In-situ synthesis of magnetite nanoparticles on cotton fabrics – structural and magnetic properties

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ABSTRACT – REZUMAT

In-situ synthesis of magnetite nanoparticles on cotton fabrics – -structural and magnetic properties

In this research, the magnetic fabric was fabricated using in situ synthesizing of Iron oxide nanoparticles. To have cotton fabrics covered by magnetic nanoparticles, prepared Iron Oxide nanoparticles were deposited on it using an in situ method with 3 different concentrations of precursors while other factors such as pH, temperature, NaOH concentration, reaction container volume, and the chemical reaction time remained constant. $FeCl_3$ and $FeSO_4{\cdot}7H_2O$ were used as precursors. The results confirmed that magnetite nanoparticles with cubic structure, spherical shape and uniform distribution were deposited on the surface of cotton fabrics. The vibrating sample magnetometer (VSM) results revealed that the cotton fabric was covered by superparamagnetic magnetite nanoparticles.

Keywords: *magnetic fabrics, magnetic nanoparticles, cotton, textile, synthesise, metal nanoparticles*

Sinteza in situ a nanoparticulelor de magnetită pe țesături din bumbac – proprietăți structurale și magnetice

În acest studiu, țesătura magnetică a fost fabricată folosind sintetizarea in situ a nanoparticulelor de oxid de fier. Pentru a obține țesături din bumbac acoperite cu nanoparticule magnetice, nanoparticulele de oxid de fier au fost depuse folosind metoda in situ cu trei concentrații diferite de precursori, în timp ce alți factori cum ar fi pH-ul, temperatura, concentrația de NaOH, volumul recipientului de reacţie şi timpul de reacţie chimică au rămas constante. $FeCl_3$ și $FeSO_4{\cdot}7H_2O$ au fost utilizați ca precursori. Rezultatele obținute au confirmat că nanoparticulele de magnetită cu structură cubică, formă sferică și distribuție uniformă au fost depuse pe suprafața țesăturilor din bumbac. Rezultatele magnetometrului cu probă vibrantă (VSM) au arătat că țesătura din bumbac este acoperită de nanoparticule de magnetită superparamagnetică.

Cuvinte-cheie*: țesături magnetice, nanoparticule magnetice, bumbac, textile, sinteză, nanoparticule de metal*

INTRODUCTION

Unique properties such as large surface to volume ratio and quantum size effects of metal nanoparticles make them important materials in scientific research and industrial applications [1, 2]. High specific surface area, super-paramagnetism, low biotoxicity, and good modification ability [3] also make magnetic nanoparticles (MNPs) considerably crucial. In addition, they are potentially used in a wide range of fields including, nanomaterial-based catalysts [4] biomedicine [5] and tissue-specific targeting [6], magnetic resonance imaging [7] data storage [8] environmental remediation [9] and textile industry [10].

Iron (Fe), nickel (Ni), and cobalt (Co) are the most important metallic MNPs whose magnetic properties are high and their size, composition, and shape can be controlled and adjusted highly [11]. Iron oxide nanoparticles (ferrites) have two crystal structures of maghemite (Fe_2O_3, γ-Fe_2O_3) or magnetite (Fe_3O_4) and are the most explored magnetic nanoparticles. These nanoparticles are superparamagnetic, below 30nm in size, and they can show magnetic properties only if an external magnetic field is applied and once the external magnetic field is switched off, the remanence falls back to zero [12]. In general, Fe_3O_4 nanoparticles can be synthesized via both chemical and mechanical methods. The co-precipitation method is one of the chemical synthesis methods that are commonly used because the process is simple and inexpensive [13]. Iron oxide nanoparticles were also synthesized using a completely green biosynthetic method by reduction of ferric chloride solution using brown seaweed water extracts [14]. Other synthesis methods like hydrothermal method [15], microwave irradiation method [16], ultrasonic method [17] and sol-gel method [18] have been used to synthesize magnetite nanoparticles.

Metals are heavy, expensive and difficult to process, and in contrast, textiles are light, inexpensive and can be shaped to form three-dimensional structures and can be tailored with scissors or folded. Thus, the fabrication of metallized textiles is important nowadays. There are different methods to coat metal on textiles, such as electroless plating [19], airbrushing [20], vacuum depositing [21], sputter coating [22],

and in situ synthesis of nanoparticles on textiles [23]. Moreover, magnetic fibres are useful as elements of magnetic cores, parts of textile gauges, transmitters, and intelligent clothing products [10]. In addition, iron oxide [24] and Ag/Ni bi-metallic nanoparticles [25] are used as the remover of textile dye, which is a significant impurity, from water. As the magnetic properties of the Fe_3O_4 nanoparticles on the treated fabrics are more interesting than those of the Iron oxide nanoparticles powder, the physicochemical properties of cotton fabrics coated with iron oxide nanoparticles by the Pad-Dry Cure method were discussed [26]. In the other research work, magnetite and magnetic core-shell mesoporous silica nanoparticles were deposited onto cotton fibres by electrostatic Layer-by-layer assembly to form a promising material for many applications. [27]. Magnetic fabrics can be used in smart textiles, flexible sensors, flexible electromagnetic shielding materials, textile wastewater treatment, medical textiles, antibacterial materials, and catalysts. [10] It is possible to use magnetic textiles as a filter for reducing and removing colour in industrial wastewater. [30]

In this research work, Iron oxide nanoparticles were in situ synthesized on cotton fabric and the magnetization properties of prepared samples were investigated.

