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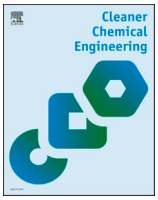

Improved coloration of hemp fabrics via low-pressure argon plasma assisted surface modification

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ABSTRACT

Interest in hemp as a viable cellulosic fibre for clothing has increased, driven partly by its economic benefits and the importance of natural renewable materials in emerging circular economies. However, the coloration and chemical finishing of lignocellulosic fibres such as hemp typically require large quantities of water and chemicals. Argon plasma pretreatment provides a way of modulating the physical properties of hemp fibres to improve the coloration process without compromising other bulk properties such as tensile strength. Such plasma treatments may contribute to alleviating the negative environmental impacts associated with liquid pretreatments, heating, or the use of auxiliary chemicals. Dyeing of hemp fibres is particularly challenging due to its crystalline chemical structure. In this study, low-pressure argon plasma-assisted surface modification of woven hemp fabrics up to 600 s at 40 and 80 Hz was explored for enhanced dyeability, resulting in enhanced dye-fibre bonding. Fourier-transform infrared spectroscopy and Raman spectroscopy of argon plasma pretreated hemp fabrics produced no noticeable changes in the functional groups of the fibres, but a physiochemical modification was observed in terms of the density of polar groups. Scanning electron microscopy (SEM) images revealed marked morphological changes including nano-etching of the fibre surface at certain argon plasma process conditions. The pretreatment process increased fibre hydrophilicity, and enhanced reactivity of the surficial –OH groups towards fibre-reactive and vat dyes, resulting in higher colour strength in dyed woven hemp fabrics. Overall, we envisage such plasma pretreatments may impact positively on the material and energy efficiency of the hemp fabric dyeing process.

1. Introduction

Hemp is a natural cellulosic fibre similar to bast fibres such as flax and ramie that are widely used in the textile industry (Manian et al., 2021). The fibres are extracted from the internal stems of the Cannabis sativa *L.* plant and comprise primary and secondary walls of long cellulose microfibrils (~72 % cellulose Chokshi et al., 2020) arranged in layered strata, with a distinctive axial orientation (Zimniewska, 2022). The high crystallinity and axially aligned cellulosic structure confers characteristically high tensile strength and attractive mechanical properties, such that hemp finds purpose in numerous textile applications, including technical textiles, fibre-reinforced composites and clothing. Opportunities for hemp in clothing are further extended by cottonisation of the coarse fibres extracted from the plant's stem, yielding smaller fibre diameters of ca. 15–20 μm, that are suitable for blending with other fibres such as cotton and spinning into fine count yarns (Zimniewska, 2022). Given the growing importance of renewable materials in the fashion and textile industry, there is an increasing interest in hemp as an economically attractive fibre for clothing fabrics, but sustainable development necessitates less resource intensive dyeing and coloration processes (Dhondt and Muthu, 2021). Compared to other natural cellulosic fibres, notably cotton, and bast fibres such as flax (linen), there is a paucity of studies relating specifically to the dyeing of hemp.

Conventional dyeing processes in the textile industry can have significant environmental impacts. It has been claimed that for every ton of fabric to be dyed, up to 200 tonnes of wastewater containing salts, dyes, surfactants, peroxides and heavy metals can be generated (Lara et al., 2022). To address these issues, alternative coloration methods such as supercritical CO_2 and ultrasonic methods are being studied (Goñi et al., 2021). Innovative coloration methods also include laser and enzyme processing technologies, particularly in relation to cotton, wool and polyester substrates (Kane et al., 2020). However, current research lacks

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Table 1
Recent studies on the coloration of hemp using exhaustion methods.

Substrate	Dyeing Conditions	Summary	Refs.
Hemp/Cotton blend	8 % w/w dye Material to liquor ratio (MLR)= 1:60 $t = 1$ h, $T = 60$ °C	Dyed using common madder and calendula achieving a colour strength of 5.6 after applying tannin as a mordant.	Mijas et al. (2022)
100 % Hemp fabric (GSM:132)	$t = 2$ h, $T = 70$ °C	Dyed using plant-based dyes and the ultraviolet protection factor was evaluated.	Grifoni et al. (2020)
100 % Hemp fabric	5 % w/w dye shade MLR= 1:20 $t = 1$ h, $T = 60$ °C	Dyed using reactive dye and compared with cotton fabric.	Kabir et al. (2017)
100 % Hemp yarn	$t = 70$ min, $T = 60$ °C	Dyed using the conventional dyeing method and fabric properties were compared with flax, linen, cotton and their respective blends.	Atav et al. (2024)

a focus on hemp. The use of hemp in the textile industry is limited primarily due to the dominance of cotton, historical stigma, complex governmental regulations and a lack of awareness about the potential advantages of the fibre (Gedik and Avinc, 2022). Table 1 highlights recent studies where hemp dyeing was accomplished using conventional exhaustion methods.

Current research interest in surface-treated hemp fibres is mainly confined to fibre-reinforced composite applications. The aim of the present research is to broaden the scope of hemp usage from composites to clothing applications by addressing two major research gaps related to the study of hemp fibre colouration. First, it addresses the issue of low colour fastness in dyed hemp fabrics, by exploring dye-fibre bonding using pyridine stripping (Sunoj Valiaparambil Sebastian et al., 2023). Second, while numerous studies have reported surface modifications on cellulosic fibres, they often overlook the chemical interactions following these surface modifications (Sunoj Valiaparambil Sebastian et al., 2023). This work investigates both morphological and chemical changes resulting from low-pressure argon plasma pretreatment.

To develop environmentally sustainable coloration techniques for hemp fabrics, it is important to understand the extent to which non-aqueous fabric pretreatments might enhance dyeability. Previously, microwave and UV irradiation of bast fibre cellulosic fabrics have shown potential to improve the colour strength and fastness of dyed fabrics (Abdelileh et al., 2021; Adeel et al., 2015; Sun et al., 2005). However, plasma pretreatment has arguably become the most ubiquitous, non-aqueous pretreatment method for natural cellulosic fibres, providing a means to modulate fibre physical structure and surface chemistry (Zhianmanesh et al., 2023). The advantage of plasma as a pretreatment is that it is a chemically independent technique, which confines its physical and chemical effects to the surface.

Plasma is defined as a state in which a significant number of atoms and/or molecules are either electrically, thermally, magnetically excited or ionised. Plasma treatment may impart physical or chemical changes with the help of radicals, ions or electrons in an excited state. Low-pressure plasma is applied in various fields such as surface cleaning, coating, etching and functionalisation of polymeric materials, with the ability to modify surface fibre morphology and/or chemistry (Chan et al., 1996). Plasma treatment can have an etching effect on the surface resulting in a nano-porous structure (Cho et al., 2001). The use of noble gases like argon can also produce highly energetic radicals in the plasma state that are able to break C-C, C-H, and hydrogen bonds, and potentially create desirable functional groups (Alves et al., 2011). As reported by Thompson et al. (2021), plasma treatment of nylon-6 using oxygen gas as a source gas resulted in an increase in the number of polar groups (C=O, C-C, C-OOH), increasing the hydrophilicity of the surface. Hemp also has a crystalline structure and is releatively hydrophobic in its parent state.

Previously, plasma treatment of hemp has mainly been confined to studies of bio-composites, specifically fibre-reinforced polymer composites, in which hemp fibres are used as a reinforcing phase (Pillai and Thomas, 2023). In this context, plasma pretreatment can be used to improve the interfacial bonding between the fibre surfaces and the matrix phase, so as to improve the bulk tensile and shear strengths, as well as the fracture resistance of the bio-composite (Barbière et al., 2021). Plasma treatment of hemp fibres using argon as a source gas has also been reported to improve the sound absorption of the resulting structures (Pavlovic et al., 2019).

Low-pressure argon plasma pretreatment of other bast fibres, such as flax, has been found to enhance hydrophilicity leading to strong interfacial bonding with vinyl silane to confer flame retardancy (Gieparda et al., 2021). In the context of fibres derived from bamboo, plasma-assisted surface modification employing gases such as oxygen and argon improved surface wetting and interfacial adhesion, thus promulgating their application as a reinforcement material in composites (Sawangrat et al., 2023). Similarly, jute fibres treated with air plasma, exhibited increased hydrophilicity due to surface etching, subsequently improving interfacial adhesion and thereby rendering them suitable for reinforcement in composites (Ullah et al., 2021; Ivanovska et al., 2023).

The potential for argon plasma irradiation as part of a pretreatment process to enhance the dyeing properties of hemp remains a topic that has not been extensively explored in the literature. Radetić et al. (2007) studied the low-temperature air plasma and enzymatic pretreatment of hemp for acid dyeing and reported an increase in the dyeing rate, final dye exhaustion and colour yield. The observed effects were attributed to plasma etching and oxidation of hemp fibre surfaces. Argon plasma treatment is believed to promote crosslinking of the polymer chains and fragmentation of polymer chains into lower molecular weight entities, and argon plasma is thought to induce a more enduring hydrophilic transformation than any other gas plasma (Luque-Agudo et al., 2021). Based on the literature survey, it is apparent that there is insufficient study exploring the extent to which plasma pretreatment influences the dyeing of hemp. Dyeing of hemp presents particular challenges due to the high degree of molecular orientation and relatively high crystallinity of the fibres. In such crystalline natural fibres, dye molecules tend to penetrate more easily through the amorphous regions than the crystalline regions (Zhu et al., 2004). Conventional dyeing procedures take place in an aqueous environment, wherein, water has a competitive role in relation to hydrogen bonding, and given the extensive hydrogen bonding in cellulose, when immersed in water, negative zeta potential arises. Similarly, when reactive dye molecules are solubilised in water, they acquire a negative zeta potential due to the presence of -SO_3H group. Therefore, the addition of salts helps neutralise the negative zeta potential acquired by cellulose, thereby promoting uniform dye adsorption. Lokhande et al., observed a decrease in a negative zeta potential, leading to proportional dye adsorption in the cellulosic structure (Lokhande and Salvi, 1976).

