data

3.6.1 Langmuir adsorption isotherm

Monolayer sorption on discrete localized adsorption sites is described by the Langmuir model.It assumes uniform energies of monolayer sorption onto the sorbent surface and no adsorbate transmigration in the plane of the surfaces [34].

The linear form of Langmuir Equation can be written as follows:

$$\mathbf{Ce / qe = 1/q_{max}\ KL + Ce/ q_{max}} \qquad \mathbf{(6)}$$

Where Ce (mgL^{-1}) is the concentration of betalains at equilibrium, q_e(mgg^{-1})is the amount of betalains adsorbed by the fabrics at equilibrium, q_{max} (mgg^{-1}) is the maximum adsorption capacity corresponding to monolayer coverage, and K_L (L/mg) is the Langmuir constant. The values of q_{max} and K_L can be calculated from plotting C_e /q_e versus C_e. The Langmuir plots for betalains adsorptions onto the fabrics are obtained and the parameters are shown in Table 3. The values of the correlation coefficient for the Langmuir plots changed in the range 0.40 to 0.70. This suggests that the adsorption of betalains onto the fabrics did not follow the Langmuir model.

3.6.2 Freundlich adsorption isotherm

The Freundlich isotherm is used to explain adsorption processes that arise on heterogeneous surfaces and active sites with various energies based on multilayer adsorption and equilibrium [35].The linear form of Freundlich Equation is given as:

$$\mathbf{\log q_e = Log K_F + 1/n \log C_e} \qquad \mathbf{(7)}$$

Where q_e is the betalains concentration on the fabrics at equilibrium, C_e (mgL^{-1}) is the concentration of betalains in solution at equilibrium, and K_F ($dm^3\ g^{-1}$) and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively . The Freundlich constants are calculated from the slope and the intercept also given in Table 3, the correlation coefficients ($R^2 > 0.99$) reflect that the experimental data agree well with the Freundlich model. The values of 1/n (0.86 and 0.92) are smaller than 1, so they represent the favourable adsorption conditions [36].

Table (2): Kinetic parameters of the dyeing process of betalains adsorbed into cotton, wool and silk fabrics at different temperatures

Temp.	First-order kinetic model			Second-order kinetic model			Elovich			Intraparticle diffusion		
(^{0}C)	q_e, cal (mg/g)	k_1 x10^{-2} (1/min)	R^2	q_e, cal (mg/g	k_2 x10^{-4} (g/mg min)	R^2	x10^{-2} (g/mg	α mg/g min)	R^2	k_i (mg/g $min^{1/2}$	C	R^2
Cotton Fabric												
50	26.22	2.2	0.9	34.52	10	0.98	17	14	0.95	2.25	8.89	0.94
70	36.45	2.7	0.9	51.99	14	0.99	12	27.4	0.94	3.03	19.03	0.95
90	55.06	3.5	0.93	81.68	20	0.99	7.3	37.3	0.89	4.88	33.84	0.85
Wool fabric												
50	75.32	3.1	0.86	129	13	0.99	45	3.75	0.93	22.16	17	0.93
70	85.58	3.6	0.94	139.5	17	0.99	43	45.68	0.96	23.01	23.2	0.97
90	109.91	5.7	0.97	152.3	22	0.99	42	132.6	0.88	23.3	38.8	0.89
Silk fabric												
50	30.08	2.4	83	160.28	22	0.99	9.5	22.48	98	3.7	122.5	0.9
70	39.63	4.3	92	169.41	23	0.99	9.4	57.06	88	3.9	130.3	0.87
90	37.67	4.4	96	173.14	26	0.99	9.1	170.8	89	3.9	135.6	0.81

Table 3: Langmuir, Freundlich isotherm constants of the dyeing process of betalains adsorbed into cotton, wool and silk fabrics at different temperatures.

