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An approach to the impact of nanoscale vat coloration of cotton on reducing agent account

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ABSTRACT

Aqueous dispersions of nanoscale vat dyes were successfully prepared through ball milling and ultrasonication of three test dyes in the presence of dispersing agent. Critical factors included the time of ball milling and ultrasonication and the molecular structure of the vat dyes have been studied. These dispersions were characterized by morphological structures with particle size determination and quality was evaluated by shelf-life stability using digital images. The nanoscale vat dyes have been applied in dyeing and printing of cotton to evaluate the effect of nanoscale dispersion on the reducing agent account and the difference of coloration performance of a nanoscale and conventionally dispersed vat dyes. Results showed that use of sodium dodecyl sulfate (SDS) maintained a high stability of dispersion with storage. The size and stability of nanoscale dispersion were greatly influenced by molecular structure of the vat dyes. Ultrasonication was helpful in decreasing average particle size. Nanoscale vat dye dispersions gave a much higher color yield than conventional vat dyes. Fastness properties were excellent for washing effects. It is clear that coloration using nanoscale vat dye dispersions offer a number of advantages in terms of reducing agent requirement, improved appearance and also in environmental protection.

1. Introduction

At present, there is no true alternative to vat dyes (Nahr & Ruppert, 1991), although the total number of vat dyes in the market has drastically diminished (Baumgarte, 1987).

The light and wet fastness of reactive dyes as the actual alternative has not yet reached the level of anthraquinone vat dyes invented a century ago (Hihara, Okada, & Morita, 2002). In the coloration of cellulose fibers, vat dyes still represent a relatively large part of the dyestuff market (about 11%); among them about 120,000 tons of vat dyes are being used annually (Roessler, Crettenand, Dossenbach, Marte, & Rys, 2002). It seems that the situation will remain constant also in the near future mainly because vat dyes yield colored cellulosic fibers of excellent all-round fastness, particularly to light, washing and chlorine bleaching (Hakeim, Abdou, El-Gammal, & El-Naggar, 2012).

Vat dyes are insoluble in water and cannot be used directly for dyeing cellulosic fibers. In the vatting process, vat dyes are reduced in an alkaline medium and converted to the soluble leuco form, which has substantivity to cellulosic fibers. The soluble leuco form penetrates into the fibers. The original insoluble structure is restored upon subsequent oxidation and the dye is retained within the fibers (Aspland, 1997; Nunn, 1979).

Until now in most industrial processes vat dyes (i.e. indigo) are reduced by the reducing agent of choice, sodium hydrosulfite, commonly known as hydro, to attain a water soluble form of the dyestuff with affinity to the cellulosic fiber. After diffusion into the fiber it will remain fixed there after having been reoxidised to the water-insoluble form. The disposal of dyeing baths and rinsing water is causing various problems (Cegarra, Puente & Valldeperas, 1992), because the necessary reducing agents will finally be oxidized into species that can hardly be regenerated. Thus, excess dithionite, sulphite, sulphate, thiosulphate and toxic sulphide heavily contaminate waste water from dyeing plants (Roessler, Crettenand, Dossenbach, Marte, & Rys, 2002). In this context, in the last decade, many attempts have been made to replace the environmentally unfriendly reduction and/or oxidation agents by ecologically more attractive alternatives using advanced chemical, electrochemical, electrocatalytic hydrogenation and biological methods (Mojca &, Vanja, 2008).

Generally, colorations produced with vat dyes impart overall higher wash fastness properties than results obtained by other classes of dyes. An insoluble characteristic of vat dyes is attributed to this superior wash fastness results (Jang, Kim & Lee, 2001; Jeong, Lee &Lee, 2002). The dyeing and fastness properties of regular viscose rayon with three vat dyes according to a different amount of reducing agent were investigated. The results found that smaller

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particle size of leuco vat dyes have a greater specific surface area than large particles, and would be expected to react more rapidly unless over reduced by adding excessive reducing agent. The color yield of the vat dyes on regular viscose rayon was dependent on the amount or concentration of the dye bath auxiliaries especially reducing agent to convert leuco vat dye (Woo, Jung & Renzo, 2006). The improvement of dispersibility of indigo was carried out by milling process to decrease the particle size distribution of indigo. The results confirmed that the particle size of indigo was decreased by milling process that a smaller particle size of indigo could provide the improved dispersibility, compared to the initial size of a commercial indigo as received (Son, Hong &Kim, 2004).

In this paper three nanoscale vat dyes were prepared using a liquid phase method including ball milling and ultrasonication in the presence of dispersing agent and applied to cotton fabric. Vat dispersion quality was evaluated by shelf life stability, morphological observation (TEM) with particle size determination. The effect of nanoscale dispersion on the reducing agent accounts for environmental and economic consideration and the difference of coloration performance of a nanoscale and conventionally dispersed vat dyes have been evaluated. Preparation variables (e.g., ball milling time and vat dye molecular structure effect on color) were investigated. In addition, the effect of ultrasonication on the shelf life stability and particle size was studied.