The dyeing of cellulosic fibres such as hemp is an equilibrium reaction, which depends on the temperature, pH and dye concentration and the extent of dye adsorption hinges on the cohesive forces inherent in the cellulosic structure. When cellulose interacts with water, the water molecules compete for some hydrogen bonding sites. Notably, cellulose carries inherent fixed positive charges that can potentially repel dye molecules seeking adsorption. The presence of these Coulombic effects inhibits dye adsorption and further dye uptake (Rattee, 1964, 1972; Rattee and Breuer, 1974). Accordingly, previous investigations into augmenting the coloration of hemp textiles have explored the application of mordants such as tannin and alum (Mijas et al., 2022). A comparable study done by Correia et al. (2021) focused on the pretreatment of cotton fabric using cationic ammonium compounds, which were

further plasma treated using oxygen gas. Similarly, nitrogen plasma pretreatment can be used to graft silver nanoparticles onto cellulosics such as cotton, viscose and linen to impart antibacterial functionality (Ibrahim et al., 2017). In a literature review, Haji et al. summarised major studies in recent years where the coloration of wool, cotton and polyester fibres was achieved (Haji and Naebe, 2020). Interestingly, the majority of the studies, aiming to achieve coloration of fibres using plasma, have employed oxygen as their plasma source.

The goal of this research is to utilise an inert, low-pressure argon plasma pretreatment to surface-modify woven hemp fabrics prior to conventional exhaustion dyeing. The extent to which the colour strength of resulting dyed fabrics is affected by the argon plasma pretreatment is studied to assess the potential for more sustainable coloration. Moreover, the impact of power and the duration of argon plasma pretreatment on surface modifications was explored in relation to reactive dyeing and vat dyeing. An analysis encompassing surface morphology, Raman spectroscopy, Fourier transform infrared spectroscopy and surface wetting properties was conducted on both untreated and plasma treated hemp fabrics.

2. Experimental

2.1. Materials

In the experimental work reported here, 100 % hemp fabric samples of different woven constructions (H, P1, P2) and yarn linear densities in the warp and weft, were industrially procured (Hemptology Ltd, UK), with material specifications as shown in Table 2.

Prior to low-pressure argon plasma pretreatment, all samples were scoured to remove any residual processing chemicals or spin finish. An alkaline boiling process was followed for the scouring of hemp (Wang and Postle, 2004). Thus, hemp fabrics were boiled for 75 min in an alkali solution containing 6 % o.w.f (on the weight of fabric) NaOH, 3 % o.w.f of Na_2CO_3 and 0.5 % o.w.f of Na_2SO_3. After the alkaline boiling, the fabrics were neutralised using 10 % o.w.f CH_3COOH and were washed thoroughly with deionised water. The scoured fabrics were dried in an air-assisted oven at 90 °C. Following drying, the scoured fabrics were stored in a standard textile testing environment with 65 % relative humidity at a temperature of 20 °C before plasma treatment. Fibre-reactive and vat dyes were procured from Atul Industries Ltd (India). Analytical research (AR) grade reagents, sodium hydroxide (NaOH), sodium dithionite ($Na_2S_2O_4$) and anionic surfactant were acquired from Sigma-Aldrich (UK). Additionally, Turkey red oil utilised for vat dyeing was purchased from Fisher Scientific Ltd (UK).

2.2. Surface modification of hemp fibres following argon plasma pretreatment

Argon plasma pretreatment of the hemp fabrics was conducted using a Denier Zepto plasma machine (Diener electronic GmbH & Co KG, Germany). The machine incorporates two needle valves for precise gas supply with gas flow controllers. The operational mode of the machine is manual, and it is furnished with a Pfeiffer Duo 3 rotary-vane vacuum pump. For the generation of plasma, an argon gas cylinder was connected to the plasma system. Argon plasma-assisted surface modification of hemp was executed employing various parameter combinations of power (intensity of plasma frequency) and treatment time (duration). Thus, the hemp fabrics underwent plasma treatment at two power levels of 80 Hz and 40 Hz at six treatment durations of $t = 30$ s, 60 s, 120 s, 180 s, 300 s and 600 s. The argon gas supply was maintained at a constant flow rate by setting the gas valve at 1 bar, with a stable pressure of 1.5 mbar within the plasma chamber. Subsequent to argon plasma pretreatment, the fabric samples were conditioned in a standard textile testing environment having a relative humidity of 65 %, maintained at 20 °C. The design of experiments (DOE) was formulated using the surface response design with two factors such as power (40 Hz, 80 Hz) and treatment time (30 s, 60 s, 120 s, 180 s, 300 s, 500 s) The results were then analysed using the surface response analysis methodology using the Minitab software.

Table 2
Product parameters of the hemp fabrics.

Fibre	Fibre Composition	Woven Fabric Structure	Yarn Linear Density (Tex)		Fabric Weight/ unit area ($g.m^{-2}$)
			Warp	Weft	
Hemp	100 %	Herringbone (H)	120	120	190
Hemp	100 %	Plain (P1)	79	79	100
Hemp	100 %	Plain (P2)	35	35	214

2.3. Analysis of fibre surface modifications

The argon plasma pretreated fabric samples were subjected to surface analysis to investigate any induced alterations in fibre surface morphology, fibre chemical modifications or wetting.

2.3.1. Method to study fibre morphological features

The surface morphology of argon plasma pretreated and untreated hemp fibres were investigated by scanning electron microscopy (SEM) images using a Jeol JSM-6610 scanning electron microscope. Using the SE mode, micrographs at magnifications of 25x-8000x were taken of the fibre surfaces for each sample, covering a scale of 1 mm to 10μm following the standard method by Juhász et al. (2021). Prior to image capture, the samples were sputter-coated with gold. Subsequently, SEM images were processed using Fiji ImageJ software to analyse morphological features such as surface roughness (Hojat et al., 2023). To measure the 'pore' structure of the fibre surfaces using Fiji Image J, an area of 30 μm on the fibre was selected within the SEM micrograph. Utilising the threshold function, surface pores within the selected area were highlighted enabling the determination of mean porosity. To assess the pore size, the pore analysis option was applied following the threshold function. The porosity measurements were conducted thrice to ensure reproducibility and to obtain consistent results.

2.3.2. Methods for analysis of chemical modifications

The chemical structure of argon plasma pretreated and untreated hemp samples were analysed utilising FT-IR and Raman spectroscopy. A Bruker FT-IR spectrophotometer which was equipped with an ATR (attenuated total reflectance) was used in the wavelength range of 600 cm^{-1}–4000 cm^{-1}. 100 scans were taken at a resolution of 4 cm^{-1} on the untreated and plasma treated samples referring to the work by Peets et al. (2019). For each fabric sample, three spectra were acquired to ensure the reproducibility of data. Raman spectroscopy of argon plasma pretreated and untreated hemp fabrics was performed using a Horiba Raman spectrometer equipped with a microscope and a 785 nm laser source. A total of 32 scans were accumulated per spectrum having a resolution of 4 cm^{-1} on the untreated and plasma treated samples following a standard method from Rygula et al. (2011) . For each fabric sample, three spectra were acquired to ensure the reproducibility of data. The resulting spectra was processed using Origin software to edit, analyse and represent spectroscopic data.

2.3.3. Method for analysis of surface wetting

The surface-wetting properties of untreated and argon plasma pretreated hemp were assessed using a Kruss DSA30E contact angle measuring equipment. The static contact angle of the hemp fabric was measured by placing 7μl sessile water droplets of deionised water having a surface tension of 72 N/m on the fabric surface. The droplets were allowed to stabilise for 20 s and the contact angle was measured using a built-in camera. Three replicates were taken for H, P1 and P2 fabric types, with each droplet positioned at a different position on the fabric sample to test the reproducibility of the data.

2.4. Method for dyeing hemp with reactive dyes

To study the effect of argon plasma pretreatment on the dyeing behaviour, a 1 % shade was applied across all the experimental procedures involving exhaust dyeing of each of the hemp fabric samples. The calculation for the amount of dye solution was done using Eq. (1). The dyeing process was conducted with a fabric-to-liquor ratio of 1:20 for all samples.

$$Amount\ of\ dye\ solution\ (mL) = \frac{Shade\ (\%)\ \times Weight\ of\ fabric\ (g)}{Concentration\ of\ stock\ solution\ (g/L)} \quad (1)$$

Similarly, the amount of auxiliaries as alkali and salt was calculated using Eq. (2), wherein 20 % of alkali namely soda ash and caustic soda along with 20 % Glauber's salt were used.

$$Amount\ of\ auxiliary\ (mL) = \frac{Auxiliary\ required\ (\%) \times Weight\ of\ fabric\ (g)}{Concentration\ of\ stock\ solution(g/L)} \quad (2)$$

For the dyeing of the hemp fabric, Glauber's salt, water and dye solution were introduced to a beaker alongside the fabric. Firstly, twenty per cent of the salt was utilised, accompanied by 20 % of soda ash and 20 % of caustic soda. Following a 15 min interval, the dye bath was stabilised at a constant temperature of 75 °C. Alkali was then added, and the dyeing was carried out for 60 min under continuous agitation. Fig. 1 summarises the complete reactive dyeing cycle.

