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Green development of methyl blue dyed electroactive cellulose fabric

S. Pathak[1], M.G.H. Zaidi*[1], S. Mehtab[1], M. Pandey[1], Shazia Mehtab[2], A. Bughani[1]

[1]*Department of Chemistry, C.B.S.H., G.B. Pant University of Agriculture and Technology, Pantnagar, India*
[2]*Fabric & Apparel Science Department, Institute of Home Economics, Delhi University, Delhi, India*

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The traditional aqueous dyeing of textiles is a water-intensive process. The textile business frequently involves wet processing and finishing methods to improve the aesthetics and utility of textile fabrics, which have a highwater usage. According to estimates, to colour 1 kg of fabric 100 and 150 L of water is required. As a result, over 280,000 tonnes of carcinogenic textile dye effluents are disposed off into the water bodies every year, endangering both human health and aquatic life. Present study demonstrates the development of a series of green methodologies pertaining to dyeing of cellulose fabrics (CFs) with methyl blue (MYB, 200 µL). Green procedures of dyeing were conducted over CFs (1 inch^2) followed by either of hot air drying (10 min), MW irradiation (3 min) and SCC treatment (3 h), each at 70^{o}C. The produced dyed fabrics (DFs) were investigated for their DC conductivity (σDC) through four probe arrangement. Cyclic voltammetry of MYB was performed at variable scan rates (25-100 mV/s) to check the cyclic stability. The leaching of dye from the DFs with time (over 120 min) was investigated through square wave voltammetry (SWV) in KCl (0.1 M). SWV reveals that the limits of detection and quantification (mg/L) of MYB up to 4.10 x 10^{-3} and 12.60 x 10^{-3}, respectively. The current study reveals that CFs undergoing SCC treatment show good dye uptake, better σDC and minimum leaching of the dye thereby making it the most efficient green methodology for dyeing in comparison to hot air and MW treatment.

Keywords: Cellulose fabric, Supercritical carbon dioxide, Cyclic voltammetry, Square-wave voltammetry, Microwave.

INTRODUCTION

Cellulose fabrics (CFs) are predominantly used in textile across the world and are tremendously employed in the apparel, décor, sanitation, and health industries[1].It is one of the most abundant natural biopolymers, which is composed of glucose chains that comprises many hydroxyls functional groups. CFs are characterized with excellent hygroscopicity, breathability, flexibility, biodegradability, heat retaining and sanitary property [2]. These characteristics make cellulose a desirable material for making conductive fabrics [3]. Conductive fabrics are now being used as wearable sensors [4], textile-integrated batteries [5], and fabric-based energy storage systems [6]. Reactive dyes are commonly used for dyeing and printing the CFs [7,8] due to strong intermolecular bonding with cellulose macromolecules[9]. Methyl blue (MYB) dye is frequently employed as a nuclear stain because it is a basic dye that can react with anionic groups like carboxylates, phosphates, and sulphates [10]. For biological staining, the dyes are used at high concentrations, which allows low affinity binding of dyes [11].

However, over a past decades, the traditional industries of textile manufacturing process have become one of the fundamental sources of environmental pollution due to discharging of large amounts of wastewater to the environment [12]. The wet processing of textile industries such as dyeing, printing and finishing techniques is a water-intensive process. It has been estimated that in a conventional dyeing, about 100-150 litres of water is used to dye 1 kg of fabric [13]. As a result, about 280,000 tons per years of textile dyes are dumped in wastewater industrial effluents and impose hazard to aquatic life and human health [14]. Dye effluents contain high chemical and biological oxygen demand which are very rich in organic and inorganic pollutants such as chlorinated compounds, heavy metals, nitrates, naphthol, sulphur, soaps, formaldehyde, chromium compounds, benzidine, sequestering agents and pigments [15, 16]. However, several toxic elements remain in the wastewater even after certain treatment processes and causes multi-contamination effects on plants, soil, air and water resources. Due to these environmental impacts, recently supercritical carbon dioxide (SCC) and microwave (MW) assisted dyeing procedures, which avoid the use of water, have been receiving growing attention [17, 18].