2. Experimental

2.1. Materials

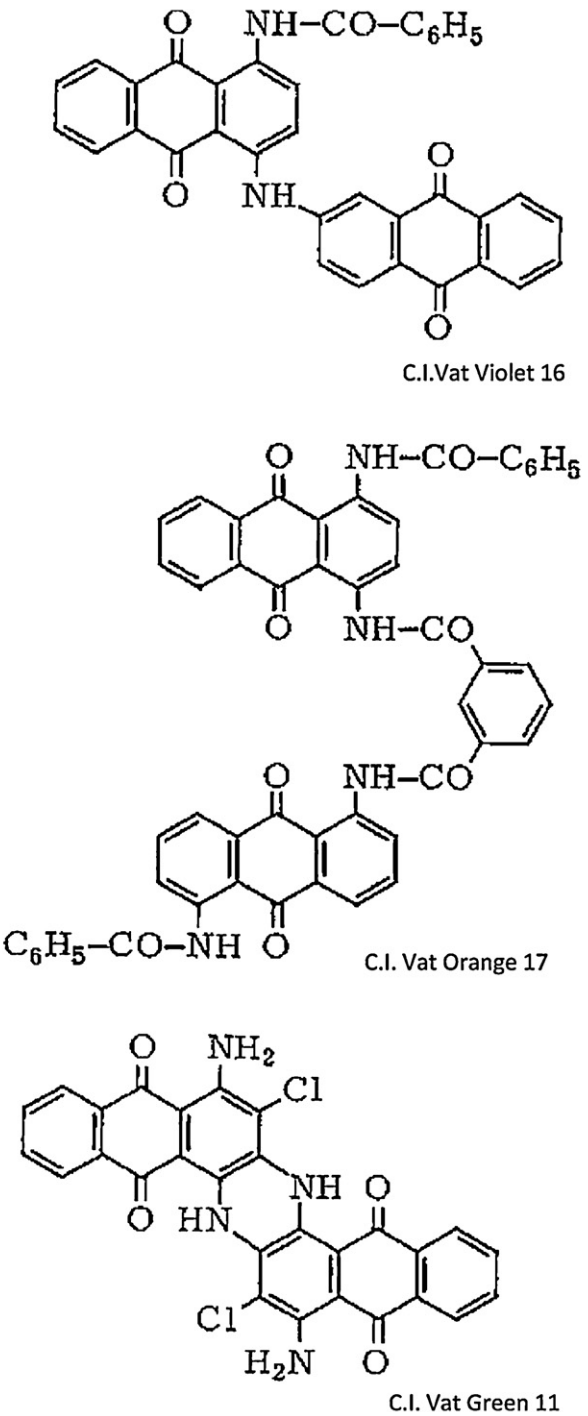
Cotton fabric used in this work was received from Misr spinning and weaving, Mehalla El-Kobrra,Egypt. This fabric was scoured, bleached, and mercerized, in which cotton fabric was 153 g/m$_2$. Surfactant tested included, sodium dodecyl sulfate, SDS purchased from Sigma. C.I. Vat Violet 16, C.I. Vat Orange 17 and C.I. Vat Green 11 were used as received from Ciba (Scheme 1). The commercial carboxymethyl cellulose (CMC) was supplied by Sichelnesp Scholten, Netherlands and sodium alginate (HV) purchased by Macrocystis pyrifera (Kelp) Sigma Chemical Co., Germany, were used as a mixture thickening agents in the vat printing. Sodium sulphoxylate formaldehyde (Rongalite C) was kindly supplied by BASF. All other chemicals and reagents used were of laboratory grade. Equipment used included the Thumblers tumbler for ball milling (Tru-Square) and the ultrasonic processor for ultrasonication process (Cole-Parmer Instrument).

2.2. Nano vat dye dispersion preparation

For vat dispersion preparation, 10 g of conventional vat dyer was mixed with 2 g of SDS and water to give 500 g total weight. This mixture was vigorously stirred with a magnetic stirrer for more than 1 h. The resulting mixture was then ball milled with 3 mm glass balls at a ball: powder weight ratio of 100:1 for 24 or 48 h. The ball-milled dispersions were then ultrasonicated for 1 h at a 90% amplitude (4 s on and 4 s off) pulsation rate.

2.3. Characterization

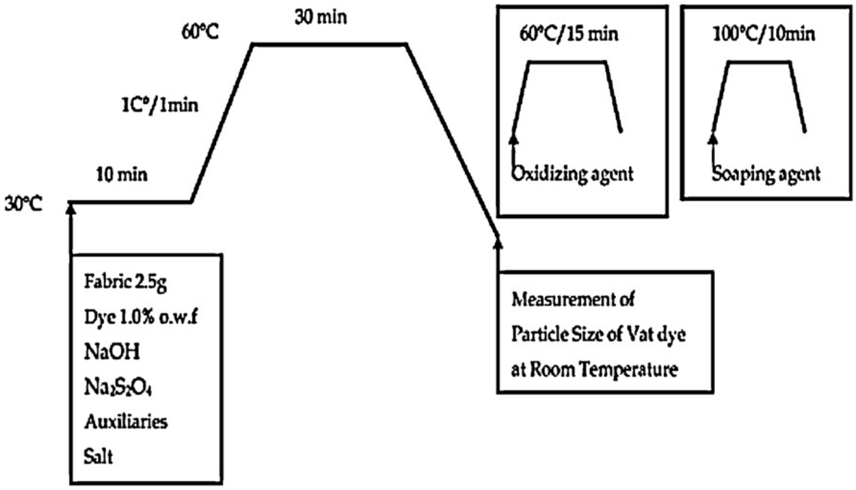
TEM (JEOL, J12300, TEM, Japan) was used to characterize vat particle morphology with particle size determination. One drop of the suspension, diluted into SDS solution, was placed on Cupper grid and dried in air before observation. Shelf-life stability was measured by placing approximately 20 ml of an mini-emulsion in a capped glass vial and observing the time necessary for a visible creaming (phase separation) line to appear. Digital photographs have been imaged using a digital camera (Sony DSC-V1) for 20 ml of mini-emulsion in a capped glass vial.



