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PHOTOCATALYTIC EFFICIENCY OF N-TIO$_2$ APPLIED ON COTTON KNIT – PART 1

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Abstract: *The main aim of the research work is the development of photocatalytic textiles materials by treating them with TiO2 doped with nitrogen. Also, the research was focused on the nitrogen-doped titanium dioxide (N-TiO2) formulation as homogeneous, stable solution, immobilization of large quantities of N-TiO2 on 100% cotton knit while preserving its genuine properties, minimize the loss of nanoparticles in wastewaters and achieve a high photocatalytic fabrics effects under visible light. The photocatalytic effect was investigated by exposing the materials to ultraviolet and visible light, and the evaluation of exposed and non-exposed fabrics was performed using a spectroscopic method. By using scanning electron microscopy, we investigated the characteristic, morphology and distribution of nanoparticles covering the textile materials, and the presence of Ti and Fe on textile materials was analyzed by X-ray energy dispersive spectroscopy and FTIR spectroscopy. The results showed the relatively uniform coating of cotton fibers by particles by using initial and re-used N-TiO2 dispersions. By using additives like polyethylene glycols and wetting agents, the stability of aqueous N-TiO2 is increased. Wetting agents, together with a higher treatment temperature represent important factors contributing to the deposition of increased amount of N-TiO2 particles existing in the dispersion remained after the first treatment of the fabric.*

Key words: *nitrogen-doped TiO_2, photocatalysis, cotton fabric, nanoparticles, scanning electron microscopy*.

1. INTRODUCTION

The N-TiO_2 was intensively studied due its extended absorption in visible light, stability and enhanced photocatalytic activity [1,2]. Most of the researches investigate the physical methods to deposit N-TiO_2 on solid substrates by spin coating [3], plasma treatment [4], DC magnetron sputtering [5–7], pulsed laser deposition [8], ion implantation method [9]. Even these methods ensure a uniform deposition of very pure thin layers of TiO_2, the disadvantages such as high investment costs, high temperatures and energy consumption needed to deposit the film make them hard to be applied on textiles. Few scientific papers are dedicated to the techniques used to deposit N-TiO_2 on textiles such as impregnation of activated carbon fibers [10], wool [11], or cotton fabrics[12]. The main aim of the research work is the development of photocatalytic textile materials by coating with TiO_2 doped with nitrogen. Also, the research was focused on: N-TiO_2 formulation as homogeneous, stable solution; depositing a high quantities of N-TiO_2 on 100% cotton knit while

preserving the genuine properties of textiles and minimize the loss of nanoparticles in wastewaters; investigation of the photocatalytic effect of N-TiO_2 deposited on textile materials under visible, UV and solar light.

2. EXPERIMENTAL PART

2.1. Materials

Chemically bleached 100% knit cotton fabric 213 g/m^2, 1.08 mm thick, TiO_2 doped with nitrogen (prepared by Kumoh National Institute of Technology, South Korea), PEG 200, PEG 20000, ethanol, ITOBINDER AG (LJ Specialities, UK), NUVA 4200 liq (Clariant), Biowet PB (nonionic tensioactive, LJ Specialities, UK), distilled water.

2.2. N-TiO_2 dispersions preparation

1N: 0.5g PEG 20000 is introduced in the mixture of 24.5mL PEG 200 and 49.5mL distilled water. The mixture is magnetically stirred at 60-65^{0}C until a clear, transparent solution is formed. The solution is cooled at 30^{0}C and 25mL ITOBINDER AG are added. 0.1g N-TiO_2 is added gradually under vigorous stirring and, the dispersion is continuously stirred for 2 hours at 25-30^{0}C. A milky white solution was obtained, which remains homogeneous after 24 hours. The so prepared solution was coded 1N. For comparison and to verify the results reproducibility, two separate 1g/L N-TiO_2 aqueous dispersions (coded **2N and 3N**) were prepared.

2.3. Method to coat the textiles with photocatalysts

N-TiO_2 was applied to cotton fabric the following pad-dry methods:

1Na: the cotton knit (16x16cmxcm) was immersed in 100mL 1N dispersion for 10 minutes and then, dried in an oven at 100^{0}C for 3 hours. The fabric remains damp and waxy.

