Application of Fe$_3$O$_4$ nanoparticles on cotton fabrics by the Pad-Dry-Cure process for the elaboration of magnetic and conductive textiles

Ayoub Nadi$^1$, Sara Jamoudi Shai$^{1,3}$, Aziz Bentiss$^{1,2}$, Mohammed Belaiche$^3$, Samir Briche$^4$, Said Gmouh$^{2,5}$.

1 Laboratoire REMTEX, ESITH, route El Jadida, km 8, BP 7731 - Oulfa, Casablanca, Morocco.
2 Laboratoire LIMAT, Université Hassan II de Casablanca, BP : 9167 Casablanca, Morocco.
3 Semiconductor and Environmental Sensor Technology Team, Energy Research Center. Faculty of Sciences, Mohammed V University, B.P. 1014 Rabat, Morocco.
4 Moroccan Foundation for Advanced Science, Innovation and Research (MASCIR), Department of Energy Storage and Multifunctional Coatings, B.P. 10100 Rabat, Morocco.
5 Author to whom any correspondence should be addressed
s.gmouh1@gmail.com

Abstract. In the present study, a magnetic textile was developed by the application of Iron nanoparticles on cotton fabrics. For this, Fe$_3$O$_4$ nanoparticles were synthetized by reverse co-precipitation. Then, the obtained magnetic nanoparticles were applied on cotton fabrics using the Pad-Dry-Cure process. Magnetic behavior of iron oxide nanoparticles was investigated to study magnetic properties by the VSM analysis. Moreover, the effect of iron oxide nanoparticles on the cotton fabrics noticed on the thermal behavior has been studied by thermogravimetric analysis. The thermal stability of cotton fabrics is positively affected after the treatment using Fe$_3$O$_4$ nanoparticles. Finally, electrical properties were studied to measure the fabrics conductivity according to the AATCC.

Keywords: Fe$_3$O$_4$ nanoparticles, Cotton fabrics, magnetic textile, Pad-dry-cure.

1. Introduction

The nanotechnology, information technologies and biomaterials have continued to evolve towards new stages of maturity[1]. They can be used for discovering new materials and developing industries with new properties such as improving the tensile strength of fabrics, flame retardant, water repellency, antibacterial and self-cleaning properties, etc.[2]. Magnetic nanoparticles continue to attract scientific researchers in order to use them in industrial applications. This interest is due to their controllable dimensions of up to 100 nm[3] and their chemical, magnetic, electrical and mechanical properties[4]. Also, they make the textile fabric recyclable through excellent separation efficiency, good recyclability, durability and better thermal resistance[5].

In the case of textile as a substrate, nanomaterials are incorporated by methods such as the Pad-Dry-Cure process. This latter consists on impregnating a textile matrix in a solution, followed by drying the fabric and curing it under appropriate conditions[6].

We have chosen reverse co-precipitation synthesis as a method for the preparation of Magnetite Fe$_3$O$_4$ nanoparticles because of its simplicity (availability of precursors, ease of control of synthesis conditions and recovery of the product) as well as its relatively high yield compared to other methods[7].
Cotton is a widely used fiber type that exhibits high absorbency, softness, and breathability. However, the use of cotton in non-classical applications is limited since its fibers have relatively low strength, low durability, easy creasing and soiling and flammability[8].

Our aim in this work is the functionalization of textiles by the surface treatment of cotton using magnetic iron oxides nanoparticles in order to design a multifunctional material with interesting magnetic, thermal and electrical properties characterized by VSM, TGA and Resistivity measurements, respectively. The principle is based initially on the deposition of the Fe₃O₄ nanoparticles on the surface of the cotton fabric by the Pad-Dry-Cure method.

2. Experimental procedure

2.1. Chemicals
Cotton (CO) woven fabric weighing 168 g.m⁻² was used. Iron oxide nanoparticles Fe₃O₄ of around 16nm (synthesized as described in our previous study [9]) ; Ethanol (EtOH, 99%), were purchased from Sigma-Aldrich. Co.

2.2. Application of iron oxide Nps onto cotton fabrics
The application of synthesized Iron oxide nanoparticles on the surface of cotton fabric is carried out by the Pad-Dry-Cure method. First, 0.35g of Fe₃O₄ nanoparticles are taken into a solution containing 9ml of Ethanol and 1.5ml on deionized water that we dispersed by sonication for 30min. Then, the fabric is emerged in the prepared solution and padded until reaching a "pick-up" of 80% and dried at 80 °C then at 120 °C for 1 hour.