Scheme 1. Chemical structures of vat dyes.

2.4. Vat dyeing

The cotton fabric was dyed using the dyeing profile shown in Scheme 2. Dyeing was commenced at 30 °C. using 5 g/l of NaOH with 0–5 g/l reducing agent. The dyebath temperature was raised 1 °C/min to 60 °C. The temperature was maintained at each temperature for 30 min, and then rapidly cooled to room temperature (RT). At the end of the dyeing process, the dyed fabrics were removed and rinsed thoroughly in cold water. Oxidation was carried out with 2 ml/l hydrogen peroxide solution (30% w/v) for 15 min at 60 °C. Finally, the dyeings were soaped in an aqueous solution of 2.5 g/l non-ionic detergent (Synperonic BD) for 15 min at a boil.



Scheme 2. Vat dyeing profile on cotton fabric.

2.5. Measurement of exhaustion

After dye solution was prepared, the initial concentration of the reduced vat dye (leuco form) was determined by measuring absorbance at the wavelength of maximum absorption (λ max) of the reduced dye using a spectrophotometer, Unicam UV 300, Thermo,England. Then dyeing was carried out without hesitation in order to prevent possible oxidation of the dye. At the end of dyeing, the absorbance of the dye solution was measured as soon as possible for the same reason (preventing oxidation). The percentage exhaustion of the vat dye on cotton was calculated using Eq. (1).

$$\text{Exhaustion}\,(\%) = \left(1 - \frac{A_1}{A_0}\right) \times 100 \qquad (1)$$

where A_0: absorbance of initial dyebath; A_1: absorbance of residual dyebath.

2.6. Vat printing

The printing with vat dyes involves the preparation of stock thickening agent and then incorporating thickening agent in the printing paste with nano vat dispersions according to the following recipes:

Nano vat dispersion[a]	500 g
Potassium carbonates	160 g
Sodium sulphoxalate formaldehyde (Ronalite C)	0–60 g
Glycerin	60 g
Thickening agents[b]	X g
Water	Y g
Total	1000 g

[a] Nano vat dispersion, 10 g of conventional vat dye was mixed with 2 g of SDS and water to give 500 g total weight, ball milled for 48 h and ulrasonicated for 1 h at a 90% amplitude.

[b] The thickening agents were a mixture of sodium alginate (25 g) and CMC (40 g).

The printing pastes were applied to fabrics through a flat silk screen. After drying, the printed fabrics were subjected to free steam air at 102 °C for 10 min. Then the fabrics were rinsed with cold water to remove the thickening agents and alkali before oxidizing the vat dye. After oxidation, the fabrics were boiled for 5 min in an aqueous solution containing 2 g/l of detergent (Synperonic BD) and sodium carbonate (1 g/l). Finally, the fabrics were rinsed in cold water and air dried.

2.7. Measurements and analysis

2.7.1. Color intensity (K/S)

Spectral reflection measurements of the dyed fabrics were carried out using a recording filter spectrophotometer. The color intensity expressed as K/S values of the dyed samples were determined by applying the Kubleka-Munk equation at λ max 520 nm (Judd & Wyszecki, 1975).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

where R: is the decimal fraction of the reflectance of the dyed substrate.

R_0: is the decimal fraction of the reflectance of the undyed substrate.

S: is the scattering coefficient.

K: is the absorption coefficient.

2.7.2. Washing fastness

Washing fastness tests were carried out according to BS1006: C02 Test 2 with a soap solution (5 g/l, liquor ratio = 50:1) for 45 min at 48–50 °C (Achwall, 1985).

3. Results and discussion

3.1. Dispersing agent effect

Nanoscale organic pigments were successfully prepared through ball milling and ultrasonication in the presence of dispersing agents (Hakeim, Fan, & Kim, 2010). The results showed that use of sodium dodecyl sulfate (SDS) maintained a high stability of dispersion with storage. In this regard, and due to the similarity of pigment and vat colors with respect to solubility, screening experiments in preparation of nanoscale C.I. Vat Orange 17 was performed in the presence and absence (presence of water only) of SDS to study its ability to stabilize vat dispersion. Formulations tested was ball-milled for 48 h. All ball-milled samples were subjected to 1 h ultrasonication. The TEM image of conventional C.I. Vat Orange 17 used is cited Fig. 1. The drawback of absence SDS as a dispersing agent during the preparation of nanoscale vat dyes is the lack of dispersion stability due to high vat agglomeration which leads to a large particle size as recorded in TEM images (Fig. 2). Lower agglomeration/aggregation was observed with use of SDS surfactant as compared to water. In addition, the particle size distribution gave better uniformity (from TEM results) with SDS. Photographs

