Microwave Assisted Reduction for Screening Banned Aromatic Amines in Azo Dyes

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Abstract: The study proposes a simple, novel and green alternative for the efficient reduction of azo dyes by the standard method, EN 14362-1:2012 (Annex. F) for detection of harmful aromatic amines in colorants, by incorporating microwave heating in place of convective heating. Basic dye response to reduction methods was explored by UV-visible spectroscopy and the results were confirmed through GC-MS and HPLC-DAD. Four azo dyes namely Acid red 1 (AR-1), Direct blue 15 (DB-15), Direct red 28 (DR-28) and Direct red 7 (DR-7) were reduced with sodium dithionite at 70 °C for 30 min in a buffered solution at pH 6.0, serving as a reference method. The decline in dye absorbance after their reduction was explored by UV-visible spectroscopy with carefully chosen bands of maximum absorbance from 300 to 700 nm. The alternative method exposed dye solutions to short microwave heating (10 s) and immediate cooling, in cycles till the desired duration of microwave heating was achieved. Results obtained from reference method were used for comparison with MAR (experimental method 1). Most prominent results of MAR were observed in the case of DR-28 dye. Hence DR-28 was further subjected to the conditions of experimental method 2, which was simply EN 14362-1:2012 (F) method modified with MAR. For standard method and experimental method 2, amines were analysed by GC-MS and HPLC-DAD. MAR methods were compared with reference and standard reduction methods for efficiencies. The total saving with MAR in terms of time and energy was ~70% and ~92% respectively.

Keywords: Green Chemistry, Azo dyes, Microwave assisted reduction (MAR), Flash microwave, Banned aromatic amines.

INTRODUCTION

Azo dyes constitute a major class of synthetic dyes. They are easy to synthesize and offer a wide variety of color shades for many applications. There are significant concerns about the presence of toxic aromatic amines and their conditional release from some azo dyes still in use. As a consequence of which the European Union and many countries have banned 22 different aromatic amines in textile and 24 in leather articles [1]. This signifies the importance of chemical tests that determine the potential of different dyes for the release of these toxic aromatic amines. The standard test methods involve a mild reduction step, followed by selective extraction of the aromatic amines and their detection and quantification by different techniques [2, 3]. It is difficult to ban dyes merely on the basis of their component aromatic amines. Therefore, the reduction conditions are intentionally kept mild so that only those dyes split off amines which have a weaker azo link. It is necessary to test each type of dyed article for the release of harmful amines, even if the same dye has been applied on a different substrate. The stability of azo dyes has been assessed with respect to pH, temperature and different reductants. The thermal stability of azo dyes depends on the presence of substituents and their positions on the aromatic rings in the dye molecule [4]. Similarly, the photochemical stability (light fastness) of a dye depends on numerous factors like the dye concentration in the fiber, the chemical and physical structure of the dye and the fiber, the spectral features of the electromagnetic radiation and various other physical factors like humidity, temperature, pollution and chemical agents used during the process of dyeing [5]. A study reveals that dyes having substituent groups that are highly electron donating are likely to photodegrade through oxidation whereas those with electron withdrawing groups tend to follow reductive decomposition pathways. However, in case of dry condition a reductive mechanism could be changed to an oxidative process [6]. The presence of a greater degree of aromaticity in a dye molecule confers stability [7].

The current era is marked by the beginning of the green revolution with constant efforts for the modification of materials, processes and methods according to the principles of green chemistry [8]. The

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utilization of microwave heating is a common practice in green chemistry as it saves time by efficiently providing energy directly to the reactants during chemical reactions [9]. The microwave heating mechanism is purely based on localized rotational molecular motion of polar compounds (localized super heating) by oscillating electric fields generated by a magnetron. The rate of energy transfer is faster than convective heating (outside to inside), mode of transfer is direct (inside to outside) yet the magnitude is not high enough to cause bond breaking [10].

Due to the efficiency of microwave assisted reactions, many catalytic reactions have been carried out using microwave heating [11]. One such example is the microwave assisted degradation of Acid orange 7 dye in 10 min, carried out on polyaniline substrate used as catalyst [12]. Microwave energy has also been utilized for degrading dyes in different combinations such as with UV radiation and O_3 [13], and sometimes with UV and H_2O_2 [14, 15]. It has also been reported that decreasing the starting reaction temperature to sub-zero levels can change the products in microwave assisted organic reactions [16]. According to another study the utilization of microwave energy in pulses is more effective than continuous microwave heating [17, 18].

