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A comprehensive review of the advances in process engineering and greener solvents in dyeing to impart sustainable textile manufacturing

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ABSTRACT

The textile dyeing industry is not only seen as one of the largest environmental polluters, but dyeing operations also have high carbon footprints. Considering the current global water and energy crisis and to address the UN's sustainable development goals, it is of utmost necessity to make textile materials and their manufacturing sustainable. Over the years, improvements in machinery design, process engineering, and the development of green solvents have been made to reduce energy, water, and chemical usage as well as the environmental impacts of dyeing. Despite their potential, significant challenges remain in developing a dyeing method that is zero-effluent, economical, industrially feasible, and eco-friendly. This review article critically discusses various aqueous and waterless sustainable dyeing methods investigated, along with their dyeing mechanisms, recyclability, merits, and demerits. The dyeing performance and colourfastness properties of the fabrics dyed by various sustainable dyeing methods have been compiled and compared. Supercritical carbon dioxide ($scCO_2$) and decamethylcyclopentasiloxane (D5) have emerged as the two most promising green alternative dyeing media. The ionic liquid, reverse-micellar, and D5-based dyeing methods are virtually zero-effluent but are not industrially feasible due to various issues, including industrial dyeing machines are not designed for solvent dyeing, requiring the handling and use of a large amounts of harmful solvents, and the difficulty of the removal of some solvents from the dyed fabrics. Conversely, $scCO_2$-based dyeing is primarily suitable for dyeing polyester fibres with disperse dyes but is unsuitable for dyeing cotton, wool and other fibres as the dyes used in their dyeing are not soluble in $scCO_2$ medium. The findings of this review will aid in the development of future industrially feasible, sustainable dyeing methods that are zero-effluent, economical, and eco-friendly.

1. Introduction

Dyeing has been used for over five thousand years to make textile fabrics colourful, to make them more appealing to consumers. The synthesis of mauve aniline dye (a purple-coloured dye) by William Parkin in 1856 heralded a new era for synthetic dye production and the colouration of textiles, although it exhibited quite poor colourfastness to light [1]. Within decades, many synthetic dyes were manufactured with varieties of colours that enabled dyeing textiles in any intended shades, heralding a revolution for the textiles and fashion industry. A range of classes of synthetic dyes, including direct, acid, basic, reactive, azoic, vat, disperse, and sulphur, have been developed for the colouration of all types of fibres. Of the dye classes, only the reactive dyes are fibre reactive, i.e., they covalently bind to the fibre. Other dyes are either electrostatically bonded to the fibres or made insoluble inside the fibres after exhaustion into them.

However, traditional aqueous dyeing produces effluent containing harmful and recalcitrant dyes, and its discharge into the environment has contaminated the local watercourses of many textile-manufacturing countries to a level that they have become almost non-treatable, endangering aquatic life. At the same time, drinking water is becoming scarce in many parts of the world, and the global energy shortage is another issue, with soaring energy prices necessitating water and energy conservation. Dyeing is conducted at a high liquor ratio (1:20 to 1:40) near the boiling temperature of water for 1–2 h, depending on the depth of shade required. The dyeing of polyester with disperse dyes requires temperatures of 130–140 °C under high pressure, significantly increasing energy usage. In aqueous dyeing, a high volume of water is used, which not only raises energy consumption but also increases the generation of effluent. A large portion of the applied dyes remains in the bath as dye absorption never reaches 100 % due to the limitation of dye absorption by fibres caused by steric hindrance and

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equilibrium [2,3]. In dyeing, not only dyes but various dyebath additives (e.g., electrolytes, surfactants, and levelling agents) are used, and they end up in the effluent, further exacerbating environmental impacts. Although dyeing with reactive dyes is carried out at moderate temperatures (40–80 °C), it uses a large quantity of salt (sodium chloride or sodium sulphate) and alkali (sodium hydroxide or sodium carbonate) to enhance the exhaustion of dyes and to fix the dye to the fibre by forming covalent bonds, respectively. Dyeing with acid and direct dyes also necessitates the addition of electrolytes to the dye bath to enhance the exhaustion of dyes into fibres. The spent dyebath is difficult to recycle because it comprises a mixture of various coloured dyes to achieve a desired shade. In the case of dyeing with reactive dyes, alkaline conditions are employed for their fixation to fibres, and the leftover dyes in the effluent become unusable due to the hydrolysis of the reactive groups at the high alkaline conditions used for dye fixation [4].

Although the major dye manufacturers have discontinued the production of carcinogenic or highly toxic dyes, some dyes used in the textile industry still could be ecotoxic. Nevertheless, some of the degradation products of dyes (such as aniline, phenols, and benzidine) were found to be more toxic compared to the parent dyes [5]. Even the presence of non-toxic dyes at high concentrations in effluent can increase the turbidity of water, obstructing the photosynthesis reaction in aquatic plants, causing oxygen depletion and eutrophication, and harming aquatic animals and microorganisms [6,7]. The dyeing operation not only uses more energy for running the dyeing machines and heating the dyebath, but also uses energy for washing to remove the unreacted dyes from dyed fabrics and for drying the washed fabrics. The high cost of energy, water, and chemicals, and the tightening of consent limits by environmental agencies are forcing the textile industry to look for sustainable alternatives. Sustainable dyeing also aligns with several United Nations Sustainable Development Goals (SDGs), particularly those related to clean water and sanitation, responsible production and consumption, and climate action. By reducing water usage, minimising water pollution, and promoting circular economy principles, sustainable dyeing contributes to making the textile industry environmentally friendly and resource-efficient.

Recently, two published articles reviewed the advancement of reverse-micellar and supercritical carbon dioxide-based waterless dyeing [8,9] but did not compare their dyeing and environmental performance with conventional and other sustainable dyeing methods. In this review article, various sustainable dyeing methods developed over the years are critically reviewed and compared, along with outlining their merits and demerits. The dyeing mechanisms of various sustainable dyeing methods are also discussed. The future perspective for the development of sustainable dyeing has been outlined. To the best of our knowledge, no published review article has compared the performance of various sustainable dyeing methods in terms of dyeing performance, such as colour yield, and colourfastness properties like this comprehensive review article.

2. Sustainable aqueous dyeing methods

To reduce the carbon footprint of dyeing and also to make dyeing environmentally friendly, various sustainable alternative dyeing methods have been developed over the years.

They can be categorised as: (i) sustainable conventional aqueous dyeing, and (ii) sustainable zero-effluent waterless dyeing. In the first category of sustainable dyeing methods, the emphasis was on the reduction of energy, water, and chemical usage, along with decreasing the generation of effluent. In the second category, sustainable dyeing methods, the use of water was greatly eliminated, resulting in the elimination of effluent generation. In the first category of methods, a considerable reduction in water, energy, and chemical usage and effluent generation was achieved, but in the second category of methods, the generation of effluent is eliminated, but very little reduction in energy and chemical usage has been achieved. The first category methods are used in the textile industry because they need minimum machinery modifications but among the second category methods only the supercritical carbon dioxide-based dyeing is used in a few textile factories, which is only suitable for dyeing polyester fibres and fabrics with disperse dyes but unsuitable for dyeing other fibres as the other classes of dyes are insoluble in this solvent. Moreover, many waterless dyeing methods developed over the years cannot be carried out in existing textile dyeing machinery.

2.1. Low-resource aqueous dyeing methods

To lower the energy usage, dyeing at low temperatures (preferably at ambient temperatures), shorter time and low liquor ratio were explored. A range of dyeing methods has been developed based on using appropriate dyeing auxiliaries that enable quick and high absorption of dyes at low temperatures or shorten dyeing time by 50 to 75 % by increasing the rate of absorption and reaching dye absorption equilibrium very quickly.

In the so-called ‘rapid dyeing’ methods, the dyebath temperature is rapidly increased (5 °C or more), which increases the mobility of dye molecules in the dyebath, their migration to the fibre surface, and their diffusion into the fibres, shortening the dyeing time. However, such a high increase in dyebath heating rate causes various issues, such as the jamming of dye molecules on the fibre surface due to entering many dye molecules at the same time into the pores of fibres causing retardation of their absorption. In package dyeing of polyester yarns, the temporary deposits of dye molecules were observed in those regions where the rate of liquor flow through the fibre/yarn package was exceptionally low [10]. For a higher heating rate, to obtain level dyeing, the exhaustion rate must be adapted to the critical dyeing rate of the system. To counter the jamming effect, an appropriate textile auxiliary, usually a dye levelling agent, is needed to add to the dyebath. Improved process engineering was also studied by modifying the dyeing process and dyeing machinery to maximise the dyebath exhaustion in the shortest time [11]. The application of sonication in dyeing can significantly speed up the dyeing process by enhancing dye penetration into fibres, resulting in reduced dyeing time and increasing colour strength and colourfastness to washing of the dyed fabrics [12,13]. Sonication creates cavitation, which breaks down dye aggregates and helps the transportation of dye molecules into the fibres more easily, leading to faster and more uniform dye absorption [14].

Dong et al. reported a continuous rapid pad-steam dyeing of nylon carpets with acid dyes as shown in Fig. 1 [15]. In this method, a slot steam applicator was used between the padding mangle and the box steamer to preheat the carpet to around 82.2 °C (above the wet glass transition temperature of nylon fibre) before the carpet entered the steamer, which increased dye diffusion into fibres, reducing the dyeing time. For the dyeing of wool, polyester, and cotton fabrics, ionic liquids (ILs), such as 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), were used either to pre-treat the fibres or as a dyebath additive/carrier to shorten the dyeing time to increase dye absorption rate [16]. However, achieving level dyeing by this method was quite challenging, and the dyed fabric showed slightly lower colourfastness to washing.

Sometimes, an appropriate dyebath auxiliary is used to modify the substantivity of dye molecules towards fibre to enhance and control their migration and diffusion into fibres to reach the dye absorption equilibrium very quickly. Chemie Impex (Germany) developed a rapid dyeing method for wool fibres where Linsegal WRD (a modified ethylene oxide condensation product) was used as a dye penetrating agent, which substantially increased the dye uptake by wool fibres, reducing the dyeing time to 30 min [17]. The pad-thermofix continuous dyeing of cellulosic fabrics with reactive dyes can also be considered rapid dyeing. In this method, the fabric is passed through the dye solution, squeezed to 100 % wet-pickup in a padding mangle, then dried, and fixation of dyes is carried out by heating the fabric at 150–170 °C. However, the pad-thermofix method is unpopular due to the poor diffusion of dyes and

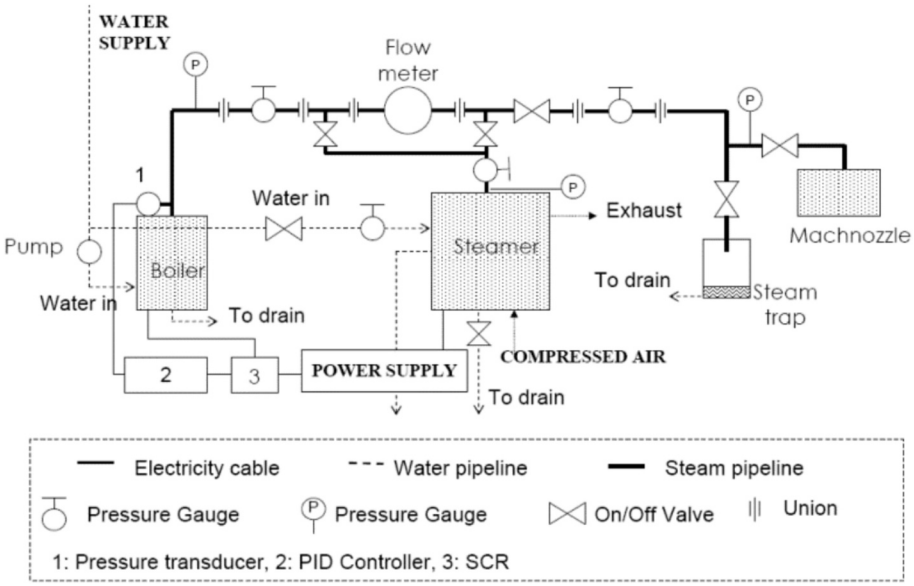

Fig. 1. Schematic diagram of continuous rapid dyeing of nylon carpets with acid dyes [15]. Reproduced with permission from Sage Publishers.

lower dye fixation efficiency compared to conventional dyeing.

Another way to reduce energy consumption is to carry out dyeing at low temperatures. However, the solubility of dye decreases at a low temperature, affecting the mobility of dye molecules in the dye bath and their diffusion into the fibres, which affects dye absorption and the colourfastness to washing. Low-temperature dyeing was initially studied for the dyeing of polyester and polyester/cotton blend fabrics. Zhang et al. modified the cellulosic part of the polyester/cotton blend fabric with cyclodextrin, enabling dyeing of the fabric at 70 °C [18]. Fibre modifications or the use of carriers in dyeing were studied to enable the aqueous dyeing of polyester at normal atmospheric conditions. The polyester fibre modified with sodium-5-sulpho-bis(hydroxyethyl)-isophthalate and 2-methyl-1,3-propanediol enabled a carrier-free and low-temperature dyeing with cationic dyes, producing deep shades along with reasonably good colourfastness to washing [19]. The possible dyeing mechanisms of low-temperature dyeing of the modified polyester with disperse and basic dyes are presented in Fig. 2. Several researchers reported pre-treatment of fibres with solvents that enabled their dyeing at comparatively lower temperatures than usually used, considerably decreasing energy consumption [20–22].

