Indian Journal of Fibre & Textile Research
Vol. 44, June 2019, pp. 141-147

Comparison of different synthesis methods for immobilization of magnetite nanoparticles on hydrolysed polyester fabric

Mohammad Mirjalili[a]

Department of Textile Engineering, Yazd Branch, Islamic Azad University, Yazd, Iran

Received 13 June 2017; revised received and accepted 1 December 2017

Attempts have been made to accomplish synthesis of magnetite nanoparticles and hydrolysis of polyester fabric in one step. Polyester fabrics are treated in a bath containing ferrous chloride, ferric chloride and sodium hydroxide under three different conditions, namely stirring, ultrasound and high temperature. The successful synthesis of Fe_3O_4 particles with different shapes on the surface of the polyester fabrics is confirmed by scanning electron microscopy, X-ray diffraction and energy dispersive X-ray spectroscopy. The treated fabrics are assessed for magnetic, antibacterial and Fenton catalytic properties. In addition, bending length and water drop absorption time of treated samples are also evaluated. The results show that magnetic, antibacterial and Fenton catalytic activities are superior for samples treated under ultrasound condition than the samples treated under stirring or high temperature conditions. Nevertheless, the hydrophilicity and flexibility of the treated polyester fabrics under various conditions are improved.

Keywords: Antibacterial property, Fenton catalytic properties, Hydrophilicity, Magnetite nanoparticles, Polyester, Ultrasound treatment

1 Introduction

Magnetite (Fe_3O_4) nanoparticles have been paid attentions among the researchers due to its strong superparamagnetic property, high adsorption ability, electronic properties, antibacterial activity, low toxicity, low cost and high bio-compatibility[1-5]. Several techniques have been established to prepare magnetite nanoparticles including coprecipitation, sol-gel, electrochemical, sonolysis, hydrothermal and high-temperature[6]. Fe_3O_4 nanoparticles have potential in important applications, such as targeted drug delivery[7], cancer therapy[8], microwave absorption[9], electromagnetic interference (EMI) shielding[10], electromechanical actuators[11] and magnetic resonance imaging (MRI)[12]. Recently, some researchers investigated the finishing of textiles with magnetite nanoparticles. For instance, Zhang and Zhu[13] produced magnetic polyamide fabrics using Fe_3O_4 nanoparticles. Along the same lines, Li *et al.*[14] obtained super-paramagnetic, conductive and EMI shielding fabrics based on magnetite coatings on polyester fabrics. Zhang *et al.*[15] prepared magnetic polyethylene terephthalate fabrics with Fe_3O_4 nanoparticles, which were prepared through the hydrothermal method. Moreover, *in situ* synthesis of magnetite nanoparticles on polyester fabric for producing multi-functional fabric with magnetic, antibacterial and sono-Fenton catalytic activities was reported by Harifi and Montazer[16]. More recently, synthesis of magnetite nanoparticles on wool fabrics was investigated by Nazari *et al.*[17]. The treated wool fabrics exhibited magnetic and antifungal properties.

Polyester is one of the most widely used versatile polymers owing to its high strength, high modulus, abrasion resistance, heat set stability, light fastness and chemical resistance[18]. However, due to its poor wettability and lack of functional groups, durable functional finishing of polyester fabrics have became concerns of the textile industry. Several studies have reported that surface modification of the polyester could be performed using different pretreatments and techniques such as plasma treatment, hydrolysis and aminolysis[19-21]. The alkaline treatment hydrolysis of the polyester fabric enhances the hydrophilicity and surface reactivity[22]. In this study, synthesis of magnetite nanoparticles and alkaline hydrolysis of the polyester fabric have been conducted in one step by three different methods, viz stirring, ultrasound and high temperature. Apart from diverse analysis employed for confirming the successful synthesis of the magnetite particles on the fabric surface, the magnetic property, antibacterial efficiency, Fenton catalytic activity, hydrophilicity and flexibility of the treated fabrics are also studied.