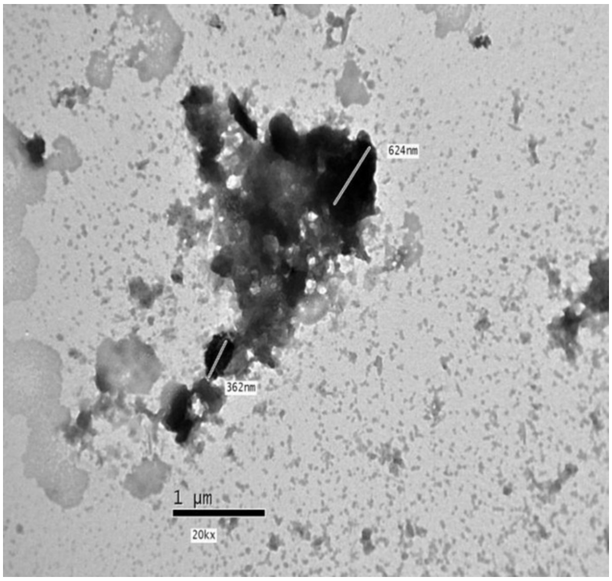


Fig. 1. TEM image of C.I. Vat Orange 17 as received.

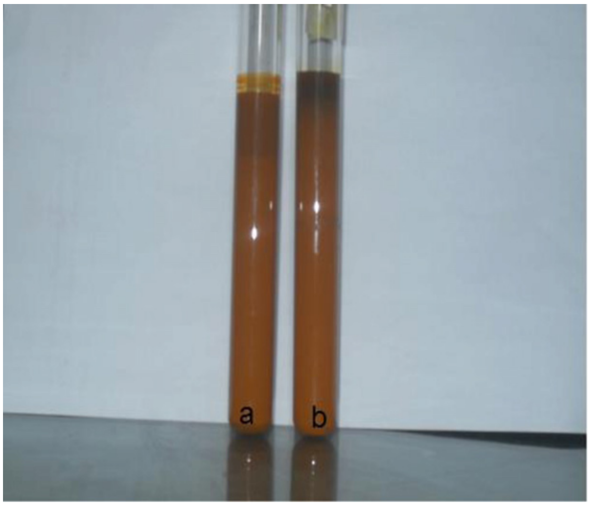


Fig. 3. Photograph of nanoscale C.I. Vat Orange 17 prepared in the presence and absence of SDS.

taken of the dispersions seven days at room temperature (RT) after preparation confirmed these results (Fig. 3). It is worthy to mention that the pigmentation of C.I. Vat Orange 17 has been carried out by ball milling in the presence of SDS producing a new crystal form. When SDS is added to the ball milling mixtures; the pigments obtained have smaller particle sizes. Since the surfaces of pigment particles can absorb SDS molecules, this may prevent pigment particles from aggregation. The results indicated that the presence of SDS is of practical importance because it has the ability to achieve a high degree of dispersion and maintain high dispersion stability in storage and therefore became the method of choice for further experiments in this study.

3.2. *Ball milling time effect*

The TEM micrographs in Fig. 4 show effect of ball milling time on the particle size of C.I. Vat Orange 17. These show that ball milling time is a key factor affecting vat dye particle size. The particle size after milling for 48 h was significantly lower than that after milling for 24 h. Although the particle size was reduced by increasing the ball milling time, the particles still showed some aggregation and agglomeration. It is known that the efficiency of dispersion is dependent on the effectiveness of the mechanical energy transfer from the milling tools to the oversized vat dye particles. The increase of ball milling time increases the opportunity of glass-ball contact with pigmented vat dye particles. During the milling process, the glass balls rolled up inside the milling bottle, and fell down, thus changing the potential energy to kinetic energy and breaking down the particle size effectively (Hakeim, Fan &, Kim, 2010).

3.3. *Vat dye structure influence on dispersion stability*

The effect of vat dye chemical structure on its dispersing level plays an important role in the application of vat colors. Attempts to correlate the ease of dispersion of the three nanoscale vat dyes with their chemical structures have been investigated in term of shelf life stability and particle morphology with particle size determination.

The morphological structure of nanoscale vat dyes was observed by TEM after 15 days of storage at RT (Fig. 5). It is clear that the violet dye was better dispersed than the other nanoscale vat dyes. It has a perfectly uniform, spherical nanoparticle shape with absence of agglomeration, uniform surface, and a mean particle size less than 20 nm. The results showed that the orange vat particles (Fig. 5b) were approximately spherical in shape with a very broad particle size distribution and with evidence of particle aggregation. On the other hand, the presence of hard agglomeration has been observed in the morphological structure of vat green with average particle size more than 100 nm. This finding may be attributed to