The key step in the standard methods for the analysis of azo colorants [2, 3] is the reduction of azo dyes with sodium dithionite at 70 ºC for 30 min in a citrate buffer adjusted to pH 6.0. The procedure takes about 60 min. The reducing property of sodium dithionite is because of two chemical species existing in equilibrium as shown by the equation:

$$S_2O_4^{2-} \rightleftarrows 2SO_2^{\bullet -}$$

Sulfur dioxide radical anion is comparatively a stronger reducing agent. The pre-dominance of the species depends upon the concentration of dithionite. At its higher concentration, dithionite is pre-dominant, otherwise the sulfur dioxide radical anion concentration is comparatively high [19] having an absorbance maxima at 315 nm [20].

Current study has explored the possibilities of finding greener alternatives to the conventional reduction methods for azo dyes (especially leather and textile dyes) that contain one or more banned aromatic amines in their structure [2] by utilizing microwave heating in place of convective heating. Four water soluble azo dyes were selected namely; direct red 7 (DR-7), acid red 1 (AR-1), direct blue 15 (DB-15) and direct red 28 (DR-28) containing 3,3'-dimethoxybenzidine, aniline, 3,3'-dimethoxybenzidine and 4,4'-benzidine respectively as the harmful aromatic amine components (highlighted as bold structures in Figure **1**). AR-1 is a monoazo acid dye whereas the other three are bisazo direct dyes.

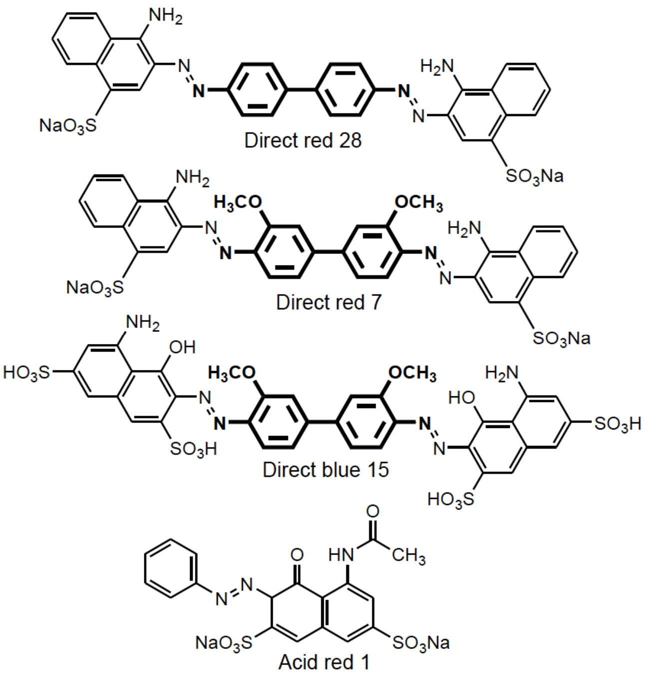

Figure 1: Dye structures with their banned aromatic amine components (in bold).

EXPERIMENTAL SECTION

The dyes; direct red 7, direct blue 15, acid red 1 and direct red 28 were purchased from a local market in Karachi, Pakistan. Citric acid, general purpose reagent grade was obtained from BDH Ltd. (UK). AR grade quality sodium hydroxide was acquired from Riedel-de haën (Germany). Silica gel 60 (70-230 mesh ASTM) and sodium dithionite, reagent grade (>87 %) were procured from Merck (Germany). Tertiary butyl methyl ether (lab reagent grade) was purchased from Fisher scientific, England.

The microwave reactions were performed on 800 W, Kentax microwave equipment, Model KG-22/AS (New Zealand). A thermostatic water bath, (Memmert, Germany) was used for performing standard reductions. A double beam spectrophotometer, Nicolet Evolution 100 was used for absorbance measurements from Thermo Electron Corporation (USA) using quartz cuvettes (1 cm). An in-house fabricated chilled water tank was used for cooling the Teflon reduction vessels (Figure **2**).

