



Intermittent Milling: An Environmental, Low-Cost, and Sustainable Strategy for Disperse Dyes

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Abstract

To improve the efficiency of disperse dyes in various applications including textiles, energy, and sensors, it is important to increase their surface area. Additionally, it is necessary to implement an environmentally sustainable approach to the milling process of these dyes. In this study, intermittent milling was utilized for the first time to mill Disperse Red 167 (DR 167) dye without the use of auxiliaries and/or additional chemicals to achieve an eco-sustainable milling approach. A comprehensive investigation was carried out to analyze the physico-chemical characteristics of DR 167 dye in its pristine and milled forms through a range of analytical techniques to uncover the effects of milling times, i. e. 2 and 10 h, on the dye properties. SEM and FTIR revealed that the pristine spherical shape of DR 167 dye deteriorated gradually with an increase in milling time, accompanied by significant variations in peak intensities and slight shifts that indicate a crystal form change. While NMR analysis indicated that there were no changes in the chemical structure of the dye. XRD data showed that the β -crystal phase of the pristine dye collapsed after 2 h of milling, followed by recrystallization to the α -crystal phase after 10 h of milling. The melting points of the β and α -crystal forms were approximately 135°C and 133°C, respectively, as revealed by thermal studies.

Keywords: Eco-sustainable milling; Intermittent Milling; Disperse dye; Environmental Sustainability; Low-Cost milling, Crystallography; Physico-chemical characteristics

1. Introduction

Azo compounds have been widely used for several years in various industries, including biological-medical research, colored plastics and polymers, paper industry and organic synthesis catalysts, as well as the textile dyeing and printing [1-6]. Azo disperse dyes are a widely used class of compounds in different industries, specifically in dyeing and printing man-made textiles such as polyester, polyamide, polyacrylonitrile, and triacetate [7-10]. They are highly desirable for their intense and brilliant colors and are considered to be one of the most efficient types of synthetic dyes, with a well-established reputation for excellence [9, 11, 12]. They are also used as sensitizers in the energy sector for dye-sensitized solar cells [13-15], in addition to being the most commonly used dye class in textiles [16, 17]. Whereas they make up more than 50% of the

total production of disperse dyes [18, 19]. These organic colorants typically have an azo chromophore group, which is often conjugated with two aromatic rings [20-22]. Azo disperse dyes, such as vat dyes and organic pigments, are a group of non-ionic compounds that exhibit low solubility in water [23, 24]. However, their hydrophobic nature and high surface energy can cause coagulation or aggregation in aqueous solutions [25-27]. Reducing the particle size of the dye not only increases its surface area, resulting in improved colorfastness by enhancing coalescence with the fabric, but it also allows for easier penetration into the synthetic fabric surface, resulting in more even dyeing and a more vibrant color. Additionally, the improved dispersion of the dye in the liquid phase is positively correlated with the decrease in particle size [28-30]. Furthermore, smaller particle size enables using less amounts of

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dye for the same color intensity, increasing dyeing process efficiency and cost savings [31-33]. Therefore, preparing small and consistent particles of dye is crucial for improving the dyeing quality of micro and nanofibers, as higher dye concentrations are typically required to achieve the desired shade depth [34, 35].

The antisolvent precipitation method produces fine dye particles with narrow size distribution and high yield, but it has disadvantages, including expensive antisolvent, difficulty in controlling size and crystal growth kinetics, and expertise required [36]. Although the supercritical fluid method can produce small particles of dye with a high yield, it is costly due to specialized equipment and energy consumption. It also has drawbacks such as safety risks, a broad distribution of particle sizes, and the use of flammable and/or toxic supercritical fluids [37-39]. While emulsion polymerization has several disadvantages such as sensitivity to changes in temperature and pH, which can lead to inconsistent particle properties. Residual monomers and initiators can also pose a contamination risk that is difficult to remove completely [40-42]. Moreover, high-pressure homogenization generates small and uniform particles but is relatively expensive and can cause the thermal degradation of dye molecules. As well, the method requires specialized equipment and expensive high-pressure pumps [43]. On the contrary, Ball milling is a milling process that involves grinding dye particles using grinding media, such as balls, within a rotating jar [44-47]. This method offers advantages such as producing small particles and having control over particle size distribution, as well as simplicity, cost-effectiveness, and scalability [48-50]. It is also widely used in industry and research, attesting to its reliability and efficiency [45, 51, 52]. However, their drawbacks in dye milling include the need for auxiliary agents to improve dispersibility and prevent agglomeration during milling [53].