EXPERIMENTAL

Materials

In this research, Iron oxide nanoparticles were in situ synthesized on cotton fabrics using ferric chloride and ferrous sulfate. For this purpose, the molar ratio of two to one of $FeCl_3$ and $FeSO_4{\cdot}7H_2O$ was used.

In situ synthesis of nanoparticles on cotton fabric

To prepare sample 1, $FeCl_3$ and ferrous sulfate with concentrations of respectively 1 and 0.5 molar were added to the petri dish containing 500 ml distilled water. Being washed cotton fabric was put in the beaker containing $FeCl_3$ and $FeSO_4{\cdot}7H_2O$ solutions while the magnetic stirrer was stirring quickly and the temperature was fixed at 75 °C. The pH of the red solution was 1.5 which increased up to 11 by adding 200 ml of 1 molar NaOH dropwise and remained at this level during the chemical reaction until a black precipitation appeared. This process continued for 30 min. Then coated textile was washed with distilled water and its impurities were removed, then it dried at room temperature (figure 1).

The other samples were synthesized using half and one-third of the initial concentrations of $FeCl_3$ and $FeSO_4{\cdot}7H_2O$, named samples 2 and 3, respectively. For preparing these two samples, the conditions which were NaOH concentration, reaction container volume, temperature, pH and the time of chemical reaction were kept the same as the sample 1 condition.

Characterization method

To examine the crystallinity characteristics of samples, X-ray Diffraction analysis was utilized by the XRD instrument (STADI MP, made in STOE, Germany). The employed radiation was Cuk with a wavelength of 1.540598 Å, 2θ between the angles of 20 and 80 degrees and the voltage and current were 40 kV and 30 mA, respectively. Moreover, the step size and step time were set, in the order at 0.04° and 1 s. Conventional SEM studies were carried out using the EM3200 machine (KYKY Co., China) to investigate the morphology of the samples. Besides, for examining the formation of iron oxide nanoparticles, FESEM analysis was employed on a treated cotton sample utilizing the MIRA3 instrument (TESCAN Co., Czech Republic) in different magnifications at 5 and 15 kV. Afterwards, Energy Dispersive X-ray (EDX) analysis was employed to identify the presence of iron oxide on cotton fabrics. To examine the magnetic properties of the samples, VSM analysis was conducted through a vibrating specimen magnetometer, (VSM, Lake-shore model 7400 with a minimum of 0.0001 emu to a maximum of 50 emu and a maximum magnetic field up to 20 kOe).

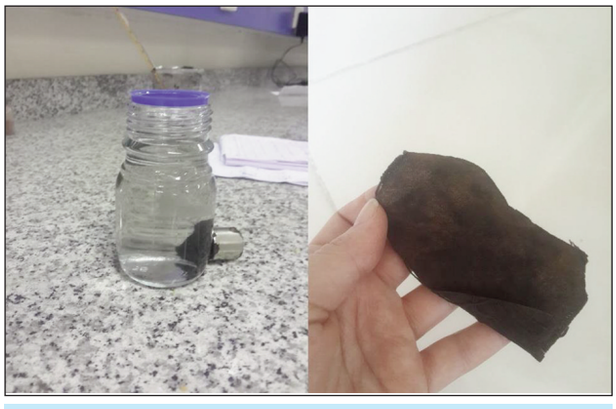


Fig. 1. The photo of magnetized fabric (sample 1)

RESULTS AND DISCUSSION

To investigate the crystallinity and type of produced nanoparticles, XRD analysis was used and the results are shown in figure 2. The results show sharp peaks, which is evidence for the formation of Fe_3O_4 nanoparticles with a high degree of crystallinity and cubic structure. The production of magnetite nanoparticles was approved by a standard card (JCPDS No. 01-087-2334).

In figure 2, the X-ray diffraction pattern shows peaks at 2θ values of 18, 30, 35, 43.40, 57 and 63.5 representing the crystal structure of Fe_3O_4 nanoparticles. Moreover, the diffraction peaks are well-adjusted to the reference Fe_3O_4 card No01-087-2334.