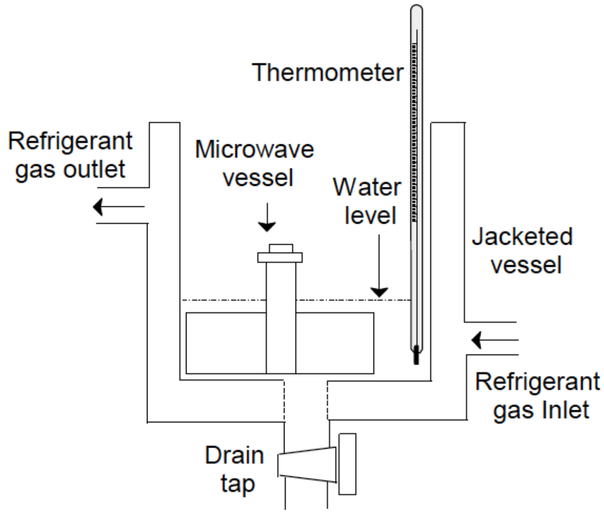

Figure 2: Jacketed steel refrigerator vessel.

The dye weights for stock solutions were 0.106 g, 0.115 g, 0.109 g and 0.140 g for DR-28, AR-1, DB-15 and DR-7 respectively, made up to 500 ml with distilled water. All the dyes were scanned in UV-visible regions ranging 285 – 700 nm on a double bean UV-Visible spectrophotometer (Figure **3**).

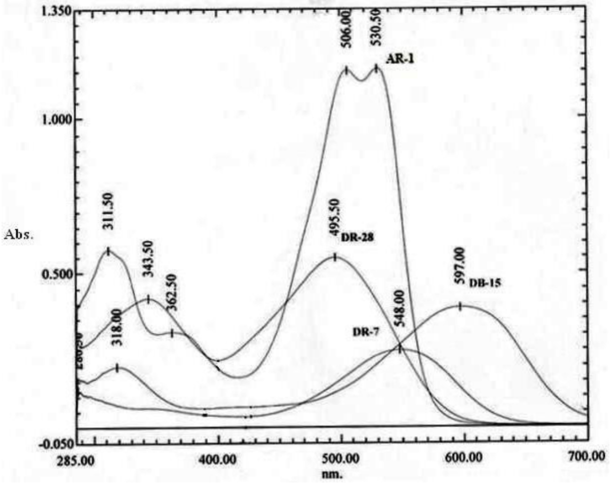

Figure 3: UV-Visible scans of Acid red 1, Direct blue 15, Direct red 7 and Direct red 28 with peaks marked.

Sodium dithionite and buffer solutions were also scanned in the working UV-visible range to avoid chances of interferences. Both the reagents showed maximum absorbance in the UV region below 300 nm, therefore adjusted appropriately in the blanks.

Reference Method

For the reference reaction, appropriate volumes from the dye stock solutions were drawn and transferred to the reaction vessels, to get the concentrations mentioned in Table **1** for a final volume of 20 ml. The volumes however, were made up to 17 ml with citrate buffer (0.03 M, pH 6.0) [21]. The initial absorbance was recorded at pre-selected wavelengths.

Dye concentrations were optimized by keeping maximum absorbance below unity. The solutions were pre-heated at 70 ºC for 20 min. After pre-heating 3.0 ml of sodium dithionite (0.04 g/ml) was added to the reaction vessels. The initial absorbance was adjusted for dilution due to sodium dithionite addition. The blank reagents were prepared in a similar fashion without the addition of dye. The temperature of the reactants was maintained at 70 ºC for 30 min and then cooled to room temperature within 2 min and the final absorbance was recorded.

Experimental Method 1

The composition of sample dye solutions for microwave experiments was exactly the same as the reference solutions. However, the pre-heating step was changed to pre-cooling. The sample solutions were cooled to around to 10 °C in a cold-water bath (Figure **2**), prior to dithionite addition. Temperature of the cold-water bath was kept in the range 2 - 8 ºC. Initial absorbance was recorded immediately after adding 3.0 ml of sodium dithionite (0.04 g/ml). Samples were then subjected to microwave heating for 10 s and the temperature was recorded. The reaction was carried out in microwave transparent and chemically inert polytetrafluoroethylene (Teflon®) vessels. Cold vessels were used to expose the reactants to maximum microwave energy and attain a certain temperature

Table 1: Experimental Parameters and Physical Properties of Selected Dyes

Dyes	CAS numbers	Selected Wavelengths 'λ'/ nm	Dye conc. mg/dl	Mol. Wt.	Buffer conc. % (v/v)
AR-1	3734-67-6	288, 312, 357, 506, 530	3.2	509.42	71
DR-28	573-58-0	280, 293, 335, 488, 505	5.1	696.66	75
DR-7	2868-75-9	288, 300, 310,320, 544, 547	7.8	756.72	57
DB-15	2429-74-5	295, 320, 330, 470, 580, 594, 608	5.5	992.80	60

(targeted around 70 ºC). At that temperature, the vessel contents were cooled in the cold-water bath to dissipate the excess heat energy, and heated again in microwave equipment for another 10 s. This cycle was repeated till the desired total microwave exposure was achieved. It is analogous to providing microwave energy in small pulses and is termed as 'Microwave flash heating' [22]. Flash microwave model was designed using easily available equipment to explore newer dimensions of existing microwave technique. The whole process is graphically represented in Figure **4**.