Subsequent to dyeing, the dyed fabrics were subjected to a soaping process that involved boiling the fabrics in a 5 % on weight of fabric anionic soap solution to remove unbound dye molecules. The soaped fabric samples were dried in an air-assisted oven at 90 °C for 4 h. The dyed fabrics were analysed using a Konica Minolta CM 700-d spectrophotometer for colour measurement to ascertain the CIE colour coordinates of the dyed fabrics.

2.4.1. Analysis of covalent bonding of reactive dyes

Hemp fabric samples that underwent dyeing with reactive dyes were subjected to a pyridine-stripping process (Uddin et al., 2015). In contrast to the conventional employment of sodium hydrosulphite and sodium hydroxide for dye-stripping, a solution containing 15 g/L of pyridine was utilised. Thus, the dyed fabrics were subjected to boiling in a solution containing 15 g/L pyridine solution. Following 5 min boiling intervals, the pyridine solution was replaced iteratively until achieving a clear solution. The colour strength of the fabrics subjected to pyridine stripping were subsequently measured using a Konica Minolta colour measurement device.

2.5. Method for dyeing hemp with vat dyes

The vat dyeing process for hemp encompassed three sequential stages: vatting, dyeing and air oxidation. The conventionally known vat dyeing process used in the denim textile industry was followed (Vat dyeing of cotton piece, 1959). Initially, the dye mixture was prepared by combining 1 g of amorphous vat dye with 5 mL of turkey red oil, forming a paste. The turkey red oil (sodium salt of sulphated castor oil) acting as a wetting agent, facilitated this process. 40 % o.w.f of sodium hydroxide (NaOH) and 2 gm of sodium dithionite ($Na_2S_2O_4$) were subsequently introduced to the dye paste and stirred until the formation of a homogeneous paste. This process yielded the soluble salt or leuco vat dye. All of the hemp fabric samples were dyed employing a 1 % shade with a fabric-to-liquor ratio of 1:20. Water, surfactant and alkali were added in accordance with calculations based on the material-to-liquor ratio and the weight of the fabric. The temperature of the dye bath was elevated to 80 °C and maintained at this temperature for a duration of 90 min. Upon cooling, the samples underwent washing and air drying to ensure uniform oxidation (Vat dyeing of cotton piece, 1959). The oxidised fabrics were then subjected to a 20 min boiling process in a 15 g/L soap solution, which served the dual purpose of removing excess non-reacted dye molecules and imparting a lustrous appearance to the fabrics. Subsequent to this soaping treatment, the colour strength of the fabrics was

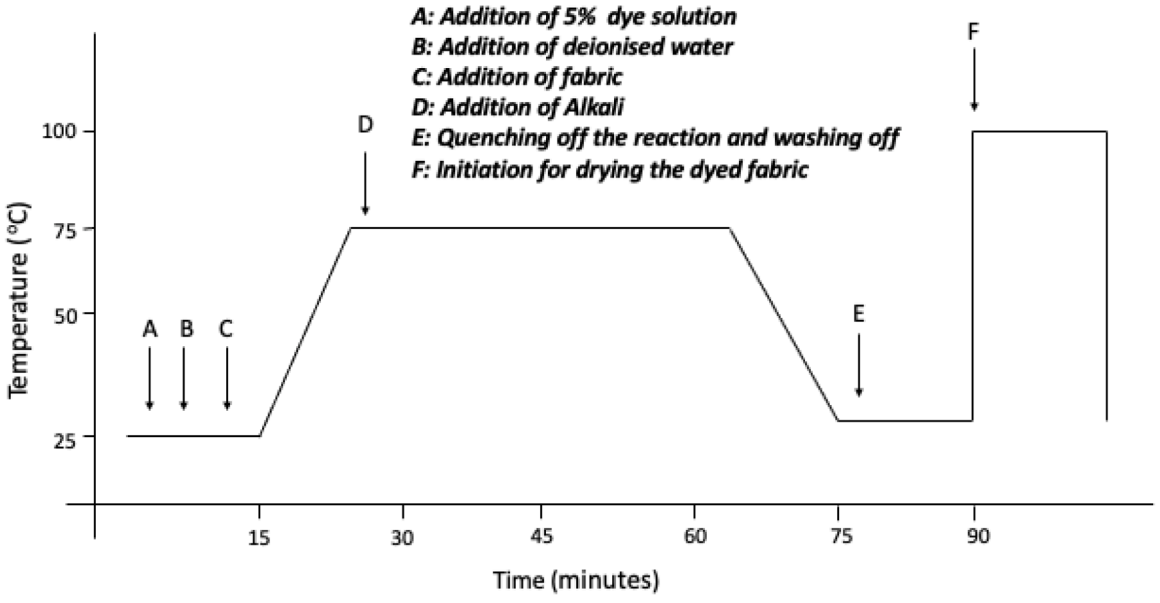


Fig. 1. Dyeing curve for dyeing of hemp fabric using reactive dye.

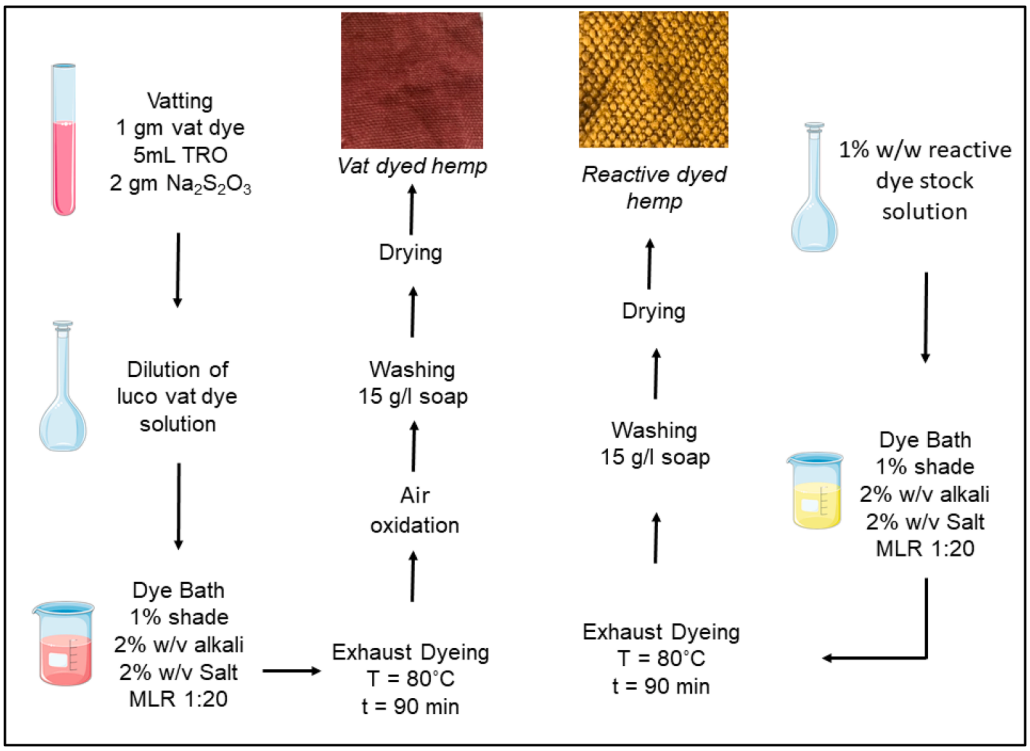


Fig. 2. Dyeing process for untreated and plasma treated hemp fabrics.

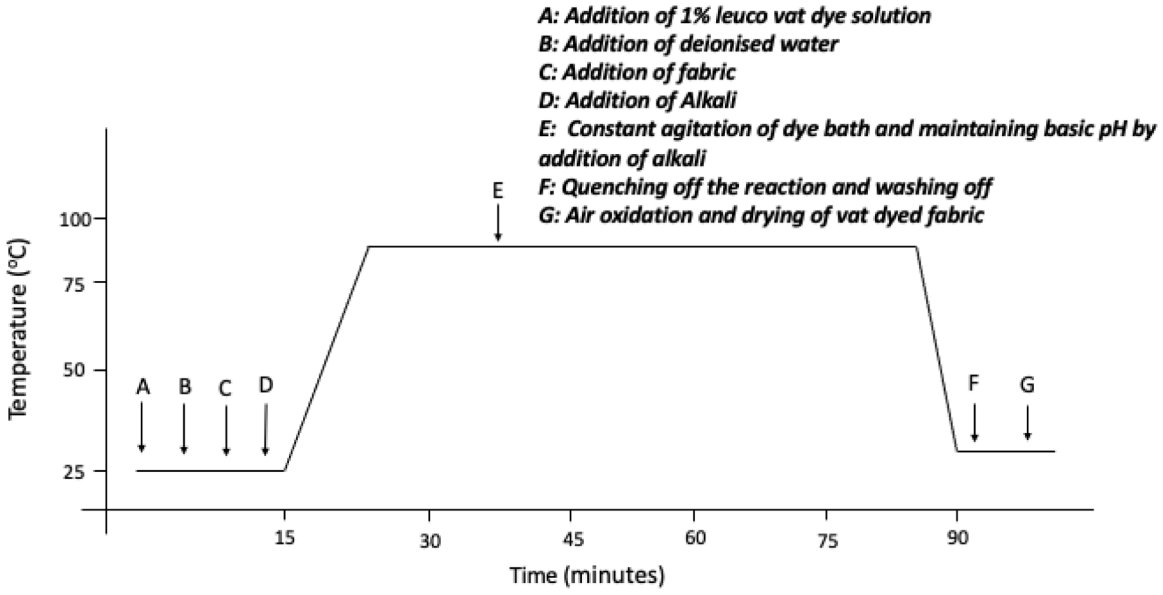


Fig. 3. Dyeing curve for dyeing of hemp using vat dyes.

assessed following drying. Fig. 2 illustrates the vat dyeing and reactive dyeing cycle of hemp fabrics used for this research, and Fig. 3 summarises the employed dyeing profile.