According to data obtained from this diffraction pattern and using Debye-Scherrer equation 1 it can be possible to calculate the mean size of Magnetite crystalline domains (*D*):

$$D = K\lambda / \beta \cos\theta \qquad (1)$$

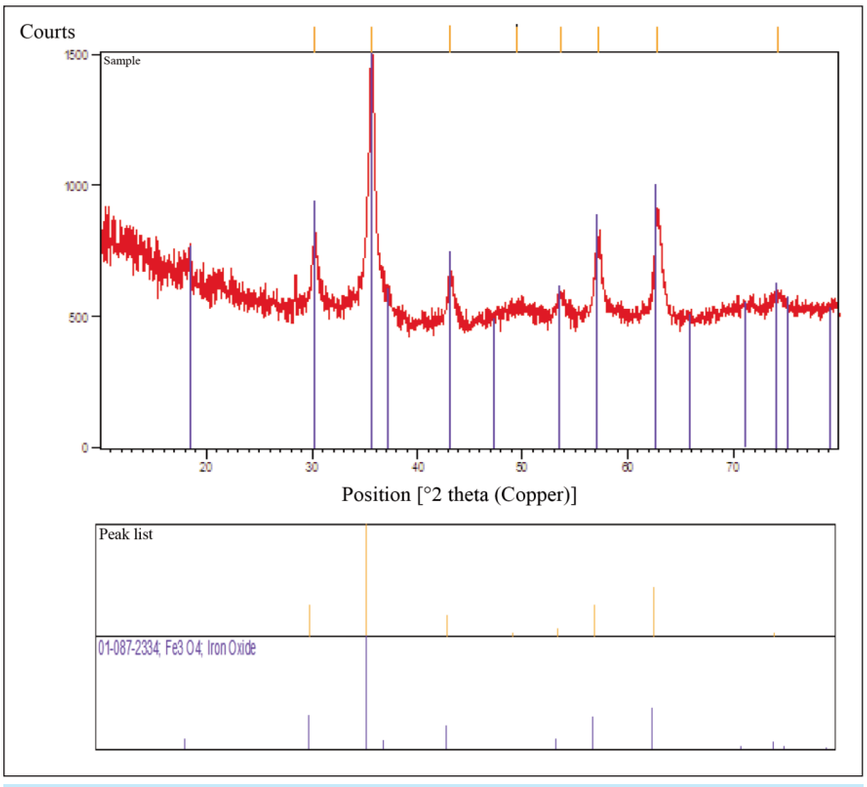


Fig. 2. X-ray pattern of nanoparticles

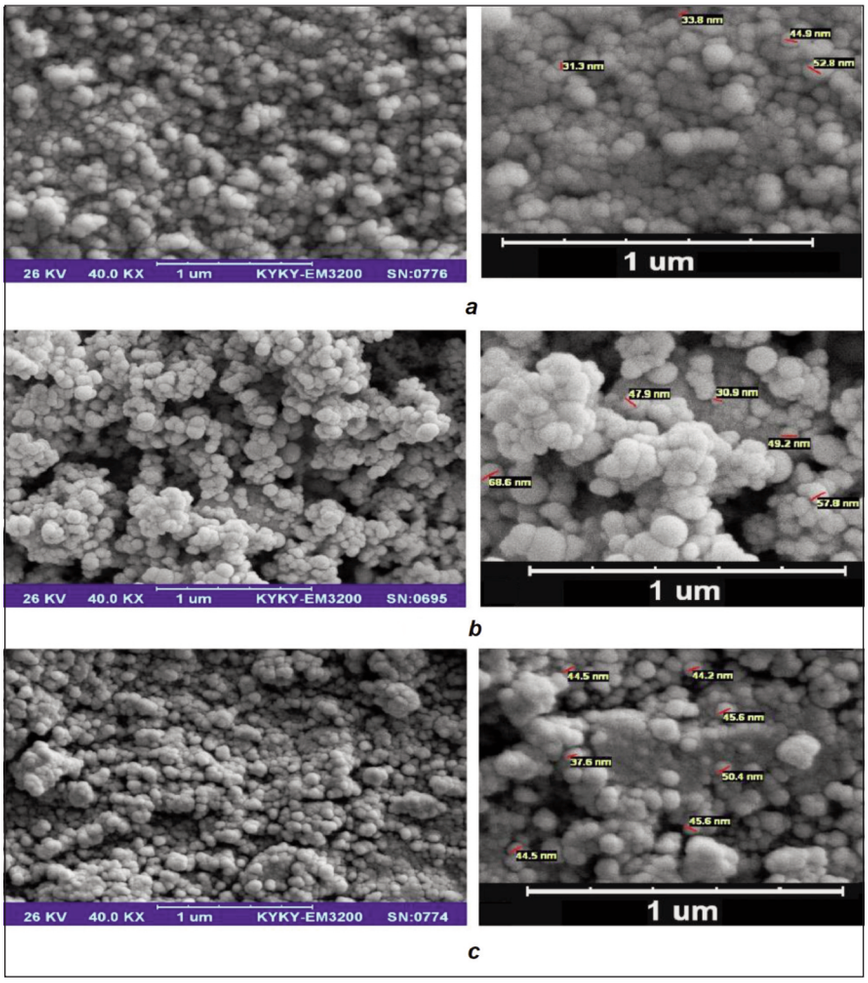


Fig. 3. SEM analyses of Magnetite nanoparticles in:
a – Sample 1; *b* – Sample 2; *c* – Sample 3

where D is the mean size of the crystalline domains, K is a dimensionless shape factor with a value close to unity, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) and θ is the Bragg angle in radians. The crystallite size of the NPs was calculated to be 13–17 nm.