Fabric type	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_{max} $X10^2$ (mg g^{-1})	K_L $x10^{-3}$ (dm^3 mg^{-1})	R^2	K_F (dm^3 g^{-1})	n/1	R^2
Cotton	1.26	3.4	0.65	1.04	0.89	0.98
	1.86	4.0	0.71	1.26	0.86	0.99
	4.77	4.5	0.71	1.40	0.92	0.999
Wool	2.94	4.9	0.90	1.53	0.88	0.99
	6.15	5.1	0.59	1.78	0.89	0.99
	6.24	5.9	0.69	1.96	0.91	0.99
Silk	10.13	4.9	0.83	1.92	0.90	0.995
	10.29	5.4	0.83	1.94	0.91	0.995
	10.32	5.8	0.82	1.95	0.92	0.998

3.7 Dyeing Thermodynamics

To establish a criterion for determining the feasibility or spontaneity of the dyeing process the chemical thermodynamic parameters had been examined. The enthalpy ΔH^0 and entropy ΔS^0 were calculated using Equation (8):

$$\ln K = \Delta S^0/R - \Delta H^0/(RT) \quad (8)$$

Where the values of ΔH^0 and ΔS^0 can be determined from the slope and intercept of the plot of ln *K* versus 1/T Figure (10)**.**

Gibbs free energy change, ΔG^0, can be calculated in terms of enthalpy and entropy as in the following Equation (9) [37-38].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

As can be seen from the data in Table (4) and Figure10, all magnitudes of enthalpy change indicate that the adsorption is physical in nature. In addition, the enthalpy change had a positive value indicate the endothermic nature of the overall dyeing process. The entropy change shows negative values, indicates that the adsorbed betalains become more ordered within fabrics sheet than the dye in solution [39]. The data also show that the positive ΔG^0 values suggest that the adsorption of betalains onto cotton, wool and silk fabrics require energy to achieve the dyeing process accounting the endothermic and spontaneous nature of the overall dyeing process.

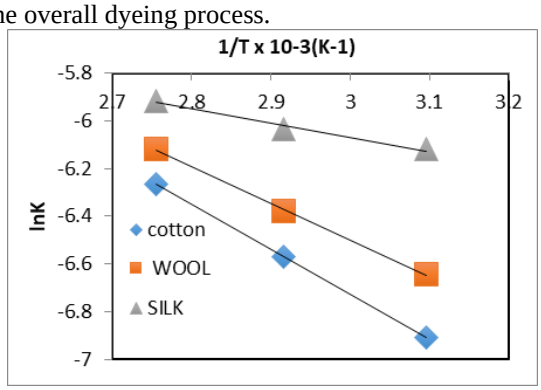

Fig.(10) Variation of lnK with 1/T (0K-1) for estimation of the enthalpy and entropy betalains into (a) cotton, (b) wool and (c) silk fabrics.

Table 4: Thermodynamic parameters for the adsorption of betalains into cotton, wool and silk fabrics at various temperatures.

Fabric	Temerature	Temperature	ΔH^0	(-) ΔS^0	$\Delta^0 G$
	C^o	k^o	**KJ/mol**	J/Kmol	**KJ/mol**
Cotton	50	323	15.63	9.02	18.55
	70	343			18.72
	90	363			18.9
Wool	50	323	12.81	15.61	17.84
	70	343			18.18
	90	363			18.46
Silk	50	323	4.97		16.43
	70	343		35.5	17.2
	90	363			17.84

3.8 Determination of Fabrics Properties

3.8.1 Color Fastness properties

The results in Tables (5) indicate well to very good color fastness grade for untreated fabrics towards washing, light and perspiration. The data assist the important requirement for comfort properties, which base the fundamental of medical fabrics. In general, the results give very good indication for enhancement the functionality of fabric's betalains. Fastness properties of the dye on treated fabrics were evaluated. The results indicated that color fastness to light, washing and perspiration of dyed samples are excellent as shown in Table (5)

3.9 Food industry and health benefits of betalains

3.9.1 Food industry

Betalains are natural plant-derived pigments that are gaining in popularity nowadays for their use as natural materials Colorants in the food industry. Consumers' growing interest in beauty, nutrition and safety Food aspects have increased the demand for natural dyes such as betalains for use as an alternative Colorings in food products [40].

Although betalains from red beetroot are one of the most widely used foods Colorants So betalain was studied, this study reviews the pharmacological properties, such as antioxidants and Anticancer of betalains derived from sources such as red beetroot, for use as functional foods. We show some figures of foods that have been dyed with bio beetroot (betalain).