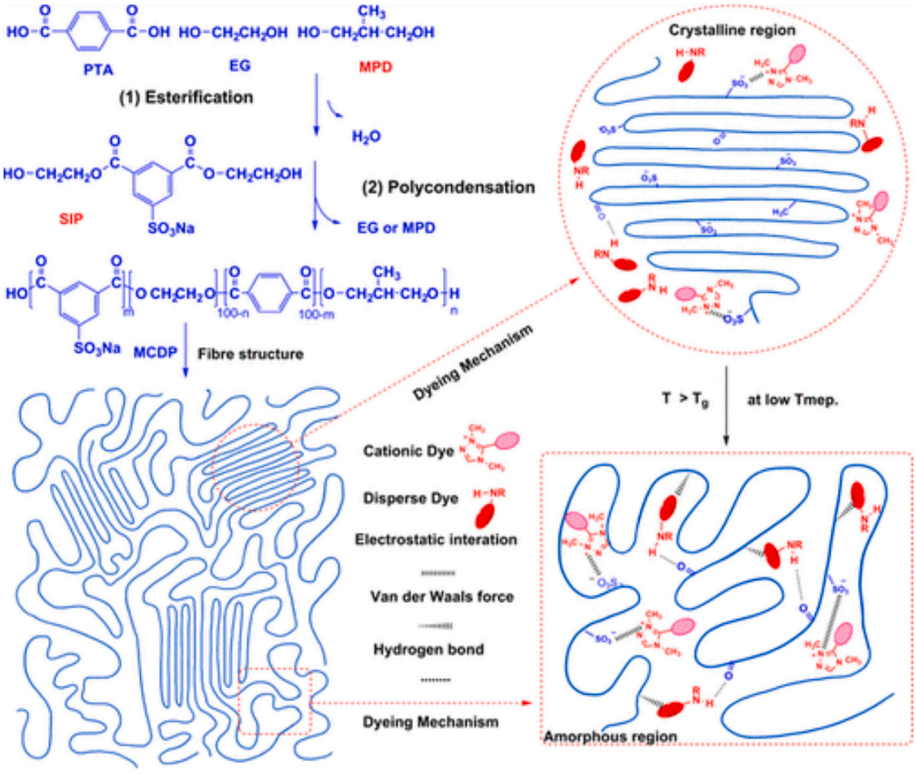

Fig. 2. Dyeing of mechanisms of polyester fibres modified with sodium-5-sulpho-bis(hydroxyethyl)-isophthalate and 2-methyl-1,3-propanediol and dyed with disperse and basic dyes [19]. Reproduced with copyright permission from the American Chemical Society (ACS).

Low-temperature dyeing is quite popular for the dyeing of cotton fabric with dichlorotriazine-type reactive dyes using the pad-batch method, which is carried out at ambient temperatures. Cold pad-batch dyeing is highly practised in the textile industry, and the dyeing is usually carried out in a jigger dyeing machine by passing the fabrics several times through the concentrated dye solution at ambient temperatures. After which, the fabric rolls are covered with plastic sheets and they are rotated at 10–15 revolutions/min on frames overnight, allowing high absorption and fixation of dyes along with uniform dyeing. Low-temperature dyeing of silk at 50–60 °C with reactive dyes showed lower colour yield, but the fibres had a lower strength loss, frictional damage, and fuzz formation compared to the fabric dyed at 80 °C [23].

Various dyebath additives were also studied for the low-temperature dyeing of various fibres. Malik et al. reported a low-temperature dyeing of cotton fibre at 50 °C with a direct dye using triethanolamine as a dyeing medium, and the depth of colour was comparable to the same fabric dyed by the traditional aqueous dyeing method [24]. A pre-treatment with UV irradiation can be used to improve the hydrophilicity and dyeability of wool fabrics with acid dyes, allowing for low-temperature dyeing [25]. It was reported that the addition of benzyl alcohol to the dyebath enabled dyeing of mohair with acid dyes at 10–20 °C lower than the usual temperature used for dyeing, but benzyl alcohol is a harmful solvent unsuitable for industrial dyeing [26]. Zhang et al. studied low-temperature dyeing of wool fibres by modifying them with the plant-derived dihydroxyacetone as a dye by the Maillard reaction, which produced quite deep shades along with enhanced UV protection [27]. Low-temperature dyeing of wool fibres with polyaniline sulphonic acid and poly(amino naphthalene sulphonic acid) produced yellowish and strong reddish-brown shades, respectively, along with high colour yield and colourfastness to washing [28,29]. To enable the dyeing of polyester fibres at normal atmospheric conditions below 100 °C., various dye absorption accelerators, such as phenol [30], para and ortho-vanillin [31], vanillin [32,33], and dimethylsulfoxide or DMSO [34], were studied. Disperse dyes were dissolved in DMSO and then dispersed in an aqueous solution using a dispersing agent, and polyester fabrics were dyed in it at 100 °C, which provided a similar colour yield produced by polyester fabric dyed by the traditional high-temperature and high-pressure aqueous dyeing method. Pasquet et al. used vanillin as a dye absorption accelerator that enabled dyeing of polyester with disperse dyes at normal atmospheric conditions at 90 °C [32]. It was reported that polylactide fibres surface treated with choline chloride/oxalic acid-based deep eutectic solvents (DESs) enabled their dyeing at 90 °C instead of 110 °C, reducing energy consumption [35].

Another means to reduce the energy, water and chemical consumption in dyeing is carrying out dyeing at a low liquor ratio (less than 1:10). However, the reduction in liquor ratio reduces the solubility of the dyes in dyebath increasing the tendency of dye agglomeration, causing uneven dyeing, poor dye absorption, and poor colourfastness to washing. Therefore, an appropriate auxiliary is needed to prevent dye molecules from agglomeration during dyeing. Radei et al. reported a dyeing process for polyester at low temperatures (95 °C and below) under sonication with a low molecular weight anthraquinone disperse dye using n-butyl acetate as a co-solvent and two bio-based auxiliaries (o-vanillin and coumarin), but o-vanillin provided better dye absorption compared to coumarin [36]. Our previous research showed that low liquor ratio dyeing of wool fabrics with acid dyes could be carried out at 1:10 or less by using an appropriate surface-active agent (Teric G12A6), which prevented the agglomeration of dyes in the dyebath [37]. In combination with sonication, we managed to carry out uniform dyeing at a liquor ratio of 1:5 [38]. The basic mechanism of ultra-low liquor ratio dyeing of wool fabric with an acid dye using various surfactants, citric acid, and sonication is shown in Fig. 3. Citric acid in combination with sonication was found to be the most effective in preventing dye agglomeration in the dyebath at a liquor ratio of 1:5. The agglomerated dye particles were loosened by citric acid and sonication further disintegrated them to the molecular level creating fully dissolved dyes, which helped their migration to fibre surfaces and diffusion into the

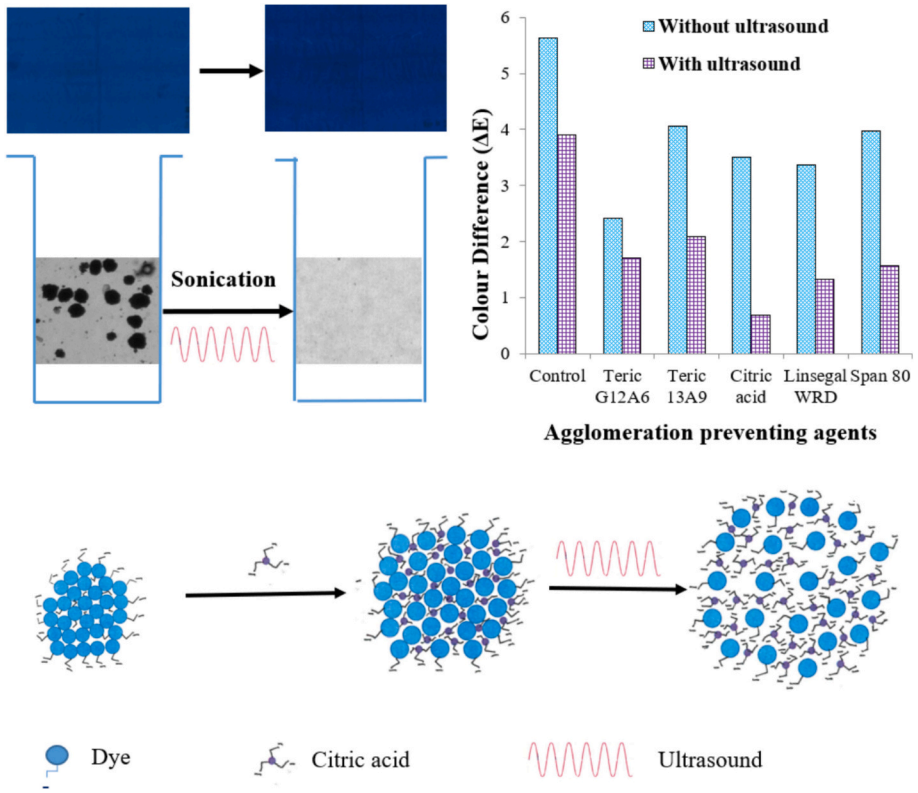

Fig. 3. Basic mechanism of ultra-low liquor ratio dyeing of wool fabrics with acid dyes using citric acid and sonication.

interior of fibres increasing the colour yield of the dyed fabric. Xie et al. reported low liquor ratio micelle dyeing of cotton fabrics with reactive dyes at a liquor ratio of 1:5, where dibutyl maleic acid ester sodium sulphate was used to produce dye-surfactant micelles [39]. The dyeing performance was comparable to conventional aqueous-dyed cotton fabrics, but the surfactant used may not be environmentally friendly. Bian et al. reported dyeing of unscoured and unbleached cotton fibre slivers with a reactive dye at a liquor ratio of 1:6 under sonication [40], increasing production efficiency by eliminating scouring and bleaching of fibres. However, they did not compare the dyeing performance of sonicated dyeing with conventional dyeing.

A large quantity of salts is used as an electrolyte in the dyeing of cellulosic, protein, and acrylic fibres with acid, direct, basic, and reactive dyes. However, high salt concentrations in effluent harm existing biological wastewater treatment processes as they inhibit the microbial activity in activated sludge [41,42]. A high concentration (40 to 10 g/l) of salts is required to use in the dyeing of cellulosic fibres with reactive dyes, depending on the depth of shade, as cellulosic fibres and reactive dyes both are anionic under the dyeing conditions. To neutralise the anionic charge of the cellulosic fibre surface, electrolytes are added to the dyebath so that dyes can migrate from the dyebath to the surface of the fibres and diffuse into the interior of the fibres. It was envisaged that the cationisation of cellulosic fibres could solve the problem, enabling the absorption of anionic reactive dyes into fibres without using any salts. The cationisation of cellulosic fibres with quaternary ammonium compounds [43], quaternised poly(2-(dimethylamino)ethyl methacrylate) [44], low-molecular-weight polyallylamine [45], polyhexamethylene guanidine hydrochloride [46], sericin [47], cationic starch [48], and polyether amine [49], was studied for this purpose. The salt-free dyeing of cotton fabric with a copper phthalocyanine and an azo-reactive dye in a ternary solvent of ethanol, carbon tetrachloride, and water (EtOH–CCl_4–H_2O) was investigated, which produced deeper shades compared to aqueous dyeing [50]. Although such a type of treatment replaces the requirement of salt, many of these cationising agents are toxic, and they create secondary pollution. They are expensive, and their applications need an extra-step treatment, resulting in considerably increased dyeing costs.

2.2. Closed-loop aqueous dyeing

Various closed-loop aqueous dyeing methods were studied for dyeing textile and fashion materials with various dyes, where the spent dyebath was recycled and reused for successive dyeing. Tincher et al. found that recycling and reuse of reconstituted acid dyebath in the dyeing of Nylon 6 and Nylon 6,6 fibres enabled a 35 % reduction in energy, a 40 % reduction in water, and a 56 % reduction in textile auxiliary usage [51]. Perkins et al. studied the reuse of spent reactive dyebath decolourised with ozone for the dyeing of cotton fabric with reactive dyes. The colour difference in textiles between using spent dyebath and fresh dyebath was negligible, which allowed 60 % recovery of salt used in dyeing [52]. Hassan and Hawkyard studied the recycling of spent reactive dyebath, where the effluent was decolourised with ozone and then applied in bleaching cotton fabric with hydrogen peroxide, whitening with optical brightener, and dyeing polyester fabric with disperse dyes [53]. The whiteness index of the cotton fabric bleached with hydrogen peroxide and whitened with a fluorescent brightener was comparable to that of the same fabric given a control treatment with fresh baths. A negligible colour difference was observed between polyester fabric dyed with a disperse dye using decolourised spent dyebath and the freshwater dyebath.