[a]E-mail: dr.mirjalili@iauyazd.ac.ir

2 Materials and Methods

2.1 Materials

The plain weave 100 % polyester fabric was used with the warp density of 32 yarns/cm (yarn count 150 den), the weft density of 24 yarns/cm (yarn count 150 den) and the fabric weight of 99 g/m^2. Iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), Iron (III) chloride ($FeCl_3$) and sodium hydroxide (NaOH) were purchased from Merck Co. (Germany). Methylene blue (CI 52015) was purchased from Uhao Co. (China).

2.2 Instrument

An ultrasonic bath Euronda Eurosonic® 4D, 350 W, 50/60 Hz (Italy) was used for sono-synthesis processing. High temperature synthesis of magnetite particles on polyester fabric was performed on a HT dyeing machine (Sima Nasaj, Iran). SEM images and EDS patterns were established by VEGA3-TESCAN, scanning electron microscope (SEM) (Czech Republic). X-ray diffraction analysis (XRD) was performed with a Bruker D8 Discover X-ray diffractometer using a Cu Kα radiation source (λ=1.5410 Å) operating at 40 kV and 30 mA to investigate the crystalline phases of the synthesized magnetite particles on the polyester fabric. The Fourier transform infrared (FTIR) spectra were carried out by Bruker FTIR (Germany) for analysis of the changes appeared in functional groups on polyester fabrics surface through the alkaline treatment. Magnetization was evaluated by utilizing a vibrating sample magnetometer at room temperature. The fabric bending length was tested on a Shirley bending length apparatus (Shirley Developments Limited, England).

2.3 Synthesis of Magnetite on Polyester Fabric

Conventional Stirrer Bath

Pre-calculated amounts of $FeCl_3$ and $FeCl_2$ (Fe^{2+}/Fe^{3+} molar ratio=2) were dissolved in 100 mL distilled water at ambient temperature under vigorous stirring using magnetic stirrer. The fabrics were immersed into the solutions. Next, different amounts of sodium hydroxide were slowly added to the aqueous solution under constant stirring, and the temperature was then increased. The solution was stirred at 90 ºC for 60 min. The treated fabrics were dried at 60 ºC for 30 min followed by curing at 130 ºC for 4 min. Finally, the treated fabrics were washed with distilled water and dried at ambient temperature.

High Temperature Bath

Diverse amounts of $FeCl_3$, $FeCl_2$ and NaOH were first dissolved in water. Polyester fabric was immersed into the aqueous solution and then transferred to a high temperature (HT) dyeing machine. The temperature was increased at a rate of 5 ºC/min to 130 °C and kept as such for 1 h. Temperature was then cooled to room temperature. Finally, the treated samples were washed with distilled water and dried at 60 ºC for 30 min.

Ultrasound Bath

To prepare magnetic nanoparticles on the polyester fabric, diverse amounts of $FeCl_3$ and $FeCl_2$ were used in 100 mL water in the ultrasound bath. The polyester fabrics were immersed into the solutions, and different amounts of sodium hydroxide were added to the bath under ultrasonic irradiation. The solution was irradiated at 70 ºC for 45 min. The treated samples were dried at 60 ºC for 30 min and then cured at 130 ºC for 4 min. At the end, the sonotreated fabrics were washed with distilled water and dried at ambient temperature. The exact formation and tests results for each sample examined in this study are summarized in Table 1.

2.4 Test methods

The Fenton catalytic activity of treated fabrics was assessed by analyzing the decrease in concentration of methylene blue under stirring in the dark. The first step was the preparation of dye solution in distilled water (10 mg/L). Then, the treated polyester fabrics (1 g/L) were added into the dye solution in the presence of hydrogen peroxide (10 ml/L). The solution mixture was stirred for 6 h without irradiation. Finally, the concentration of dye in the solution was calculated by Varian Cary 300 UV–Vis spectrophotometer using calibration curve. A computer program determines absorbance of dye solution at maximum wavelength of methylene blue - 663 nm. The Fenton catalytic efficiency has been calculated using the following equation:

$$\text{Efficiency } (\%) = (C_0 - C_e)/ C_0 \quad \ldots(1)$$

where C_0 and C_e correspond to the initial and final concentrations of dye before and after stirring respectively.