1Nb: assuming that the solution has a relatively large amount of N-TiO_2 and to increase the ability of particles to migrate on fabrics, 50 ml of distilled water were added to 50 ml of 1Na solution remained after the first treating of the cotton knit. In this solution, a new knit (16x16cm) was introduced and treated under identical conditions as 1Na.

2N & 3N: the cotton knit (21.5x21.5cmxcm) is immersed in 1000mL solution 2N and respectively 3N, it is brought to 80^{0}C in 60min and held at this temperature on ultrasonic bath for 30 minutes. The fabric is removed from the treatment bath, immersed in 1L of 50 mL/L NUVA 4200 liq. (pH 4.5) and kept under magnetic stirring for 10 minutes at 30^{0}C. The fabric is removed from the bath and is dried in oven at 100^{0}C.

2N bis: in 2N dispersion remaining after first knit treatment, 50mL absolute ethanol, 50mL PEG 200, 10mL Biowet PB, and 50mL Itobinder AG are added. A milky white emulsion was obtained, which remains stable for 24 hours at room temperature. In so prepared solution, two pieces (16x16cm each) of white knitted cotton were immersed. The temperature was raised to 75-80^{0}C in 15 minutes and the knit was maintained under magnetic stirring at this temperature for 30 minutes. The knit was removed and dried in oven at 100^{0}C.

3N bis: the method is similar to method 2Nbis except the addditon of 50mL of water instead of ethanol and the treatment temperature which was raised to 85-95^{0}C.

2.4. Characterization

The morphology, shape, size and distribution of the nanoparticles covering the textiles were investigated by scanning electron microscopy (SEM, Quanta 200, FEI, Holland). The presence of Ti and Fe on the textiles surface was analyzed by X-ray energy dispersive spectroscopy and FTIR spectroscopy (Excalibur FTS 3000, Digilab).

To evaluate the photocatalytic effect of the materials coated with N-TiO_2, the fabrics were immersed for 30minutes in 0.0064 g/L MB aqueous solution, dried under an IR lamp and exposed to UV (254 nm) and visible light (Xenotest, 1000 W xenon arc lamp, irradiance 4.5mW/cm^2 at 300-400 nm, Heraeus Industrietechnik, Hanau, Germany). The trichromatic coordinates of the exposed and non-exposed samples were measured on Hunterlab spectrophotometer, with CIELAB 1976 color space and D65-light source.

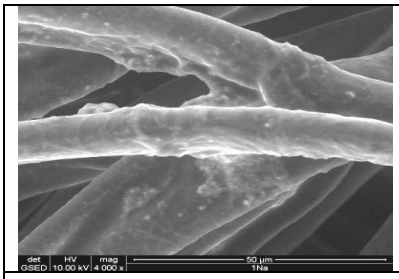
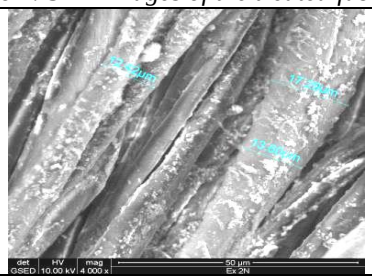
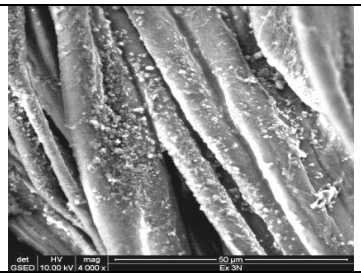
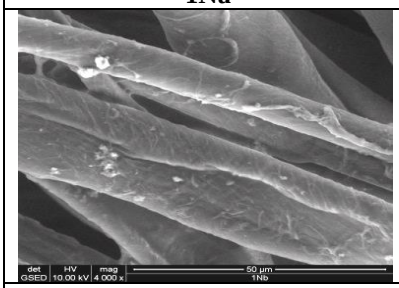
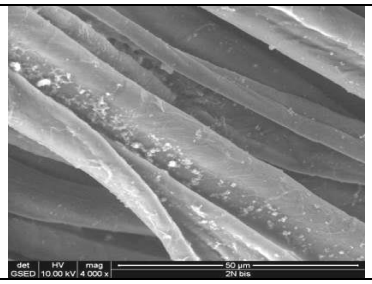
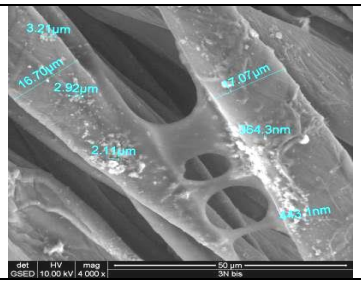
To test the particles adherence to the surface, the materials were subjected to five washing cycles under the following conditions: (5x5cmxcm) materials were washed in 100ml of distilled water containing 0.4g ECE detergent without phosphate and optical brighteners at 40^0C for 30min, then were rinsed 2 times with 100 ml water at 40^0C for 3 minutes. Washings were carried out in order to assess the adherence of N-TiO_2 particles on the fabrics surface. The remained TiO_2 particles were quantified by SEM/EDAX.