3. Results and discussion

The physical and chemical properties of the hemp fabrics and their constituent fibres were studied before and after pretreatment with argon plasma to determine any structural and chemical effects and their potential influence on the dyeing process.

3.1. Influence of argon plasma treatment on hemp fibre surface morphology

The fibre surface morphologies of untreated and argon plasma treated hemp fabrics were investigated by means of SEM (Fig. 4A–F). Fig. 4A shows a typical example of the surface morphology of fibres in the untreated sample, having relatively smooth surface. Evidence of dry etching is apparent in hemp fibres that had been argon plasma treated for 600 s at 40 Hz power (Fig. 4F). A progressive dry etching can be observed as the argon plasma treatment time increases (Moradkhani et al., 2023). The dry etching can be attributed to a chain scission at the

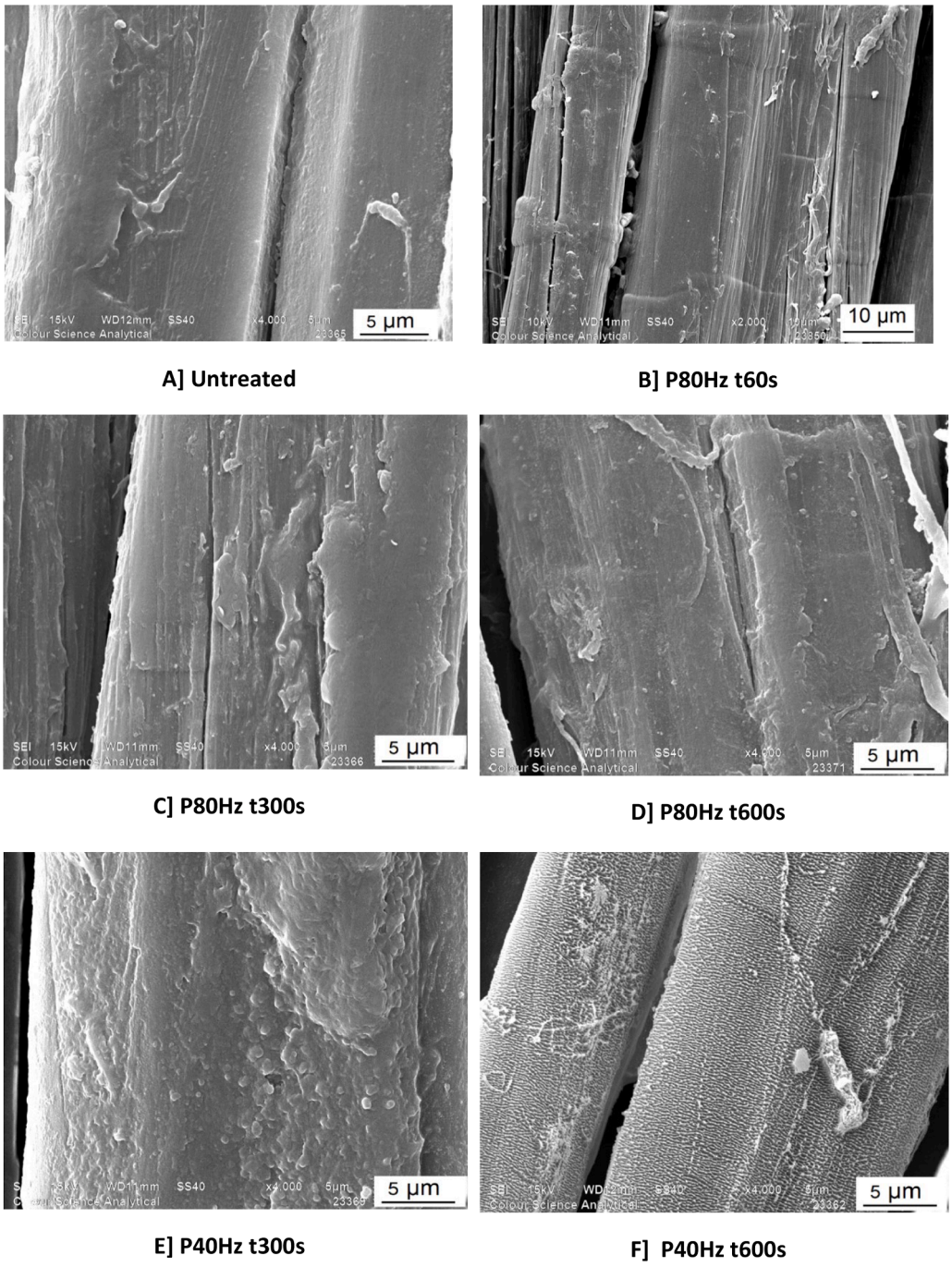


Fig. 4. SEM micrographs showing the surface morphologies of the untreated P1 hemp fabric and the argon plasma treated P1 hemp fabric at different powers (Hz) and treatment times (s) at magnifications of x2000 (micrograph 4B) and x4000 (micrographs 4A, 4C, 4D, 4E and 4F).

surface of the fibre and has been previously observed in plant-based fibres (Moradkhani et al., 2023) as well as regenerated cellulose fibres such as viscose (Sawangrat et al., 2023). This type of effect can be observed highlighting a high degree of sub-micron surface etching in the argon plasma treated hemp samples (comparing Fig. 4A and F).

Plasma is known to be capable of nano-etching surfaces (Palumbo et al., 2019) and etching at this scale was evident in the argon plasma treated samples at x4000 (Fig. 4F). By means of image analysis (Fiji Image J), the size of 'pores' on the surface of the fibres before and after argon plasma treatment were estimated. It was found that, in the untreated sample, the detectable pore structure covered a very small portion of only 0.5 % of the total fibre area of 30 μm, and the mean size of these pores was 3 nm. Following argon plasma treatment, the mean pore size increased to 17 nm, with the pores covering 24 % of the 30 μm fibre area shown in the SEM micrograph. With regard to the change in surface pore structure, the etchant gas, in this case, argon, evidently accelerates onto the surface with a force capable of dislodging atoms or molecules on the surface monolayer. A similar type of nano-porous surface was obtained by the action of argon gas plasma on cellulose paper (Shu et al., 2023). In previous research carried out on the surface of diamond, with oxygen and hydrogen as source gases for plasma generation, the etching mechanism was studied using molecular dynamic simulation, and it was concluded that the etching is a layer-by-layer process involving the generation and desorption of gaseous molecules (Xu et al., 2021). This type of layer-by-layer etching process can be visible in the micrographs whereby an initiation in the

etching is observed in the hemp fabric plasma treated for a lower treatment time of the 60 s (Fig. 4B).

When argon gas comes in contact with the electrodes in the plasma generator, they govern a type of quasi-neutrality. At this stage, the density of positively charged species and negatively charged species is equal (Kortshagen et al., 2016). Ar(18) is a relatively large atom when charged using high-voltage electrodes, it possesses a high potential to be ionised to form Ar^+. Typically, the velocity of travel of an Ar^+ ion is approximately 800 m s^{-1} (Kortshagen et al., 2016). Thus, argon gas plasma can be considered to be in a state of high entropy and highly rapid Ar^+ ions on reacting with the amorphous or semi-crystalline or crystalline regions present in the hemp fibres, may dislodge atoms and molecules present on the surface monolayer resulting in an etched surface. Kortshagen et al. (2016) has postulated a detailed explanation of the mechanism of nonthermal plasmas. Thus, with reference to the SEM images shown in Fig. 4, it can be postulated that plasma preferentially etches the amorphous or semi-crystalline regions of the surface monolayer. Such a change in the surface morphology of the fibres may be expected to modulate interfacial properties such as water droplet interaction, and consequently, surface-wetting behaviour.

3.2. Chemical properties of hemp before and after argon plasma treatment

In order to investigate the alterations induced in the chemical structure of cellulose, both the untreated and argon plasma treated hemp fabrics were subjected to analysis via FT-IR spectroscopy and Raman spectroscopy.

3.2.1. Fourier-transform infrared spectroscopy of hemp fabrics

Prominent peaks corresponding to the stretching vibration of functional groups, namely -OH, -CH and -C-O can be observed within the frequency range of 3500 to 3000 cm^{-1}, 2900 cm^{-1} and 1200 to 1000 cm^{-1} respectively (Kondo, 1997). Fig. 5 shows the FT-IR spectra pertaining to the untreated hemp fabric and the hemp fabric plasma treated for 600 s with 40 Hz of power.