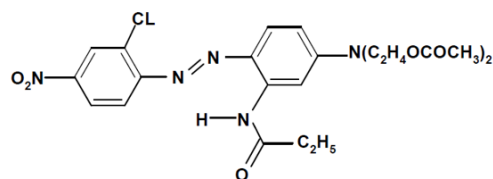
The use of large amounts of auxiliaries not only results in dye degradation [54], but also leads to environmental contamination, including toxicity to aquatic life and persistence in the environment. This can result in bioaccumulation, disruption of aquatic communities and food webs, and contamination of sediments, which may have long-term consequences for the health of marine ecosystems [55-57]. Thus, improper management of the production and use of these auxiliaries may contribute to environmental issues such as climate change and other problems that caused by the emission of greenhouse gases and pollutants. Additionally, in the ball milling process, the collisions of the balls generate thermal energy that can increase the surface energy of dye molecules,

potentially altering their chemical, physical, and thermal properties [58-60]. So, this study aims to investigate the use of intermittent milling as a simple, low-cost, and environmentally friendly strategy for milling DR 167 dye without adding auxiliary agents or additional chemicals. This method involves alternating periods of milling with intervals of rest, during which the milling jar is opened to dissipate the heat produced by the collision of the grinding balls and to deagglomerate any agglomerated dyes. The effects of milling duration on the surface morphology, chemical and crystal structures, as well as thermal properties of the dye were evaluated using various analytical techniques, including scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), Fourier transform infrared spectrometry (FT-IR), Nuclear magnetic resonance spectroscopy (NMR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

The chemical structure of DR 167 dye is depicted in Scheme 1 and was sourced from DyStar (Egypt).



Scheme 1. Chemical structure of DR 167 [1].

2.2. Dye Milling

DR 167 was subjected to intermittent milling, which included short periods of milling lasting 30 minutes followed by rest intervals lasting 15 minutes, using a high-energy ball mill (Planetary Ball Mill PM 100, Retsch, Germany). Prior to the milling process, the dye undergoes a drying procedure for a duration of 15 minutes, at a temperature of 60 °C, with the aim of eliminating any remaining moisture content that could lead to an increase in particle aggregation and a decline in the quality of the dye.

A total of 200 g of DR 167 was placed in a 500 mL stainless steel jar, along with 7 balls (2 cm in diameter) and 40 balls (0.5 cm in diameter). The jar was subjected to intermittent milling at a fixed rotational speed of 450 RPM, until a total milling time of 2 h was achieved. Following this, the milled dye was passed through a sieve with a mesh size of 38 µm, resulting in the collection of particles larger than 38 µm, which were labeled as DR 167-B. The remaining particles, with sizes smaller than 38 µm, underwent an additional 8 hours of milling to produce a new sample, designated as DR 167-C.

3. Characterization

3.1. Morphological Investigations

The alterations in surface texture and shape of DR 167 and the milled dyes were evaluated using scanning electron microscopy (SEM) (JSM 6700F/JEOL/Tokyo/Japan) at a beam energy of 30 kV and a working distance of 11.1 to 12.2 mm. The samples were imaged at a magnification of 400X after being coated with gold using a coater device (JEOL-JSM-420, Japan). Additionally, the particle size of the samples was analyzed using Image J software. The specific surface areas of the samples were also investigated using Nova Touch LX4 equipment (Quantachrome, USA). The surface area was evaluated by the N₂ adsorption/desorption tests at 77.35 K by applying the BET approach. 2.3.2. Surface Area Measurements.

3.2. Functional Groups and UV-Visible Analysis

The functional groups of the DR 167 before and after milling for 2 and 10 h were characterized using Fourier transform infrared spectroscopy (FT-IR) in the wavenumber range of 400 to 4000 cm⁻¹. The analysis was performed using a Bruker FTIR-2000 Spectrometer with a spectral resolution of 4 cm⁻¹. The dye particles and KBr (Merck) were mixed in a 1:10 ratio to make a translucent pellet disk that was utilized to identify the functional groups of the addressed dyes. Using a UV-3600 spectrophotometer, UV-vis absorption spectra were recorded.