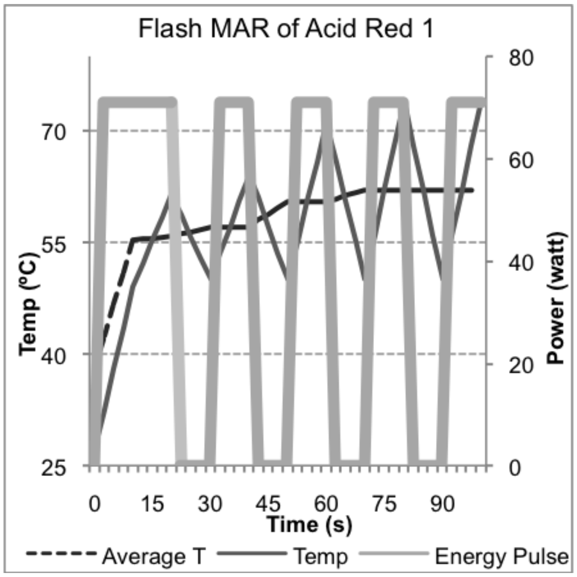

Figure 4: Temperature profile with alternate microwave heating and cooling cycles (Power scale figures are arbitrary).

The positive slopes on the thin grey line show the increasing temperature whereas the negative slopes show the cooling of the reaction solution. For quick cooling at the end of the reaction, the vessels were shaken in cold water to bring at room temperature and final absorbance was recorded.

Standard Method BS EN 14362-1:2012

Direct red 28 was further subjected to screening for banned aromatic amines through the standard method BS EN 14362-1:2012 (F) [3]. The final extract was analysed by GC-MS and HPLC-DAD for identification and quantification of aromatic amines.

A GC-2010 gas chromatographic system from Shimadzu (Japan) was employed having AOC-20i+s, attached assembly of injector/auto sampler with software assisted program (GC-MS Real time analysis). The GC unit was directly linked to a mass specific detector QP2010. A GC column specific for aromatic amine analysis, DB-35MS, with dimensions 25.0 m x 0.20 mm, 0.33 µm df was employed.

26 amines including aniline and 1,4-phenylenediamine as per standard method (ISO DIS 17234-1 for leather) used for calibration were Ehrenstofer Quality (EQ) from Germany. Individual stock solutions of 2000 ppm of all aromatic amine standards were prepared. A 200 ppm working standard solution was made having all the amines mixed together in one dilution. Calibration of GC-MS method was carried out with 1, 5, 15 and 30 ppm diluted standard solutions.

GC temperature program was kept constant at 60 °C for one min, gradually raised to 320 °C at a rate of 14 °C/min and held for 5 min at the end, giving a total run time of approx. 25 min. Split mode was set at 1:10 Split ratio for the standard and sample injections. SIM mode was used for acquisition to obtain improved limits of detection.

LabAlliance high performance liquid chromatography system (model: 2500 Plus, USA), coupled to diode array detector (LabAlliance, model: UV6000LP, USA) linked to a desktop computer via EZchrome Elite software was employed. Other pertinent features were quaternary pump system, column oven and a reverse phase ODS1 Spherisorb® column (0.4x25 cm) from Waters with 5 µm particle size. A gradient method was optimized for eight selected amines by the modification of the HPLC method suggested in the standard method for the analysis of amines in leather (ISO DIS 17234-1). Column temperature was adjusted to 40 °C. Sample loop volume was 10 µl. Three wavelength channels were programmed to record data at 240, 280 and 305 nm. HPLC grade methanol having 30% acetonitrile was used as eluent 1, whereas eluent 2 was simply an aqueous phosphate buffer solution, having a pH of 6.9. Method run time was 30 min with a linear gradient starting with 25% eluent 1 increasing up to 80%. Combined solvent flow rate was 0.65 ml/min. 2, 20 and 40 ppm standard solutions, each containing eight preselected banned amines were used for calibration.