Over a past few years, green methodologies have been received growing consideration in the development of sustainable technologies at the cost of reduced disposal of hazardous substances to environment [19,20]. SCCis the most frequently utilised material over other supercritical fluids due to

* To whom all correspondence should be sent:
E-mail: mgh_zaidi@yahoo.com

its inexpensive, harmless, low surface tension, non-flammable nature and has critical conditions that are simple to access at Tc = 304.2 K and Pc = 7.37 MPa[21]. The low gas-like viscosity of SCC allows it to penetrate various solid substrates, and its liquid-like solvent power allows it to solubilize a wide range of organic molecules [22]. The high diffusion rates and low mass transfer resistance of SCC has reduced the dying time [23]. Hence, SCC has shown numerous advantages, such as short dyeing time highuptake rate, recycling of CO_2, no usage of water and any effluent discharged into environment over conventional aqueous dyeing process [24,25].

Another green methodology employed for dying is MW irradiation due to its mass transfer kinetics, which consumes less time, energy and solvent [26]. This technology provides an eco-friendly and pollution-free heating source for cotton dyeing due to its non-contact, uniform, efficient and quick heating properties [27-30]. This technique provides more colour depth in a shorter time over traditional dying methods [31]. The mass transfer effect provides good dye exhaustion, higher absorption abilityand energy consumption, resulting in a high treatment speed [32,33]. Inthis method, microwave energy penetrates easily to inside CFs and all particles of CFs can be heated simultaneously which leads to reduce the heat transfer problem [34].

In the present investigation, a kind of electrically conducting CFs has been fabricated through dying with methyl blue followed by conventional, SCC and MW assisted methods. Electrochemical behavior of DFs has been investigated in KCl (0.1 M) at 7.0 pH in view to explore their future applications in biomedical research of staining.

EXPERIMENTAL

Materials

MYB (purity ≥99.98%) and CFs were procured from Ms Molychem India PVT Limited and Abdos India PVT Limited, respectively. Other chemicals and solvents including carbon dioxide (≥99.0%) were locally organised and used without further purifications. MYB solution (0.04g) was dissolved in 100 mL of deionized water to create a 400 ppm-strength solution for dying CFs.

Dyeing of CFs under hot air

Specimen of CFs were dyed in a bath with an alcoholic solution of MYB (200µL) in two aliquots of 100 µL followed by hot air (70ºC) drying over 10 min. DFs were stored at 400mmHg/25±1ºC.

Dyeing of CFs under MW irradiation

Specimen of CFs were placed in a dying bath and was dyed with MYB solution (200µL) in aliquots of 100 µL followed by MW irradiation (22.4Hz, 70ºC) over 3min. DFs was stored at 400mmHg/25±1ºC.

Dyeing of CFs in SCC

A 100 mL high-pressure supercritical fluid reaction system equipped with needle valves, a chiller, and PID-controlled heating tape was used to dye CFs. A required mass of CO_2 and MYB (200 µL) moistened were introduced to the reactor vessel at a temperature of 25±1°C. For the vessel to achieve the requisite supercritical pressure (psi), between 1400 and 1800 over 3 h, the temperature was raised to 70±1ºC. Depressurizing the reactor system at a rate of 10 psi per minute at 10±1ºC allowed DFs to be separated from the vessel.

DFs of identical size were developed through hot air, MW irradiated, SCC treatment at 1400 and 1800 psi and were abbreviated as CF_1, CF_2, CF_3 and CF_4.

Characterizations

DC conductivity measurements were conducted over Keithley nanovoltmeter equipped with 6221 DC current source and 2182A nano voltmeter at selected voltages ranging 1 to 100 V at 25±1ºC. Electrochemical behaviour of CFs and respective DFs was performed over IVIUM Potentiostat-Galvanostat equipped with triple electrode cell assembly comprising glassy carbon electrode as working electrode, Pt foil (1 cm^2) as auxiliary electrode and Ag/AgCl as reference electrode in KCl solution (0.1M). Calibration curve was plotted at selected concentrations of MYB over current response in SWV. Limit of detection (LOD) and limit of quantification (LOQ) of MYB were obtained from calibration curve using the relation: LOQ = 10×S/m, LOD = 3.33×S/m, where s represents standard deviation of the peak current for the blank and m indicates slope of the analytical curve in calibration curve [35].