3.3. NMR analysis

The ¹H NMR of the respective spectra were confirmed for the investigation of the effect of milling on the chemical structure of dye by employing a Bruker DRX-300 instrument operated at 400 MHz using DMSO-d₆ as solvent.

3.4. Crystallographic Investigations

To determine the crystallinity and phase identification of the samples, an X-ray diffractometer (XRD, PANalytical Empyrean) equipped with a Cu-K α radiation source (= 1.5406) that worked at an accelerating voltage of 40 kV and a current of 30 mA in the 2 θ range of 5°-80° with a 0.04° detector step size and a 5.0 min scanning time was used.

3.5. Thermal Studies

The effects of milling duration on the thermal characteristics of DR 167 were studied using the SDT Q 600 (TA, Company, USA) instrument. TG, DTG, and DSC curves were obtained at a 10 °C/min uniform heating rate under the nitrogen atmosphere, and temperatures ranged from room temperature to 550 °C. These tests were done under ASTM E 1621 [2].

3.6. UV-Visible Study

4. Results and Discussion

4.1. Morphological Investigations

Figure 1 indicates the influence of milling time on the morphological features and particle size distribution of dyes. The milling for 2 h caused a shift in the shape of DR 167 particles (Fig. 1a) from spherical to sheet-like structures. This change in morphology is attributed to the mechanical force introduced during the milling process [3]. Also, an increase in total surface from 18.56 to 24.37 m²/g was observed (Table 1). that was attributed to the reduction in particle size and changes in particle shape, which can lead to an increase in the amount of surface area per unit mass of material exposed, as reported in previous studies [4]. The heterogeneous particle diameter distribution also observed ranged from 17.9 to 87.7 μ m with an average of 42.2 μ m, which may suggest that the milling duration of 2 h was insufficient to achieve a complete dye milling (Fig. 1b).

The increase in milling duration to 10 h resulted in the grinding of the sheet-like shapes of DR167-B into fine particles, increasing the aggregation of particles and causing a decrease in total surface area to 21.31 m²/g. The results also indicate that milling for 2 h led to a slight enhancement in particle diameter distribution (from 0.4 to 42 μ m), with about 63% of the particles having a diameter in the range of 0 to 10 μ m and an average diameter of 13.8 μ m. While milling for 10 h led to a high degree of uniformity in the particle diameter distribution (0.13 to 26.38 μ m, average of 3.85 μ m), about 92% of the dye particles had a diameter in the range of 0 to 10 μ m, (as shown in Fig. 1c).

The minimization of dye particles can be attributed to the increase of frictional forces on the dye particles within the ball mill jar, which gradually convert the particle size to finer as the duration of milling increases [3]. The increase in particle aggregation can be attributed to the formation of small particles during the milling duration [5,6]. The results of this investigation highlight the significance of milling time on the morphological structure and particle size distribution of dyes, providing insights for further optimization and improvement in the field of dye production.

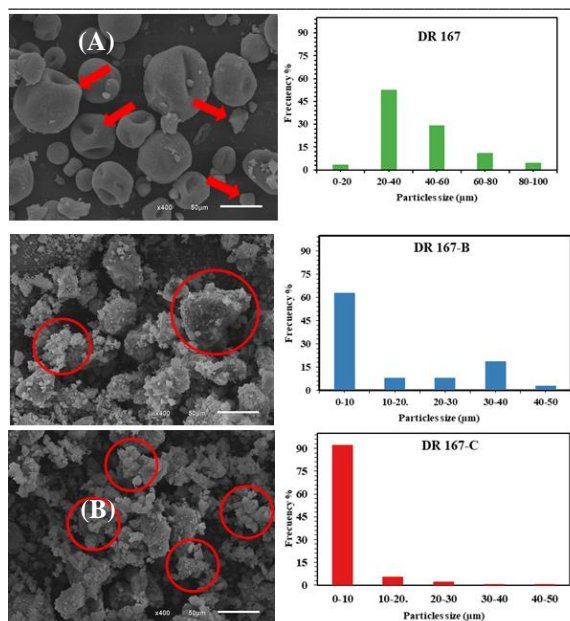


Figure 1. SEM Images and diameter distribution of dye particles; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