The advantage of this method for producing Iron oxide nanoparticles is its simplicity, low cost, and possibility to be done in every chemistry lab with simple chemical reagents. The chemical reaction goes on by the following equations:

$$FeSO_4 \cdot 7H_2O + 2FeCl_3 \cdot 6H_2O + 8NaOH \rightarrow Fe_3O_4 + 6NaCl + Na_2SO_4 + 17H_2O \quad (2)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (3)$$

SEM analyses of three different samples depicted in figure 3 show that the magnetite nanoparticles are spherical in shape and their uniform size remained constant, ranging from 30 nm to 70 nm, by varying the concentration of precursors.

The morphology of the nanoparticles on cotton samples was investigated using FESEM analysis. FESEM analyses of the raw cotton without any deposited Magnetite nanoparticles have been shown in figure 4 with different magnifications. As it is seen, no nanoparticles, as it was expected, appear on the surface.

FESEM analyses of samples 1, 2 and 3 have been shown in figures 5, 6 and 7, respectively. It is seen that the surface of cotton fabrics has been covered by magnetite nanoparticles. The morphology of the nanoparticles on the surface of fabrics is spherical and it shows that the shape of in situ synthesized nanoparticles on cotton samples remains constant. According to these figures, as expected, the concentration of magnetite nanoparticles has

decreased with a decrease in concentration of the initial precursors, from sample 1 to sample 3.

The amount of Fe_3O_4 magnetite nanoparticles on the surface of cotton samples was compared via using EDS (Energy Dispersive X-ray) analysis as an elemental analysis. EDS analysis of a piece of raw cotton, used as a substrate, is shown in figure 8. As it was expected, there were not any Fe atoms on the textile before depositing.

Comparing the amount of Fe element in three samples (figures 9–11) the results show that its weight percent in sample three is minimum which is compatible with the concentration of the initial precursor of this sample that was the least and this result confirms the results of SEM analyses.

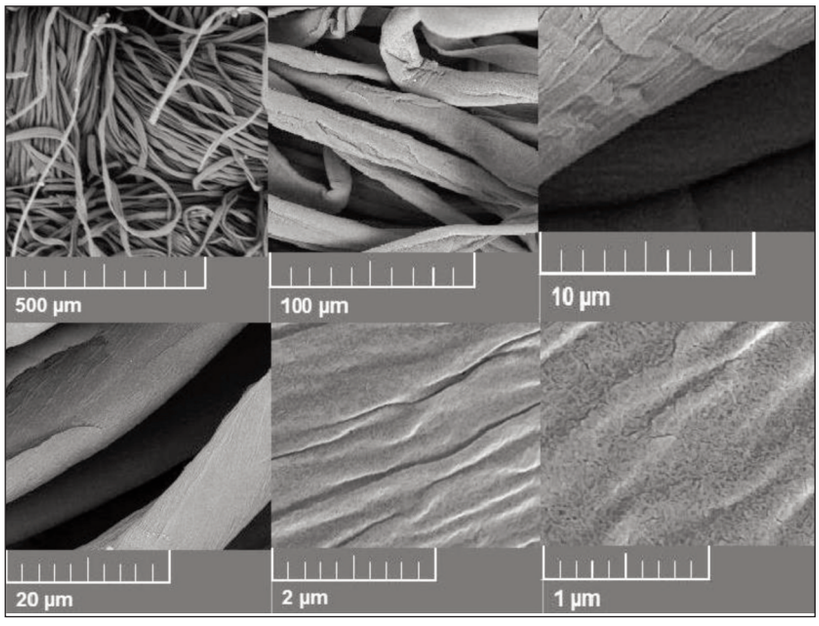


Fig. 4. FESEM analyses of raw cotton samples in different magnifications (in the absence of Magnetite nanoparticles)