3.9.2 Antioxidant activity

The antioxidant activity of betalains has been demonstrated in several chemical and biological models such as trolox equivalent antioxidant capacity (TEAC) and 1,1-diphenyl-2-picryl hydrazy (DPPH) study. The free radical-scavenging activity of betanin measured in a 1,1-diphenyl-2- picrylhydrazy (DPPH) assay is higher, than that of vitamin C, which is an effective natural antioxidant [41-42].Pre-treatment of HT-29 cells with betalains significantly reduced hydrogen peroxide induced DNA damage [43]

indicating the potential DNA-protective effect of betalains. Betalains identified by the DPPH method were found to be among the most powerful antioxidants as ascorbic acid and other powerful antioxidants, such as rutin and catechins [41].

The Figure 12 (a,b) shows that the DPPH scavenging % of Betalain is generally close to that obtained by using ascorbic acid under the same conditions. Improvements observed in DPPH scavenging %, which reaches to 93.95% for Betalain, compared to 98.91 % for ascorbic acid.

Fig. (11) some foods before and after dyed with bio beetroot (betalain)

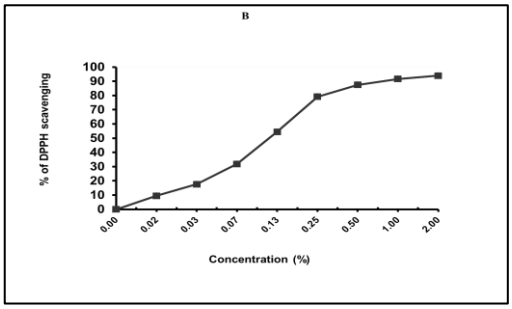

Fig. (12 a) the DPPH scavenging % of Betalain

3.9.3 Anti-cancer properties

Betalains are actively involved in the removal of free radicals. Thus, it may prevent the onset of cancer and cardiovascular disease. Betalains have been found to transactivate the major nuclear erythrocyte nuclear factor 2 (Nrf2) that stimulates the antioxidant defense mechanisms of endogenous cells [43].

The carcinogenic human liver cell (Huh7 Cell) Supplement with 15mM Betalains from Beetroot. It resulted in a significant increase in cellular glutathione (GSH), which are important cellular antioxidants that lead to cell cycle arrest and apoptosis[43] indicating the possibility of chemoprevention properties of betalains. Betalains are found from beetroot Anti proliferative activity in cancer cells. Extracts of beets Contains betalains, which suppress the growth of human colon and breast cancer cells significantly. Future research combining neoplastic cell lines with in vivo testing in a model that closely resembles the targeted human cancer will have a better chance of evaluating betalains' anticancer effectiveness.The Inhibitory percent of Betalains against colon carcinoma cells is 60.59 percent, while the low Inhibitory percent of Betalains against breast carcinoma cells is 26.16 percent, as shown in Figures 13 (a,b).

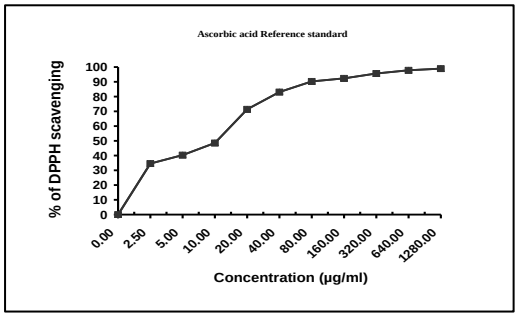

Fig. (12 b) The DPPH scavenging % of Ascorbic acid.

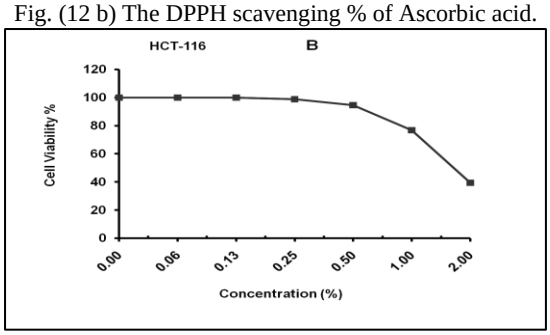

Fig.(13a) Betalain inhibition effect against colon carcinoma cells

Table (5) Color fastness to light, washing and perspiration of dyed sample

Type of fabrics	Untreated fabrics				Treated fabrics			
	Washing	Light	Perspiration		Washing	Light	Perspiration	
			Acid	Alkali			Acid	Alkali
Cotton	3	3-4	3-4	3-4	4	4-5	4-5	4-5
Wool	3-4	4	4	4	4-5	5	5	5
Silk	3-4	4	4	4	5	5	5	5