In Fig. 5, the blue FTIR spectrum refers to the P1 fabric (see Table 2 for sample details) after argon plasma treatment for 600 s at 40 Hz power. Sharper peaks of functional groups such as -OH (hydroxyl) corresponding to 3000 cm^{-1} and 2900 cm^{-1} wavelength is seen. C-H bond stretching vibration at a wavelength of 1500 cm^{-1} and a sharp peak at 1600 cm^{-1} can be attributed to the bond vibration of C=O (carbonyl) (Gerullis et al., 2022; Geminiani et al., 2022). The distinct peak of the carbonyl group may have resulted from oxidation induced by the argon plasma. Additionally, the sharp peak at 1000 cm^{-1} corresponds to the vibration of -C-O- group of secondary alcohols and ether bonds within cellulose. There are noticeable alterations in the absorption envelope within these regions of the spectrum, following plasma treatment, suggesting possible modifications to the interaction of the -C-O-vibrational groups.

Following argon plasma treatment for 600 s at 40 Hz of power, the intensity of -OH, -C=O and -C-O- bond vibration increases leading to prominent sharp peaks associated with polar groups. The presence of these surface active polar groups indicates a strong reactivity of the surface-treated fabric towards dyes. Moreover, it can be hypothesised that after plasma treatment of hemp fabric, the inter and intra-molecular hydrogen bonding in the cellulose molecule was weakened leading to an etched surface and an enhancement in hydrophilicity.

The wetting behaviour of fabric is closely linked to the presence of polar groups on the constituent fibre surfaces, which play a role in attracting water molecules and facilitating liquid spreading through capillary action. The presence of these polar groups signifies that a higher surface energy is to be expected (Jothi Prakash and Prasanth, 2021). Concerning argon plasma treated hemp fabrics, it is apparent that plasma treatment induced a physiochemical modification to the fibre surfaces by increasing the density of polar groups. In a study on oxygen plasma treated carbon nanotubes (CNTs), the wettability of the CNTs increased following plasma treatment because of the surface etching combined with the functionalisation of the CNTs by oxygen plasma (Ramos et al., 2011).

3.2.2. Raman spectroscopic analysis of argon plasma treated hemp

Raman spectroscopy provides a non-destructive means of identifying surface modifications in textile fabrics. It enables the detection of chemical alterations in surface-modified cellulosic fibres, providing insights into molecular interactions, crystallinity and chemical structure (Agarwal, 2019). In Raman spectroscopy, polar molecules with a dipole moment can be detected as they are polarised by a high-energy laser source. To discern the mechanism of plasma penetration and its interaction with either amorphous or crystalline cellulose, Raman spectroscopy was performed on hemp fabrics before and after argon plasma

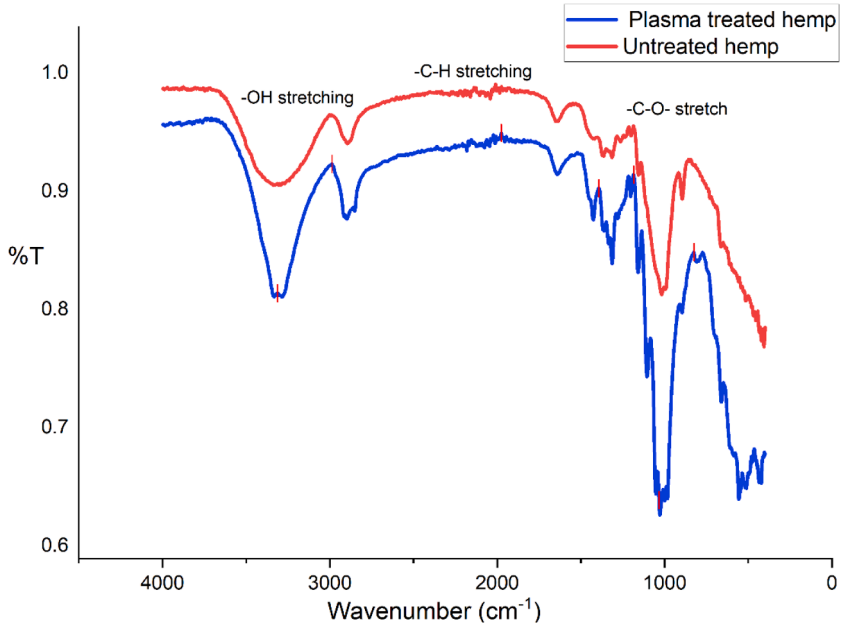


Fig. 5. FT-IR spectroscopy of P1 hemp fabric before and after argon plasma treatment for 600 s at 40 Hz of power.

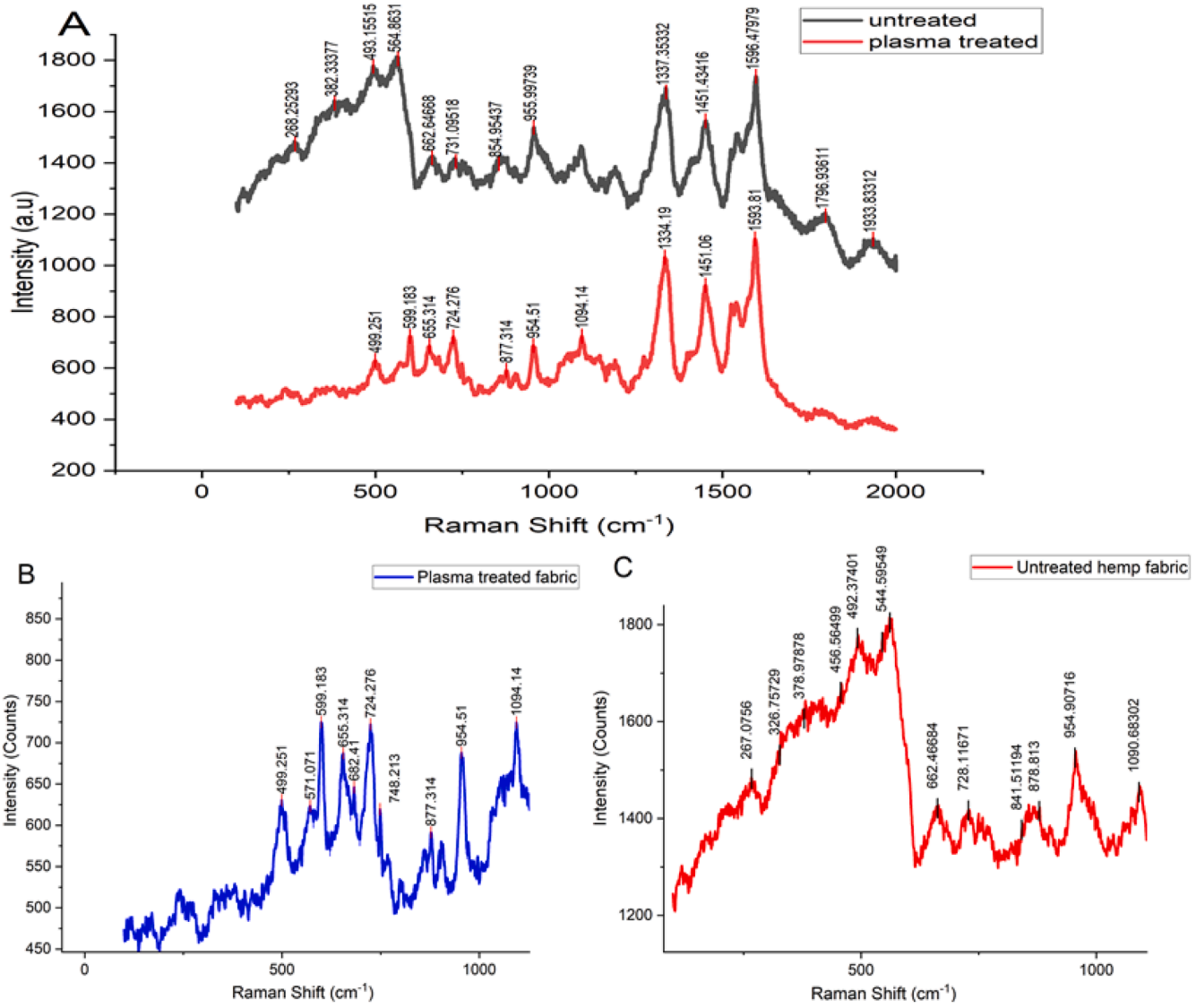


Fig. 6. (A) Raman spectroscopy of P1 hemp fabric before and after argon plasma treatment for 600 s at 40 Hz power; (B) Raman shift in P1 hemp fabric after plasma treatment for 600 s at 40 Hz power ranging from 0 to 1000 cm^{-1}; and (C) Raman shift in P1 hemp fabric in the untreated state ranging from 0 to 1000 cm^{-1}.

treatment. The frequency of bond vibrations in a Raman spectrum is influenced by the mass of a molecule. To validate the hypothesis of plasma penetration into the surface monolayer, thereby inducing changes in the masses of surface molecules, Raman spectroscopy was conducted on P1 hemp fabrics treated with argon gas plasma for 600 s at 40 Hz power. A distinct Raman shift is visible in Fig. 6A, where the Raman fingerprint spectrum of untreated P1 fabric in black noticeably differs from that of the plasma treated P1 hemp fabric shown in red.

The vibrational and stretching frequencies present within the cellulose molecule are manifested in the peaks spanning the range of 1000 cm^{-1}–2000 cm^{-1} corresponding to the -C-C-C-, -C-C-O-, -C-O-C-, and -C-OH, bonds in the a-D-glucopyranose ring (Proniewicz et al., 2002).