2.3. Foam dyeing

Foam dyeing technology has become popular in the textile industry because of its low energy and water consumption. Foam is defined as gas dispersed in a liquid phase of another substance, such as dye, which is in a state of equilibrium or non-equilibrium. Fig. 4 shows the foam dyeing process for the dyeing of cotton and wool fabrics with reactive and acid dyes [54]. In foam dyeing, foam of aqueous dye solution is prepared by high-speed stirring using a foaming agent and a stabiliser. The fabric is either soaked in foam or coated with a foam solution of dyes using a coating machine. Different foaming agents, such as alkyl dimethyl amine oxide, sodium alkane sulphonate salt (SAS), ethoxylated decanol [55], polyoxyethylene ether [56], sodium dodecyl sulphate (SDS) [57], and hydrolysed keratin [58], were studied in the foam dyeing of textile fabrics. Foam dyeing was mainly studied for the dyeing of cotton with reactive [58], pigment [59,60], and vat dyes [61,62], and polyamide and wool fabric with acid dyes [54,63]. In the case of reactive dyes, an electrolyte and an alkali are added to the foam formulation as a dye absorption enhancer and dye-fixing agent, respectively. The coated fabric is kept in flat conditions for a long time to allow the adsorption of dyes into the fibres and their fixation with the fibre. Sometimes, no heating is used for such a kind of foam dyeing, saving energy costs. Foam dyeing is also possible for dyeing cotton textiles with vat dyes. A foam of leuco vat dye solution is prepared after the solubilisation of vat dyes using sodium dithionite and alkali, and then fabric/yarn is passed through the foamed dye solution, followed by drying and oxidising in the air [61]. In the case of foam dyeing with pigments, a binder is added to the foam formulation, and the dyed fabric is dried and cured to bind the pigments to textile surfaces.

Fig. 5 shows the effect of pigment content in the pigment dispersion on the colour strength of a cotton fabric dyed by foam dyeing. The colour yield and the depth of shade increased with an increase in the pigment concentration. Foam dyeing is highly beneficial as the foam of highly concentrated dye solutions is used in foam dyeing, which reduces water usage as the fabric has only a small amount of water to dry, considerably reducing energy consumption in drying.

2.4. Transfer dyeing

Transfer dyeing was mainly studied for the dyeing of polyester fabrics, where dye is heat-transferred from the coated paper to the fabric. The basic mechanism of transfer dyeing is shown in Fig. 6. In this method, one side of the transfer paper is coated with an aqueous paste of disperse dyes having a low sublimation temperature by rotary-screen printing dried. The polyester fabric is placed over the coated and dried paper, and they are passed through calendaring rollers heated above the sublimation temperature of the dyes used. The dyes from the coated paper are transferred to the polyester fabric during calendaring. Only a small amount of water is used to make the dye paste, and therefore, no effluent is generated. However, transfer dyeing cannot be carried out in a conventional dyeing machine, only suitable for dyeing polyester fabrics with disperse dyes having low sublimation temperatures.

2.5. Gel dyeing process

Gel dyeing is a process in which textile fibres are dyed when they are still in a gel state, as shown in Fig. 7, and this method is mainly used for the dyeing of polyacrylonitrile (PAN) fibres with basic dyes. During wet spinning, the concentrated polymer solution is passed through a spinneret to the coagulation bath to form a fibre. After the formation of fibre, it is still in gel conditions with very high amorphousness. The extruded fibres are washed and then passed through the dyebath containing dye solutions, enabling high exhaustion of dyes and easy diffusion of dye molecules into the highly amorphous fibres at a low temperature, resulting in saving energy and time. On the contrary, in the traditional dyeing process, the dyeing operation is carried out after the drawing process, which considerably increases the crystallinity of the fibre, making the fibre strong, but the dyeing needs a high temperature and a long time to diffuse the dye molecules into the fibres. A small percentage of anionic polymers (e.g., polystyrene sulphonate) is added to PAN dope

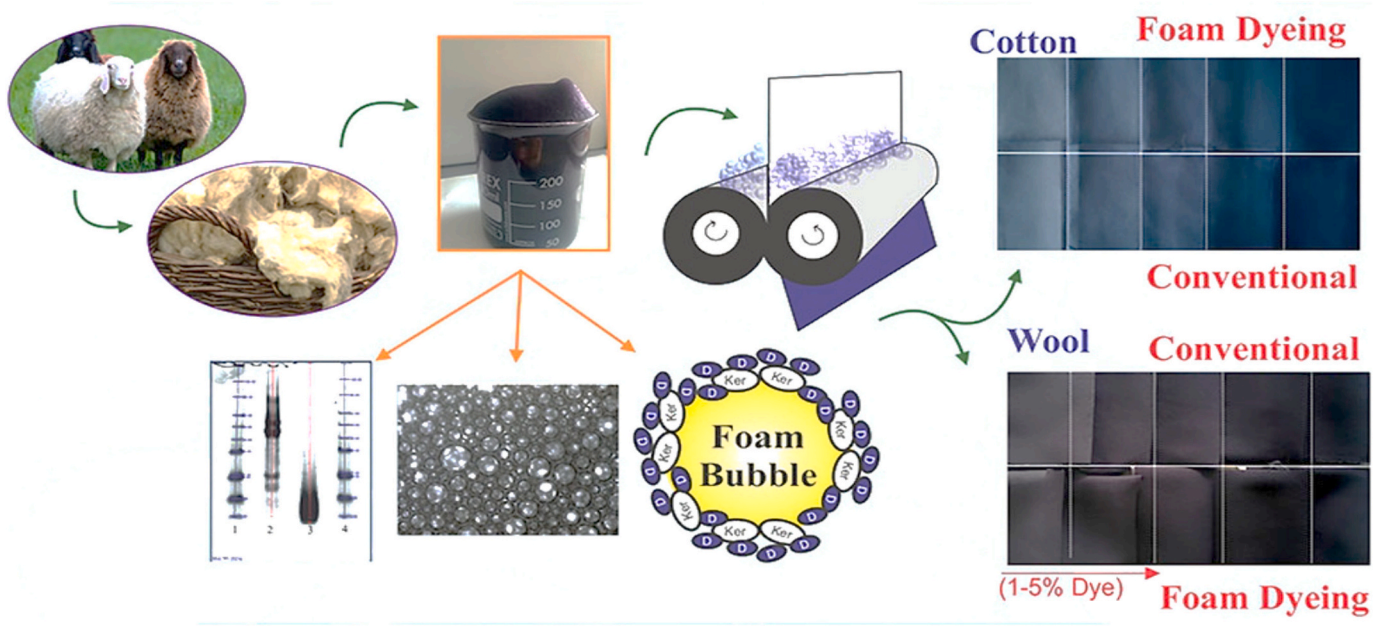

Fig. 4. Schematic representation of foam dyeing of textiles with reactive and acid dyes [54]. Reproduced with copyright permission from the American Chemical Society.

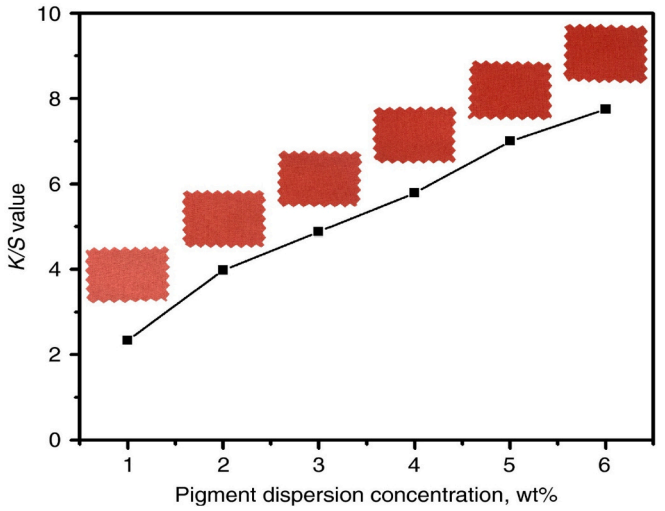

Fig. 5. Effect of pigment dispersion concentration on the colour yield of cotton fabric dyed by foam dyeing method [56]. Reproduced with copyright permission from John Wiley and Sons.

to enable dyeing with basic dyes, and they electrostatically bind to the sulphonate groups of the resulting fibres. Hou et al. reported successful gel dyeing of acrylic fibres at 50 °C using a low liquor ratio [64]. The dyed fibres showed excellent colourfastness to washing and rubbing (4–5), and the dyeing time was only 45 s. Houghton et al. reported successful gel dyeing of casein fibres with natural dyes [65].

2.6. Dyeing performance

Table 1 shows the colour yields and colourfastness to washing of fabrics dyed by low-temperature and rapid dyeing methods. Of them, the polyester fabric modified with ß-CD/citric acid and then dyed with a basic dye showed poor colour yield and colourfastness to washing and wet rubbing [18]. The polyester fabric dyed with C·I. Disperse Blue 56 and C·I. Disperse Blue 79 using vanillin as a dyebath additive also showed poor colourfastness to washing [31,36]. All other treatments provided excellent colour yield and also colourfastness properties. In the case of wool fabric pre-treated with [Bmim]Cl and dyed with the C·I. Acid Red 249, the dye absorption equilibrium was reached within 15 min compared to 120 min for the conventional dyeing [17]. The dyed fabric showed excellent colour yield, but the colourfastness to wet rubbing was quite poor, suggesting poor diffusion of dyes.

Mohair fibres dyed with acid dyes using benzyl alcohol as a dye adsorption accelerator produced excellent colour yield and good colourfastness to washing and light [26]. The brown colour-producing effect of dihydroxyacetone (DHA) in sunless tanning products encouraged textile chemists to apply it as a colourant for textile applications. Wool fabric dyed with dihydroxyacetone as a colourant provided an acceptable level of colour strength, and excellent colourfastness to washing and wet rubbing [27]. The modification of cotton, polyester, and polyester/cotton blend fabrics with ß-cyclodextrin and citric acid enabled low-temperature dyeing at 70 °C, and the treated fabrics showed a colour yield of 10.2, 4.00, and 8.6 compared to 0.5, 0.1, and 0.7, respectively, for the untreated fabrics [18]. Polyester fabric dyed with various disperse dyes dissolved in DMSO at 100 °C provided colour yield, and colourfastness to washing and wet rubbing like the fabric dyed with the same dyes at 130 °C by conventional dyeing using DMSO [33]. However, the synthesised dyes exhibited poor colourfastness to light.

Table 2 shows the dyeing performance and colourfastness properties of various fabrics dyed by the foam dyeing method. Wool fabric dyed with pigment and reactive dyes showed poor colour yield but reasonably good colourfastness to washing and wet rubbing. Of the various types of fabric dyed by foam dyeing with pigment dyes, polyester fabric produced the deepest colour [60]. Of the dyes studied in foam dyeing, pigment-dyed fabrics provided good colourfastness to washing and wet rubbing, but fabrics dyed with acid and reactive dyes showed poor colourfastness to washing and rubbing. In the case of foam dyeing, the wet pick is only 30–40 %, which limits the diffusion/penetration of dyes into fibres, providing poor colourfastness to washing. Pigment-dyed fabrics showed reasonable colourfastness to washing and rubbing because of the use of a binder, and pigments are not absorbed into the fibre but rather coat the fibre. As most of the sustainable aqueous dyeing methods still generate effluent, and some of the virtually effluent-free dyeing processes produce uneven dyeing, waterless dyeing was

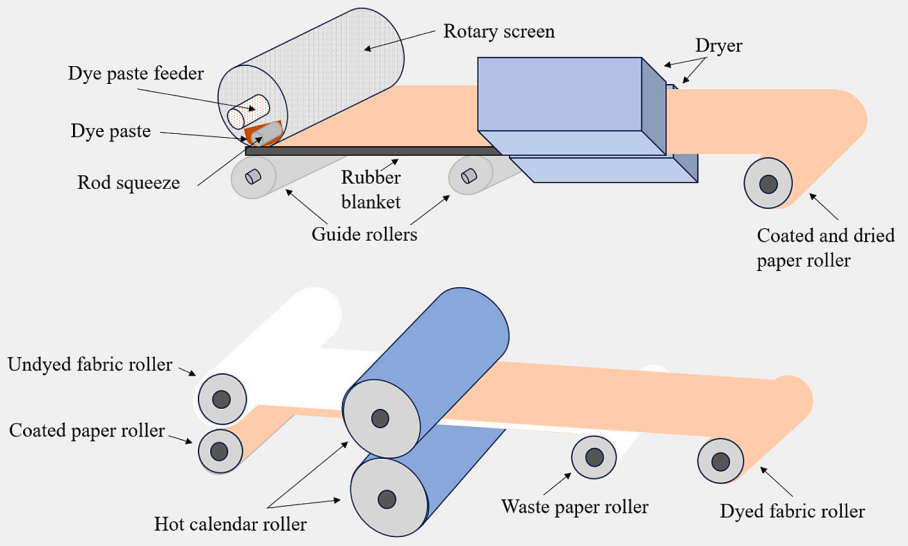

Fig. 6. Schematic diagram of coating of paper with disperse dyes (top) and then transfer dyeing of polyester fabric with that disperse dye-coated paper (bottom).