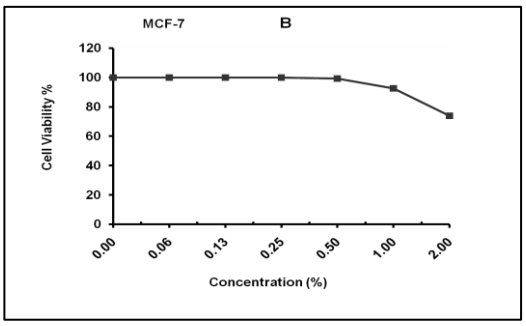

Fig.(13b) Betalain inhibition effect against breast. carcinoma cells.

4. Conclusion

The extraction condition plays an important role in the extracting content of betalain(beetroot peel extract) and the physical character. Water was used in this study as a green solvent for almost the entire experiments. The optimum extraction conditions were 0.5 g /10 ml water, 50ºC for a duration of 3min and extraction pH optimized at 5. The characteristic analyses showed that betalain have a maximum absorbance at 535 nm, FTIR spectroscopy showed the presence of C=O and COOH groups that characterize the betalain dye, the mass spectrum of Beetroot solution gives the molecular ion peak at 551 m/z, the dyeing process for different fabric showed improvements in the presence of chitosan, the kinetic adsorption mechanism showed that the dyeing process follow the second order rate constant. Also follow the freundlich isotherm; all magnitudes of enthalpy change indicate that the adsorption is physical in nature. In addition, the enthalpy change had a positive value indicate the endothermic nature of the overall dyeing process. The entropy change shows negative values, indicates that the adsorbed betalains become more ordered within fabrics sheet than the dye in solution. The data also show that the positive ΔG^{0} values suggest that the adsorption of betalains onto fabrics require energy to achieve the dyeing process accounting the endothermic and spontaneous nature of the overall dyeing process. Betalain showed marvelous results as colorant agent. The antioxidant activity of betalains has been demonstrated, Improvements observed in DPPH scavenging %, which reaches to 93.95% for Betalain, compared to 98.91 % for ascorbic acid. Beet extracts Contains betalains that have a significant growth inhibitory effect on Human colon and breast cancer cells.

5. Conflicts of interest

There are no conflicts to declare.

6. Formatting of funding sources

No funding sources.

REFERENCES

[1] Kumar V, Prabha R. Extraction and analysis of natural dye. J. Nat. Prod. Plant Resour. 2018;8(2):32-8.

[2] AL-Khateeb DS. Extraction Dyes From Two Natural Plants Olive Leaves and Beta vulgaris And The Uses In dyeing Textile. InJournal of Physics: Conference Series 2019 Sep 1 (Vol. 1294, No. 6, p. 062109). IOP Publishing.

[3] Cai Z, Jiang G, Yang S. Chemical finishing of silk fabric. Coloration technology. 2001 May;117(3):161-5.

[4] Vankar PS, Shanker R, Verma A. Enzymatic natural dyeing of cotton and silk fabrics without metal mordants. Journal of Cleaner Production. 2007 Oct 1;15(15):1441-50.

[5] Ali NF, El-Khatib EM, EL-Mohamedy RS. Improvement in Properties of Wool Fibers Pretreated with Chitosan and Nano-Chitosan and Dyed with Saffron Natural Dye. Egyptian Journal of Chemistry. 2019 Dec 1;62(Special Issue (Part 1) Innovation in Chemistry):357-66.

[6] Gengatharan A, Dykes GA, Choo WS. Betalains: Natural plant pigments with potential application in functional foods. LWT-Food Science and Technology. 2015 Dec 1;64(2):645-9.

[7] Ravichandran K, Saw NM, Mohdaly AA, Gabr AM, Kastell A, Riedel H, Cai Z, Knorr D, Smetanska I. Impact of processing of red beet on betalain content and antioxidant activity. Food research international. 2013 Mar 1;50(2):670-5.

[8] Prabha R, Singh DP, Verma MK, Sahu P, Kumar P.Bacterial diversity in rhizosphere of Paspalum scrobiculatum L.(kodo millet) is revealed with shotgun metagenome sequencing and data analysis. Data in brief. 2018 Oct 1;20:1653-7.