In the Raman spectra (Fig. 6), the profound change in peak height is notably observed within the wavelength interval of 0 cm^{-1} to 750 cm^{-1}. These peaks denote the presence of -C-H bending vibration at 330 cm^{-1}, C-O stretching at 490 cm^{-1} and -OH bending of absorbed water molecules visible within the frequency range of 500 cm^{-1}–650 cm^{-1}. In the case of the plasma treated hemp, a prominent Raman shift is observed with decreasing peak height. This observation suggests that plasma treatment is capable of dehydrating the hemp fibres and can be detected between the wavelength range of 1600 and 1700 cm^{-1} which is the H_2O bending mode (Fischer2, 2000).

In Fig. 6A, a prominent difference can be observed in the frequency range spanning 0–600 cm^{-1}. This difference is characterised by a decreasing intensity of bond vibrations in the Raman spectra of the plasma treated hemp, suggestive of alteration in the surface energy. Fig. 6B and C showcase the Raman spectrum of plasma treated hemp and untreated hemp fabric across the wavelength frequency range spanning 0–1000 cm^{-1}. In spite of plasma treatment, the functional groups inherent to cellulose remain unaltered as observed in Fig. 5. Noteworthily, Raman shifts are discernible in plasma treated substrates, these vibrations are clearly seen in the Raman spectra belonging to the region of 1200–1500 cm^{-1} (Fischer2, 2000) indicating the presence of acid (-COO) or -C=O (carbonyl) on the surface monolayer. Below 900 cm^{-1}, complex vibrational modes corresponding to C-C-C, C-C-O, C-O-C, O-C-O and C-O-H are detected on the surface of the plasma treated hemp fabric (Sukhov, 2003). The shifts in hydrogen bonding are discerned in Raman spectroscopy as peaks transition beyond the 3000 cm^{-1} realm (Fujisawa et al., 2016). This phenomenon occurs due to the challenging polarisation of inter and intra-molecular hydrogen bonds in cellulose primarily due to steric hindrance. Additionally, the vibrational frequency of the hydrogen atom changes as it interacts with an electronegative atom like oxygen. Referring to Figs. 5 and 6, it appears that H—OH bonds on the surface monolayer of the hemp fabric are impacted,

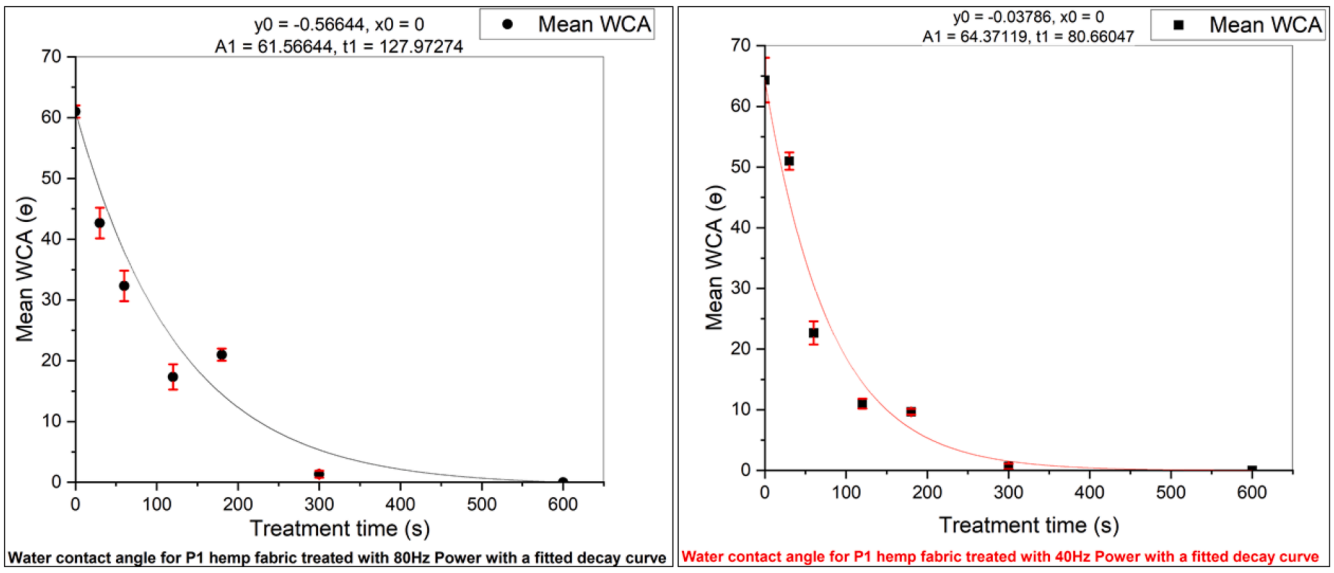


Fig. 7. Change in fabric water contact angle with the duration of argon plasma treatment.

leading to the emergence of sharp peaks associated with -OH groups in the IR spectrum and the absence of H_2O bending mode in Raman spectroscopy. This suggests the hypothesis that Ar^+atoms generated by plasma are capable of cleaving the inter- or intra-molecular hydrogen bonds in cellulose present on the surface monolayer or hemp.

3.3. *Modification of wetting characteristics of hemp fabrics after plasma treatment*

Water droplet contact angle measurements were made on the H, P1 and P2 hemp fabric samples to assess their surface wettability before and after argon plasma treatment. In their untreated states, all the fabrics exhibited partially hydrophobic (θ=60°) wetting characteristics, evident by the presence of a stable water droplet on the fabric surface, with no lateral spreading. Water droplets on the surface resided for at least 20 min before measurement was concluded. By contrast, argon plasma treatment led to a marked change in hydrophilicity and wettability, with a water droplet contact angle of θ=0°. Lateral liquid spreading was evident in all three argon plasma treated hemp fabrics following wetting, with wetting occurring within >1 s from the moment that the droplet made contact with the surface. It was reasoned that argon plasma treatment initiates surface etching (Section 3.1), thereby increasing the surface energy and contributing to a reduction in the water contact angle. Fig. 7 illustrates the water contact angle measurements for hemp fabric samples (P1) subjected to plasma treatment for a duration from 0 s to 600 s based on three replicates for the H, P1 and P2 fabric samples. Line fit curves in Fig. 7 marked in blue and red for P1 hemp fabric samples treated at 40 Hz power and those treated with 80 Hz power follow a decay type of curve. With an increase in plasma treatment duration, a marked decrease in water contact angle is observed and a constant water contact angle of θ=0° is obtained approaching a treatment time of 600 s.

Surface morphology is known to influence wetting characteristics. The role of surface free energy is of key importance in wetting behaviour and the relation is described by Young's equation for ideal surfaces in which the surface morphologies considered are for smooth surfaces. Following plasma treatment, if a non-ideal smooth surface is modified into a roughened surface, the modified Cassie-Baxter theory can be applied to theoretically analyse the wetting behaviour. Taking into consideration all three models namely, the Young's model, the Wenzel's equation and the Cassie-Baxter theory, it was found that the degree of surface roughness controls the wetting behaviour because of its influence on free energies between the solid-vapour and the solid-liquid phases (Godeau et al., 2016; Staudt et al., 2019).

Water is a polar liquid possessing a number of forces, specifically London force, dispersion forces and hydrogen bonding. When a droplet of water is applied onto the interfacial monolayer of a fibre surface, attractive forces exist in the phase with higher surficial energy. The interaction between the two phases depends upon the type of individual forces present (Fowkes, 1964). Therefore, it can be hypothesised that the increased hydrophilicity observed in argon plasma treated hemp is a consequence of a modulation in fibre surface topography, combined with the increase in the attractive forces of the fibre surface monolayer (Du et al., 2022) (Ivanovska et al., 2023). Previous research examining the modification in the surface energy of inert materials such as polypropylene following plasma treatment serves as a reference, suggesting that Argon gas plasma has the capability of enhancing the surface energy of the substrate (Gomathi and Neogi, 2009). The extent of surface modification is contingent upon the duration of argon plasma treatment. Consequently, the reduction in water contact angle in a hemp fabric is affected by the duration of argon plasma treatment. Surface modification is notably enhanced with a longer plasma treatment duration as illustrated in Fig. 7. This is because of an increase in surface etching with pores up to 17 nm being formed following plasma treatment.

3.4. *Influence of argon plasma treatment on the dyeability of hemp*

To examine the potential change of the dyeability of hemp fibres following argon plasma pretreatment, both untreated and treated hemp fabrics were dyed using fibre-reactive and vat dye types (Fig. 2). Fibre-reactive dyes were selected to explore the hypothesis of an increase in the extent of covalent bonding of cellulose surface molecules after plasma treatment. To further explore any potential alteration of bonding sites following argon plasma treatment, hemp fabrics were also subjected to dyeing with vat dyes.

3.4.1. *Hemp fabrics dyed using fibre-reactive dyes*

The impact of argon plasma treatment on H, P1 & P2 hemp fabric, dyed using fibre-reactive dyes was evaluated through the analysis of colour space values. Table 3 displays the outcomes of colour space analysis, encompassing L*(brightness), a* (redness or greenness), b* (blueness or yellowness) and K/S (colour strength) for the dyed P1 hemp fabrics that underwent argon plasma treatment under variable conditions. Significantly, the colour strength of the dyed, argon plasma

Table 3
L*, a*, b* and K/S values of the dyed P1 hemp fabrics.

Power (Hz)	Treatment Time (s)	L*	a*	b*	K/S (420 nm)
40	300	65	28	72	16
0	0	77	2	14	0.6

Table 4
Colour strength of the dye-stripped fabrics.