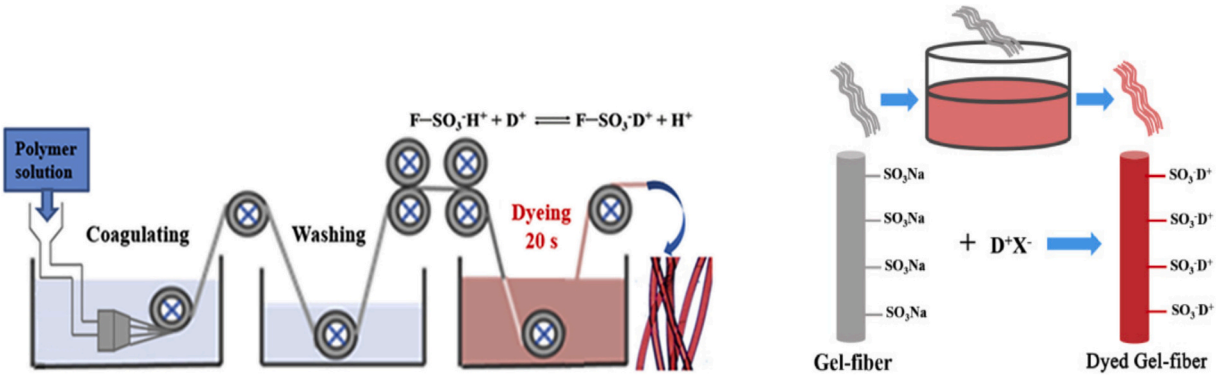

Fig. 7. Schematic diagram showing the wet-spinning and gel-dyeing of PAN (left), and also the mechanism of dyeing of PAN with basic dyes (right) [64]. Reproduced with copyright permission from Elsevier.

studied to completely eliminate the generation of effluent.

3. Zero effluent waterless dyeing methods

In the zero-effluent dyeing methods, virtually no aqueous effluent is produced as dyeing is carried out in a non-aqueous solvent or an extremely low amount of water is used just to produce a dye solution, which is evaporated from the dyed fabric during drying.

3.1. Solvent dyeing

3.1.1. Dyeing in organic solvents

In this method, instead of water, various polar and non-polar solvents are used as a dyeing medium, which can be recycled by evaporation and condensation. Some dyes, such as water-soluble direct, acid, and reactive dyes, are soluble in polar solvents at some levels. On the other hand, hydrophobic dyes, such as disperse dyes, are soluble in non-polar solvents. By using a solvent, it is possible to dye textiles at a very low liquor ratio, enabling transport of dye molecules from the dye bath to the interior of the fibre. Initially, the solvent dyeing method was mainly studied for the low-temperature atmospheric dyeing of polyester fibres.

Different solvents, such as triethanolamine or TEA [24], liquid ammonia [66], palm oil [67], decamethylcyclopentasiloxane (D5) [68–71], linear silicone [72], etc., have been studied as an alternative to the aqueous medium for the dyeing of textiles with various classes of dyes. The dyeing of polyester with natural dyes, such as polyphenols extracted from henna, was also studied in a solvent medium [73]. Solvent dyeing was also studied for the dyeing of various natural fibres, such as cotton, and the studied solvents were D5 [74–76], ethyl octanoate (EO)/DMSO binary solvent (3:7) [77], water/dichloromethane (DCM) binary solvent [78], ethanol (EtOH)/carbon tetrachloride (CTC)/water ternary solvent [79,80], polar aromatic solvents [81,82], and DESs [83–85], for the dyeing of nylon and other polyamide fibres. The ILs were studied for the dyeing of cotton [86,87], wool [88,89], and silk [90], with various dyes. The dyeing of wool, polyester, and cotton fibres with disperse dyes was studied in an aqueous solution containing 0.2 to 3 % 1-(2-hydroxyethyl)-3-methylimidazolium chloride-based IL at 95 °C without using any dyebath additives [91], which produced deeper shades compared to the fabric dyed by the traditional aqueous dyeing method. However, it does not reduce water and energy usage and also produces effluent containing harmful IL. The dyeing of wool fibres in a ternary solvent of Et-OH/CTC/water with reactive dyes increased dye utilisation by reducing the hydrolysis of dyes and decreasing dye content in the generated effluent [80]. The dyeing of polyester with a photochromic dye in a solvent medium (DCM) was reported to show reversible photochromism, developing colour on ultraviolet exposure and fading after removal of the ultraviolet source [92]. Deng et al. studied the dyeing of cotton fabrics with reactive dyes in a binary solvent with temperature-dependent miscibility that reduced the hydrolysis of

Table 1
Dyeing performance of low-temperature aqueous dyed textiles using appropriate auxiliaries with various classes of dyes.

Fibre types	Class of dyes	Auxiliary agent	Applied dosage (% owf)	Dyeing conditions		Colour yield (K/S)	Colourfastness to			Ref.
				Temp. (°C)	Time (min)		Washing (Grade)	Wet rubbing (Grade)	Light (Grade)	
Cotton	C.I. Basic Red 14	β-cyclodextrin and citric acid	2	70		10.2 ± 0.4	–	–	–	[18]
Polyester/ cotton						8.6 ± 0.4	3–4	4	4–5	
Polyester						4.0 ± 0.1	–	–	–	
Mohair	C.I. Acid Blue 324	Benzyl alcohol	3	90	90	33.6	4	n/a	7–8	[26]
	C.I. Acid Blue 193					23.3	4–5	n/a	7	
Polyester	C.I. Disperse Blue 79	Vanillin	2	90	120	11.2	4–5	n/a	n/a	[31]
	C.I. Disperse Red 167					19.3	5			
Polyester	C.I. Disperse Blue 56	Vanillin	3	90	60	8.0	4–5	4–5	–	[32]
	C.I. Disperse Blue 79					2.4	3–4	4		
Polyester	Disperse dye 2	DMSO	2	100	60	15.1	4–5	4	3	[34]
	Disperse dye 5					19.4	4–5	4	3	
Polyester	C.I. Disperse Blue 56	O-vanillin	2	95	120	16.2	4	n/a	n/a	[36]
Wool	C.I. Acid Red 249	Pre-treated with [Bmim]Cl	2	100	120	21.1	4	3–4	–	[17]
Wool	Dihydroxy-acetone	–	360	85	180	8.6	4–5	4–5	–	[27]
Wool	C.I. Acid Red 336	Teric G12A6	5	98	60	29.2	–	–	–	[37]
	C.I. Acid Blue 350					26.7				
	C.I. Acid Orange 67					27.7				

Table 2
Dyeing performance of fabrics dyed with various classes of dyes by foam dyeing methods.

Fibre types	Class of dye	Foaming agent	Applied dosage (% owf)	Colour yield (K/S)	Colourfastness to			Ref.
					Washing (Grade)	Wet rubbing (Grade)	Light (Grade)	
Wool	Pigment Red	SAS	2	1.4	3–4	4	–	[55]
	Pigment Blue			1.7	4	4		
	C.I. Reactive Red 3			4.1	3–4	3–4		
	C.I. Reactive Yellow 176			4.6	4	4–5		
	C.I. Reactive Blue 198			4.1	4	4		
Cotton	CI Reactive Red 120	SDS	1.8	15.2	–	2–3	–	[58]
Cotton	Indigo vat dye	SDS	3	6.38	–	–	–	[61]
			5	9.09				
Cotton	Pigment	SDS	2	8.10	5	3–4	–	[60]
Silk				7.80	5	4	–	
Polyester				9.85	5	3–4	–	
Polyamide	C.I. Acid Blue 80		0.9	6.3	4–5	3–4	–	[63]

reactive dyes [93]. Chen et al. reported the application of a non-nucleophilic solvent (a 1:4 mixture of DMSO and dimethyl carbonate or DMC) as an alternative to water for the dyeing of cotton fibres with reactive dyes, eliminating hydrolysis of reactive groups and enabling recycling/reuse of the spent dyebath [94]. A 30–40 % reduction in dye consumption, along with a 97.5 % reduction in alkali consumption, was achieved. Solvent dyeing was also studied for the dyeing of polyamide fibre with vat dyes [95]. Lim et al. reported the dyeing of cotton fabric with C.I. Reactive Red 2 and C.I. Acid blue 113 in DCM/water (92:8) immiscible solvent at 50 °C for 60 min [78]. The dyeing produced uniform shades, and the used solvent can be easily recovered. In the case of C.I. Reactive Red 2, the dye uptake increased with an increase in water content in the mixed solvent, but in the case of C.I. Acid Blue 113, the increase in water content did not affect dye uptake by the fibres. The dyeing of partially oriented yarns of polyester and polyamide on the melt spinning unit with crude disperse dyes dissolved in benzyl alcohol using the solvent crazing technique produced deeper shades compared to the fully oriented yarns dyed by conventional methods [96].

3.1.2. *Dyeing in silicone oils*

Silicone oils are used as a solvent for various purposes, including as an industrial lubricant, hydraulic oil, and thermic fluid oil for high-temperature dyeing applications. The silicone oils can be divided into two categories, inert and functional. The inert silicone oils don't have any reactive groups. Polydimethylsiloxane, polymethylphenylsiloxane, D5, and fluoroalkylpolysiloxane are a few examples of inert silicone oils [69–72]. On the other hand, functional silicone fluids have methoxy, ethoxy, or epoxy functional groups, and they are unsuitable for use as a dyeing medium as they react with fibres. Of them, D5 was the most studied silicone oil for dyeing.

3.1.3. *Dyeing performance*

Table 3 shows the colour yield and fastness properties of textile fabric dyed with various classes of dyes by solvent dyeing. Of the solvent

Table 3
Colour depth and fastness properties of textile fabric dyed with various classes of dyes by solvent dyeing.

Fibre types	Class of dyes	Solvent/ emulsifier	Applied dosage (% owf)	Dyeing conditions		Colour yield (K/S)	Colourfastness to			Ref.
				Temp. (°C)	Time (min)		Washing (Grade)	Wet rubbing (Grade)	Light (Grade)	
Cotton	C.I. Direct Red 81	TEA	2.0	50	70	5.2	3–4	–	–	[24]
	C.I. Direct Blue 71					7.2	4			
	C.I. Direct Yellow 44					5.9	4			
Cotton	C.I. Reactive Red 2	Water/DCM	1.0	50	60	n/a	n/a	n/a	n/a	[78]
	C.I. Acid Blue 113									
Cotton	C.I. Reactive Yellow 2	DMSO/DMC	3	95	120	6.8 ± 0.2	5	4–5	–	[94]
	Reactive Red 24					25.9 ± 0.3	5	4–5		
	Reactive Orange 5					23.4 ± 0.2	4–5	5		
	Reactive Blue 14					11.3 ± 0.2	4–5	4–5		
Cotton	C.I. Reactive Blue 222	EtOH/CTC/water (55:40:5)	2.0	60	70	15.5				[79]
	C.I. Reactive Blue 256					13.0				
	C.I. Reactive Yellow 3					11.2				
	C.I. Reactive Blue 20					20.9				
Wool	Reactive Yellow 4G	D5/water (90:10)	1.0	95	90	5.5 ± 0.4	n/a	4–5	n/a	[74]
	Reactive Blue 5G					5.7 ± 0.2		4–5		
	Reactive Red 6GN					5.2 ± 0.4		4		
Wool	Lanasol Red CE (reactive)	EtOH/CTC/water	2.0	80	60	17.5	4–5	4	n/a	[80]
	Lanasol Yellow CE (reactive)					14.3	4–5	3–4		
	Lanasol Blue CE (reactive)					13.5	4–5			
Polyester	C.I. Disperse Red 177	D5	0.5	140	90	14.7	4–5	4–5	3–4	[71]
Nylon	C.I Acid Red 249	D5	4.0	98	60	19.9	4–5	5		[81]
	C.I Acid Blue 83					40.8	4–5	4		
	C.I Acid Orange 6					33.6	4–5	5		
Nylon 6,6	Monascus rice pigment	D5	n/a	80	30	2.64 (1.66)	4–5	n/a	n/a	[82]

dyeing studied, only the cotton fabric dyed in TEA medium with direct dyes showed the worst results [24], which is not unexpected as direct dyes do not bind to cotton fibres. Cotton fabric dyed with various reactive dyes in DMSO/DMC medium showed excellent colourfastness to washing. Even wool fabric dyed with reactive dyes in D5/water and EtOH/CTC/water media also showed excellent colour yield and colourfastness to washing [75,81], Nylon 6,6 dyed with natural pigments (pigments extracted from Monascus rice) showed excellent colourfastness to washing [83], Polyester fabrics dyed with disperse dyes in a D5 medium exhibited excellent colour yield and colourfastness to washing [71], but the colourfastness to light was poor, which was the inherent properties of dyes not affected by the dyeing medium or method.

N.B. owf = on the weight of fibre.

3.2. *Reverse-micellar dyeing*

The reverse-micellar dyeing system is one of the most viable zero-effluent dyeing systems, an alternative to traditional aqueous exhaust dyeing systems [97–100]. It was originally developed for the dyeing of cotton fabrics, but later its application has been explored for other natural fibre dyeing. It is a kind of solvent dyeing process where dyes dissolved in a minimum amount of water are encapsulated with reverse micelles of a surfactant and then dispersed in a solvent. The textile fibres are then dyed in that solvent dispersion eliminating the generation of effluent.