Table 1. Total surface area of dyes; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

Dye	DR 167	DR 167- B	DR 167- C
Surface area	18.56 m ² /g	24.37 m ² /g	21.31 m ² /g

4.2. Functional Groups Analysis

The chemical composition of a dye, including the nature of its linking bonds, the presence of specific functional groups, and its segment structure, significantly influences its physicochemical properties and performance in its intended applications [7]. The Fourier Transform Infrared (FT-IR) spectroscopy was utilized to gain a deeper understanding of the effects of milling duration on the chemical structure of the dye (Fig. 2 a-c). Concerning DR 167, the FT-IR spectra revealed that the peak around 3413.61 cm⁻¹ indicates the presence of N-H stretching vibration (ν N-H) in the coupling components. With milling for 2 and 10 h, the intensity of such a group has increased and slightly shifted to 3418.59 and 3425.26 cm⁻¹, respectively. Whereas the FT-IR was performed on the sample after the last milling time without drying, thus, the shift in the N-H stretching band is due to the formation of hydrogen bonds between the dye molecules, resulting in the aggregation of the dye particles [8]. The formation of hydrogen bonds can be a result of the heat generated by the collision of the balls in a jar during milling, which causes the functional groups of the dye molecules to vibrate and interact with one another. Therefore, to address these challenges, the intermittent milling method was adopted, and drying was used to prevent temperature

rise and particle aggregation inside the jar, respectively. While the characteristic peak observed at 3093.95 cm⁻¹ ascribed to =CH- stretching vibrations (ν =CH-) of DR 167 little shifted to 3093.32 and 3091.14 cm⁻¹ in DR 167 -B and DR 167-C, respectively. This can be attributed to the formation of new C-H bonds during the milling process. The new C-H bonds are a result of the rearrangement of the dye molecules and the breaking and reformation of existing C-H bonds.

The FT-IR spectra also revealed the presence of C=O stretching vibrations (ν C=O) at 1738.58 cm⁻¹ for DR 167, 1737.69 cm⁻¹ for DR 167-B, and 1736.04 cm⁻¹ for DR 167-C. At the same time, the C=O band for DR 167 was separated into asymmetric and symmetric stretch vibrations at 1174.97 and 1038.44 cm⁻¹, respectively. This observation was recorded for DR 167-B and DR 167-C with little peaks shifting, indicating the presence of re-arranged dye molecules with increased milling duration. The FT-IR spectra also confirmed the presence of -N=N- stretching vibrations of the azo groups in DR 167, recorded at 1684.3 cm⁻¹. The C=C stretching vibration for aromatic rings was confirmed with strong peaks at 1614.69 cm⁻¹.

With milling, the -N=N- stretching vibrations were observed with the slight shifting of bands, and the C=C stretching vibration for aromatic rings was almost recorded at the same peak. These observations indicate the stability of the azo and aromatic rings even after milling, which can be attributed to the strong chemical bonds present in these functional groups. The nitro group's characteristic adsorption bands of asymmetric and symmetric stretching vibration were recorded at 1521 and 1329 cm⁻¹. The peak at 1226.5 cm⁻¹ is attributed to the C-O-C stretching vibration of the ether bond. Finally, the very weak peaks at 751.03, 751.42, and 751.5 cm⁻¹ can be correlated to the C-Cl stretching vibration of DR 167, DR 167 -B, and DR 167 -C, respectively. In general, an increase in the intensity of peaks with an increase in milling duration was observed, which confirms the re-arrangements and re-crystallizations of dyes during the milling process [5]. This finding matches the XRD results (Fig. 3). This can be attributed to generated heat through the collision of the balls in a jar milling [9,10].

4.3. UV-Visible Study

The impact of various milling durations on the color properties of DR 167 was examined using UV-Vis spectroscopy. The results, which are not presented here, revealed that all samples had a relatively wide, single absorption peak with a good shape in the visible absorption band between 410 nm and 630 nm. DR 167 had a maximum absorption wavelength of 525 nm. Additionally, DR 167-B and DR 167-C samples had similar absorption peaks after

the milling process. These findings suggest that the dye's color characteristics remained unchanged after milling and that a pure red color with a high visual light absorption capability was preserved in all DR 167 samples.

