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Ultrasound mediation for one-pot sonosynthesis and deposition of magnetite nanoparticles on cotton/polyester fabric as a novel magnetic, photocatalytic, sonocatalytic, antibacterial and antifungal textile

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ABSTRACT

A magnetic cotton/polyester fabric with photocatalytic, sonocatalytic, antibacterial and antifungal activities was successfully prepared through in-situ sonosynthesis method under ultrasound irradiation. The process involved the oxidation of Fe^{2+} to Fe^{3+} via hydroxyl radicals generated through bubbles collapse in ultrasonic bath. The treated samples were analyzed by X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy and vibrating sample magnetometry. Photocatalytic and sonocatalytic activities of magnetite treated fabrics were also evaluated toward Reactive Blue 2 decoloration under sunlight and ultrasound irradiation. Central composite design based on response surface methodology was applied to study the influence of iron precursor, pH and surfactant concentration to obtain appropriate amount for the best magnetism. Findings suggested the potential of one-pot sonochemical method to synthesize and fabricate Fe_3O_4 nanoparticles on cotton/polyester fabric possessing appropriate saturation magnetization, 95% antibacterial efficiency against *Staphylococcus aureus* and 99% antifungal effect against *Candida albicans*, 87% and 70% dye photocatalytic and sonocatalytic decoloration along with enhanced mechanical properties using only one iron rich precursor at low temperature.

1. Introduction

Different techniques have been proposed for preparing iron oxide nanoparticles, among which co-precipitation is one of the most convenient and low-cost methods [1]. Conventional co-precipitation methods for synthesis of iron oxide nanoparticles such as magnetite (Fe_3O_4) mainly require deoxygenated conditions and Fe^{2+}/Fe^{3+} molar ratio control [2]. Based on previous studies [3], the Fe^{2+}/Fe^{3+} molar ratio for the formation of Fe_3O_4 should be kept at 0.5. However, creation of Fe_3O_4 with $Fe^{2+}/Fe^{3+} = 2$ has been proposed by Harifi and Montazer in 2015, which led to more consumption of FeOOH in an excess of $Fe(OH)_2$ [4]. Therefore, Fe_3O_4 preparation was effectively carried out in an open container [5].

In case of using one iron salt precursor, a reductive or oxidative agent is required to be added to the synthesis reaction providing both ions in sufficient quantity [6]. For instance, when Fe^{2+} alone was used for precipitation, H_2O_2 [7] or $NaNO_2$ [8] were selected to partially oxidize Fe^{2+} to Fe^{3+} in the precipitated product. On the other hand, instead of using two iron precursors an aqueous iron (III) salt solution was used and reduced by potassium iodide or Na_2SO_3 to maintain the appropriate Fe^{2+}/Fe^{3+} molar ratio [9].

Instead of using external oxidizing agents for ferrous to ferric oxidation, hydroxyl radicals generated by bubbles collapse induced through ultrasonic irradiation can be applied to mediate the oxidation reaction [10]. The synthesis of magnetite nanoparticles was achieved by sonochemical oxidation of an aqueous solution of iron (II) acetate under Ar at 298 K for 3 h [11]. Preparation of Fe_3O_4 nanoparticles with 10–30 nm was carried out through sonochemical reaction of $Fe(OH)_2$ in diethylene or triethylene glycol/water solutions [12]. Recently, 2-D magnetite nanoplates were prepared by ultrasonic irradiation using $FeSO_4$ and NaOH at low temperature without deoxygenated conditions [2].

Sonochemistry not only provides the condition for synthesis of magnetite nanoparticles using one iron salt, but also prepares great benefits in uniform size distribution, high surface area, fast reac-

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tion time and low temperature reactions [13]. This arises from the physicochemical effects of sonochemical causes the formation, growth, and implosive collapsing of bubbles in liquid medium [14].

Nowadays, sonochemical method has introduced as a promising technique to synthesize nanoparticles on textiles [15]. In addition to Abramov [16] who was one of the pioneering researchers interested in materials synthesis using ultrasound, different groups led by Gedanken [17–19], Suslick [20,21], Perelshtein [22–26] and Montazer [27–31] published various papers on sonosynthesis of nanomaterials onto various textile substrates. However, in this area the only research focusing on producing magnetic fabric using sonochemical synthesis route was the recent study carried out by Harifi and Montazer [32] proposing the preparation of superparamagnetic TiO_2:Fe_3O_4:Ag nanocomposite on polyester fabric via one step sonosynthesis method. Following this study, here for the first time we aimed at producing magnetic, antibacterial, antifungal, sonoactive and photoactive cotton/polyester fabric through sonosynthesis and sonofabrication of magnetite iron oxide nanoparticles. Herein we report the one-pot feasible, rapid and easy sonochemical synthesis of Fe_3O_4 nanoparticles on cotton/polyester fabric using only one iron rich precursor (Fe^{2+} ions) without any external oxidizing agent and deoxygenated conditions. Sonosynthesis of iron oxide nanoparticles was achieved due to the effect of radicals generated during water sonolysis under collapse of bubbles providing sufficient amount of Fe^{2+} and Fe^{3+} ions required for Fe_3O_4 nanoparticles formation. The synthesis parameters including iron precursor and surfactant concentration along with pH were optimized using statistical analysis based on central composite design. For the first time in this study, photocatalytic activity of the Fe_3O_4 treated fabrics toward decoloration of Reactive Blue 2 was confirmed, suggesting the potential of sonochemical method to produce magnetic fabrics with appropriate saturation magnetization, antibacterial and antifungal properties along with photocatalytic and sonocatalytic efficiency.