3.2.1. *Mechanism of dyeing*

Reverse micelles are nanosphere aggregates of water droplets dispersed in a non-polar solvent by surfactants to provide a stable aqueous microenvironment, a so-called water pool, in non-aqueous media. In reverse-micellar dyeing, a small quantity of water is used to dissolve the dye, which is then dispersed in a non-polar solvent by using a surfactant. The polar heads of the surfactant encapsulate the water pool of dye molecules, and the long non-polar tails are extended into the non-polar solvent medium as shown in Fig. 8. Surfactants can effectively reduce interfacial tension to form microemulsions [101]. The amount of water used in this dyeing method is so little that it is virtually a waterless dyeing method. In this method, only water-soluble dyes, such as acid, direct, reactive, and basic dyes, can be used. During dyeing, a water pool of dyes surrounded by reverse micelles meets water and is absorbed by the fabric, leaving the micelles in the solvent phase, resulting in uniform dyeing of the fabric. Various hydrocarbon-based solvents such as n-heptane, hexane, cyclohexane, isooctyl silane, alkane [102], polyethylene glycol [103,104], and soybean oil [98] have been used as the continuous phase media in the reverse micelle dyeing system, but these solvents, except soybean oil, are not environmentally friendly. Moreover, the selection of the right surfactants can be considered a major parameter for investigating the quality of dyeing, including colour yield.

3.2.2. *Dyeing performance*

Table 4 shows the dyeing performance of various textile fibres by reverse micellar dyeing methods. Polyamide fabrics dyed with acid dyes using soybean oil, using Span 40 as an emulsifier, produced good depth of shades with excellent colourfastness to washing and rubbing [105]. The cotton fabrics dyed with reactive dyes in PEG also exhibited excellent colourfastness to rubbing, but the colour yield and colourfastness to washing were not measured. The wool fabric dyed with various reactive dyes in EtOH-CTC-H_2O solvent using polyoxyethylene *tert*-octylphenyl ether (TX-100) and sorbitan monopalmitate (Span 40) as an emulsifying agent produced quite deep colours, and the dyed

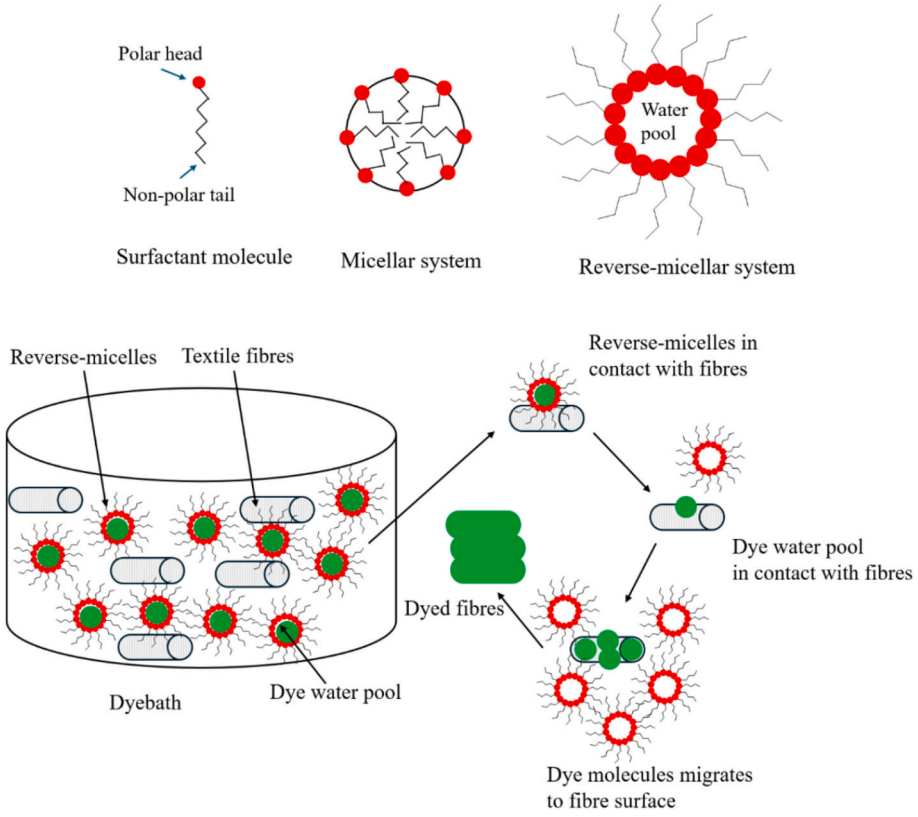

Fig. 8. Schematic diagram showing reverse-micelle formation (top) and reverse-micellar dyeing of textiles (bottom).

Table 4
Colour depth and fastness properties of textile fabric dyed with various classes of dyes by reverse micellar dyeing.

	Class of dye	Solvent/ emulsifier	Applied dosage (% owf)	Dyeing conditions		Colour yield (K/S)	Colourfastness to			Ref.
				Temp. (°C)	Time (min)		Washing (Grade)	Wet rubbing (Grade)	Light (Grade)	
Cotton	C.I. Reactive Blue 52	PEG/PEG-12/n-octanol	2.5	90	120	–	5	4–5		[63]
	C.I. Reactive Red 55					–	5	4		
	C.I. Reactive Yellow 41					–	5	4–5		
Cotton	Levafix CA (reactive)	PEG-12/heptane/ n-octanol	6.0	70	90	33.9	n/a	n/a	n/a	[97]
Polyamide	C.I. Acid Blue 260	Soybean oil/Span 40	1.0	98	30	5.2	4–5	4–5	n/a	[106]
	C.I. Acid Yellow 127					5.3	4–5	4–5		

fabrics showed excellent colourfastness to washing, but their colourfastness to wet rubbing was only moderate. The dye adsorption process in mixed TX-100/Span40 reverse micelles followed pseudo-second-order kinetic equations, and the repelling force and competitive adsorption between the dyes and cotton fabric were decreased with an increasing amount of Span40.

3.3. Dyeing in ILs and DESs

3.3.1. Dyeing mechanisms

ILs and DESs have become quite popular solvents for a wide range of applications including textile dyeing due to their good solvation power and low toxicity. ILs are made by mixing two opposite ionic compounds, such as organic heterocyclic cations and organic or inorganic anions [106]. On the other hand, DESs are a new class of ionic liquid (IL) analogues as they share many characteristics and properties of ILs, and they are a eutectic mixture of Lewis or Brønsted acids and bases or hydrogen bond donors, such as a combination of choline chloride and urea [107]. The phase diagram of a two-component DES is shown in Fig. 9. They are usually considered highly polar solvents and therefore various water-soluble dyes are soluble in them. Rani et al. used Kamlet–Taft empirical polarity scales α, β and π^* with *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline liquid dye sets to determine the polarity of various ILs [108]. They found that the use of polarity scales based on charged solutes can give very different values for the polarity of ILs compared to those based on neutral probes. It was found that the necessity of the use of electrolytes is redundant in the case of dyeing in ILS/DESs as the deposition of cationic charge on fibre surfaces increases the substantivity of anionic dyes towards charged fibres.

The mechanism of dyeing of textiles in an IL with an acid dye is shown in Fig. 9. Acid dyes are soluble in ILs. When the dye molecules in an IL encounter textile fibre, they migrate to the fibre surfaces with the

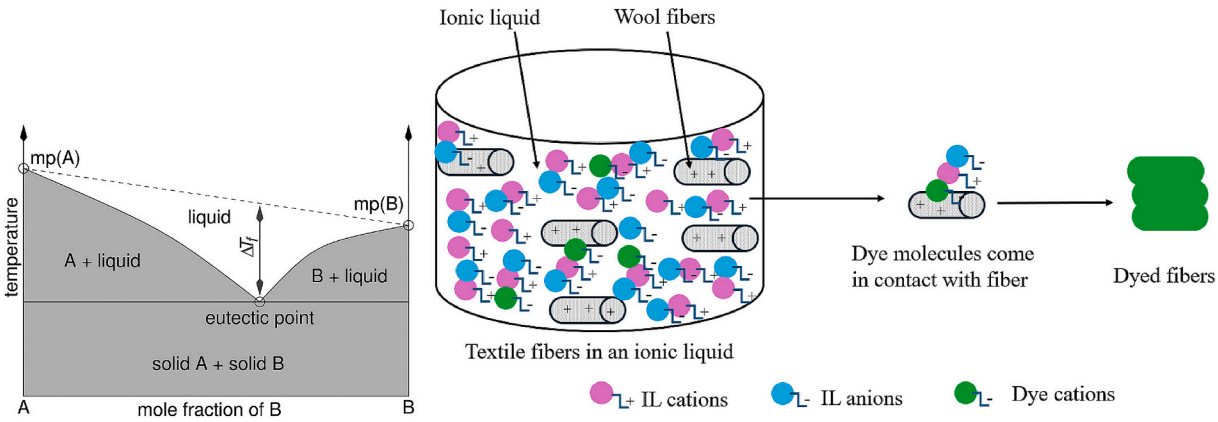

Fig. 9. Phase diagram of a two-component DES (left) and mechanism of dyeing of wool fibres in an ionic liquid with an acid dye.

ionic liquid and then diffuse into the fibres where they electrostatically bind to fibres.

3.3.2. *Dyeing of textile fibres in various ILs and DESs*

For the dyeing of polyester with disperse dyes, dicationic imidazolium [109], choline chloride (CC)/ethylene glycol (EG) [110–113], and a 1:1:1 mixture of CC/urea/ glycerol [114], were studied. Qi et al. reported that 25.5 % energy savings were achieved in the case of dyeing of PLA in CC/urea/ glycerol DES. On the other hand, for the dyeing of cellulose nanofibres with reactive dyes, PLA with disperse dyes, and silk fibre with chestnut shell extracts, CC/EG, 1:2 mixture of thymol/ coumarin, and CC/urea, respectively were studied [115,116]. The ILs studied for the dyeing of textiles may include 3,3′-[1,2-ethanediylbis (oxy-2,1-ethanediyl))-bis[1-methyl-imidazolium)-dibromide or DImD Br, and 1-(2-hydroxyethyl)-3-methylimidazolium chloride for the colouration of cotton, silk, wool, and polyester fabrics [91,110]. The other ILs studied for the dyeing of cotton with reactive dyes were 10 % imidazolium (1-ethyl-2,3- dimethylimidazolium ethyl sulphate-E) or Basionics® ST 67 /EtOH, and 10 % ammonium (methyl-tri-n-butylammonium methyl sulphate B) or Basionics® ST 62/EtOH mixtures [117]. For the dyeing of wool fibre with natural madder and *Reseda lutea* extracts, acetic acid/hexamethylenetetramine IL [118], and 1-ethyl-3-methyl-imidazolium acetate or [Emim]Ac, and 1-ethyl 3-methyl imidazolium acetate and 1-butyl 3-methyl imidazolium chloride, were studied [89,119].

3.3.3. *Dyeing performance*

The colour yields and colourfastness to washing, rubbing, and light of various types of fabrics dyed with different classes of dyes in various ILs and DESs are presented in Table 5. The fabric dyed in various DESs and ILs media showed quite good colour yield and colourfastness to washing and rubbing. Of them, cellulose nanofibres dyed with two reactive dyes showed quite poor colour yield but the colourfastness to washing and rubbing was quite good [112]. The cotton fabric dyed with C.I. Reactive Red 238 in 10 % Basionic ST 67/EtOH DES medium also showed good colour yield but colourfastness to washing and wet rubbing

Table 5
Colour depth and fastness of textile fabrics dyed with various dyes in ILs/DESs.

Fibre types	Class of dye and Dosage (% owf)	IL/ DES	Solvent	Applied dosage (% owf)	Dyeing conditions		Colour yield (K/S)	Colourfastness to			Ref.
					Temp. (°C)	Time (min)		Washing (Grade)	Wet rubbing (Grade)	Light (Grade)	
Polyester	C.I. Disperse Red 343	DES	CC/EG	n/a	130	30	1.)	n/a	4–5	n/a	[111]
	C.I. Disperse Blue 79						1.35		4		
Polyester	C.I. Disperse Blue 56	DES	CC/urea/ glycerol (1:1:1)	5	130	45	17.50	4–5	n/a	7	[113]
PLA	C.I. Disperse Red 167	DES	thymol/ coumarin (1:2)	0.5	90	120	10.5	4–5	4	n/a	[114]
	C.I. Disperse Orange 30						12.4	4–5	4–5		
	d C.I. Disperse Blue 79						5.4	4	4		
Cellulose nanofibre	C.I. Reactive Red 195	DES	CC/EG	3	70	60	4.4	n/a	n/a	n/a	[112]
	C.I. Reactive Blue 19						3.6				
Cotton	Reactive Red 238	IL	10 % Basionic ST 67/EtOH	1	60	120	7.7 (4.9)	5	4–5	n/a	[116]
			10 % Basionic ST 62/EtOH				3 (4.9)	4–5	4		
Silk	Chestnut shell extract	DES	CC/urea								[115]
Wool	C.I. Acid Blue 7	IL	IL (Emim)Ac	4	100	120	31.1	4	3–4	n/a	[89]
Wool	C.I. Acid Blue 203	IL	[Emim]Ac	1	60			4	3–4	n/a	[118]
	C.I. Reactive Red 84		[Bmim]Cl					4–5	4		

was excellent [116]. The same fabric dyed with the same dye in 10 % Basionic ST 62/EtOH DES medium showed only half of the colour yield provided by the fabric dyed in 10 % Basionic ST 67/EtOH DES medium and also showed slightly lower colourfastness to washing and wet rubbing. The polyester and PLA fabrics dyed with disperse dyes in DES medium showed very good colour yield and colourfastness properties. On the other hand, wool fabric dyed with C.I. Acid Bue 7 in IL (Emim)Ac showed excellent colour yield but the colourfastness to rubbing was poor.