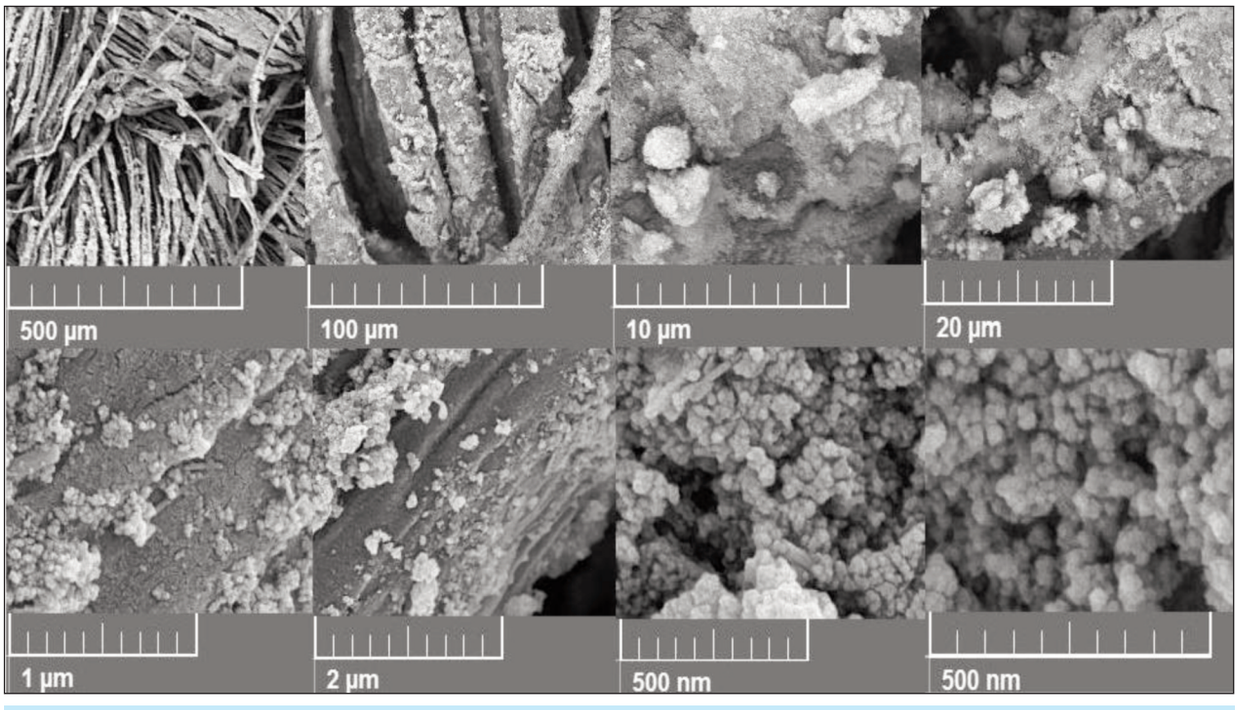


Fig. 5. FESEM analysis of Sample 1 (with magnetite nanoparticles)

As was mentioned in the experimental part, for measuring the magnetic properties of deposited samples, VSM analysis was used. Hysteresis loops of samples 1, 2 and 3 at room temperature with a maximum applied magnetic field of 10 kOe were measured and shown in figure 12. Magnetic analysis shows that magnetic hysteresis loops are not linear in average magnetic fields, which is evidence that the samples are not paramagnetic. Iron oxide displays superparamagnetic properties at room temperature when its size is below 30 nm [12]. As it is shown, all samples are superparamagnetic due to the presence of these nanoparticles. The reversibility of magnetic loops clarifies that the samples are isotropic without coercivity. According to what is seen, the magnetic saturation and the slope of the hysteresis loop showing magnetic susceptibility have decreased due to the presence of less Fe content, from sample 1 to sample 3. The magnetic properties of prepared samples are enough high to be adsorbed by a magnet (figure 1). Magnetic nanoparticles have many applications in the textile industry [24–28]. As such nanoparticles

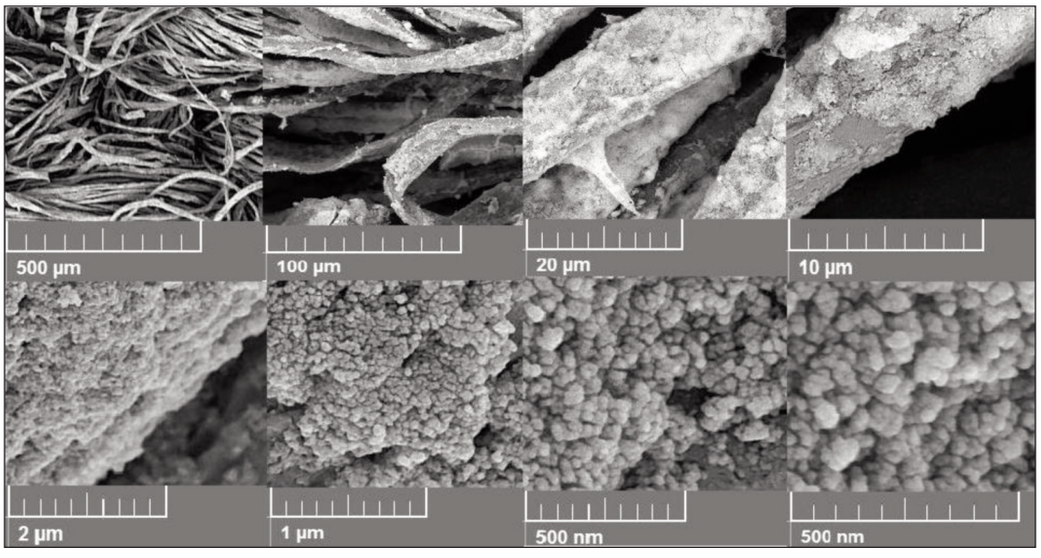


Fig. 6. FESEM analysis of Sample 2 (with magnetite nanoparticles)