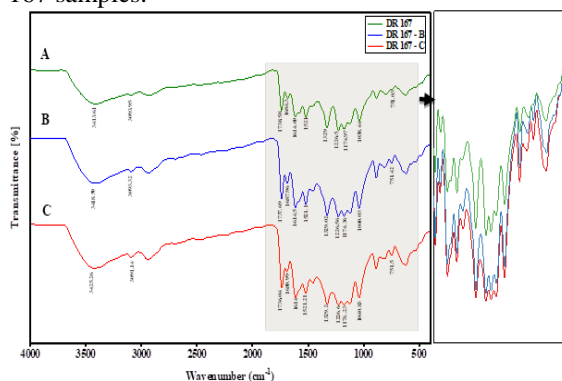


Figure 2. FT-IR spectra of dyes; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

4.4. NMR analysis

^1H NMR is a widely utilized analytical technique in the field of dye analysis that provides comprehensive information about the chemical and physical properties of dyes [11-17]. This analytical technique is based on the interaction between the nuclei of specific atoms in a magnetic field and radiofrequency waves [18]. This interaction results in the resonance and emission of signals by the nuclei that can be detected and analyzed to provide information about the molecular structure, composition, and environment [19]. In this study, the chemical structures of DR 167 dye before and after milling were extensively analyzed through ^1H NMR analysis, and the findings are presented in Figure 3. The outcomes of this analysis strongly suggest that the structure of the dyes was obviously changed after milling that matches with SEM, FTIR, and XRD data.

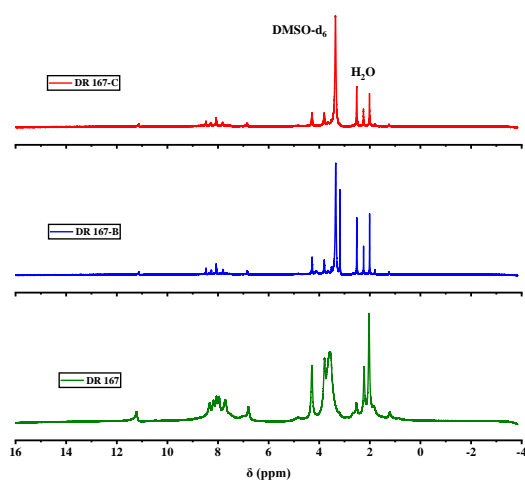


Figure 3. NMR spectra of dyes; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

4.5. Crystallographic Investigations

DR 167 is a monoazo dye, that is composed of a planar azobenzene skeleton with a dihedral angle of 1.5° between the planes of the two aromatic rings. To study the impact of milling time on the crystal structure of DR 167, X-ray diffraction (XRD) analysis was conducted. The XRD data was plotted before and after milling, with milling times of 2 and 10 hours, and is shown in Fig. 4. DR 167 belongs to the $C2/c$ space group, and its crystals are monoclinic, which is typical of organic pigments and vat dyes, and exhibits polymorphism [20]. From the XRD pattern of DR 167 (Fig. 4a), it can be concluded that the main crystalline peaks at $2\theta \approx 25.13, 23.87, 21.66,$ and 29.07° with d-spacing values of 3.54, 3.72, 4.10, and 3.07 Å, respectively, confirm the formation of the β -crystal phase of the DR 167 [21]. After grinding for 2 h (DR 167-B), the main crystalline peak of the β -crystal phase (at 2θ of 25.13°) was notably reduced to a weaker and broader peak (Fig. 4b). As well, the other characterized peaks of the β -form were approximately dispersed, and the overall amorphous nature was amplified [22]. However, the appearance of weak diffraction peaks at $2\theta \approx 32.2$ and 34.0° with d-spacing values of 2.78 and 2.64 Å, respectively, reflects the initial transformation to the α -crystal phase [7]. This can be attributed to the partial activation of the crystal lattice electrons by mechanical forces during ball milling, bringing out the electrons with higher energies. Therefore, the structural breakdown of the β -crystal form occurred, followed by the initial recrystallization process through the applied milling time [23]. This was assured by the appearance of weak diffraction peaks at 2θ of 32.2 and 34.00° with d-spacing values of 2.78 and 2.64 Å, respectively. After milling for 10 h (DR 167-C), a complete transformation to the α -crystal form was observed (Fig. 4c). This was approved by the improved intensity of the defining peaks at $2\theta \approx 32.23$ and 34.00° (Fig. 4c). Similarly, the height of crystallite stacking (L_c) of such peaks was also improved from 38.11 to 53.34 and from 26.02 to 30.07 (Table 2). Furthermore, the emergence of two new diffraction peaks at $2\theta \approx 26.92$ and 23.17° with d-spacing values of 3.312, and 3.84 Å, respectively, confirms the complete transformation to the α -form of the addressed dye. Such a recrystallization process of dyes may be attributed to both the produced friction temperature of the milling process as well as the size reduction of the involved particles.