RESULTS AND DISCUSSION

Electrical conductivity

I-V characteristics of undyed fabric (CF_0) and their respective DFs has revealed ohmic behaviourin current range 0.18 to1.01 µA up to 30V at 25±1 ºC (Fig. 1). Fig. 2 demonstrates the effect of voltage ranging 1 to 100 V on σDC of CFs and respective DFs at 25±1 ºC. CF_0 and respective DFs has shown comparable σDC (mS/cm) at 1V ranging 0.30 to 0.35. Further increase in voltage to 10 V, no remarkable changes were observed in value of σDC, which revealed the electrically insulating nature of

CF_0 and DFs up to 10V [36]. However, at 100 V, σDC of CF_0 and respective DFs increased due to their electrically conducting nature. CF_0 showed lower value of σDC (0.38) over hot air (0.45) and MW (0.56) assisted DFs. Furthermore, SCC assisted DFs showed relatively higher value of σDC at 1400 psi (0.68) and 1800 psi (0.64) over the rest of DFs.

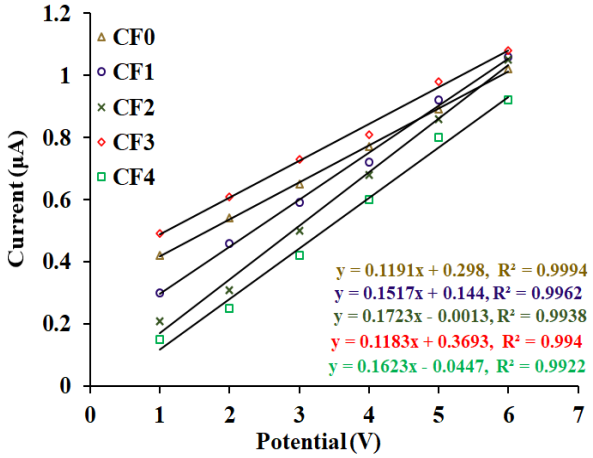

Fig. 1. I-V characteristics of DFs

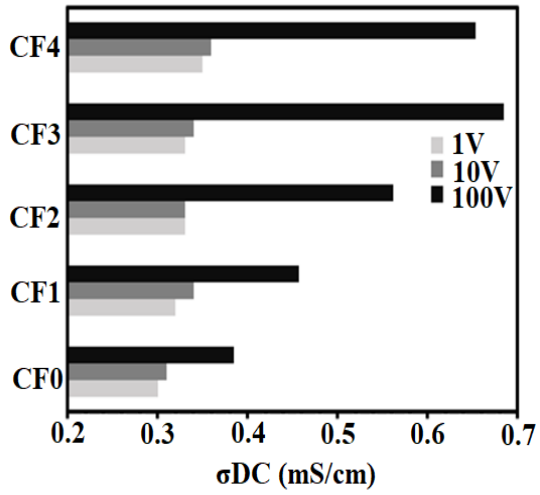

Fig. 2. Effect of voltage on σDC of DFs

Electroanalysis

In order to investigate the I/V characteristics of MYB dye (400 ppm), CV measurements were conducted at pH 7.0, 25±1 ºC under potential window -0.4 to 1.0 V with 25-100 mV/s scan rate (SR) in KCl (0.1 M) (Fig. 3). CV reveals free from redox characteristics of MYB in current range (-2 to 23 µA) and a potential window (-0.52 to 0.9V). MYB has shown relatively higher anodic peak current (I_{Pa}) over cathodic peak current (I_{Pc}) with SR. With SR, MYB showed I_{Pc} (µA) ranging 143.50 to 182.50 at constant 0.29 V anodic peak potential (E_{pa}). However, MYB showed I_{Pc} (µA) 236.90 at 25 mV/s SR. Further rise in SR ranging 50 to 100 marginally raised I_{Pa} in the range of 303.00 to 316.00. Results showed the highest I_{Pa} value obtained for MYB dye at 100 SR.