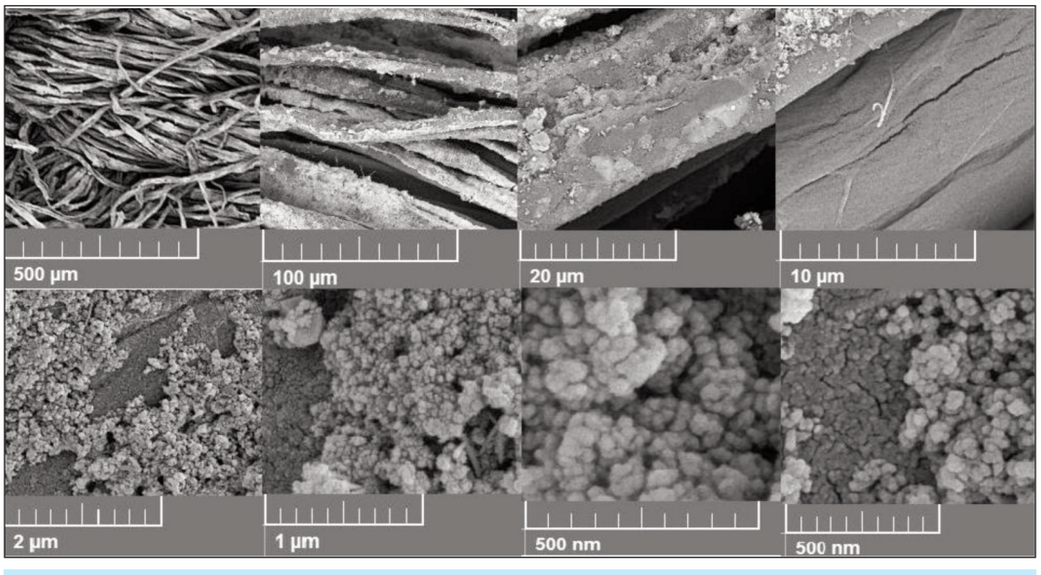
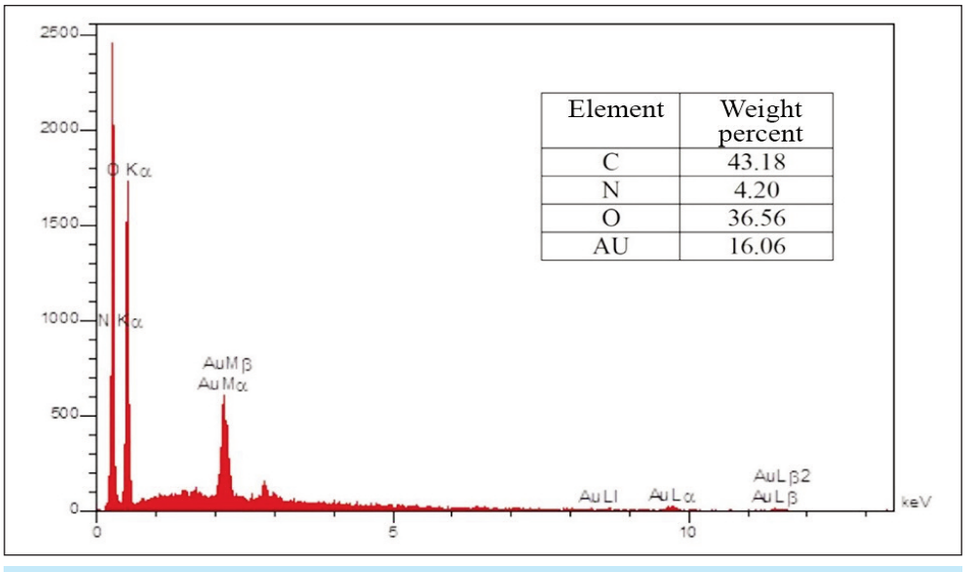
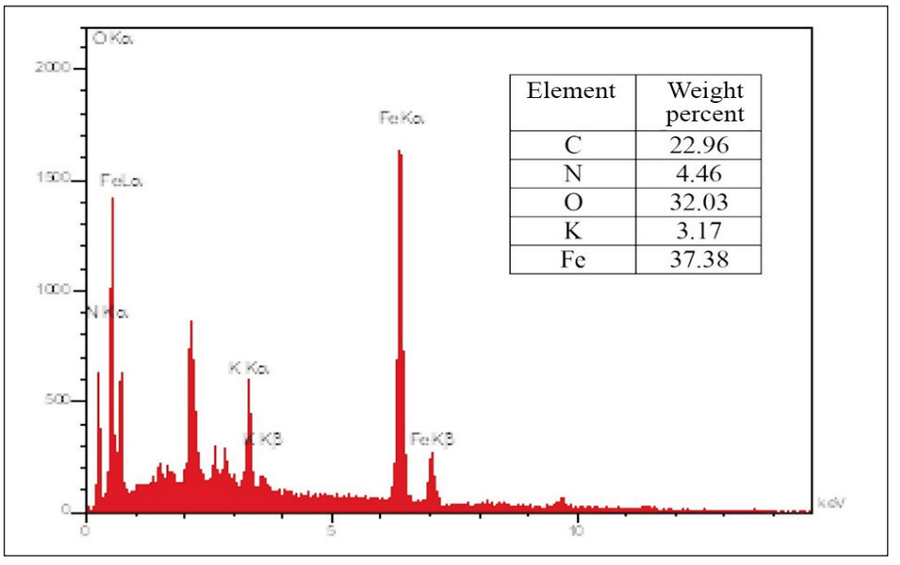