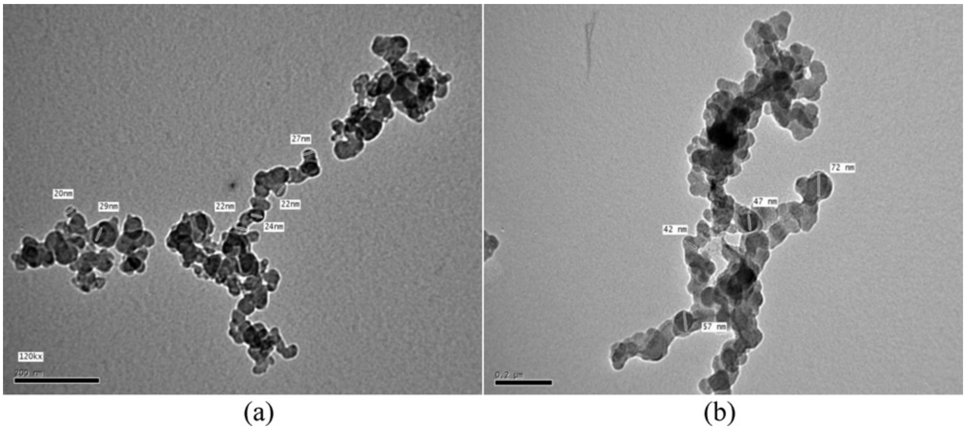


Fig. 2. TEM images of nanoscale C.I. Vat Orange 17 prepared in the presence and absence of SDS.

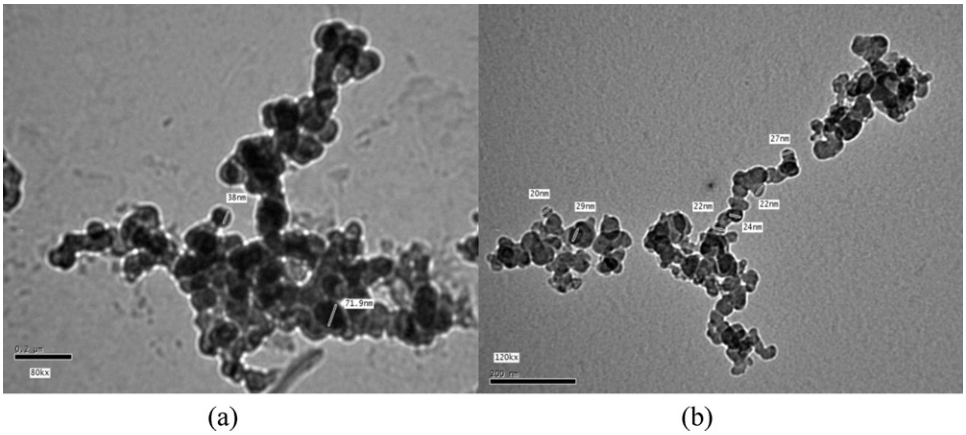
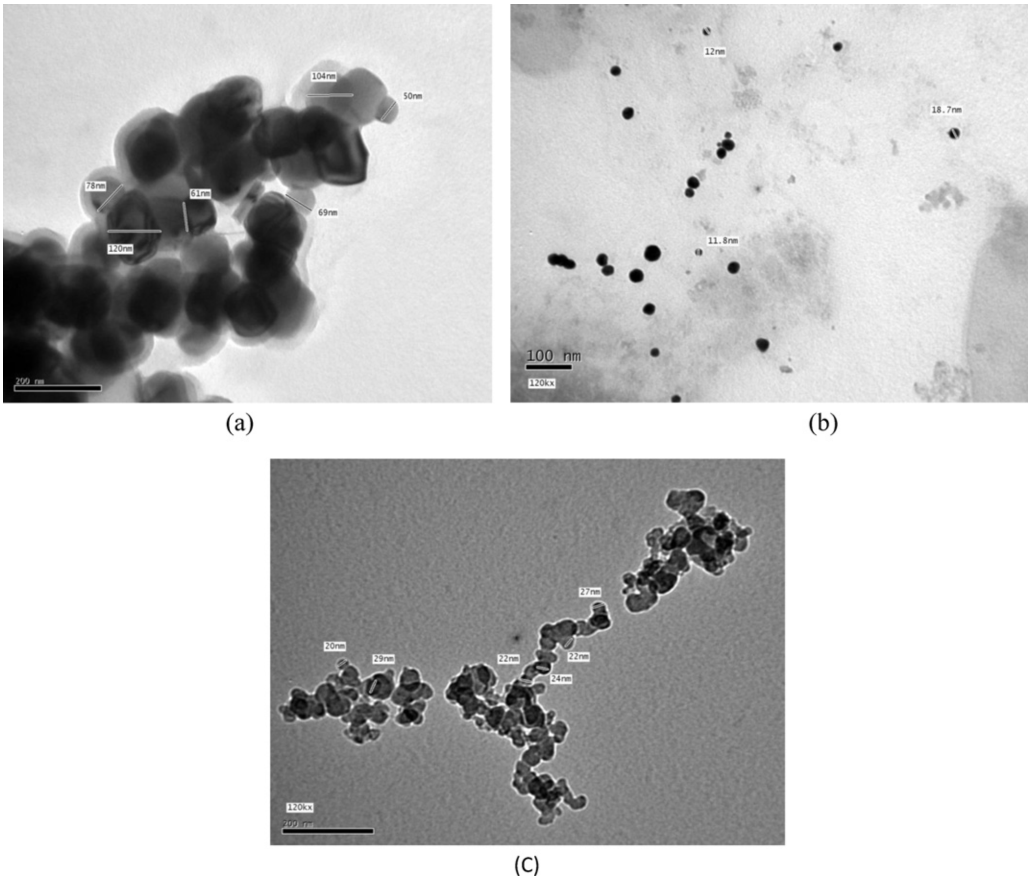


Fig. 4. TEM images of nanoscale C.I. Vat Orange 17 prepared in the presence of SDS and ball milled for 24 h and 48 h.

non-planar structure and the steric hindrance of the vat green, which in turn, decreased colorant hydrophobicity and the ease of dispersion stability. Shelf-life stability of C.I. Vat Violet 16 and C.I. Vat Orange 17 was measured by placing ~20 ml of prepared nanoscale vat dye dispersion in a capped glass vial and observing the time it took for a visible phase separation and agglomeration of colors at RT. It was appeared that the violet vat dispersion had better storage stability than the orange vat. Fig. 6.