Experimental Method 2

Experimental method 2 was actually the standard method BS EN 14362-1:2012 (F) with the standard reduction procedure replaced with MAR. Rest of the method, dye and reagent quantities as well as the final determinations were same as in the standard method.

RESULTS AND DISCUSSION

Experimental Method 1

The selected wavelengths for each dye are presented in Table **1**. The change in absorbance of the sample solutions present a good picture of the effect of microwave heating for different time durations (Figure **5**). In case of acid red 1, both the wavelengths, 506 and 530 nm follow the same trend i.e. the overall absorbance gradually decreases from 0.83 ± 0.002 to 0.78 ± 0.003 after 4 min of total microwave exposure. A similar absorbance change is also observed in the UV region at the other wavelengths. The only noticeable difference is the rate of absorbance change as dyes mostly show higher molar absorptivities in the visible region.

The absorbance trend in case of DB-15 at 580, 594 and 608 nm wavelengths is quite similar to the visible region of AR-1. The results at these wavelengths suggest that the drop in absorbance achieved in the first minute of microwave exposure is greater than that observed in the last 2 min of microwave heating. The absorbance changes at other wavelengths also showed an overall drop but with slopes not comparable to the visible region. The visible region in DR-7 also shows a slow and gradual trend of dye degradation through MAR. The wavelengths (544 and 547 nm) show a gradual drop in absorbance especially in the first three minutes of MAR. The UV region follows a similar trend, but the change is again less noticeable as compared to the visible region.

Direct red 28 is the only dye among the four dyes which shows the greatest level of degradation through MAR. Prominent indications of change are noticed at the wavelengths 488 and 505 nm in the visible region, showing identical slope values. The absorbance trend at 335 nm is similar to the visible region but the rate of