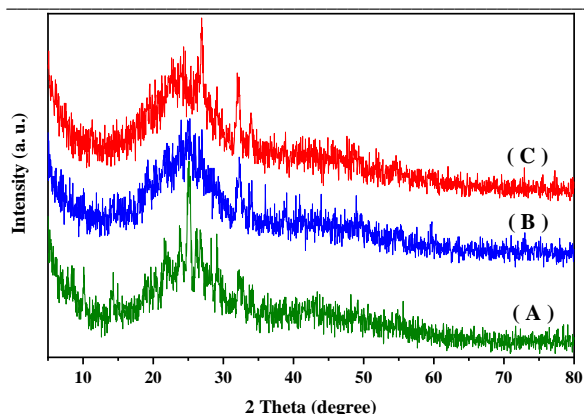


Figure 4. XRD patterns of dyes; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

4.6. Thermal Studies

Thermal analysis can provide valuable information about the stability and behavior of disperse dyes at different temperatures, which is important for the optimization of their processing and applications [24]. TGA measures the change in weight of a sample as a function of temperature, DTG records the change in weight of a sample as a function of time at a constant temperature, and DSC measures the change in heat flow into a sample as a function of temperature [7]. By using these techniques, researchers can determine the temperature at which the dye begins to decompose or undergo a phase

transition, as well as the amount of heat required for the process to occur. This information can be used to optimize the processing conditions for the dye and ensure its stability in high-temperature applications. Additionally, it is critical to understand the thermal properties of disperse dyes, especially for those used in high-temperature processes and in high-technology applications, to ensure their performance and reliability in these environments [17].

The thermal behavior diagram of DR 167 dye before and after milling is shown in Figure 5a-c. The TG and DTG curves demonstrated that the initial weight loss stage of DR 167 dye occurs between 37°C and 172°C and is due to the evaporation of adsorbed moisture. This is evident from the downward slope of the TG curve during this temperature range. Moreover, the major weight loss stage, which is the most significant, occurs between 240°C and 530°C and is characterized by two endothermic peaks in the DTG curve. The first peak is observed between 250°C and 350°C, while the second peak is observed between 350°C and 530°C. These peaks indicate a decomposition reaction of the DR 167 dye and a release of volatile products. The endothermic nature of these peaks suggests that energy is being absorbed by the sample, which is in line with the thermal degradation of the material.

Table 2. XRD characteristics of dyes; a) DR 167, b) DR 167 -B, and c) DR 167 -C.

	[2°Th]	Height [cts]	d-spacing [Å]	Rel. Int. [%]
DR167	25.1313	101.01	3.54359	100.00
	23.8745	57.73	3.72721	57.16
	21.6641	48.59	4.10224	48.11
	29.0692	45.11	3.07190	44.67
DR 167- B	25.0280	68.22	3.55799	100.00
	32.2054	38.11	2.77956	55.86
	34.0078	26.15	2.63625	38.34
DR 167- C	26.9201	91.61	3.31205	100.00
	32.2260	53.34	2.77783	58.23
	23.1748	52.54	3.83813	57.35
	34.00	30.07	2.64317	32.82

The crystal lattice of disperse dye is a molecular crystal, which means that the bonds between the dye molecules are weak. This results in a low melting point and hardness. The overall structure of the dye is flexible and organic, which contributes to its low thermal stability compared to inorganic materials. [25]. The melting point is defined as the temperature at which the maximum tangent intersection of the baseline and front slope of the exothermic peak of the DSC curve occurs. This exothermic peak is due to the release of heat energy as the material changes from a solid to a liquid state. The melting point is an

important parameter for understanding the thermal stability of a material and its behavior under different conditions [26]. The DSC data (Fig. 5c) showed that milling DR 167 dye for 2 hours (DR 167-B) resulted in a reduction of the melting point from 135°C to 71°C. This decrease can be attributed to the structural breakdown of the β -crystal form of the dye.