3. Characterization
The characteristic bonds of cotton fabric and iron oxide nanoparticles has been analyzed by Fourier Transform Infrared Spectroscopy with attenuated total reflection (FT-IR) by Thermo Scientific BRUCKER HYPERION 1000. Surface morphology of the untreated and treated cotton fabrics was observed using Scanning Electron Microscope (SEM) by ESEM FEI QUANTA 200 effect Scanning Electron Microscope (SEM). Thermal properties of the cotton fabrics were estimated by thermogravimetric analysis (TGA) from 25°C to 600°C with a heating rate of 10 °C/min under a nitrogen atmosphere using a thermogravimetric analyzer (Mettler Toledo, TGA2). The magnetic characteristics and behaviors of iron oxide and before and after their application on cotton fabrics were studied using a vibrating sample magnetometer (SQUID Quantum Design PPMS-9) at room temperature (300 K) and at low temperature (10 K). Electrical conductivity was measured according to the AATCC test method of the American Association of Textile Chemists and Colourists. The fabric (10 x 13 cm²) was placed between two metal electrodes separated by 3 cm under standard conditions (65% RH and 24 °C). The electrical resistance was recorded with a Multimetrix DMM 120.3.

4. Results and discussion

4.1. X-ray diffraction
These results showed that Fe₃O₄ nanoparticles on the surface of cotton fabrics preserve their crystalline nature and size after their application on the cotton fabric surface. The crystallite size that was determined by Scherrer equation on the samples of the treated textiles gave average values around 15 nm[10], which is in agreement with the measurements on the nanoparticles powder according to our previous works [9].

4.2. Morphology analysis
After coating cotton fabrics with iron oxide nanoparticles using the Pad-Dry-Cure technique, we noted that the treated fabric has a smooth surface with a very uniform color. This result is confirmed by the SEM as shown in (Figure.3b, 3b’). However, at the level of the modified fabric (Figure. 3b), it is noted that the nanoparticles covered the surface of the cotton fabric homogeneously.
4.3. **FT-IR analysis**

The chemical interactions of Fe$_3$O$_4$ Nps on the surface of cotton fabrics were investigated by FT-IR analysis. Figure 2a represents FT-IR spectra of UCF and TCF-CN and figure 2.b represents spectrum of iron oxide Nps powder. For the uncoated cotton surface (UCF): the absorption peak at 3467.47 cm$^{-1}$ is related to hydroxyl groups -OH vibration and the band at 2896 cm$^{-1}$ is assigned to the C-H stretching. On the other spectrum of Iron oxide coating Cotton fabric (TCF-CN) the band corresponding to the group Fe-O appeared at 526.88 cm$^{-1}$ and 434.60 cm$^{-1}$ which is the characteristic band of Iron oxide nanoparticles, as seen in the Fe$_3$O$_4$ Nps powder spectrum (figure 2.b)[11].

![Figure 1](image1.png)

**Figure 1.** Pictures of untreated (a) and treated cotton fabric (b); SEM images of untreated (a’) and treated cotton fabric (b’).

![Figure 2](image2.png)

**Figure 2.** (a) FT-IR spectra of uncoated cotton (UCF) and treated cotton fabrics (TCF-CN) and (b) Fe$_3$O$_4$ Nps powder.

4.4. **Thermal properties**

The thermal stability of uncoated cotton fabric (UCF) and coated cotton with magnetic iron oxide nanoparticles (TCF-CN) was studied by thermogravimetry under a nitrogen atmosphere (Figure 3). In the case of cotton treated with nanoparticles (TCF-CN), the sample showed the same stages of degradation of the untreated one until the last stage. In this latter, we observed an improvement in the thermal properties of the sample by retaining about 25% of its mass at 600°C, while the residue of untreated cotton (UCF) is about 3.46% at 600°C[12]. This is due to the good thermal properties of iron oxide nanoparticles as described in the literature [13]. A similar result has been reported by Harifi, indicating that the thermal stability of polyester fabric was enhanced after the coating with Fe$_3$O$_4$ nanoparticles [14].
4.5. Magnetic properties
The measurement of magnetic properties (figure 4) showed that the cotton fabric covered by iron oxide nanoparticles has an identical magnetic behavior as the powder nanoparticles with a difference of $M_s=94.1$ emu/g in favor of the fabric. This may be due to the agglomeration caused by the pressure of the rollers in the Pad-Dry-Cure process.

Moreover, we can see the absence of coercivity and remanence at 300K, which indicates a superparamagnetic behavior for both samples. However, at low temperature (10K) both samples have a hysteresis cycle, which reflects the transition to ferrimagnetic behavior.

It is established that the size and shape of nanoparticles influence the physical properties of the material, due to dipole-magnetic interactions at long distances, between agglomerations and intra-agglomeration that impact the magnetic response of the sample[15].