The pigmentation of vat dyes can be carried out by wet ball milling in the presence of SDS, consequently the dispersion stability of vat dyes can be explained on the basis of pigment crystal form of hydrophobic colorants. With this in mind, in a dispersion bath of hydrophobic colorants, the colors probably exist in the form of complexes consisting of many pigment particles and dispersant molecules linked together by Van der Waals and hydrophobic-hydrophobic interactions. Consequently, the ease of dispersion increases with an increase in pigment hydrophobicity which increases the interaction with dispersants. On the other hand, the solvation chain of dispersant (SDS) on the hydrophobic surface of vat color can cause steric hindrance and prohibit pigment particles from aggregation (Hakeim, Fan &, Kim, 2010), and also leads to an improvement in dispersing the pigment. Based on the aforementioned facts, C.I. Vat Violet 16 was better dispersed than orange vat. The extensive aggregation of C.I. Vat Orange 17 after 15 days can be attributed to the higher molecular weight of its molecule in comparison with the violet one.



(a) (b)

(C)

Fig. 5. TEM images of nanoscale C.I. Vat Green 1, C.I. Vat Violet 16 and C.I. Vat Orange 17, upon 15 of storage at RT.

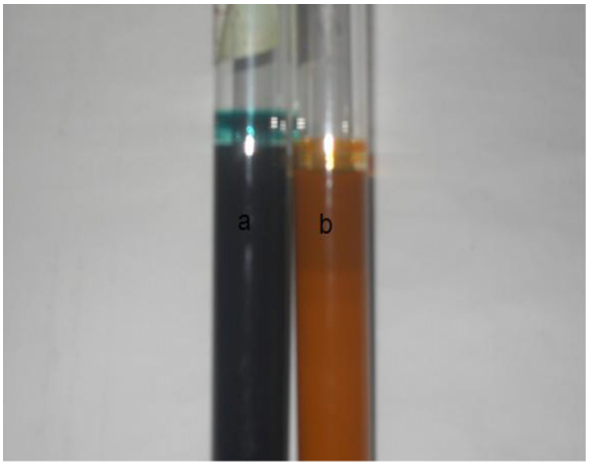


Fig. 6. Photograph of of nanoscale C.I. Vat Violet 16 and C.I. Vat Orange 17, upon 15 of storage at RT.

3.4. Ultrasonication time influence on particle size and dispersion stability of vat dye

The role of ultrasonication in preparation of C.I. Vat Violet 16 nanoscale was investigated with respect to morphological structure with particle size determination. For this purpose, another batch of nanoscale vat violet was prepared at different time intervals of ultrasonication (30, 60 and 90 min). It is apparent from Fig. 7 that ultrasound application helped reduce the vat particle size, generating more particles less than 20 nm at ultrasonication for 90 min. The main mechanical effect of ultrasonication is to deagglomerate pigment particles in the presence of SDS dispersant (Hakeim, Fan &, Kim, 2010). Generated ultrasound waves make similarly-charged particles collide into one another with great force; consequently the problem of agglomeration is greatly reduced. In addition, high energy produced from particle collisions at high temperatures is responsible for breaking down the particles and decreasing particle size which has an impact on dispersion stability of vat dyes.