The antibacterial properties of the polyester samples were measured by AATCC 100-2004 test method against *Escherichia coli* (*E. coli*, ATCC 25922, Gram-negative bacterium) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923, Gram-positive bacterium) as common pathogenic bacterium. Antibacterial activity was expressed in terms of the percentage reduction (R) of microorganisms and calculated as:

Table 1 — Experimental conditions and tests results for three different methods.

Sample	$FeCl_3$ mg	$FeCl_2$ mg	NaOH wt.%	E%	SM [a] emu g^{-1}	BL [b] cm	BR [c] mg.cm	WDAT [d] s
Stirring method								
1	81	49.5	1	19.3	0.1	3.4	389.10	22
2	81	49.5	2	19.4	0.1	3.2	324.40	16
3	81	49.5	4	20.3	0.5	3	267.30	14
4	162	99.5	1	22.5	1	3	267.30	22
5	162	99.5	2	27.3	1	2.7	194.86	18
6	162	99.5	4	29.8	1.5	2.8	217.32	16
7	324	199	1	29.5	2	3.2	324.40	18
8	324	199	2	33.1	2.5	3	267.30	20
9	324	199	4	35.7	3	3	267.30	20
High temperature method								
10	81	49.5	1	20.4	1	2.2	105.41	7
11	81	49.5	2	28.1	1	2	79.20	5
12	81	49.5	4	33.9	1.5	1.8	57.73	4
13	162	99.5	1	42.1	2	2.3	120.45	12
14	162	99.5	2	48.6	2.5	2.1	91.68	9
15	162	99.5	4	52.3	2.5	2	79.20	9
16	324	199	1	59.7	3	2.4	136.85	10
17	324	199	2	62.6	3.5	2.2	105.41	8
18	324	199	4	65.4	4.2	2.1	91.68	9
Ultrasound method								
19	81	49.5	1	28.2	1.5	3	267.30	18
20	81	49.5	2	33.1	2	2.8	217.32	16
21	81	49.5	4	37.4	2.5	2.4	136.85	14
22	162	99.5	1	61.9	3	3	267.30	9
23	162	99.5	2	68.4	3.5	2.8	217.32	7
24	162	99.5	4	69.6	4.2	2.8	217.32	7
25	324	199	1	72.1	4	2.8	217.32	10
26	324	199	2	72.6	5.5	3	267.30	9
27	324	199	4	73.9	6.5	3	267.30	7
Raw polyester fabric				19.1	-	3.6	461.89	95

[a]Saturation magnetization; [b]Bending length; [c]Bending rigidity; and [d]Water droplet adsorption time.

$$R(\%) = [(A\text{-}B)/A] \times 100 \quad \ldots(2)$$

where A and B are the number of microorganisms colonies on untreated and treated fabrics respectively.

Fabric stiffness as expressed in terms of bending length was measured according to ASTM D 1388-96 (2002) test method. The bending rigidity of the fabrics was calculated using the following equation:

$$G = M \times (C)^3 \quad \ldots(3)$$

where G is the bending rigidity (mg cm); *M*, the fabric weight (mg/cm^2); and *C*, the average bending length (cm). Also, hydrophilicity of the samples was conducted according to AATCC 79-2000 test method.