Fig. 7. FESEM analysis of Sample 3 (with magnetite nanoparticles)



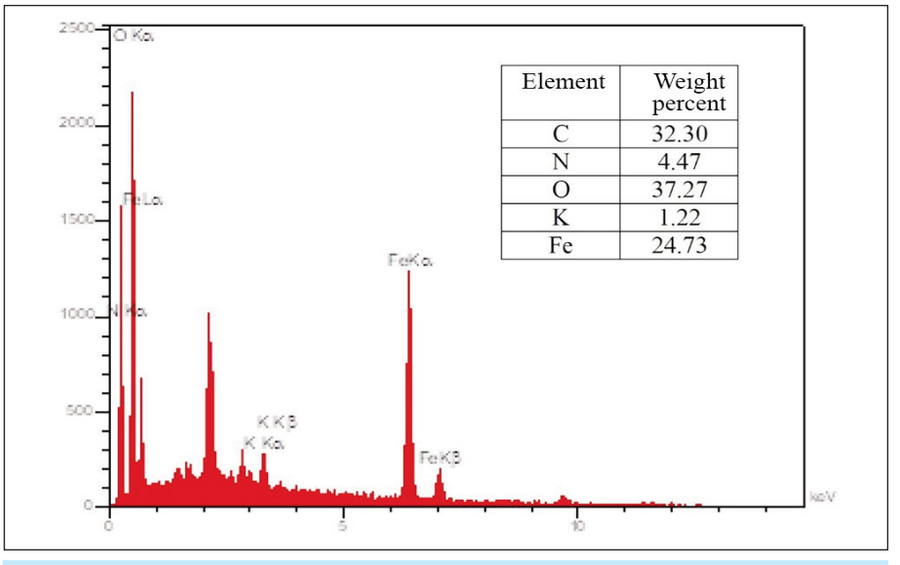
Element	Weight percent
C	43.18
N	4.20
O	36.56
AU	16.06

Fig. 8. EDS analysis of a raw cotton sample (in the absence of Magnetite nanoparticles)



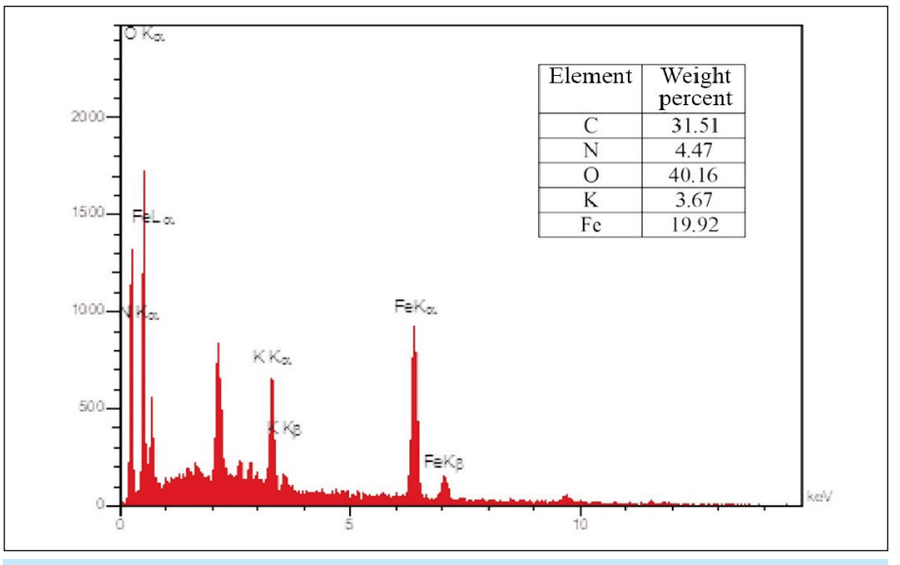
Element	Weight percent
C	22.96
N	4.46
O	32.03
K	3.17
Fe	37.38