[9] Bhuiyan MR, Shaid A, Khan MA. Cationization of cotton fiber by chitosan and its dyeing with reactive dye without salt. Chemical and materials engineering. 2014;2(4):96-100.

[10] Hilal NM, Gomaa SH, ELsisi AA. Improving Dyeing Parameters of Polyester/Cotton Blended Fabrics by Caustic Soda, Chitosan, and Their Hybrid. Egyptian Journal of Chemistry. 2020 Jun 1;63(6):2379-93.

[11] Fakhari AR, Salehi P, Heydari R, Ebrahimi SN, Haddad PR. Hydrodistillation-headspace solvent microextraction, a new method for analysis of the essential oil components of Lavandula angustifolia Mill. Journal of Chromatography A. 2005 Dec 9;1098(1-2):14-8.

[12] Herbach KM, Maier C, Stintzing FC, Carle R. Effects of processing and storage on juice colour and betacyanin stability of purple pitaya (Hylocereus polyrhizus) juice. European Food Research and Technology. 2007 Mar;224(5):649-58.

[13] Sadowska-Bartosz I, Bartosz G. Biological properties and applications of betalains. Molecules. 2021 Jan;26(9):2520.
[14] Kushwaha R, Kumar V, Vyas G, Kaur J. Optimization of different variable for eco-friendly extraction of betalains and phytochemicals from beetroot pomace. Waste and Biomass Valorization. 2018 Sep;9(9):1485-94.
[15] Sadowska-Bartosz I, Bartosz G. Biological properties and applications of betalains. Molecules. 2021 Jan;26(9):2520.
[16] Attia GY, MOUSSA MM, SHEASHEA EE. Characterization of red pigments extracted from red beet (Beta vulgaris, L.) and its potential uses as antioxidant and natural food colorants. Egyptian Journal of Agricultural Research. 2013 Sep 1;91(3):1095-110.
[17] Adenam NM, Pirdaus NA, Yunin MY, Azmie K, Wong KN, Adli HK, Salleh H. Study of Beta vulgaris (Beetroot) Extraction in Polar Solvents as Photoabsorber in Dye-Sensitized Solar Cells Application. InIOP Conference Series: Earth and Environmental Science 2020 Dec 1 (Vol. 596, No. 1, p. 012014). IOP Publishing.
[18] Syafinar R, Gomesh N, Irwanto M, Fareq M, Irwan YM. FT-IR and UV-VIS spectroscopy photochemical analysis of dragon fruit. ARPN J. Eng. Appl. Sci. 2015;10:6354-8.
[19] Aztatzi-Rugerio L, Granados-Balbuena SY, Zainos-Cuapio Y, Ocaranza-Sánchez E, Rojas-López M. Analysis of the degradation of betanin obtained from beetroot using Fourier transform infrared spectroscopy. Journal of Food Science and Technology. 2019 Aug;56(8):3677-86.
[20] Yusuf M, Shabbir M, Mohammad F. Natural colorants: Historical, processing and sustainable prospects. Natural products and bioprospecting. 2017 Feb;7(1):123-45.
[21] Wang H, Li Y, Zhang K, Ma Y, Li P. Feasibility and transcriptomic analysis of betalain production by biomembrane surface fermentation of Penicillium novae-zelandiae. AMB Express. 2018 Dec;8(1):1-0.
[22] Popescu V, Blaga AC, Pruneanu M, Cristian IN, Pîslaru M, Popescu A, Rotaru V, Crețescu I, Cașcaval D. Green chemistry in the extraction of natural dyes from colored food waste, for dyeing protein textile materials. Polymers. 2021 Jan;13(22):3867.
[23] Tamirat AG, Sendek A, Libsu S. Optimizing Dyeing Parameters of Remazol Golden Yellow G Dye upon Cotton Fabric. International Journal. 2014;2(10):234-40.
[24] Mane VS, Mall ID, Srivastava VC. Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution. Dyes and Pigments. 2007 Jan 1;73(3):269-78.
[25] Ali NF, El-Khatib EM, EL-Mohamedy RS. Improvement in Properties of Wool Fibers Pretreated with Chitosan and Nano-Chitosan and Dyed with Saffron Natural Dye. Egyptian Journal of Chemistry. 2019 Dec 1;62(Special Issue (Part 1) Innovation in Chemistry):357-66.
[26] Silva LP, Pereira TM, Bonatto CC. Frontiers and perspectives in the green synthesis of silver nanoparticles. InGreen synthesis, characterization and applications of nanoparticles 2019 Jan 1 (pp. 137-164). Elsevier.
[27] Perumalraj R. Effect of sliver nanoparticles on wool fibre. International Scholarly Research Notices. 2012;2012.
[28] Tseng RL, Wu PH, Wu FC, Juang RS. A convenient method to determine kinetic parameters of adsorption processes by nonlinear regression of pseudo-nth-order equation. Chemical Engineering Journal. 2014 Feb 1;237:153-61.
[29] Chen Y, Zhang D. Adsorption kinetics, isotherm and thermodynamics studies of flavones from Vaccinium Bracteatum Thunb leaves on NKA-2 resin. Chemical Engineering Journal. 2014 Oct 15;254:579-85.
[30] Shahwan T. Sorption kinetics: obtaining a pseudo-second order rate equation based on a mass balance approach. Journal of Environmental Chemical Engineering. 2014 Jun 1;2(2):1001-6.
[31] Kumaresan M, Palanisamy PN, Kumar PE. Application of eco-friendly natural dye on cotton using combination of mordants. Indian Journal of Fibre & Textile Research.2012 June 2(37):194-98.
[32] Ghasemi N, Tamri P, Khademi A, Nezhad NS, Alwi SR. Linearized equations of pseudo second-order kinetic for the adsorption of Pb (II) on pistacia atlantica shells. Ieri Procedia. 2013 Jan 1;5:232-7.
[33] Lorenc-Grabowska E, Gryglewicz G. Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon. Dyes and pigments. 2007 Jan 1;74(1):34-40.
[34] Edet UA, Ifelebuegu AO. Kinetics, isotherms, and thermodynamic modeling of the adsorption of phosphates from model wastewater using recycled brick waste. Processes. 2020 Jun;8(6):665.
[35] Yuan X, Xia W, An J, Yin J, Zhou X, Yang W. Kinetic and thermodynamic studies on the phosphate adsorption removal by dolomite mineral. Journal of Chemistry. 2015 Jan 1;2015.
[36] Shama SA, Gad MA. Removal of heavy metals (Fe3+, Cu2+, Zn2+, Pb2+, Cr3+ and Cd2+) from Aqueous Solutions by using Hebba Clay and Activated Carbon. Portugaliae Electrochimica Acta. 2010 Sep 18;28(4):231-9.
[37] Tserendulam S, Yu G, Nadmid G, Kh SU. Studies of kinetics and thermodynamic parameters of cashmere dyeing with bio-preparation of Urtica