Power (Hz)	Treatment Time (s)	K/S (430 nm)
40	300	12
80	60	3
0	0	0.2

treated hemp increased compared to the untreated hemp fabric. Similarly, the colour strength of the dyed hemp fabrics following a pyridine stripping test was measured and is represented in Table 4. It is evident that the colour strength of the untreated hemp fabric after pyridine stripping was markedly lower, indicative of reactive dye being removed by pyridine stripping. However, as the duration of plasma treatment increases, the reactive dye becomes more resistant to washing off, resulting in higher K/S values. This is because of the chemical functionalisation of the surface polymer chains. Ar^{+}plasma is capable of generating oxygen-rich groups like -OH following a free radical mechanism (Zhang et al., 2017). Hence, a greater concentration of hydroxyl groups can contribute to the formation of strong covalent dye-fibre bonds. Upon comparing the data in Tables 3 and 4, it becomes evident that the argon plasma treatment strengthens the dye-fibre bonding by making it more resistant to strong alkali as indicated by the similar K/S values before and after pyridine stripping reaction of dyed, plasma treated hemp fabrics.

The effect of plasma treatment on K/S and L* can be seen in Fig. 8A and C. Fig. 8A illustrates that the K/S value increases with extended treatment time, while Fig. 8C demonstrates that L* increases with higher power (intensity) during plasma treatment. The interaction plots in Fig. 8B and C suggest that plasma treatment facilitated an efficient coloration of fabric, particularly in cases where the fabric had a lower yarn count compared to those with densely woven structures. In comparison to the P1 and P2 fabric types, the fabric type H has a herringbone type of weave. Referring to the interaction plots in Fig. 8B, it is evident that the K/S values for H type sample increased after argon plasma treatment. This can be attributed to the herringbone weave structure, which comprises half warp and half weft yarns giving a broken twill effect. Consequently, employing a much longer plasma treatment duration can lead to a more enhanced coloration of the herringbone weave (Palaskar et al., 2020).

Sometimes, the presence of surface roughness on a fabric can contribute to optical reflection creating an impression of a deeper

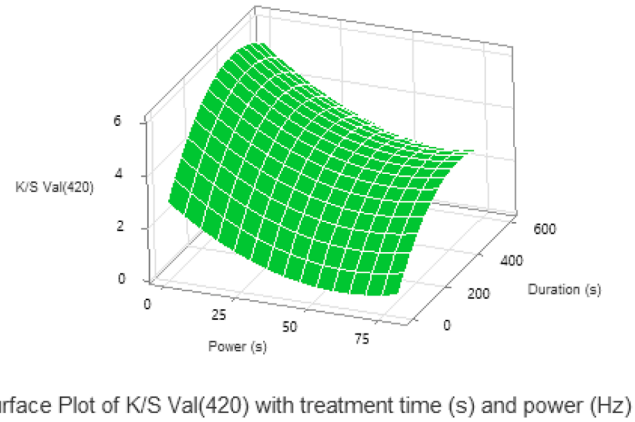


Fig. 8. The influence of argon plasma treatment parameters (treatment duration and power) on the colour strength (K/S) and brightness (L*) of hemp fabrics dyed with fibre-reactive dyes.

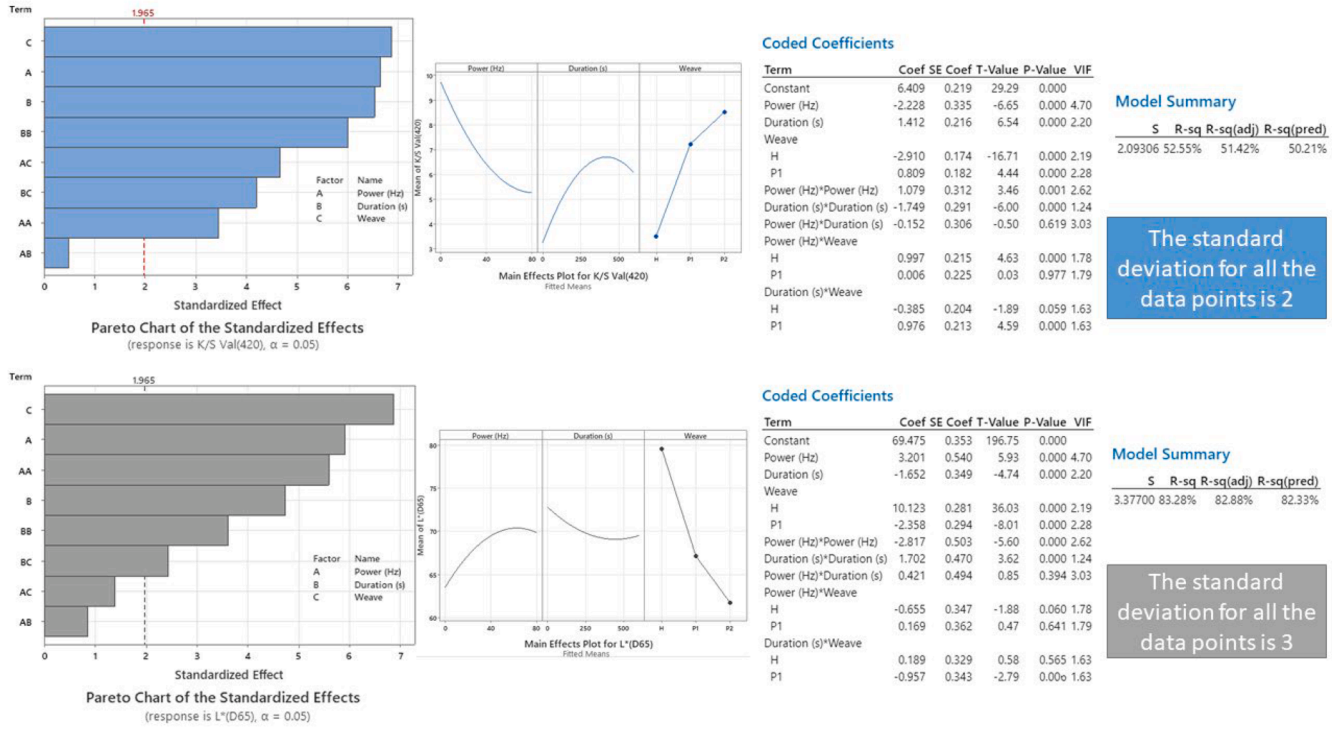


Fig. 9. Statistical analysis of reactive dyeing using surface response model.

coloured dyeing. A rough surface scatters light diffusely, potentially creating a matte-like effect (Liu et al., 2002). The colour strength, representing the ratio of the absorbed light to the incident light is a critical parameter. Therefore, it can be inferred that the observed increase in colour strength is not an effect of optical reflection but is due to the enhanced dyeability of the fabric.

It was observed that plasma treatment improves the diffusion of reactive dyes, which could primarily be due to enhanced penetration of the dye facilitated by the increased surface energy. Such a change in surface energy plays a vital role in facilitating the formation of a strong covalent bond between the dye molecules and cellulose molecules (Amin and Blackburn, 2015). Furthermore, plasma treatment is observed to result in surface etching as evidenced in SEM micrographs (Fig. 4). This has effected in the formation of a nano-porous structure which inturn leads to an increase in surface area of the fabric (Hegemann and Balazs, 2007). Rattee et al. mention, the factors affecting the physical chemistry of dye adsorption which include surface area, the enhancement of which in turn promotes the adsorption of reactive dye resulting in a uniform fixation making the fabric visually brighter and more lustrous.

Fig. 9 provides a factorial analysis of the increased colour strength resulting from reactive dyeing on both untreated and argon plasma pretreated hemp fabric. The Pareto chart indicates power (Hz), and weave type have similar impacts on enhancing colour strength. Therefore, it can be concluded that power is a crucial factor that influences the increased colour strength after reactive dyeing of plasma pre-treated hemp.

3.4.2. *Hemp fabrics dyed using vat dyes*

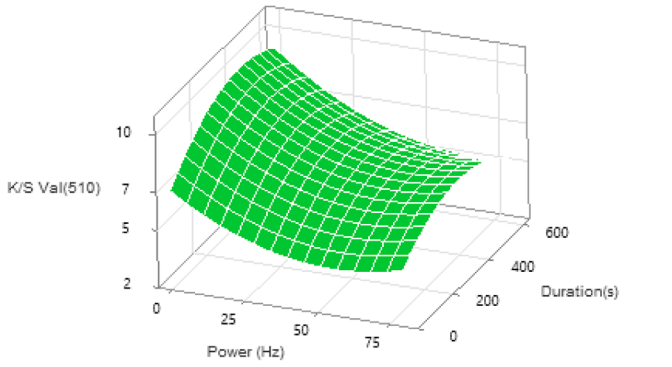
The impact of argon plasma treatment on the vat dyeing process of hemp fabric was assessed through colour space analysis, and the results are presented in Table 5. Notably, the colour strength of the argon plasma treated hemp fabric with a K/S of 22 demonstrates a substantial increase compared to untreated hemp fabric which has a K/S of 6.4.

Fig. 10A and C reveal the effect of factors, such as treatment time and power, on the colour strength and the brightness of the dyed fabric. It is evident that, as the duration of plasma treatment is extended, the colour strength of the dyed fabric increases. Similarly, higher plasma power values led to increased fabric brightness. The interaction plots in Fig. 10B and D indicate the influence of plasma treatment on the reactivity of hemp towards vat dye molecules. These plots suggest that longer duration and higher power setting in plasma treatment enhances the reactivity of the fabric with vat dye molecules.