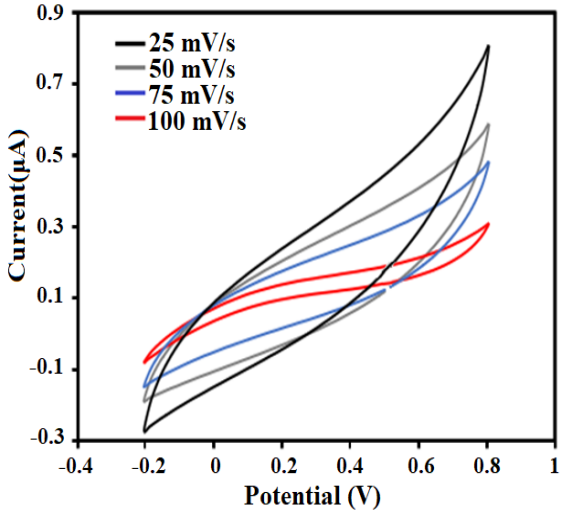

Fig. 3. CV of MYB in KCl (0.1M) at variable SR

Quantitative analysis of MYB released from DFs was performed by SWV. Trends of SWV for CF_1 (Fig. 5), CF_2 (Fig. 6) and CF_3 (Fig. 7) and CF_4 (Fig. 8) were investigated through SWV of DFs in KCl (0.1 M). Different green assisted dying procedures rendered a remarkable effect on the compatibility of MYB with dyed CFs. In general, DFs derived through hot air and MW assisted dying showed significant and identical quantitative release of MYB from DFs. However, DFs derived through SCC assisted methodology showed enhanced compatibility of MYB with DFs. Quantification of MYB during release from DFs was monitored through SWV in the potential range varying from -1.20 to 1.00 V, within specified optimal parameters at 50 Hz and pulse amplitude of 10 mV.

Prior to investigation of quantitative release of MYB from DFs, a calibration curve was drawn between the peak current of SWV against successive increase in concentration of MYB (ppm) ranging 0.006 to 0.14 in KCl (0.1M at pH 7.0, 25 ±1 ºC). In the calibration curve peak current linearly increased ranging from 0.003 to 0.057 mA (regression coefficient of 0.99) with the concentration of MYB (Fig. 4). The calculated value of LOD and LQD for MYB was 4.1×10^{-3} mg/L and 12.6×10^{-3} mg/L, respectively.

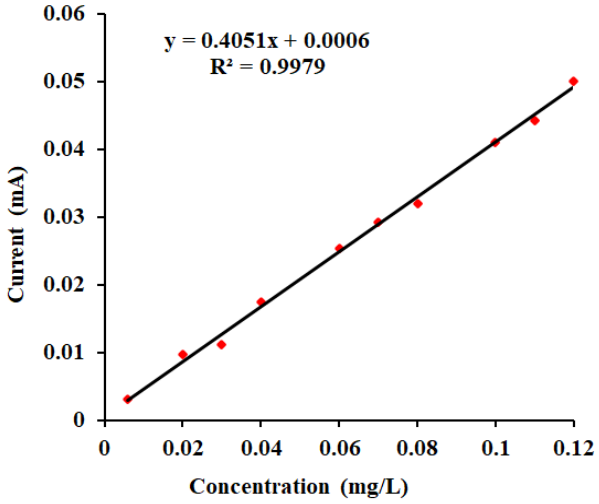

Fig. 4. SWV derived calibration curve of MYB

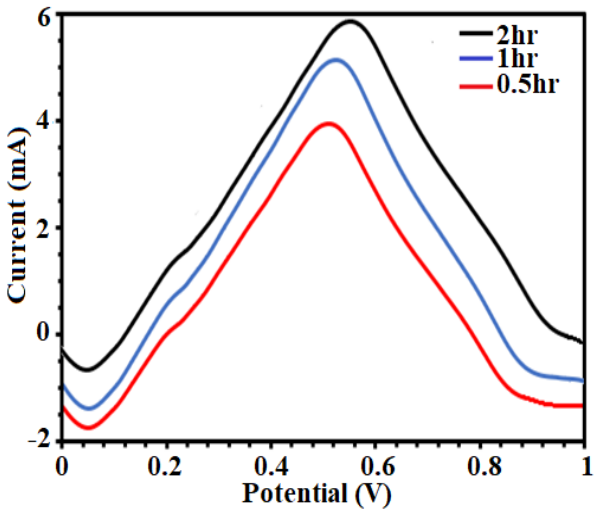

Fig. 5. Monitoring of MYB release from CF_1 in KCl (0.1M)