3 Results and Discussion

3.1 Characterization

The surfaces of the treated and untreated polyester fabrics are observed with scanning electron microscopy. The SEM images of raw polyester (A and B), polyester treated with magnetite at stirrer (C and D), HT (E and F), and ultrasound (G and H) baths are presented in Fig. 1. While the surface of the raw polyester fabric is smooth, the synthesized magnetite particles are distributed on the surface of the treated fabrics. Through finishing treatment at conventional stirrer bath, magnetite sheets with disparate dimensions are coated over the entire polyester surface. Also, it is thoroughly possible to recognize the magnetite nanoparticles on the surface of polyester fabrics treated in HT and ultrasound baths. Alkaline hydrolysis of polyester leads to controlled degradation of the surface, in which hydroxide ions react with polymer chains and the polymer is hydrolyzed to monomer units, and terephthalate anions and ethylene glycol are removed[22]. Due to the vigorous conditions at HT bath, alkaline hydrolysis is

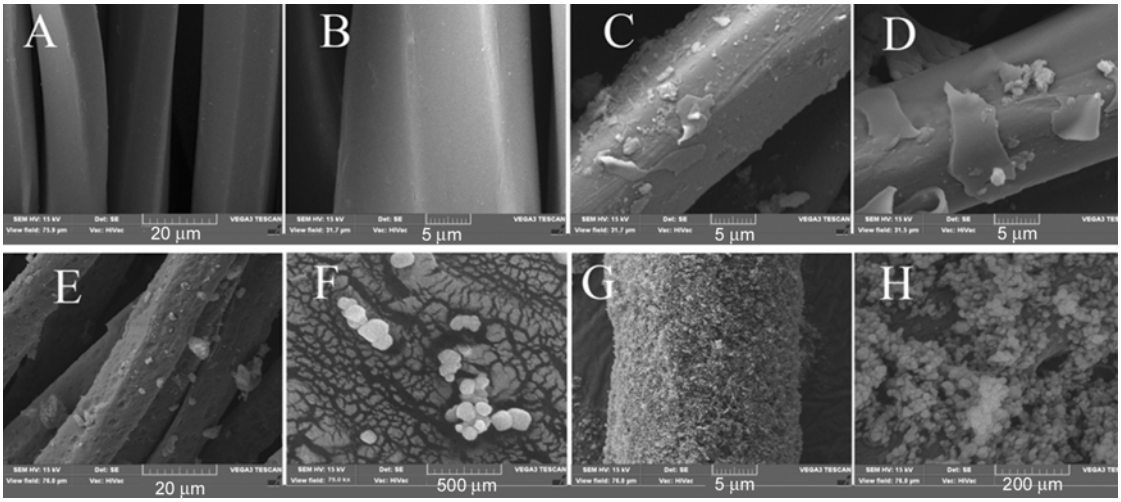

Fig. 1 — SEM images of various polyester fabrics: (A and B) raw, (C and D) treated at conventional stirrer bath (sample 6), (E and F) treated at HT bath (sample 15), and (G and H) treated at ultrasound bath (sample 24)

found more prominent at higher temperature, resulting in the creation of deeper pits. The sonosynthesized magnetite nanoparticles are uniformly spread on the surface of the sample due to the ultrasound irradiation. The images at higher magnification indicate the presence of spherical-shaped particles, with an average size of 25 nm [Fig. 1(H)].

The successful formation of the magnetite nanoparticles on the treated fabrics is verified using the chemical compositions analysis by EDS. As shown in Fig. 2, iron and oxygen are the two elements on the treated samples apart from the carbon that relates to the polyester fabric. As the fabrics are coated by gold layer before SEM observation, Au peaks are also included in the spectra. The Fe contents on the treated fabrics are found 10.7, 11.5 and 22.3 wt% for samples 6, 15 and 24 respectively. The percentage of Fe on the treated fabric at ultrasound bath is found higher than either HT or stirrer baths, thus confirming the influence of ultrasound irradiation on the generation of Fe_3O_4 nanoparticles.

XRD patterns are used to confirm the presence of magnetite on the fabric surface and to study crystalline status (Fig. 3). The peaks at 2θ values of 17°, 23.1°, and 26.4° are the diffraction peaks of the original polyester substrate. All treated fabrics confirm the formation of cubic spinel structure of Fe_3O_4 in the XRD patterns. The successful synthesis of magnetite particles on the polyester fabrics can be established by the characteristic peak at 2θ value of 35º.