Fig. 10 shows the effect of dyeing time and initial dye concentration on the dye fixation efficiency of IL dyeing with C.I. Reactive Red 24 (RR24) in comparison with aqueous dyeing. Solvent dyeing provided superior dye adsorption and dye fixation efficiency compared to aqueous dyeing.

3.4. Dyeing in supercritical carbon dioxide

Supercritical carbon dioxide ($scCO_2$) was considered a green solvent for the waterless dyeing of textiles. Compared to other solvents studied, it is non-toxic, and it also does not produce any byproducts. Although organic compounds are more soluble in liquid CO_2 compared to $scCO_2$, the latter is the more popular sustainable alternative solvent than the former because of its higher diffusivity, lower viscosity, and lower surface tension compared to the former [119]. $scCO_2$ was identified as an ecological and non-toxic solvent, but the need for new high-pressure dyeing technology for high batch rates to make the process economically viable was realised only recently. Fig. 11 shows the schematic diagram of a $scCO_2$ dyeing machine. Dyeing is carried out in a pressure vessel filled with CO_2, equipped with a heat exchanger, which maintains the temperature of the pressure vessel.

3.4.1. Dyeing of textiles with various dyes

Of the dye classes, disperse dyes are non-polar, and therefore dyeing of textiles with disperse dyes is mostly studied using this solvent [120–123]. The dyeing of cellulose diacetate fabric with dispersed dyes in $scCO_2$ produced an excellent level of dyeing [124]. It was also studied for the dyeing of cotton with acid and reactive disperse dyes [125,126].

Fig. 12 shows optical images of cotton fabrics dyed with three acyl fluoride-containing reactive disperse dyes in $scCO_2$ [126]. All of them produced quite uniform brown colour shades. The dyed polyester and polyamide with disperse dyes produced shades with excellent levelness and colourfastness to washing [127–129]. The dye adsorption by polyester fibre follows a linear isotherm [130]. Wide-angle X-ray scattering analysis showed that the surface morphology, crystallinity, and dimensions of crystallites of the dyed polyester were affected by the $scCO_2$ treatment [131]. It was reported that the Disperse Red 167 dye transformed from β-type to α-type due to the dissolution and melting recrystallisation. The thermal decomposition temperatures are shifted to a lower temperature when the CO_2 temperature is higher than 120 °C in $scCO_2$ dyeing [132]. De Giorgi et al. dyed polyester fibre with thiadiazolyl azo dyes in $scCO_2$ and found that polyester dyed at 80 °C and ~ 24 MPa without using any dispersing agent produced shades as the fabric dyed using the same dosage of dyes in traditional high temperature and high-pressure aqueous dyeing at 120 °C [133].

Not only in lab-scale dyeing but the dyeing of polyester was also studied in a mini plant with disperse dyes [134]. It was found that $scCO_2$ dyeing of polyester carried out at 21 MPa instead of the normally used 25 MPa resulted in a 17 kWh decrease in energy consumption [135]. Miyazaki et al. dyed unmodified polypropylene with a series of 1-amino-4-hydroxy-2-phenoxyanthraquinone derivatives substituted with various hydrophobic groups. They found that the type and position of the hydrophobic group attached to the substituted phenoxy ring affected dyeing performance [136]. The dyeing of polyester in $scCO_2$ with photochromic dyes was also studied [137]. Cotton fabric modification with 2, 4, 6-trichloro-1,3,5-triazine enabled its dyeing with hydroxyl or amino group-containing disperse dye that showed improved colourfastness properties [138]. Jia et al. studied $scCO_2$ dyeing of polyester fabrics with 1,8-naphthalimide-based fluorescent dyes [139].

Zhao et al. studied the dyeing of cotton fabrics with reactive dye in ethanol and DMSO-incorporated $scCO_2$ [140]. A similar dyeing technique was also studied for the dyeing of acrylic fibres with a basic dye [141]. Huang et al. studied continuous dyeing of the polyester zipper with dispersed dyes in $scCO_2$, which not only decreased the processing cost by 20 % but also the dyed zipper showed excellent colourfastness to washing, light, and rubbing, between grades of 4 and 5 [142]. Other than polyester, disperse dyes were also studied for the dyeing of polypropylene [143], aramid [144], polyester/cotton blends [145], ramie [146], nylon [147], wool [148], cotton [149], and polylactide fibres [150]. It was found that the addition of methanol to the $scCO_2$ dyebath increased the solubility of disperse dyes, and increased dye adsorption by fibre and colour yield of the dyed polyester [151].

In the case of beam dyeing in $scCO_2$, the levelling properties and colour strength of fabrics were improved with an increase in dyeing temperature, pressure, dyeing time, and a time ratio of fluid circulation to static dyeing but decreased with an increase in number of fabric layers on the beam under an identical condition [152]. The dyeing mechanism of polyester fibres with disperse dyes is quite different from the dyeing of natural fibres with the same class of dye. In the first case, polyester fibre swells in $scCO_2$ allowing diffusion of dye into the fibre as the dye, fibre, and $scCO_2$ all are non-polar. After the completion of dyeing, when the

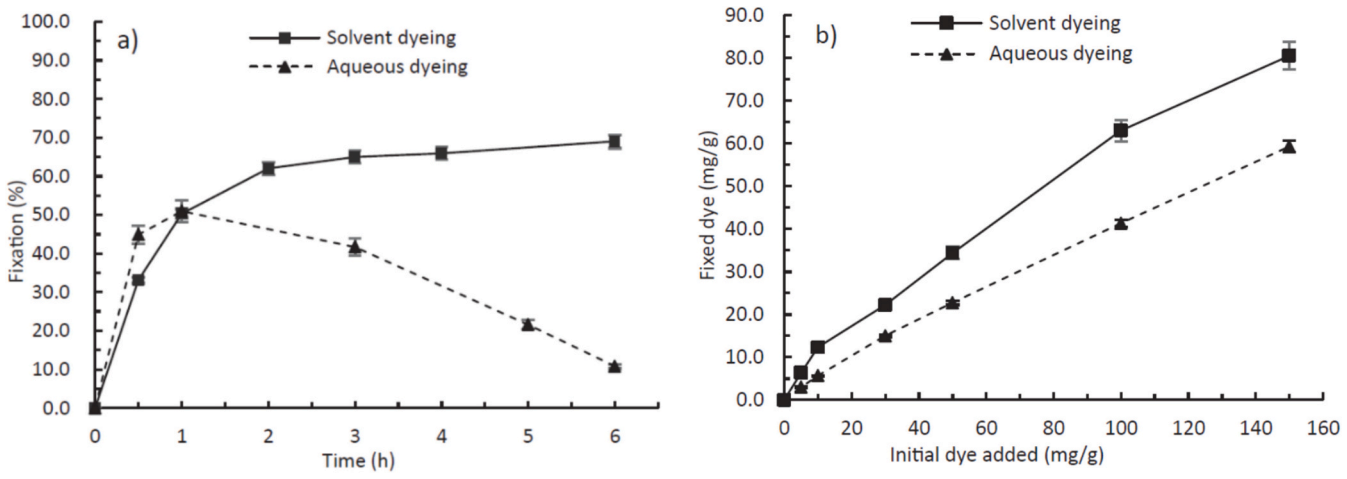

Fig. 10. Effect of dyeing time and initial dye concentration on the dye fixation efficiency. a) dye fixation (%) of RR24 as a function of time in solvent and aqueous dyeing; and b) build-up properties of RR24 dye in solvent and aqueous dyeing [94]. Reproduced with permission from Elsevier.

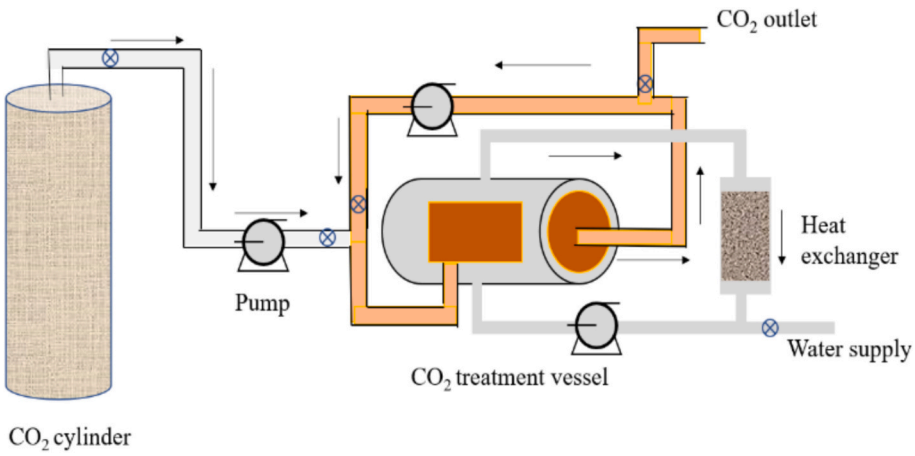

Fig. 11. Schematic diagram of a $scCO_2$ dyeing machine.

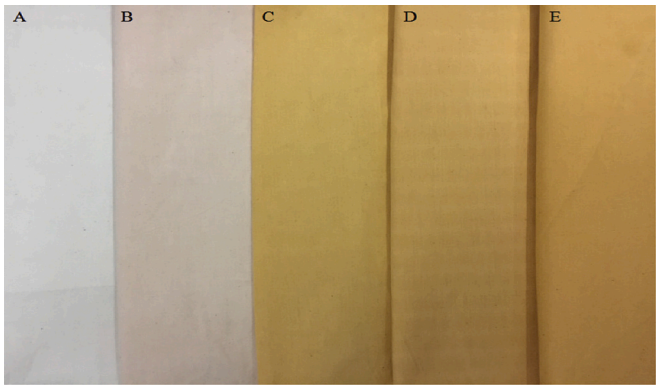

Fig. 12. Photograph of cotton fabrics dyed with three reactive disperse dyes in $scCO_2$: before dyeing (A); dyed with dye 3 (B), dye 2 (C), and dye 1 at 20 MPa, 80 °C, 1 h (D); dyed with dye 1 at 20 MPa, 80 °C, 3 h (E) [126]. Reproduced with copyright permission from Elsevier.

$scCO_2$ is evaporated and the fibre is cooled, dye molecules are trapped inside the fibres due to their shrinkage. As polyester fibre is highly hydrophobic with ultra-low moisture regain, in contact with water the fibre does not swell and therefore the trapped dyes are not released from the dyed fibres. However, for natural fibres, the dyeing mechanism is quite different as natural fibres are hydrophilic, and in contact with water, they will swell releasing the trapped dyes as there is no bonding between the disperse dyes and the fibres providing very poor colourfastness to washing.