However, milling the dye for 10 hours (DR 167-C) resulted in an increase in the melting point to 133°C. This is likely due to the re-arrangement and recrystallization of the dye to the α -crystalline phase. Additionally, the DSC data showed that the thermal decomposition temperatures of the dye milled for 2

hours shifted to a lower value, indicating the formation of an amorphous form of the dye [22] (Fig. 5a &b). The results showed that dye milling for 10 hours (DR 167-C) resulted in thermal decomposition temperatures that were nearly the same as those of DR 167. This is different from the findings of Zheng et al. [7], the α -crystalline phase enhanced the thermal decomposition temperature, which had approximately the same decomposition temperature as the β -crystalline dye. This is possibly due to particle size reduction, resulting in much better stability in the dye bath.

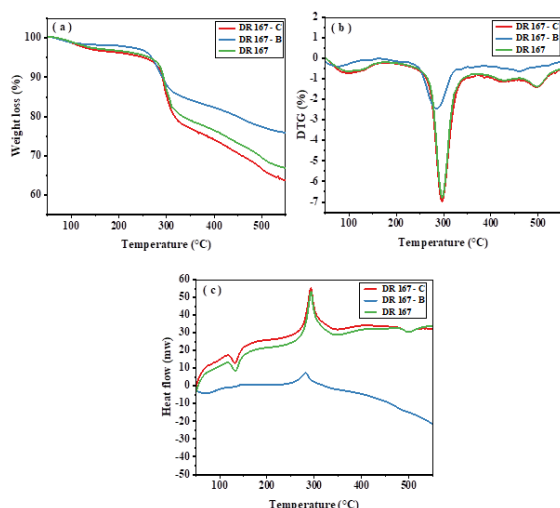


Figure 5. TG (a), DTG (b), and DSC (c) curves of dyes.

Conclusions

The data presented in this study lead us to the following conclusions:

- Minimization of dye particle size enhances colorfastness, facilitates even dyeing, and enables using less amounts of dye, resulting in increased dyeing process efficiency and cost savings, making it crucial for improving the dyeing quality of micro and nanofibers.
- The intermittent milling as simple, low-cost, and environmentally strategy to milling of disperse red 167 dye without auxiliaries was applied.
- The results showed that milling for 2 hours increased total surface area from 18.56 to 24.37 m²/g, with a particle diameter ranging from 17.9 to 87.7 μ m (average 42.2 μ m) and 63% of the particles had a diameter of 0 to 10 μ m (average 13.8 μ m).
- Milling for 10 hours decreased total surface area to 21.31 m²/g and increased uniformity in particle diameter. Results showed 92% of the dye particles had a diameter of 0 to 10 μ m, with an average of 3.85 μ m.

- The FT-IR spectroscopy results indicated the formation of hydrogen bonds, new C-H bonds, re-arranged dye molecules, and re-crystallization of the dyes during the milling process. The stability of the azo and aromatic rings was confirmed even after milling, which can be attributed to the strong chemical bonds present in these functional groups. The increase in the intensity of peaks with an increase in milling duration confirmed the previous finding.
- DR 167 dye's chemical structure was analyzed through ¹H NMR before and after milling, and the results from Figure 2 indicate that the structure remained unchanged.
- The XRD analysis showed that after 2 hours of milling, the main crystalline peak of the β -crystal phase of DR 167 was reduced, and the overall amorphous nature was amplified. The appearance of weak diffraction peaks reflected the initial transformation to the α -crystal phase.
- After 10 hours of milling, a complete transformation to the α -crystal form was observed, confirmed by the improvement in the intensity of the characterizing peaks and the emergence of two new diffraction peaks.
- The thermal analysis showed that milling the dye for 2 hours resulted in a reduction in the melting point from 135°C to 71°C and the thermal decomposition temperatures shifted to a lower value.
- Milling dye for 10 hours resulted in an increase in the melting point to 133°C and thermal decomposition temperatures that were nearly the same as those of DR 167. The findings suggest that the thermal stability of the dye depends on the milling time and particle size reduction.
- UV-Vis spectroscopy showed that the color characteristics of DR 167 remained unchanged after milling, as evidenced by the similar absorption peaks observed in all samples.