The finishing of polyester fabric with sodium hydroxide is a versatile method for producing hydrophilic groups such as hydroxyl and carboxyl on

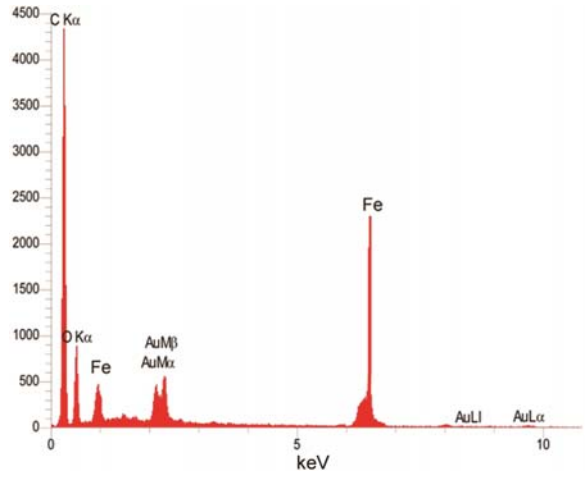

Fig. 2 — EDS spectrum of treated polyester fabric with magnetite nanoparticles at ultrasound bath

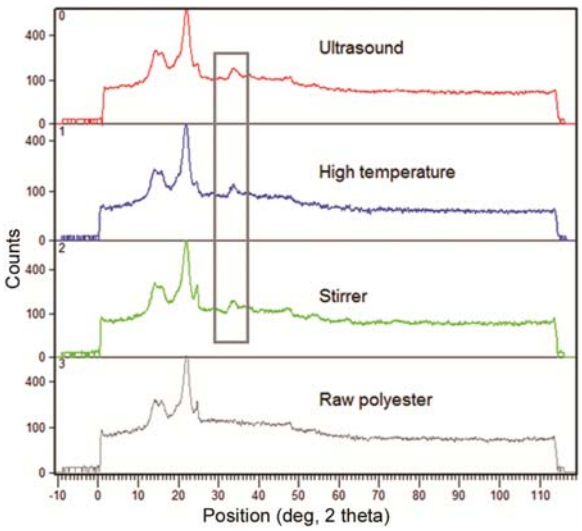

Fig. 3 — XRD patterns of various polyester fabrics

the surface of the fabric. The effect of alkaline hydrolysis on the chemical properties of polyester fabric is studied by FTIR spectroscopy (Fig. 4). The FTIR spectrum of the treated sample with NaOH indicates the characteristic peaks attributed to C=O (carboxylic acid), C–O (ester acid), C–H (stretching vibration), and C–H (bending vibration) at 1715, 1000–1500, 2928 and 722 cm^{-1} respectively. Also, the peak at approximately 3450 cm^{-1} confirms the presence of terminal groups of –OH on the surface of polyester fabric after the alkaline process, which is derived from the interaction of the hydroxide ions with the electron-deficient carbonyl groups[16].

3.2 Magnetic properties

The magnetic sensitivity of the treated polyester samples is confirmed by attraction towards a magnet (Fig. 5). The values of the saturation magnetization of treated polyester fabrics are given in Table 1. The saturation magnetization of treated polyester fabric increases with increasing magnetite precursors concentrations at constant concentration of NaOH. Based on the obtained results, the saturation magnetization of coated polyester samples increases from 0.1 emu g^{-1} to 6.5 emu g^{-1} by increasing the amounts of $FeCl_2$ and $FeCl_3$ in the impregnating bath. This could be considered as a result of the higher magnetite content on the polyester samples. Also, the increase in the NaOH concentration has a tangible effect on the magnetic properties of treated polyester fabrics, and the saturation magnetization of treated samples increases progressively. Increasing the concentration of sodium hydroxide increases the polar groups such as carboxyl and hydroxyl groups on the surface of the fibres, which may favor the adsorption of magnetite particles on the samples. Moreover, the ultrasound treated fabrics confirm more magnetic property in comparison with stirrer or HT treated samples. Ultrasound irradiation prevents particles from aggregation on the surface of polyester fibres. As seen in SEM images, the distribution of magnetite on ultrasound treated sample is more uniform due to using ultrasonic in comparing with stirrer or HT treated sample. Also, as verified through the EDS analysis, ultrasound treated polyester fabrics has the highest iron content.