Fig. 9. EDS analysis of sample 1



Element	Weight percent
C	32.30
N	4.47
O	37.27
K	1.22
Fe	24.73

Fig. 10. EDS analysis of sample 2



Element	Weight percent
C	31.51
N	4.47
O	40.16
K	3.67
Fe	19.92

Fig. 11. EDS analysis of sample 3

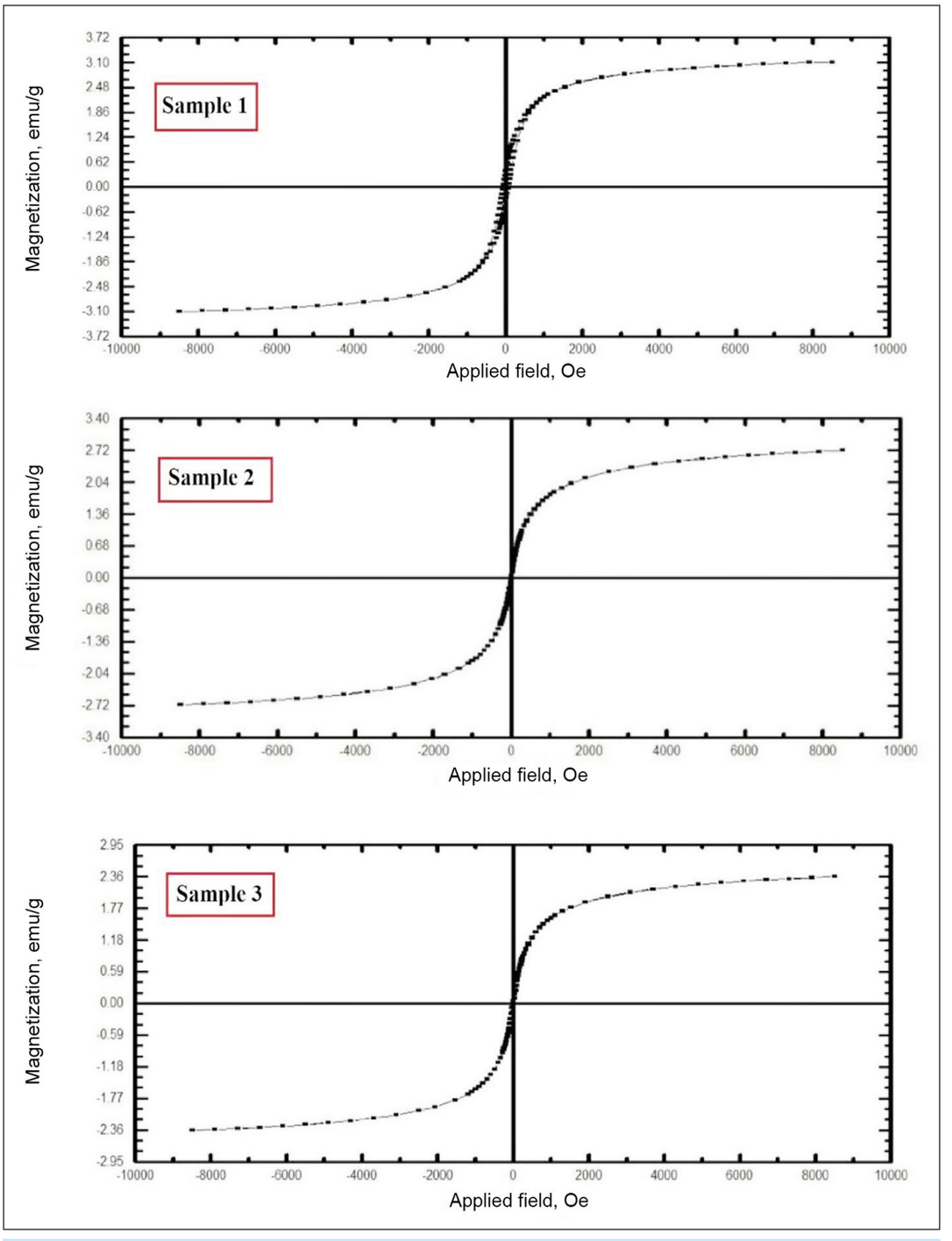


Fig. 12. Magnetic hysteresis loop for synthesized magnetic fabrics

can be simply dispersed in water, after dying the fabrics, wastewater was subjected to magnet, and unbounded magnetic dyes were collected, recycled, and saved for the next dyeing procedures, which is an environmentally friendly way for the wastewater treatment process [29]

CONCLUSIONS

XRD, SEM and FESEM analyses confirmed that magnetite nanoparticles with cubic structure, spherical shape and uniform distribution have been fabricated and in situ synthesized on cotton fabric. The precursors' concentration did not affect the size of nanoparticles and it just changed the concentration of nanoparticles. Based on the results of EDS, the amount of Fe deposited on the fabric sample is in direct proportion to the concentration of precursors. VSM analysis reveals that the in situ synthesized magnetite nanoparticles on cotton samples are superparamagnetic.

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