4.6. Electrical properties
The effect of the coatings on the surface resistivity of the cotton fabrics is shown in Table 1. The samples after padding have similar thicknesses, around 0.32 mm. First, we measured the surface resistivity of the uncoated fabric (UCF) and the fabric treated by the iron oxide Nps (TCF-CN). After the treatment with iron oxide nanoparticles, we noted that the surface resistivity of the fabrics becomes measurable and is of 7.07 MΩ/m² (Ohm). These results showed that the coating of cotton fabric by Iron oxide nanoparticles gives an electrical conductivity to the fabric which makes it a semi-conductor material[16].
5. Conclusions
The physicochemical properties of cotton fabrics treated with iron oxide nanoparticles by the Pad-Dry-Cure method were discussed in this article. One of the main characteristics of this work is that the magnetic properties of the Fe₃O₄ nanoparticles on the treated fabrics are more interesting than those of the iron oxide nanoparticles powder by itself. This is due to the padding process that favors a uniform agglomeration of the nanoparticles on the surface of the fabric. The conductivity of cotton fabrics was significantly increased by iron oxide NPs. The thermal properties of cotton fabrics are positively affected after the treatment by magnetic nanoparticles. In summary, Fe₃O₄ nanoparticles treated cotton fabrics can be more effective through improvements by new functionalization in order to enhance the mechanical and thermal resistance.

References
[1] Afzali A and S Maghsoodlou, 2016, Modern application of nanotechnology in textile. Nanstructured Polymer Blends and Composites in Textiles, p. 41-85.
[2] Boukhriss A, 2015, Elaboration de revêtements hybrides par le procédé sol-gel pour conférer de nouvelles fonctions à des matériaux textiles, Clermont-Ferrand 2.
[3] Xu P et al., 2012, Use of iron oxide nanomaterials in wastewater treatment: a review. Science of the Total Environment, 424, p. 1-10.
[4] Qian T et al., 2019, Fabrication of magnetic phase change n-eicosane@ Fe3O4/SiO2 microcapsules on wood surface via sol-gel method. Journal of Alloys and Compounds, 772, p. 871-76.
[5] Yan T et al., 2018, A magnetic pH-induced textile fabric with switchable wettability for intelligent oil/water separation. Chemical Engineering Journal, 347, p. 52-63.
[6] Nadi A et al., 2018, Evolution in the surface modification of textiles: a review. Textile Progress, 50(2), p. 67-108.
[7] Chen Y et al., 2016, Preparation of size-controlled magnetite nanoparticles with a graphene and polymeric ionic liquid coating for the quick, easy, cheap, effective, rugged and safe extraction of preservatives from vegetables. Journal of Chromatography A, 1448, p. 9-19.
[8] Yetisen A K et al., 2016, Nanotechnology in textiles. ACS nano, 10(3), p. 3042-3068.
[9] Nadi A et al., 2018, Immobilisation of bacteria onto magnetic nanoparticles for the decolorisation and degradation of azo dyes. IET nanobiotechnology, 13(2), p. 144-149.
[10] Anbarasu M et al., 2015, Synthesis and characterization of polyethylene glycol (PEG) coated Fe₃O₄ nanoparticles by chemical co-precipitation method for biomedical applications. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 135, p. 536-539.
[11] Soares S F et al., 2019, Trimethyl Chitosan/Siloxane-Hybrid Coated Fe₃O₄ Nanoparticles for the Uptake of Sulfamethoxazole from Water. Molecules, 24(10), p. 1958.
[12] Thi V H T and Lee B K, 2017, Development of multifunctional self-cleaning and UV blocking cotton fabric with modification of photoactive ZnO coating via microwave method. Journal of Photochemistry and Photobiology A: Chemistry, 338, p. 13-22.
[13] Wang Q et al., 2014, Fe₃O₄ nanoparticles grown on graphene as advanced electrode materials for supercapacitors. Journal of Power Sources, 245, p. 101-106.
[14] Harifi T and M Montazer, 2014, In situ synthesis of iron oxide nanoparticles on polyester fabric

| Measures           | Samples | UCF  | TCF-CN   |
|--------------------|---------|------|----------|
| Thickness (mm)     | 0.32    | 0.30 |          |
| Resistivity        | -       | 2.83Ω |         |
| Surface Resistivity| -       | 7.07Ω/m² |      |

Table 1. Electrical properties measurements of the elaborated cotton fabric.
utilizing color, magnetic, antibacterial and sono-Fenton catalytic properties. *Journal of Materials Chemistry B, 2*(3): p. 272-282.

[15] Unni M et al., 2017, Thermal decomposition synthesis of iron oxide nanoparticles with diminished magnetic dead layer by controlled addition of oxygen. *ACS nano, 11*(2): p. 2284-2303.

[16] Liu X et al., 2010, Polyelectrolyte-bridged metal/cotton hierarchical structures for highly durable conductive yarns. *ACS applied materials & interfaces, 2*(2): p. 529-535.