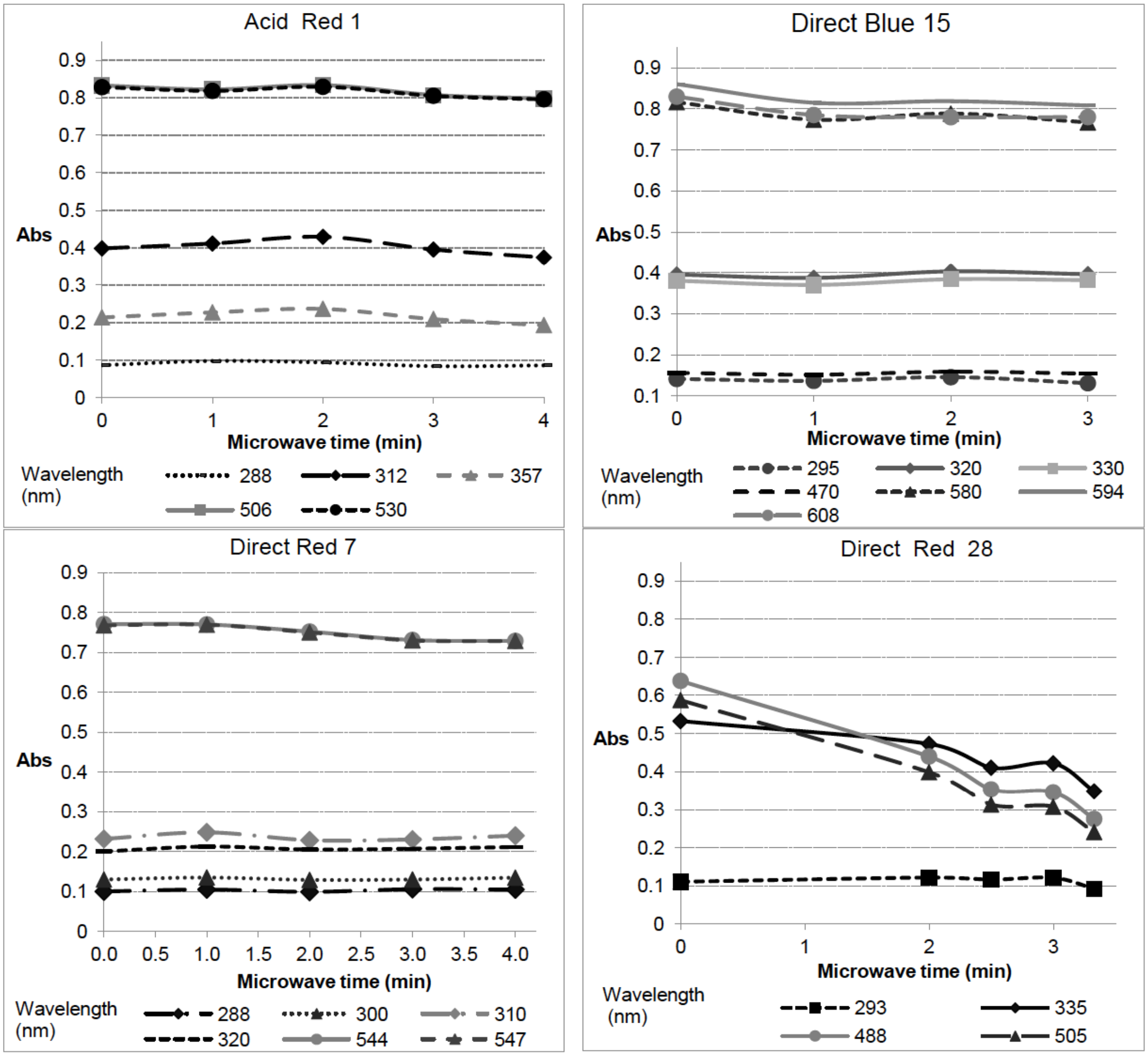

Figure 5: Absorbance as a function of microwave exposure time for different dyes.

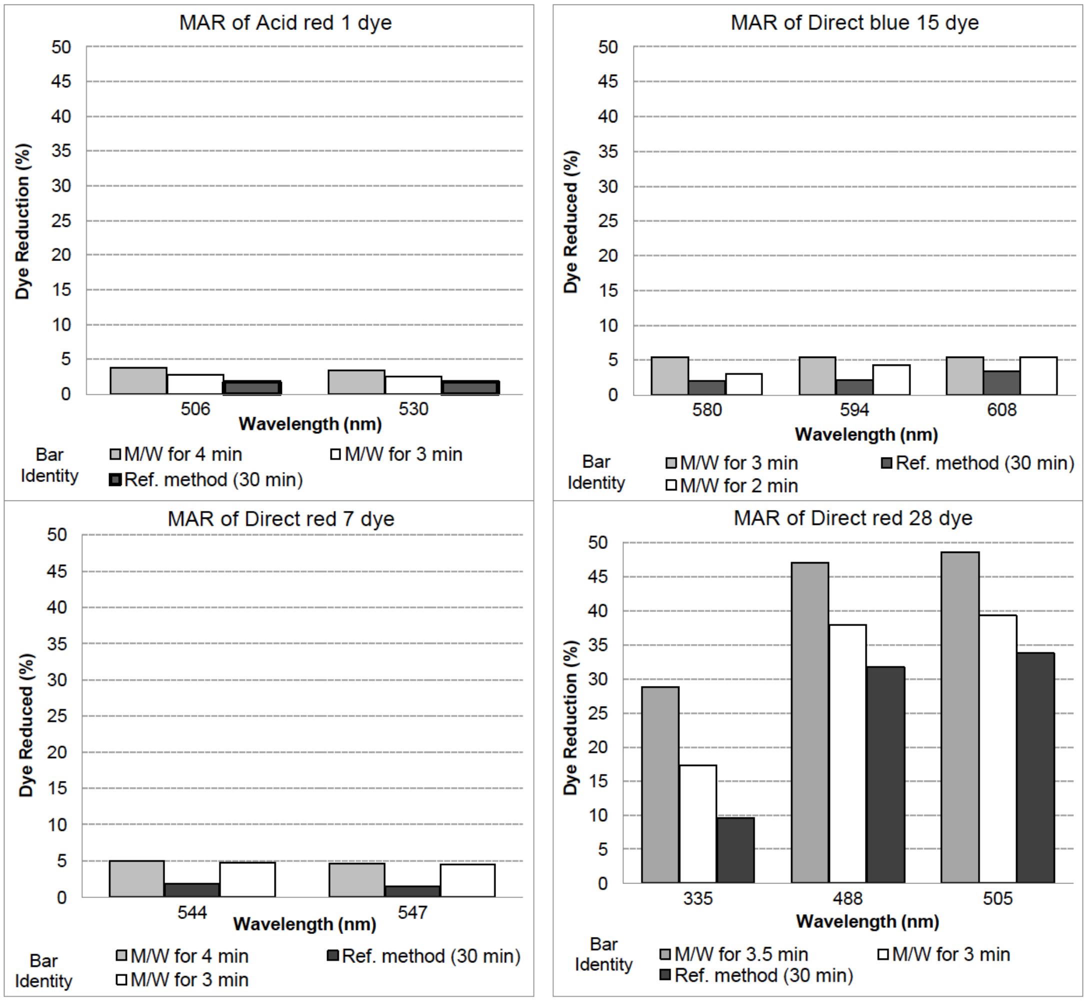

Figure 6: Comparative account of percentage dye degradation through MAR and reference method at selected wavelengths.