2. Experimental

2.1. Materials and methods

The cotton/polyester fabric with 30% cotton and 70% polyester was purchased from Yazdbaft Co. (Iran). Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and sodium hydroxide were supplied from Sigma Aldrich (USA). Cetyltrimethylammonium bromide shortly called CTAB was also purchased from Merck, Germany and used as surfactant. Prior to the synthesis procedure, fabrics were washed with nonionic detergent at 70 °C for 20 min, rinsed with distilled water and finally dried at room temperature.

The samples were then put in a bath containing pre-calculated amount of ferrous sulfate (0.02–2 W/V%) and CTAB (0–10 W/W%) under different pH conditions (9–13) adjusted using sodium hydroxide in aqueous solution based on statistical design (Table 1). The reaction mixture was irradiated in sonicator bath (50 kHz, 50 W) for 2 h at 80 °C. Thereafter, the treated fabrics were thoroughly washed with water and dried at room temperature. A sample was only treated with NaOH and CTAB under the same sonosynthesis conditions at 80 °C for 2 h and regarded as control sample. In this study ultrasonic bath was used as an alternative to ultrasonic probe. As the actual ultrasonic power density of an ultrasonic bath is less than the probe, the processing time required for complete formation of Fe_3O_4 nanoparticles was 2 h.

2.2. Characterization and multifunctional properties testing

X-ray diffraction analysis (XRD) was performed with XPert MPD (Philips, Holland) to investigate the crystalline size and phases of the synthesized iron oxide nanoparticles on the treated fabric. The surface morphology of the treated sample and particle size of the synthesized nanoparticles were analyzed by field emission scanning electron microscope (MIRA, Tescan) equipped with energy-dispersive spectroscopy (EDX) to characterize the elemental composition.

Table 1
Central composite design for weight changes, color differences and magnetism properties.

Run	Ferrous sulfate (W/V%)	CTAB (W/W%)	pH	ΔW (%)	Magnetism (s)	ΔRGB
1	0.42	7.97	10	5	70	233
2	1.60	2.03	10	11	59	295
3	1.60	7.97	12	10	59	308
4	1.02	0.00	11	8	67	293
5	1.02	5.00	11	10	63	310
6	0.42	2.03	12	5.6	69	287
7	2.00	5.00	11	9.6	63	289
8	0.42	7.97	12	4.5	72	255
9	0.02	5.00	11	0.01	77	170
10	1.60	7.97	10	11.3	58	323
11	1.02	5.00	11	7	61	246
12	1.02	5.00	9	4	75	180
13	0.42	2.03	10	3	74	197
14	1.02	5.00	13	2	73	230
15	1.60	2.03	12	9.1	64	278
16	1.02	5.00	11	10	62	297
17	1.02	10.00	11	9.5	65	269

The percentage of weight change due to the treatment ($\Delta W\%$) was determined according to Eq. (1):

$$\Delta W\% = [(W_2 - W_1)/W_1] \times 100 \quad (1)$$

where W_1 and W_2 are weight of samples before and after the treatment, respectively.

Coloring effect of the treatment on the fabrics was evaluated by scanning the samples and measuring the color differences between the untreated fabric and the Fe_3O_4 treated samples using image processing in RGB color space according to Eq. (2) using Matlab software:

$$\Delta RGB = [(R_2 - R_1)^2 + (B_2 - B_1)^2 + (G_2 - G_1)^2)]^{1/2} \quad (2)$$

where $R_1G_1B_1$ and $R_2G_2B_2$ are color coordinates of untreated and treated samples, respectively.

Quantitative antibacterial and antifungal efficiency of the treated fabric was determined against *Staphylococcus aureus* (ATCC 6538) as Gram-positive and diploid fungus *Candida albicans* according to AATCC100 guideline. After preparation of a fresh culture of each bacterial strain on nutrient agar (18 h at 37 °C), bacteria were cultured, washed and suspended in normal saline to an optical density (OD) 620 of 0.1 which is equal to 1.5×10^8 CFU/mL. A dilution of 1:10 from each bacterial suspension was prepared subsequently. The treated and untreated (control) fabrics were placed in a sterile 50 mL polystyrene conical tubes (Jet-Biofil, Canada) and sterilized in autoclave (15 min at 121 °C). Fabrics were separately inoculated with bacterial suspension (10^6 CFU/mL) and incubated for 18 h at room temperature. 20 mL normal saline was then added to each tube and stirred vigorously for 2 min. Three serially dilution of 1:10 from each sample was prepared and 0.1 mL from each dilution was inoculated on Mueller–Hinton agar and spread on the surface thoroughly. Plates were incubated for 18 h at 37 °C, the colonies were then counted and total CFU/mL was determined for each experiment. The antibacterial and antifungal efficiency were calculated according to Eq. (3).

$$R\% = [(A - B)/A] \times 100 \quad (3)$$

where R is the reduction rate, A and B are the number of microorganism colonies from control and treated samples, respectively.