Conflicts of interest

The authors declare that they have no competing interests.

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References

- [1] Y.Z. Zhan, X. Zhao, W. Wang, *Color Technol* 133 (2016) 50.
- [2] V. Tirth, A. Algahtani, M.A. Aziz, A. Edacherian, *Metal Science and Heat Treatment* 61 (2020) 750.
- [3] H. Osman, M. Khairy, *Indian Journal of Fibre and Textile Research* 38 (2013) 202.
- [4] M. Jonnalagadda, V.B. Prasad, A.V. Raghu, *Journal of Molecular Structure* 1230 (2021) 129875.
- [5] D. Maamoun, H. Osman, S. Nassar, *journal of international environmental application & science* 9 (2014) 90.
- [6] S.C. Endres, L.C. Ciacchi, L. Mädler, *Journal of Aerosol Science* 153 (2021) 105719.
- [7] H. Zheng, Y. Zhong, Z. Mao, L. Zheng, *J. CO2 Util.* 24 (2018) 266.
- [8] A. Datyner, A.G. Flowers, M.T. Pailthorpe, *Journal of Colloid and Interface Science* 74 (1980) 71.
- [9] F.A. Hamm, E. Van Norman, *J Appl Phys* 19 (1948) 1097.
- [10] A. Stolle, T. Szuppa, S.E. Leonhardt, B. Ondruschka, *Chem Soc Rev* 40 (2011) 2317.
- [11] T. Abou Elmaaty, M. Sofan, S. Ayad, E. Negm, H. Elsisy, *J. CO2 Util.* 61 (2022) 102053.
- [12] A. Honda, S. Kakihara, M. Kawai, T. Takahashi, K. Miyamura, *Crystal Growth & Design* 21 (2021) 6223.
- [13] X. Li, Y. Yang, H. Zhang, Z. Quan, X. Qin, F. Li, R. Wang, J. Yu, *Applied Nanoscience* 10 (2020) 2025.
- [14] K. Bártová, I. Císařová, A. Lyčka, M. Dračínský, *Dyes Pigm.* 178 (2020) 108342.
- [15] N.K. Balakrishnan, K. Koenig, G. Seide, *Polymers (Basel)* 12 (2020) 2321.
- [16] S. Babaei Golshan Abadi, M.E. Yazdanshenas, R. Khajavi, A. Rashidi, M. Varsei, *J. Text. Inst* (2020) 1.
- [17] M.G. Al-Khuzai, S.M. Al-Majidi, Synthesis and characterization of new azo compounds linked to 1, 8-naphthalimide as new fluorescent dispersed dyes for cotton fibers, *Journal of Physics: Conference Series*. IOP Publishing, 2020, p. 012065.
- [18] C. Fontana, G. Widmalm, *Chem. Rev.* 123 (2023) 1040.
- [19] S.A. Richards, J.C. Hollerton, *Essential practical NMR for organic chemistry*, John Wiley & Sons, 2023.
- [20] H. Freeman, *Dyes Pigm.* 20 (1992) 279.
- [21] W. Biedermann, *Journal of the Society of Dyers and Colourists* 87 (2008) 105.
- [22] W. Liu, Y. Wang, J. Yang, X. Li, X. Wang, L. Ma, *Dyes Pigm.* 175 (2020) 108149.
- [23] J. Miao, R. Zhang, L. Zhang, *Materials Research Bulletin* 97 (2018) 109.
- [24] S. Gaisford, V. Kett, P. Haines, *Principles of thermal analysis and calorimetry*, Royal society of chemistry, 2019.
- [25] S.Y.R. Shengwu, *journal of east china insitiute of chemical technology* (1986).
- [26] S. Zhao, Z. Gao, G. Jiang, J. Wang, X. Miao, A. Wan, *Text. Res. J.* 91 (2020) 580.