decrease is comparatively lower. Similarly, at 293 nm the drop in absorbance is hardly noticeable except after three minutes of microwave heating. It is worth to mention here that despite of a carefully designed experimental setup the wavy lines indicate the difficulty of controlling reaction parameters and the fluctuation of temperatures after flash microwave heating. And despite of keeping most of the parameters under control, the peak temperature of the sample solutions deviated slightly from 70 °C.

The results obtained after MAR and reference reductions are compared in Figure **6**. The percent dye reduction is paralleled for the four dyes at selected wavelengths. The results of acid red 1 at all selected wavelengths of the visible region clearly indicate that the order of dye degradation is 4 min MAR > 3 min MAR > reference reaction. In the visible region of DB-15, all the three wavelengths 580, 594, and 608 nm clearly show highest dye degradation after 3 min of MAR, followed by 2 min of MAR and finally the reference method. The visible region in case of DR-7 can be interpreted easily and has the order 4 min MAR > 3 min MAR > reference method reduction at both the

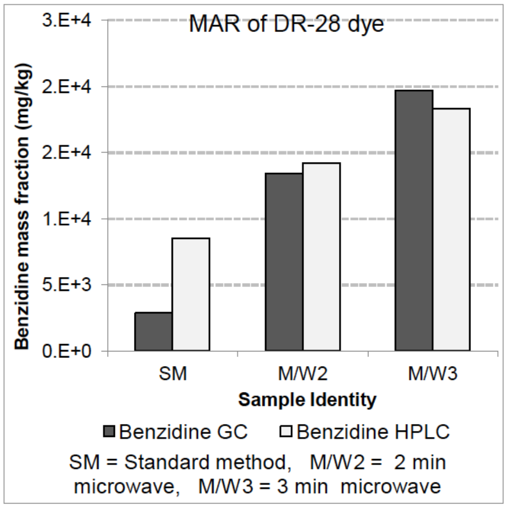

Figure 7: Comparative benzidine profile of DR-28 analysis by standard method reduction and MAR (experimental method 2).

wavelengths. However, there is not a drastic difference between the absorbance change after 4 and 3 min of MAR. The correlation between 544 and 547 nm is also in agreement with Figure **5**. The results of DR-28 at 335, 488 and 505 nm indicate that the dye degradation is in the order 3.3 min MAR > 3 min MAR > reference reaction.

Experimental Method 2

Results of DR-28 analysed by standard method EN 14362-1:2012 (F) were used for comparison. Comparative profile for benzidine mass fractions obtained from DR-28 analysis by standard and microwave assisted method (experimental method 2) are presented in Figure **7**.

Results from both techniques are in agreement. The detected high concentration of benzidine is a direct indication of dye degradation. It was quite evident that the highest dye degradation was observed in the following order, MAR for 3.3 min > MAR for 2 min > standard method reduction. Chromatograms obtained from GC-MS and HPLC-DAD are shown in Figure **8**.

For each dye the conditions of temperature and the duration of microwave exposure to match the reduction level of standard method with are slightly different. This could be attributed to individual dye behavior as some dyes are prone to reduction where as others are chemically resilient. It is difficult to pinpoint all the parameters affecting microwave heating as there are several parameters contributing to it, such as dipole moment and size of absorbing molecules, solvent viscosity, frequency of the applied field [23] and ionic strength of the solution [24]. It has also been established that the dipole moment of excited state of a