3.3 Fenton Catalytic Properties

The Fenton technique is one of the most effective methods for the oxidation of organics in water. Recently, magnetite nanoparticles has received significant interest in Fenton systems due to their facile recovery and recycling, potential to catalyzing hydrogen peroxide to form hydroxyl radicals to decompose organic pollutants[23,24]. In this study, Fenton catalytic ability of the treated polyester fabrics has been estimated by the rate of discoloration of methylene blue. The Fenton catalytic efficiencies of the samples are shown in Table 1. Results show that the Fenton catalytic efficiencies for the treated polyester fabrics are higher when treated at alkaline condition. Increasing the concentration of NaOH increases the discoloration of methylene blue. Further, introducing more magnetite precursor into the impregnating bath leads to increase in Fenton catalytic efficiency from 19.3% to 35.7%, from 20.4% to 65.4% and from 28.2% to 73.9% for samples treated at stirring, HT and ultrasound baths respectively. The presence of magnetite leads to the *in situ* generation of highly

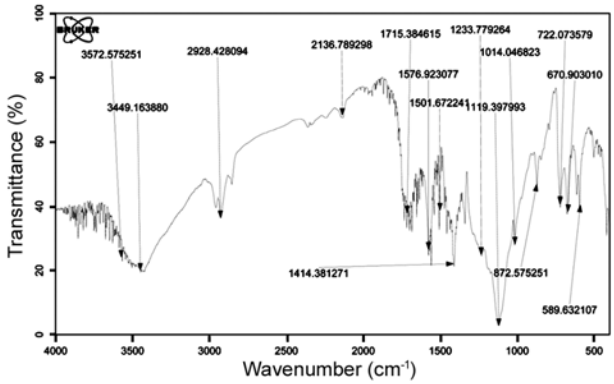

Fig. 4 — FTIR spectrum of alkaline treated polyester fabric with sodium hydroxide at ultrasound bath

Fig. 5 — Magnetic sensitivity of magnetite powder and treated polyester fabric towards a magnet

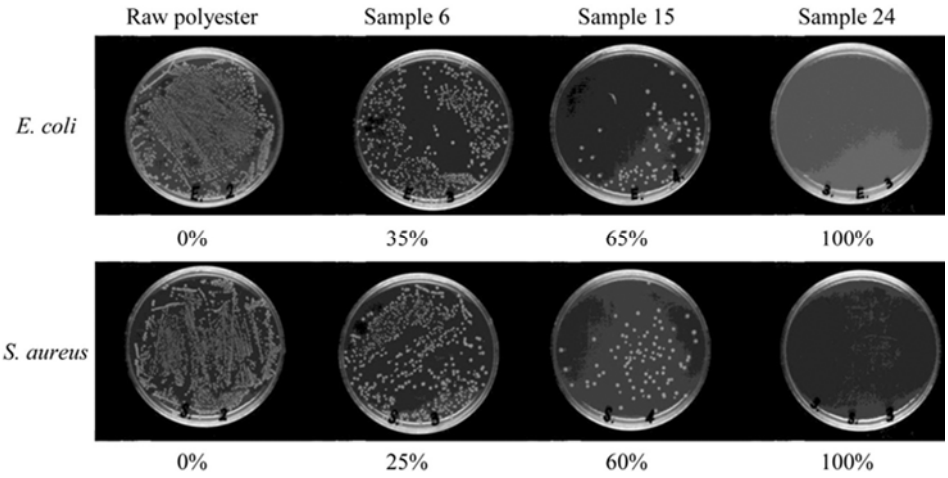

Fig. 6 — Antibacterial efficiency of the polyester samples

oxidative species, i.e. hydroxyl radicals, according to the process, as shown below:

$$Fe^{+2}{}_{(aq)} + H_2O_2 \rightarrow Fe^{+3} + OH^{-} + OH^{\bullet} \quad \ldots(4)$$