To improve the colourfastness to washing, cellulosic fibres are chemically modified by introducing hydrophobic groups to decrease water hydrophilicity and to bind hydrophobic disperse dyes by hydrophobic-hydrophobic interaction. For example, hydrophilic hydroxyl groups of cotton cellulose were partially modified with benzoyl chloride (B-m-C) and then dyed with a disperse dye at 100 °C in $scCO_2$, which considerably improved colour yield and colourfastness to washing [144]. Beltrame et al. found that cotton pre-treated with poly (ethylene glycol) dyed with disperse dyes in the presence of benzamide crystals considerably improved the dye uptake and colourfastness to washing and light [153]. Guzel and Akgerman studied mordant dyeing of wool fibres in $scCO_2$ with 2-nitroso-1-naphthol, 5-(4-aminophenylazo) salicylic acid, and 1,2-dihydroxyanthraquinone using various metal ions at 60–80 °C under 15–23 MPa pressure and the dyed fabrics showed excellent colourfastness to washing [154]. However, dyeing of modified cotton with disperse dyes did not provide the desired level of colourfastness to washing, as only weak bonding was formed between hydrophobic groups of modified cotton and disperse dyes. To bind disperse dyes to cotton and other natural fibres, reactive groups were introduced in disperse dyes and applied for the dyeing of cotton, wool, silk, and polyester/cotton blend fibres [138]. Wool and silk fibres had deeper shades compared to cotton and all of them exhibited colourfastness to washing, and light, between grades 4 and 5. The reactive groups introduced in disperse dyes are tricyanopyrrolidone coupled with triazine [155], carbamates and cyanuric chloride [156], 2-bromoacrylic acid and 1,3,5-trichloro-2,4,6-triazine [138], fluorotriazine [157], vinyl sulphonyl [158], mono- and bi-acyl fluoride [99], and halogenated acetamide [159], for the dyeing of cotton, wool, and other natural fibres. It was also investigated for the dyeing of wool fibres with natural dyes, such as madder (*Rubio tinctorum*) using chemical and biomordants (e.g., *Punica granatum*) [160]. Zhao et al. studied the dyeing of cotton fabrics with normal reactive dyes in $scCO_2$ using dimethyl sulfoxide as a cotton fibre swelling agent and ethanol as a dye dissolution solvent, which provided excellent absorption of dyes along with good colourfastness to washing and rubbing for the dyed fibres [140]. 1-amino-4-hydroxy-2-phenoxyanthraquinone derivatives, substituted with various hydrophobic groups were studied for the dyeing of polypropylene, and the type and position of the hydrophobic group attached to the substituted phenoxy ring affected dyeing performance [143]. Jia et al. studied the dyeing of wool fibres with 1,8-naphthalimide-based fluorescent dyes and a dye with an active group N-hydroxysuccinimide group reacted with amino groups of wool fibres reaching dye fixation up to 91 % [139]. The recycling and reuse of $scCO_2$ dyebath is complicated as the dye of the previous bath remains in the machine parts, which may contaminate when the next batch is dyed with another dye. To solve this issue, the Netherland-based Dyecoo BV developed a closed loop industrial scale $scCO_2$ dyeing machine (DYEOX 4) where residual dyes remaining in the spent bath are separated by evaporation and the reclaimed CO_2 is reused in the next batch of dyeing. The reclaimed dyes can be reused and 95 % of the used CO_2 is recovered in this process. The other demerits of this process are a few percentages of CO_2 are lost, and highly purified dyes need to be used in $scCO_2$ dyeing, which increases the dye cost.

3.4.2. *Dyeing performance*

Table S1 (Supplementary Materials) shows the dyeing performance of various types of textile fibres dyed with various classes of dyes. Of them, polyester fibres dyed with various disperse dyes produced excellent colour yield, and the dyes fabrics showed the maximum colourfastness to washing and rubbing [122,123]. However, nylon fibres dyed with disperse dyes produced good colour yield but the colourfastness to washing was quite poor [120]. The pilot-scale dyeing of cellulose diacetate with disperse dye produced excellent colour yield but the colourfastness to washing and wet rubbing were only 4 and 4 respectively [124]. The cotton fabric dyed with reactive disperse dyes also produced

poor colour yield, but the colourfastness to washing and wet rubbing was quite poor [126]. The TCT-modification of cotton enhanced the colour yield when dyed with C.I. Disperse Yellow 23, but still, the colour yield and colourfastness to washing and wet rubbing were very poor [140]. Cotton and nylon fabric dyed with tricyanopyrrolidone reactive disperse dye produced good colour yield and excellent colourfastness to washing and wet rubbing, but the colourfastness to light was very poor [155].

Luo et al. found that cotton and wool fabrics dyed with a reactive disperse dye containing vinyl sulphone reactive group in $scCO_2$ under 14 MPa pressure, the dye fixation reached almost 96 % in the case of wool but for cotton, it was only 61 % when the fabric had 40 % water of its mass [158]. The wool fabric showed better colourfastness to washing and wet rubbing compared to cotton fabric. Of the cotton fabrics dyed with azo disperse dyes containing chloroacetamide and bromoacetamide, and also anthraquinone disperse dye containing bromoacetamide group, the fabric dyed with the anthraquinone disperse dye showed the highest colour yield (14.4), but all showed poor colourfastness to washing [159]. Overall, polyester fabric dyed with disperse dyes in $scCO_2$ showed excellent colour yield and colourfastness to washing, but for other fabrics, the colourfastness to washing was poor.

3.4.3. Mechanism of dyeing textile and cellulosic fibres in a $scCO_2$ medium

The phase diagram of CO_2 is shown in Fig. 13 (left). At room temperature, under 6 MPa or more pressure, gaseous CO_2 becomes liquid, but above its critical temperature (31.1 °Celsius) and pressure (7.3 MPa), it turns into a supercritical fluid with the density of a liquid, which is known as $scCO_2$.

The basic mechanism of dyeing of textile fibres under $scCO_2$ is shown in Fig. 13 (right). As $scCO_2$ is considered a non-polar solvent due to its low dielectric constant and zero molecular dipole moment, mainly non-polar dyes are soluble in it. Purified disperse dyes are soluble in $scCO_2$, and under high pressure, dye molecules are quickly diffused into the interior of fibres. As polyester fibres are hydrophobic, $scCO_2$ can diffuse into swollen polyester fibres, taking hydrophobic dye molecules and enabling dyeing. At the dyeing temperature, increasing the size of pores in the fibres allows the adsorption of dye molecules in $scCO_2$ into the interior of the fibres. When the CO_2 is released and the fibres are cooled, the fibres shrink to their original state, entrapping dye molecules inside the fibres. When the fibres are washed in water, the dye molecules are not released as they are water-insoluble and trapped inside the fibres.

A new type of disperse dyes containing reactive groups was developed mainly for the dyeing of cotton/polyester blend fabrics. In the case of polyester/cotton blend fabric dyeing, polyester fibres swell in $scCO_2$ fabrics and reactive disperse dyes are absorbed and entrapped inside polyester fibres like normal disperse dyes and do not covalently bind to the fibres. However, in the case of cellulosic components, Yang et al. proposed that the absorbed reactive disperse dye molecules bind to the C6 hydroxyl groups of fibres by forming a hydrogen bond as shown in Fig. 14 [126]. Normal covalent bonding between the cellulosic fibres and dye molecules cannot occur in a $scCO_2$ medium. It can only take place when dyeing is carried out in an aqueous medium under highly alkaline conditions. Therefore, the cellulosic fabric dyed with reactive disperse dyes in $scCO_2$ medium shows poor colourfastness to washing compared to the cellulosic fabric dyed with reactive dyes in an alkaline aqueous medium.

4. Comparison of various sustainable aqueous and waterless dyeing methods

Table 6 shows the merits and demerits of various aqueous and waterless sustainable dyeing methods developed over the past two decades. Conventional dyeing is easy, economical, and proven, providing excellent dye absorption, consistent colour yield and colourfastness to washing, and minimal batch-to-batch variation. Moreover, most of the commercial dyes and dyeing machinery are manufactured for conventional dyeing. The key issue of conventional aqueous dyeing is that it generates effluent requiring tertiary treatments. Low-resource-consuming sustainable alternative dyeing methods (e.g., rapid dyeing) greatly reduce energy usage compared to conventional dyeing methods and can be used for dyeing using conventional dyeing machinery. Modern dyeing machinery can achieve some levels of energy and water savings without much process modifications, still, some of the low resource-consuming aqueous dyeing methods could be beneficial to achieve further savings in energy. However, rapid and low-temperature dyeing has risks of uneven and ring dyeing, along with lower colourfastness to washing compared to the conventional dyeing methods. Of the low resource-consuming dyeing methods, cold pad-batch dyeing and ultra-low liquor ratio dyeing are highly advantageous over rapid and other low-temperature dyeing methods as they save not only energy but also water and chemicals, along with reduced effluent generation. However, cold pad-batch dyeing is only suitable for dyeing cellulosic textiles with dichlorotriazine-type reactive dyes, and ultra-low liquor ratio dyeing needs an extra auxiliary and also sonication transducer installation in existing dyeing machines.

Foam dyeing is highly beneficial in terms of reducing energy, water, and textile auxiliary usage, but may cause uneven dyeing or ring dyeing due to the very low water content of the foam-soaked fabric not restricting diffusion of dyes into the interior of the fibres and reducing the colourfastness to washing and rubbing. Therefore, sometimes the foam-soaked dried fabrics are steamed to diffuse the dye molecules into the interior of the fibre to increase their colourfastness to washing and rubbing, but that operation increases the energy usage, increasing the production cost. Foam dyeing is more effective for dyeing textiles with

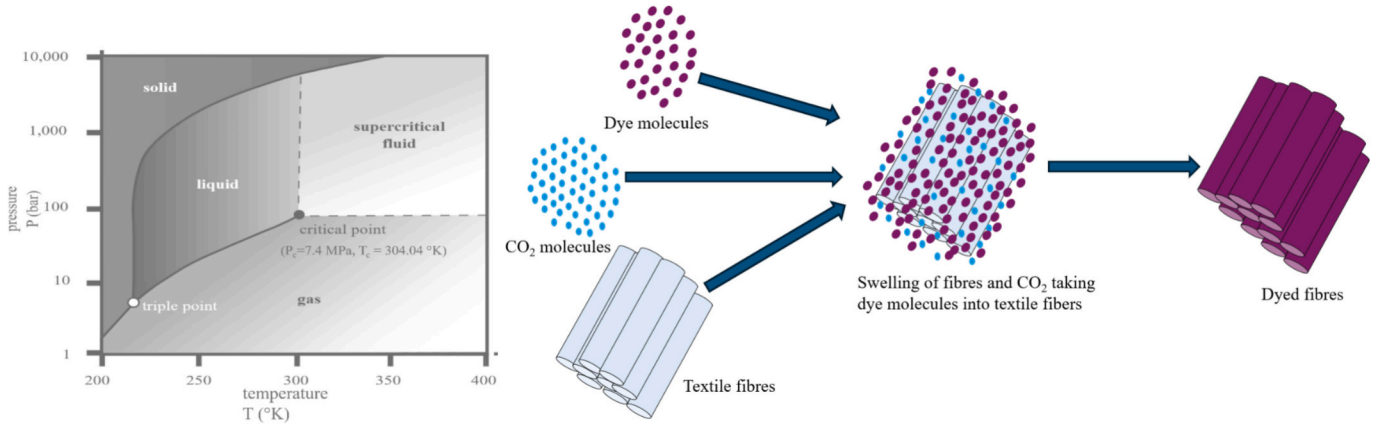

Fig. 13. The phase diagram of CO_2 gas (left) and dyeing mechanism of polyester fibres in $scCO_2$ medium (right).

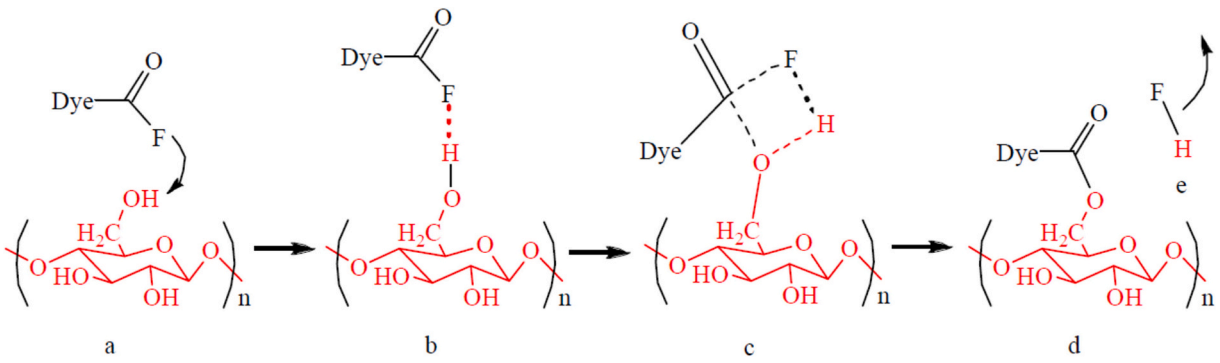

Fig. 14. Proposed mechanism of the reactive disperse dyes reacting with cellulose fibre [126]. Reproduced with copyright permission from Elsevier.

pigments due to the use of binders, which effectively bind pigment particles to the textile surface, providing good colourfastness to washing and rubbing. However, it is less effective for dyeing unmodified wool fabrics with acid dyes due to the lack of functional groups on fibre surfaces. Gel dyeing is not as water and energy-efficient as foam dyeing, but the dyed fabrics provide better colourfastness to washing and rubbing compared to foam dyeing. Gel dyeing can be used only for the fibres that are manufactured by wet spinning (e.g. acrylic fibres) and are unsuitable for fabric-stage dyeing. Spent dyebath recycling and reuse by dyebath reconstitution highly reduces the carbon footprint with the generation of a very low volume of effluent, but is not economical for short batches of different colours and unsuitable for reactive dyes. Spent dyebath recycling and reuse by dyebath decolourisation not only reduces carbon footprints but also eliminates effluent generation, but adds cost for decolourisation of effluent.