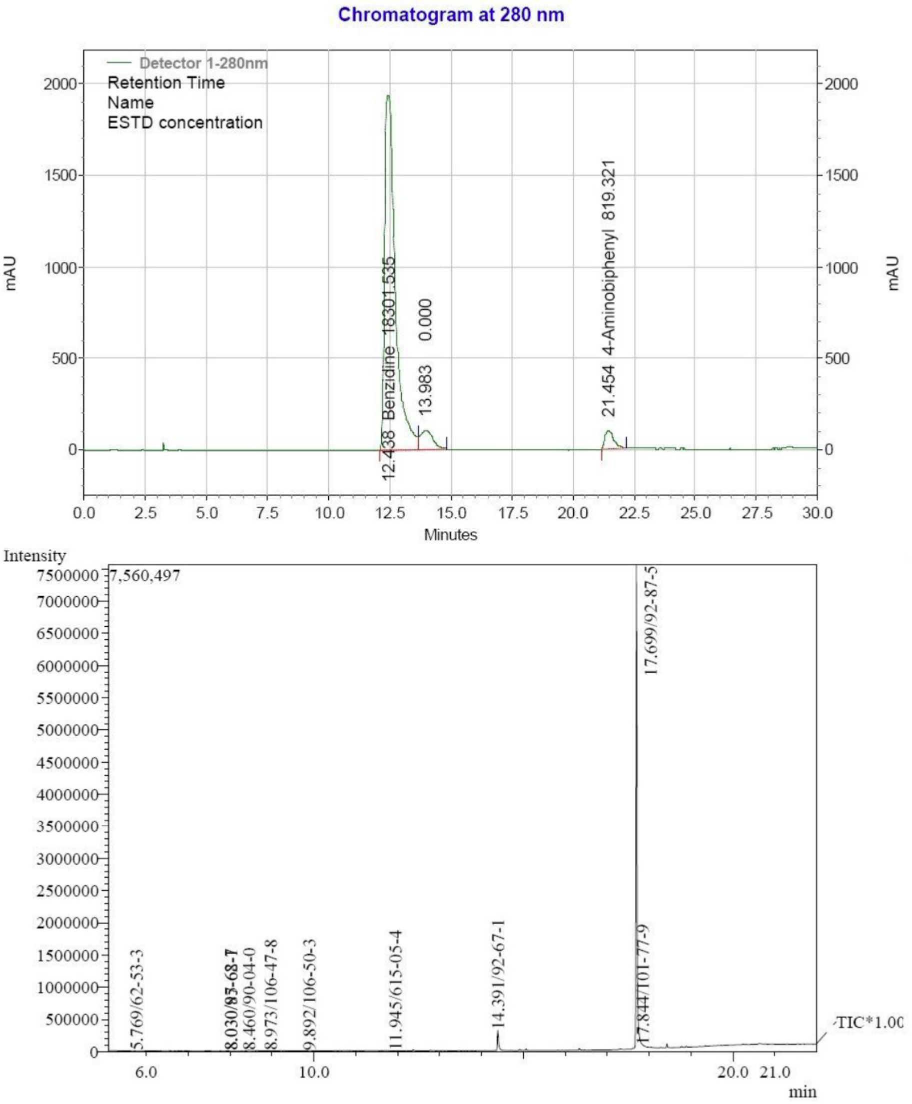

Figure 8: Chromatograms of DR-28 dye subjected to MAR for 3.3 min Above: HPLC-DAD (at 280 nm), Below: GC-MS.

dye is generally higher than its ground state [25]. Under such circumstances it is likely that the effect of microwave heating near the onset of a chemical reaction would be profound. As higher dipole moment would bring more heat into the system, similarly more heat would cause a greater number of molecules to attain the excited state and so on, just like a chain reaction.

CONCLUSIONS

As compared to the reference method, all selected dyes (AR-1, DB-15, DR-28 and DR-7) responded well to MAR when analysed through UV-visible spectroscopy (experimental method 1). Considering comparative approximations, reduction equivalent to the reference method could be achieved in less than 1.5 min of MAR for DR-7 and DB-15. However, in case of AR-1 and DR-28, it could be accomplished in 2 and less than 3 min of MAR, respectively.

DR-28 was further subjected to standard method (experimental method 2) modified with MAR, and analysed through GC-MS and HPLC-DAD. Effective exposure time observed for MAR was 3 min which saved ~ 70% time as compared to the standard method of reduction as in BS EN 14362-1 (F), for colorants. Similarly, the total power saving in MAR was ~92%. Hence, MAR could be considered as a greener method of reduction as compared to the standard method. Microwave heating is very fast and convenient but in case of flash microwave, a rapid cooling mechanism is also very important to augment the effectiveness of the technique. In case of a commercial laboratory scale flash microwave, automation is the best choice.

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