3.5. Effect of amount of reducing agent on dyeing and printing properties of nanoscale and commercial vat dyes

The particle size of the dyestuff plays a vital role for considering suitability of any dyestuff for continuous processing. During dyeing, the dye molecule has to enter the intercellular spaces of the fiber in which it has to be fixed. The particle size of leuco vat dye converted by reducing agent influenced the time of reduction required to establish the vat dyeing process. A decrease in the particle size thus shortens the time required for dyeing in equilibration. Large particles would mitigate high resistance to enter the fiber (Woo, Jung & Renzo, 2006). Table 1 shows the variation in amount of reducing agent and their effect on exhaustion %, color strength and washing fastness of nanosize (~20 nm) and commercial C.I. Vat Violet 16. Cotton fabric was dyed with nanosize dye prepared at the optimum conditions (48 h ball milling and 90 min ultrasonication) and the exhaustion of the dye was measured. It is clear that the decrease in particle size of vat dye on using nanosize vat color in vatting process decreases the reducing agent requirement. When we added no reducing agent to the dye solution the nanosize vat color can be behaved as a leuco form. Thus, dye molecules could be fixed to make color in the fiber and automatically penetrate with fixation in the internal region of cotton fabrics. The opposite holds true on using the commercial vat color. This can be clearly indicated from the good result of color yield of nanosize vat color on cotton fabric using 0 g/l reducing agent in comparison with commercial dye. It is also clear that as the amount of reducing agent is increased in the vatting process, a little increase of color strength of the nanosize dye was observed. However, excessive reducing agent (6 g/l) has a negative effect on dyed cotton fabrics. With increasing concentration of reducing agent in the dyeing process, the dyed fabric could not produce high color yield. This is because the reducing agent is dissolving the leuco vat dye which can represent the color. Table 1 shows the percentage exhaustion values of C.I. Vat Violet 16 at different amounts of reducing agent. It seems that the nanosize vat violet exhausted more than the commercial vat one in absence of reducing agent. The percentage exhaustion values of nanosize and commercial C.I. Vat Violet 16 at 0 g/l reducing agent which were 94.9 and 74.4% respectively support this finding. This might result in reaching saturation of color yield for nanosize earlier than the commercial vat dyes. In exchange for their cost, vat dyes can deliver dyeing with arguably the highest levels of washing and wet fastness properties. Vat dyeing has several good properties which make them very difficult to overlook for dyeing some industrial yarns, terry cloth, and industrial work clothing and shirting fabrics. Table 1 shows the fastness to washing of nanosize and commercial vat dyes on cotton fabric. The results showed that the vat dyeing displayed very good fastness properties to washing in term of shade change with reducing agent (0–4 g/l) and that very little staining to the adjacent fabric occurred over 4 g/l. This result can be also attributed to the insolubility of the vat dyes characteristics.

Based on the above results few points may be concluded; (1) the pigmentation of vat dyes can be carried out by wet ball milling in the presence of dispersant producing a new crystal form. (2) The nanosize C.I. Vat Violet 16 was better dispersed with storage and gave the smaller particle size than the other vat colors due to its higher hydrophobic nature, while the nanosize C.I. Vat Green 1 with its non-planar structure and steric hindrance has the hard agglomeration with larger particle size and the least dispersion stability with storage. (3) The nanosize C.I. Vat Violet 16 can behaves as a leuco form in absence of reducing agent and could be fixed to make color in the fiber and automatically penetrate with fixation in the internal region of cotton fabrics and gave the satisfactory color yield, on the other hand, the commercial vat dyes were not converted to the leuco form in absence of reducing agent, the fabric could not be dyed and inquire a high amount of reducing agent. Also, vat dye with a larger proportion of small particles (nanosize) would be expected to reduce more rapidly than a sample with predominantly large particles (commercial dye) at the same reducing agent ratio. This focus on using the nanosize vat dye reflects on the environmental concern which inquires to reduce the use of environmentally unfavorable reducing agents by improving dyeing with vat dyes.

Vat printing is one of the most complicated printing methods which need a lot of chemistries including reduction and oxidation. The conventional vat printing was performed in two steps; steaming at elevated temperature followed by oxidation process. In this work, the vat printing on cotton fabrics using the nanosize vat orange was compared with the vat printing with the same commercial colors. In this method the vat dye was incorporated in a paste containing sodium alginate and carboxymethyl cellulose as a base thickener. Sodium sulphoxylate formaldehyde was used as a reducing agent and potassium carbonate was used as the alkaline medium. The printed cotton fabrics were dried and finally fixation is conducted using saturated steam at 102 °C for 10–15 min. Table 1 shows also the effect of particle size of vat color on the color yield of cotton fabrics printed at different amounts of reducing agent. Generally, the color strength of printed cotton fabric with nanosize vat color is higher than the commercial one. It is apparent that the nanosize vat dye follows the same trend in printing process as in dyeing with respect to color yield, and behaves as a leuco form at 0 g/l of reducing agent and fixed on the surface of fabrics and the