It could be considered that the gain in surface energy and concurrent increase in overall surface area due to the change in surface fibre morphology, following plasma treatment, facilitated an enhanced attachment of vat dye molecules to the surface of hemp fibres (Gomathi and Neogi, 2009). A similar increase in the colour strength of vat-dyed cotton was observed following a surface treatment using ultrasound and microwave treatments (Kamran et al., 2022).

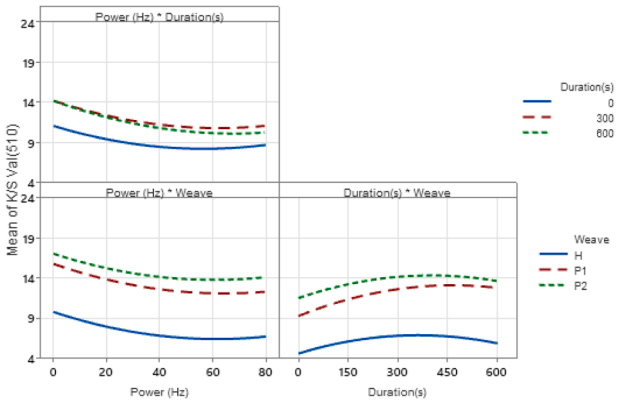
Table 5
Colour space analysis of P1 hemp fabrics dyed using vat dye.

Plasma Parameters		Colour Space Analysis			Colour Strength
Power (Hz)	Treatment time (s)	L* (D65)	a* (D65)	b* (D65)	K/S (510 nm)
0	0	37	42.1	20.5	6.4
40	300	47	46	13.5	18
80	300	54	44	3	22



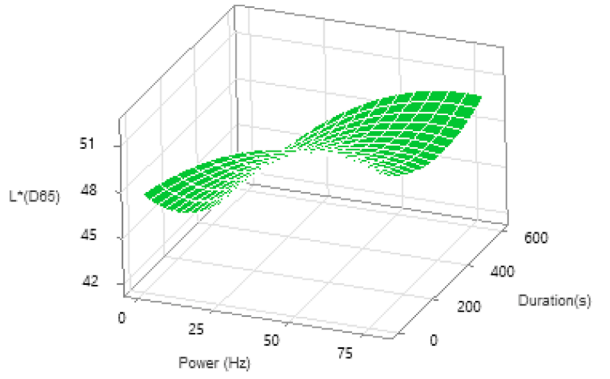
Surface Plot of K/S Val(510) vs Duration(s), Power (Hz)

A



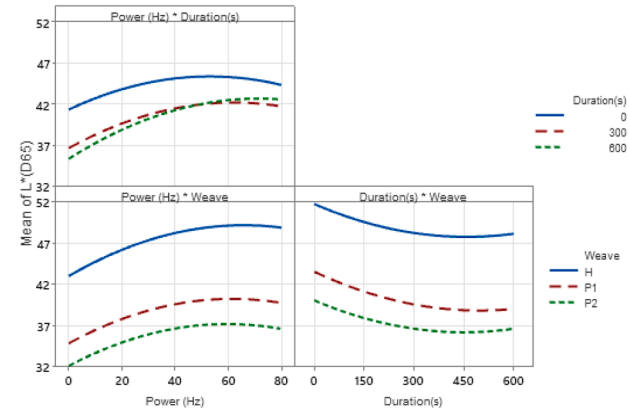
Interaction Plot for K/S Val(510) with power (Hz) and treatment time (s) factors

B



Surface Plot of L*(D65) vs Duration(s), Power (Hz)

C



Interaction Plot for L*(D65) with power (Hz) and treatment time (s) factors

D

Fig. 10. The influence of argon plasma treatment parameters (treatment duration and power) on the colour strength (K/S) and brightness (L*) of hemp fabrics dyed with vat dyes.

Fig. 11 is a factorial analysis that explains increased colour strength following vat dyeing. Factors such as power (Hz), treatment time(s) and the weave type collectively enhance the colour strength. The main effect plot highlights the influence of each factor after vat dyeing of H, P1 and P2 hemp fabrics. Consequently, it can be concluded that the effectiveness of argon plasma pretreatment significantly depends on the weave type and duration of argon plasma treatment.

4. Conclusions

Low-pressure argon plasma pretreatment of hemp fabrics enhances the colour strength that can be achieved in reactive and vat dyeing. This is attributed to morphological and physiochemical changes to hemp fibre surfaces, specifically nano-etching and an increase in the density of polar groups, which increases aqueous wettability.

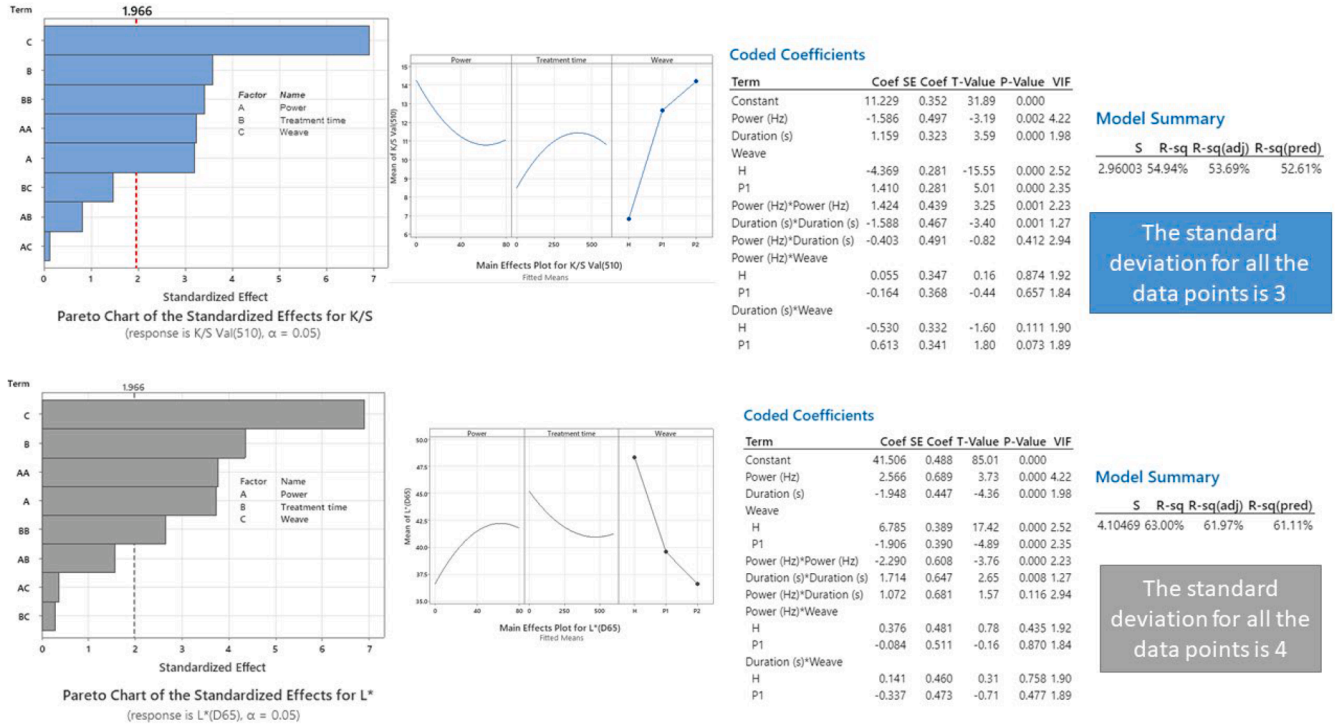


Fig. 11. Statistical analysis of vat dyeing using surface response model.

Based on the FTIR analyses of the argon plasma treated fabrics, distinct carbonyl (C=O) peaks have been observed at 1500 cm^{-1} signifying oxidation induced by argon plasma. Furthermore, sharper polar group peaks were evident indicating a physiochemical alteration of the substrate. A prominent Raman shift has been observed within the frequency range of 0 cm^{-1}–1000 cm^{-1} implying a shift in the surface energy of the fibres after argon plasma pretreatment. Moreover, the water contact angle measurements confirmed an increase in the surface energy following argon plasma treatment and the hydrophilicity of hemp gradually increases with longer plasma treatment duration. The morphological modifications using argon gas plasma include the development of a nano-porous fibre surface associated with progressive dry etching. Such a nano-porous surface contributes to an increase in the available surface area for improved dye adsorption. Moreover, the change in surface energy of plasma treated hemp promotes the formation of strong covalent bonds with reactive dye molecules, while also facilitating the attachment of bulkier vat dye molecules to the fibre surfaces (Fig. 11).

Given the challenges associated with the coloration of hemp, argon plasma pretreatment represents a potentially valuable means of preparing hemp fabrics for dyeing to maximise colour strength without liquid pretreatments, heating, or the use of auxiliary chemicals. This approach holds promise for addressing some of the limitations and environmental impacts associated with conventional dyeing and wet treatment of hemp fibres to magnify its commercial value. Argon gas plasma treatment offers a method to uniformly dye the hemp fabric by reducing overall treatment time and temperature required for dye-fibre fixation.

Hemp fabrics possess complex surface chemistry and the induced surface modification through low-pressure plasma treatment was detected after coloration of fabrics. Although this study provides significant insights, further investigations on fibre surface topography and surface energy employing specialised analytical equipment would be beneficial in establishing the detailed mechanism involved in the interaction between Ar^{+} plasma and hemp fibres.

CRediT authorship contribution statement

Kunal S. Bapat: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **T.P. Kee:** Writing – review & editing, Supervision. **S.J. Russell:** Writing – review & editing, Supervision. **L. Lin:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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