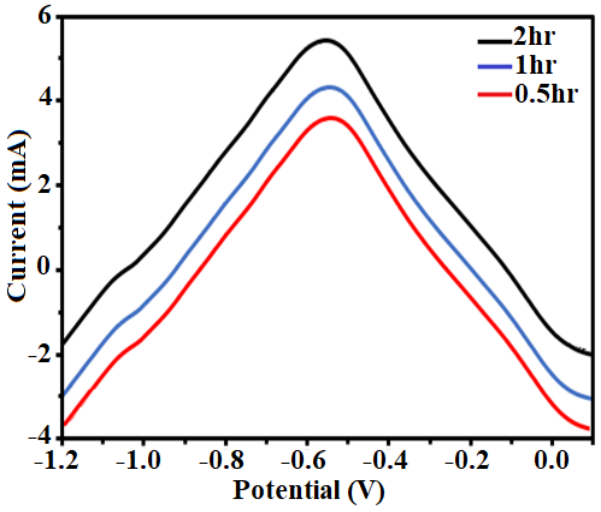

Fig. 6. Monitoring of MYB release from CF_2 in KCl (0.1M)

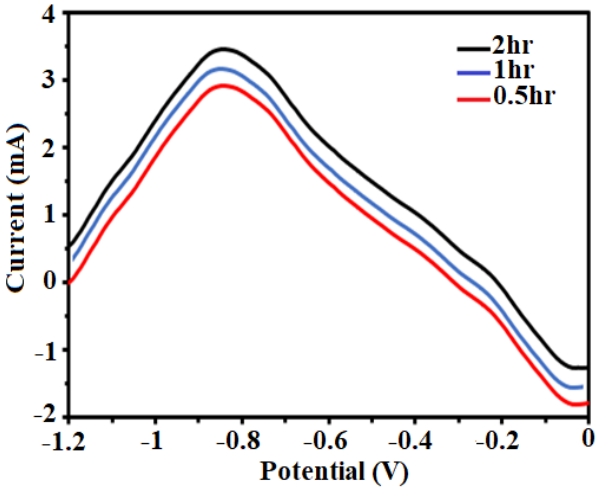

Fig. 7. Monitoring of MYB release from CF_3 in KCl (0.1M)

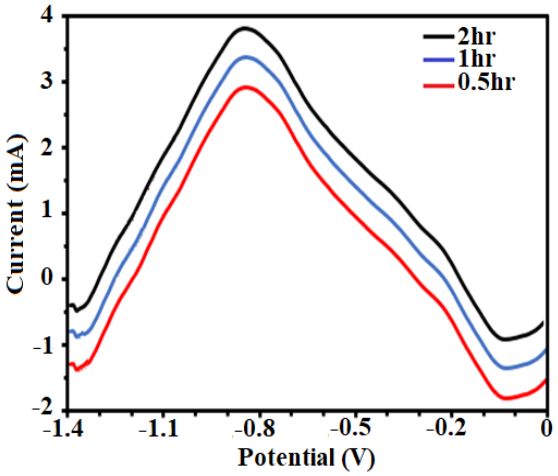

Fig. 8. Monitoring of MYB release from CF_4 in KCl (0.1M)

CONCLUSION

Methyl blue (MYB)-dyed electroactive cellulose fabrics (CFs) has been developed through implication of a series of different green methodologies. In this context CFs (1.0 $inch^2$) was investigated for dying with methyl blue (400 ppm, 200µL) in hot air, microwave irradiation (MW) and supercritical carbon dioxide (SCC) treatments at 70°Cover selected periods. Study reveals enhanced potential of SCC towards dyeing of CFs in comparison to MW and hot air. I-V characteristics of undyed fabric (CF_0) and their respective dyed fabrics (DFs) has shown ohmic behaviour in voltage (V) ranging from 5 to 30 under four probe conditions at 25±1^{0}C. All DFs showed comparable σDC (mS/cm) at 1V ranging 0.30 to 0.35 at 25±1^{0}C. Increase in voltage to 10V showed no remarkable change in σDC of DFs at 25±1^{0}C. CF_3 (0.62 mS/cm) and CF_4 (0.59 mS/cm) showed higher value of σDC over CF_1

and CF_2 at 100V. Cyclic voltammetry (CV) revealed the redox behavior of MYB @ 25, 50, 75, and 100 mV/s. Release of MYB from DFs was performed by square wave voltammetry (SWV) in KCl (0.1 M) in the potential range -1.20 to 1.00 V. LOD (4.1×10^{-3} mg/L) and LOQ (12.6×10^{-3} mg/L) of MYB were obtained over GCE through SWV in KCl (0.1 M).

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