Ultimately, highly oxidative species can oxidize the dye molecules. The highest Fenton catalytic efficiency is found 73.9% for treated fabric in ultrasound bath ($FeCl_3$ 342 mg, $FeCl_2$ 199 mg, NaOH 4%). The Fenton catalytic efficiency of treated polyester fabrics at various conditions is ranked as ultrasound > HT > stirrer. Therefore, treatment condition has a tangible effect on the Fenton catalytic property of treated polyester fabrics.

3.4 Antibacterial Assay

Magnetite nanoparticles possess unique characteristics such as photocatalytic, magnetic, antifungal and antibacterial, which can make it possible to produce a textile with multifunctional properties. Moreover, Fe_3O_4 naoparticles are bio-safe and biocompatible for applications in medicine textile[25]. The Fe_3O_4 treated textile can inhibit the growth of bacteria possibly by two mechanisms. The first important reason is the production and penetration of reactive oxygen species, which causes bacterial cell oxidation and subsequent bacterial death. The second reason is the strong electrostatic attraction toward bacterial outer membranes, resulting in binding of magnetite nanoparticles to bacterial cell walls, thereby causing membrane disruption[26].

The antibacterial activities of the samples are evaluated quantitatively by suspension method against both *E. coli* and *S. aureus* bacteria. The percentage of the bacteria reduction by ultrasound/Fe_3O_4 treated, HT/Fe_3O_4 treated, stirrer/Fe_3O_4 treated and raw polyester samples are reported in Fig. 6. The raw polyester fabrics provide a suitable media for growth of microorganisms. The antibacterial efficiencies of the ultrasound, HT and stirrer treated fabrics against *E. coli* bacteria are 100%, 65% and 35% respectively. Also, antibacterial activity of the ultrasound treated sample against *S. aureus* is higher than either HT or stirrer treated samples, which is due to more and homogeneous loading of magnetite on the treated fabric surface under ultrasound irradiation. It is certificated that the transmission of finer size materials establishes more antibacterial activity comparing with the usual size[27].

3.5 Flexibility and Wettability

Bending length, bending rigidity and hydrophilicity properties of the polyester samples are summarized in Table 1. The bending lengths of the ultrasound, HT and stirrer treated samples are reduced in comparison to the raw polyester fabric, indicating higher flexibility. This clearly indicates the alkaline hydrolysis of polyester fabric with sodium hydroxide. A similar result has been reported by Allahyarzadeh *et al.*[28], indicating that the alkaline hydrolysis resulted in production of lightweight polyester fabrics with silk like properties. Also, the treated samples indicate the shorter time of the water droplet adsorption compared to that of the untreated fabrics, which further demonstrate the formation of hydrophilic groups on polyester fabric surface after alkaline hydrolysis.

4 Conclusion

A mechanism of simultaneous synthesis of magnetite nanoparticles and alkaline hydrolysis of polyester fabric surface has been developed. Polyester fabrics with magnetic property, Fenton

catalytic activity, antibacterial efficiency, improved hydrophilicity and flexibility are obtained by finishing process in ultrasound, high temperature and stirrer baths. Through SEM, XRD and EDS patterns, the presence of the magnetite on the surface of the treated polyester fabrics is confirmed. It is found that Fe_3O_4 nanospheres are synthesized on the fabrics treated at ultrasound and high temperature baths. All properties of the treated polyester fabric at ultrasound bath are superior compared to the treated sample in either HT or stirrer bath. Applying ultrasound irradiation in finishing process leads to synthesis of magnetite with finer size and homogenous distribution on the fibre surface.