On the other hand, existing dyeing machinery in the textile industry is not designed for waterless dyeing and solvent recovery. Most of the hydrocarbon solvents studied for solvent dyeing of textiles, such as phenols, dimethyl sulfoxide, and chlorinated solvents, are volatile, smelly, harmful, flammable, and unsuitable for industrial dyeing. Palm oil and other edible oils are also highly flammable and viscous with poor flow properties, and their application as a dyeing medium produces oil-stain marks in the dyed fabrics that are difficult to remove. Reverse-micellar dyeing is also based on water-immiscible hydrocarbon solvents with 5–10 % water used for dye dissolution, and they also have demerits like other solvents, such as being harmful, volatile and flammable, and also the risk of poor dye absorption and producing uneven shades. ILs/DESs are relatively toxic, have a strong odour, and have high viscosity. Many of them have an affinity towards fibre and can ionically bind to fibres with opposite charges, making their removal from dyed textiles difficult. Silicone-based solvents are odourless, non-volatile, and have high flashpoints and low flammability, making them ideal replacements for water for dyeing textiles. It is reported that the use of D5 solvent in non-aqueous dyeing could reduce water consumption by water for textile dyeing up to 61.3–80.0 % and greenhouse gas emissions by 43.70 % compared to the traditional aqueous system [161]. However, it is expensive, has a high viscosity, and its removal/recovery from dyed textiles is cumbersome. Moreover, D5 is considered a toxic substance by Environment Canada, and the EU classified it as a high-concern substance due to its persistence, bioaccumulation, and toxic potential, with the potential to accumulate in aquatic organisms [162]. Still, it is one of the most promising solvents for the industrial dyeing of textiles. Most of the above-mentioned dyeing methods are considerably more expensive than conventional methods and were studied at a lab scale. Therefore, their scaling up and success in the real industrial environment are difficult to assess. Moreover, handling, storage, and removal of solvents from the dyed fabrics are not straightforward. None of the waterless dyeing systems, except $scCO_2$, have been trialled in an industrial environment. As a result, such dyeing methods are not used in the textile industry.

The main merits of $scCO_2$ are that it is harmless, non-flammable, recyclable, and easily available. In $scCO_2$ dyeing, the use of no dyebath additive, acid or alkali is required, and no drying of dyed fabrics is necessary, saving energy. However, $scCO_2$ suffers from a range of inconvenient physicochemical properties generally required to be an effective solvent, such as low viscosity, dielectric constant, and surface tension [163,164]. Because $scCO_2$ is a weakly non-polar solvent, polar and ionic compounds are not soluble in it, which limits its application for dyeing polyester fabrics with the disperse class of dyes. For $scCO_2$ dyeing, highly purified disperse dyes need to be used, which substantially increases the price of dyes. However, the colour yield, uniformity of the shade, and colour colourfastness to washing and rubbing by $scCO_2$-dyed polyester fabrics are excellent. Nevertheless, in the case of dyeing polyester/cotton blends with reactive disperse dyes, colourfastness properties are poor to moderate as reactive groups of reactive disperse dyes are not designed to react in a solvent medium other than water. Therefore, only a handful of textile factories in China, Thailand, and the Netherlands use $scCO_2$-based dyeing, and companies like DyeCoo (The Netherlands) are leading its development and deployment. The high cost of dyeing machinery and highly purified disperse dyes, the availability of only a limited number of dyes, high maintenance costs, and safety risks associated with high-pressure vessels are limiting their widespread use.

5. Future directions

The advancement in sustainable dyeing achieved over the years considerably reduced energy, water, and chemical usage, along with partial or complete elimination of effluent generation. However, significant challenges remained in their implementation in the textile industry. Future research needs to look for the optimisation of closed-loop aqueous dyeing methods based on recycling of spent dyebath through dyebath reconstitution for dyeing with acid, basic, direct, and disperse dyes and spent dyebath recycling through decolourisation for dyeing with reactive dyes. Economy dyebath decolourisation techniques will need to be developed to reduce the cost of dyebath decolourisation. The spent dyebath can be stored and reconstituted or decolourised in the addition tank of the dyeing machines, resulting in minimum disruption of the existing dyeing machinery compared to sustainable waterless dyeing methods. The key barriers are that most of these developed methods were studied at the laboratory bench, and no scaled-up or pilot trial was conducted. Most of them use solvents that could be harmful, have strong odours, are highly volatile, and are difficult to handle at an industrial scale, and existing dyeing machinery in the textile industry is not designed for their use. Although they do not generate effluent, their recycling and recovery are costly, and the textile industry does not have facilities for their recycling. Of them, D5 and $scCO_2$-based dyeing methods are the most promising, with various disadvantages, and therefore, only $scCO_2$-based dyeing is used at a handful of textile manufacturing facilities globally. Reactive disperse dyes were developed

Table 6
Merits and demerits of various sustainable aqueous and waterless dyeing of textiles.

Dyeing methods	Merits	Demerits and industrial feasibility	Ref.
Conventional aqueous dyeing			
	1. The dyeing process is easy, economical, and produces brilliant and uniform shades along with consistent colourfastness properties 2. Almost all the commercial dyes are made for conventional dyeing methods 3. Flexibility in dyeing and shades can be adjusted easily 4. Suitable for dyeing all types of fibres with almost all types of dyes 5. More than 90 % of the textile dyeing machinery is made for conventional aqueous dyeing.	1. Very high energy, water and chemical consumption with increased carbon footprints. 2. Needs several textile auxiliaries. 3. Produces a high volume of effluent. 4. For dyeing cellulosic fibres with reactive dyes, 5–45 % hydrolysed dyes remain in the effluent along with a large quantity of salts and alkali. 5. Extensively used in industry.	[12,28]
Sustainable aqueous dyeing			
Rapid dyeing	1. Decreases the dyeing time by 50 to 75 %. 2. Decreases energy usage, cost of dyeing, and fibre damage. 3. Increases production efficiency.	1. Does not reduce water usage and effluent generation. 2. Needs an extra textile auxiliary, risk of producing uneven dyeing, and therefore is less used in industry.	[12,16,17]
Low-temperature dyeing	1. Reduces energy usage, cost of dyeing, and fibre damage. 2. Reduces wear of dyeing machinery.	1. Does not reduce water usage, dyeing time, and effluent generation. 2. Risk of producing uneven dyeing and lower colour yield, except for cold pad-batch dyeing. 3. Long dyeing time for cold pad-batch dyeing. 4. The dyed textiles show lower colourfastness to washing compared to the traditional dyeing, except for cold pad-batch dyeing.	[23,24]
Low-liquor ratio dyeing	1. Reduces energy, water, and chemical usage, and effluent volume. 2. They are used in the textile industry. 3. Minimum machinery modification is needed.	1. Risk of producing uneven dyeing. 2. Still produces effluent, although at a lower volume. 3. Industrially feasible.	[37–39]
Foam dyeing	1. One or both sides of the fabric can be dyed. 2. Saves energy by more than 50 % and chemicals by 10–40 %, resulting in lower dyeing costs and generating almost no effluent. 3. Improve production efficiency due to continuous dyeing. 4. Considerably reduces the carbon footprint of dyeing and effluent generation.	1. Problem with dye penetration into the fibres causing uneven and ring dyeing, and lower colourfastness to washing and rubbing than conventional dyeing. 2. Mainly suitable for pigment dyeing. 3. Some foaming agents studied may not be environmentally friendly. 4. Because of various demerits, they are not used in the textile industry.	[54–56]
Gel dyeing	1. Reduced dyeing temperature, dyeing time, and energy usage. 2. Continuous dyeing. 3. Quite good colour yield, and colourfastness to washing. 4. Produces less effluent compared to the conventional aqueous dyeing.	1. Only suitable for dyeing fibres that are produced by wet spinning. 2. Dyeing cannot be carried out in traditional dyeing machines 3. Rarely used in the textile industry because it is unsuitable for fabric-stage dyeing, which is a common industry practice.	[64,65]
Waterless dyeing			
Solvent dyeing	1. Various types of solvents are used instead of water, and 95 % of the solvents can be recycled. 2. Rapid wetting, faster dyeing and drying, and does not produce effluent. 3. Reduces energy cost and produces no effluent (except for D5-based dyeing). 4. In the case of D5, the solvent recovery is almost 95 %.	1. Most of the solvents are harmful and flammable. 2. Mainly suitable for water-insoluble dyes. 3. Dyeing machinery needs modification. 4. Approx. 5–10 % of solvents are lost. 5. Except for D5, other solvents are unsuitable for industrial dyeing. 6. Expensive and no textile industry uses solvent dyeing, even D5-based dyeing.	[75,78,81]
Reverse-micellar	1. Mainly water-immiscible solvents are used. 2. Very little water is used for the dissolution of dyes. 3. Virtually waterless and therefore does not generate effluent. 4. Most of the solvents can be recycled	1. Reduce energy usage only marginally, and it is mainly suitable for cellulosic and polyamide fibre dyeing. 2. Approx. 5 % of the solvents are lost. 3. Most of the solvents are harmful and flammable. 4. Not industrially feasible and costly.	[97–99]
ILs/DESs	1. ILs and DESs are used instead of water for dyeing. 2. Waterless dyeing that does not generate effluent.	1. Does not reduce energy usage. 2. Approx. 5–10 % ILs/DESs are lost and mixed with the washing effluent 3. Dye adsorption is not as good as aqueous dyeing. 4. Most of the ILs/DESs are harmful and smelly, and not industrially feasible. 5. Removal of solvents from dyed fabrics is cumbersome.	[117,118]
$ScCO_2$	1. The solvent used is $scCO_2$, which is non-toxic. 2. Very good diffusion of dyes into fibres. 3. Provides excellent colourfastness to washing for the polyester textiles dyed with disperse dyes. 4. Generates no effluent, and 99 % of the solvent can be recycled.	1. A specialised and expensive dyeing machine is needed. 2. It does not reduce dyeing time much, and dyes suitable for this dyeing are highly expensive. 3. Mainly suitable for polyester fibre dyeing with disperse dyes. 4. A limited number of suitable disperse dyes are available commercially. 5. Other types of fibres dyed with disperse and reactive disperse dyes exhibit poor colourfastness to washing. 6. Only a very few textile factories use this dyeing method because of the high cost of dyeing machinery and explosion risks.	[123,124,126]

for the dyeing of polyester/cotton blends, but the poor colourfastness to washing exhibited by the dyed textiles suggests that they do not react with cellulose efficiently like aqueous dyeing, as reactive groups are designed to react with cellulosic and polyamide fibres mainly at alkaline aqueous conditions. Therefore, novel reactive disperse dyes with reactive groups that enable covalent binding with hydroxyl groups of cellulose in $scCO_2$ or solvent medium will need to be developed.

For waterless dyeing, new solvents with low viscosity, low toxicity, odourless, non-flammability, low volatility, compatible but no affinity towards textile fibres that can be cheaply recycled and recovered, will need to be developed. Existing dyeing machinery available in the textile industry is not suitable for such types of dyeing methods, as they are not designed for solvent dyeing and recovery of spent solvents. The design of dyeing machinery and dyeing processes should be further optimised to

reduce the carbon footprint. As the recalcitrance of synthetic dyes is a major issue, the development of biodegradable synthetic dyes may solve that issue, although there is a risk of compromising the lightfastness properties of those dyes.

Although natural dyes are eco-friendly, they are not alternatives to synthetic dyes because of their very poor colourfastness to light and washing, unavailability of an industrial-scale supply of dyes, and they are expensive compared to many synthetic dyes. Most of the synthetic dyes are derived from petroleum-derived feedstocks, and the dependence on these feedstocks can be eliminated by manufacturing such a type of dyes by biochemical engineering or from bio-derived feedstocks. Such a type of dye will need to provide not only high colour yield at an affordable price but also high colourfastness to washing and light. The dyes having novel on-demand binding reactive groups can also be developed so that they can be easily removed from post-consumer textiles for their recycling. The use of artificial intelligence may help in the development of such a type of dye and dyeing methods that will be cost-effective, low environmental footprint, and are industrially feasible.

6. Conclusions

The improvement in dyeing machine design and dyeing process has revolutionised the aqueous dyeing of textiles, which has considerably reduced water, energy, and chemical usage in dyeing, resulting in a reduced carbon footprint, but the problem of effluent generation and associated water pollution was not eliminated. Of the low-resource consuming aqueous dyeing methods, rapid, low liquor ratio, and low temperature have various disadvantages, such as the need for extra textile auxiliaries, poor dye absorption, poor colour yield, and the risk of producing uneven shades. On the other hand, all the waterless methods, although eliminating water pollution, may cause air pollution if the solvents are liberated into the surrounding environment. They are suitable for dyeing selective types of fibres with selective dyes. Dyeing in $scCO_2$ is mainly suitable for polyester fibres with disperse dyes, but other fibres dyed with disperse and reactive disperse dyes show poor colour yield and colourfastness to washing. Hydrocarbon solvent dyeing is also mainly suitable for dyeing polyester fibres with disperse dyes. On the other hand, reverse-micellar dyeing is mainly suitable for dyeing natural and synthetic polyamide fibres with acid, disperse, reactive, and natural dyes. However, the solvents used in reverse micellar dyeing are flammable and harmful to the environment. IL and DES are suitable for dyeing polyester, cellulosic, and polyamide fibres with disperse and water-soluble dyes, respectively. Further research is necessary to address the barriers to implementing various sustainable dyeing methods developed over the years in the textile industry. Moreover, new reactive disperse dyes containing novel reactive groups that can react with cellulosic and polyamide fibres in a solvent medium, the development of novel dyes from biobased feedstocks, and new harmless, industrially feasible, and easy recoverable solvents for dyeing will need to be developed to make the future textile dyeing industry clean and green.

CRediT authorship contribution statement

Mohammad M. Hassan: Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

None.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.susmat.2025.e01490.

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