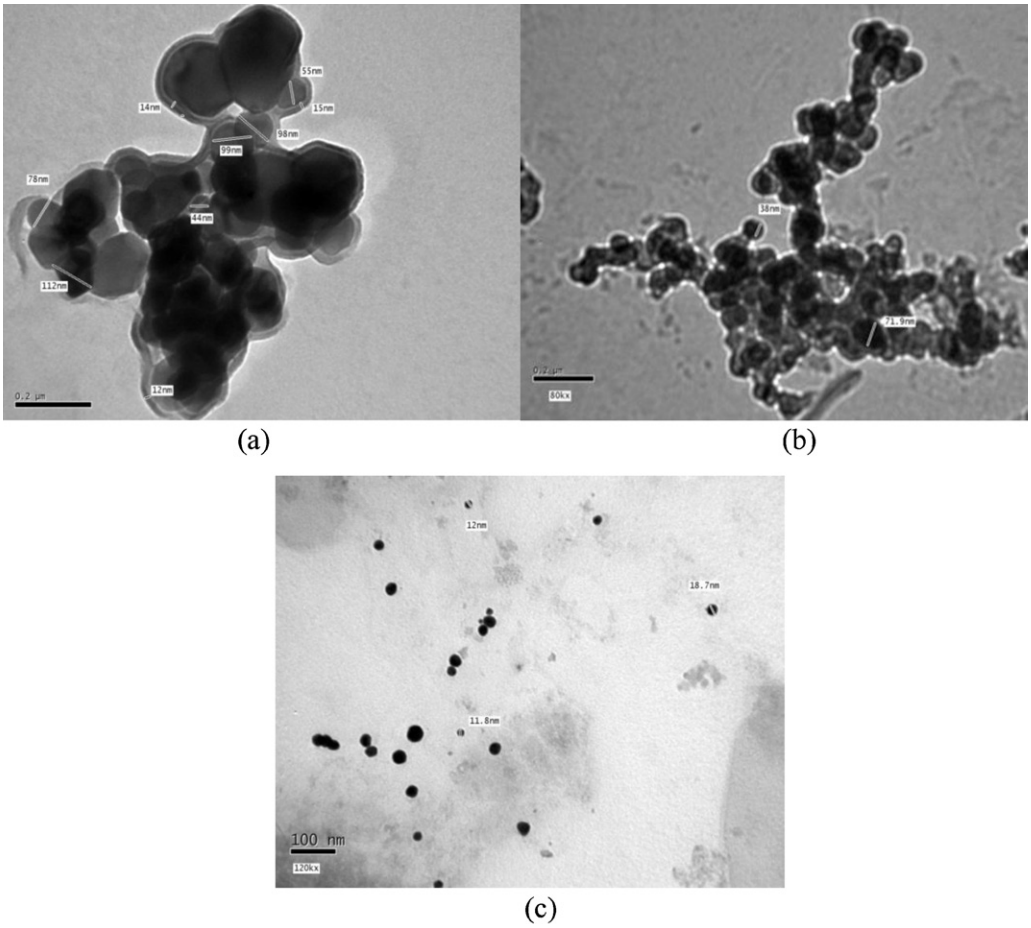


Fig. 7. TEM images of nanoscale C.I. Vat Violet 16 ball milled for 48 h in the presence of SDS and ultrasonicated for 30 min, 60 min and 90 min.

smaller particle size was able to impart a satisfactory color yield. Smaller sizes of vat dyes are suitable for printing the fabric because the leuco vat dye can easily penetrate and fix on cotton. A smaller particle size of vat dyes could provide an improved dispersion. Thus, because the reduction in particle size of vat dye could enhance dispersibility in the vat printing process, there was an increase in the color strength of prints. However, the commercial dye cannot be printed in absence of reducing agent. Actually the reduction of commercial dye and formation of leuco form which has substantivity to cellulose fiber, for satisfactory dye uptake inquire more

Table 1
Effect of reducing agent amount on the dyeing and printing properties of nanosize and commercial vat dyes.

Concentration of reducing agent	Dye	Exhaustion %	*K*/*S*	Washing fastness		
				Sc	Sw	Alt
Dyeing[a]						
0.00 g/l	Commercial	74.4	0.81	5	5	5
	Nanosize	94.9	3.36	5	5	5
2.00 g/l	Commercial	79.6	1.42	5	5	5
	Nanosize	93.1	3.44	5	5	5
4.00 g/l	Commercial	80.01	1.96	5	5	4–5
	Nanosize	96.8	3.56	4–5	4–5	4–5
6.00 g/l	Commercial	81.01	2.22	4	4	4–5
	Nanosize	90.03	2.88	4	4	4–5
Printing[b]						
0.00 g/l	Commercial	–	0.54	–	–	–
	Nanosize	–	3.11	5	5	5
200 g/l	Commercial	–	1.12	5	5	5
	Nanosize	–	3.65	5	5	5
4.00 g/l	Commercial	–	1.68	4–5	4–5	4
	Nanosize	–	3.91	5	5	4–5
6.00 g/l	Commercial	–	2.96	4–5	4–5	4
	Nanosize	–	2.99	4–5	4–5	4

SC = staining on cotton; SW = staining on wool; Alt = change of color.

[a] C.I. Vat Violet 16 is used in dyeing.

[b] C.I. Vat Orange 17 is used in printing.

amounts of reducing agents and this reflect a negative impact on ecological consideration. The larger molecules inquire high concentration of reducing agent and have a harder time diffusing into the fiber and take more time, while the smaller ones can behave as a leuco form and easily penetrate and fix on cotton fabrics. On other word, the small particle size of nano vat dye compensates partially the requirement of reducing agent. It was also apparent that irrespective of dye used, the printed cotton fabrics dyes exhibited good wash fastness in terms of shade change and very little staining to the adjacent fiber.

4. Conclusions

The dyeing and printing of cotton with nanosize and conventional vat dyes according to a different amount of reducing agent was investigated. Nanoscale vat dyes with particle sizes ~20 nm were successfully prepared by using ball milling and ultrasonication in the presence of SDS. The pigmentation of vat dyes was carried out by this method producing a new crystal form. The influence of vat dye structure on the quality of vat color dispersion and particle size was found to be of major importance. Vat Violet 16 was better dispersed with storage and gave the smaller particle size compared to the other vat colors. Ultrasonication obviously played a determinant role in decreasing vat particle size. The nanosize vat colors can behave as a leuco form in absence of reducing agent in dyeing and printing of vat dyes and could be fixed to make color in the fiber and penetrate with fixation in the internal region of cotton fabrics and gave the satisfactory color yield. On the other hand, the commercial vat dyes were not converted to the leuco form in absence of reducing agent. This focus on using the nanosize vat dye is ecologically and economically acceptable and reflects on the environmental concern which inquires to reduce the use of environmentally unfavorable reducing agents by improving dyeing and printing with vat dyes.

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