References

1 Gao J, Gu H & Xu B, *Accounts Chem Res*, 42 (2009) 1097.

2 Teja A S & Koh P Y, *Prog Cryst Growth Charac Mater*, 55 (2009) 22.

3 Ling D, Lee N & Hyeon T, *Accounts Chem Res*, 48 (2015) 1276.

4 Arami H, Khandhar A, Liggitt D & Krishnan K M, *Chem Soc Rev*, 44 (2015) 8576.

5 Xu P, Zeng G M, Huang D L, Feng C L, Hu S, Zhao M H, Lai C, Wei Z, Huang C, Xie G X & Liu Z F, *Sci Total Environ*, 424 (2012) 1.

6 Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L & Muller R N, *Chem Rev*, 108 (2008) 2064.

7 Mody V V, Cox A, Shah S, Singh A, Bevins W & Parihar H, *Appl Nanoscience*, 4 (2014) 385.

8 Chu M, Shao Y, Peng J, Dai X, Li H, Wu Q & Shi D, *Biomaterials*, 34 (2013) 4078.

9 Wang G, Chang Y, Wang L, Liu L & Liu C, *Mater Res Bulletin*, 48 (2013) 1007.

10 Dhawan R, Kumari S, Kumar R, Dhawan S K & Dhakate S R, *RSC Adv*, 5 (2015) 43279.

11 Liang J, Huang Y, Oh J, Kozlov M, Sui D, Fang S, Baughman R H, Ma Y & Chen Y, *Adv Functional Mater*, 21 (2011) 3778.

12 Patsula V, Kosinová L, Lovric M, Ferhatovic Hamzić L, Rabyk M, Konefal R, Paruzel A, Slouf M, Herynek V, Gajovic S & Horák D, *ACS Appl Mater Interfaces*, 8 (2016) 7238.

13 Zhang H & Zhu G, *Appl Surf Sci*, 258 (2012) 4952.

14 Li Y, Lan J, Guo R, Huang M, Shi K & Shang D, *Fiber Polym*, 14 (2013) 1657.

15 Zhang H, Liu Y, Zhou Y, *J Text Inst*, 106 (2015) 1078.

16 Harifi T & Montazer M, *J Mater Chem B*, 2 (2014) 272.

17 Nazari A, Shishehbor M R & Poorhashemi S M, *J Text Inst*, 107 (2016) 1617.

18 Cameron D J & Shaver M P, *Chem Soc Rev*, 40 (2011) 1761.

19 Mirjalili M & Karimi L, *J Text Inst*, 104 (2013) 98.

20 Dave J, Kumar R & Srivastava H C, *J Appl Polym Sci*, 33 (1987) 455.

21 Poortavasoly H, Montazer M & Harifi T, *Mater Sci Engin C*, 58 (2016) 495.

22 Hashemizad S, Montazer M, Mireshghi S S, *J Text Inst*, 108 (2017) 117.

23 Costa R C, Moura F C, Ardisson J D, Fabris J D & Lago R M, *Appl Catal B: Environ*, 83 (2008) 131.

24 Huang R, Fang Z, Yan X & Cheng W, *Chem Engin J*, 197 (2012) 242.

25 Kharisov B I, Dias H R, Kharissova O V, Jiménez-Pérez V M, Perez B O & Flores B M, *RSC Adv*, 2 (2012) 9325.

26 Rastgoo M, Montazer M, Malek R M, Harifi T & Rad M M, *Ultrason Sonochem*, 31 (2016) 257.

27 Behzadnia A, Montazer M, Rashidi A & Rad M M, *Ultrason Sonochem*, 21 (2014) 1815.

28 Allahyarzadeh V, Montazer M, Nejad N H & Samadi N, *J Appl Polym Sci*, 129 (2013) 892.