Cannabina L. Proceedings of the Mongolian Academy of Sciences. 2019 Apr 26:4-15.

[38] Gohr MS, Abd-Elhamid AI, El-Shanshory AA, Soliman HM. Adsorption of cationic dyes onto chemically modified activated carbon: Kinetics and thermodynamic study. Journal of Molecular Liquids. 2022 Jan 15;346:118227.

[39] Kongkachuichay P, Shitangkoon A, Chinwongamorn N. Thermodynamics of adsorption of laccaic acid on silk. Dyes and pigments. 2002 May 1;53(2):179-85.

[40] Gengatharan A, Dykes GA, Choo WS. Betalains: Natural plant pigments with potential application in functional foods. LWT-Food Science and Technology. 2015 Dec 1;64(2):645-9.

[41] Cai, Y., Sun, M., & Corke, H. (2003). Antioxidant activity of betalains from plants of the Amaranthaceae. Journal of Agriculture and Food Chemistry, 51, 2288e2294. Chemistry and Toxicology, 73, 119-126.

[42] Gliszczyńska-Świgło A. Antioxidant activity of water soluble vitamins in the TEAC (trolox equivalent antioxidant capacity) and the FRAP (ferric reducing antioxidant power) assays. Food chemistry. 2006 May 1;96(1):131-6.

[43] Esatbeyoglu T, Wagner AE, Motafakkerazad R, Nakajima Y, Matsugo S, Rimbach G. Free radical scavenging and antioxidant activity of betanin: Electron spin resonance spectroscopy studies and studies in cultured cells. Food and Chemical Toxicology. 2014 Nov 1;73:119-26.