3. RESULTS

3.1. Characterization of the fabrics treated with N-TiO_2 nanoparticles by Scanning Electron Microscopy (SEM)

The SEM images of the cotton knit covered with N-TiO_2 are shown in Table 1.

***Table 1**: SEM images of the treated fabrics*

		
1Na	**2N**	**3N**
		
1Nb	**2Nbis**	**3Nbis**

Cotton fibers are coated in a polymer film, thicker for 1Na than for 1Nb fibers. Most of the particles are embedded in polymer and a small percentage in the form of relatively large agglomerations visible on fibers surface.

2N cotton fibers are coated uniformly with the N-TiO_2 particles of relatively small sizes while **2N bis** cotton fibers are enveloped in a polymer film and rare particles with different sizes (437.1nm, 804.7nm, 1.17 μm), mostly crowded, unevenly dispersed on the surface.

3N: fiber surface is covered almost entirely with particle with different sizes (the smallest being 231.8nm. 361.5nm) evenly dispersed, some of them forming small clumps.

3N bis: the deposition of the polymer and N-TiO_2 particles is demonstrated by the increased diameter (17.07- 16.70 μm) of the cotton fibers treated with 3N bis compared to the untreated fibers of 8.34- 15.17 μm. Most of the particles are deposited in the form of large clusters (364.3nm to 3.21 μm) embedded in the acrylic polymer.

3.2. EDAX elemental analysis of the fabrics treated with N-TiO_2

The energy dispersive spectroscopic (EDX) microanalysis results are shown in the Tables 2 and 3.

***Table 2**: EDAX spectra of the treated fabrics*

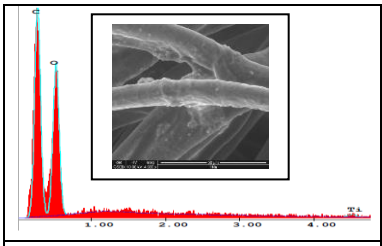
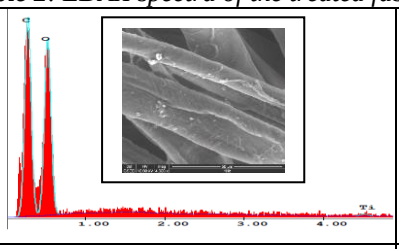
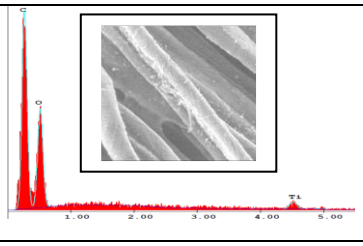
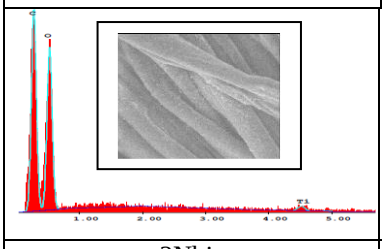
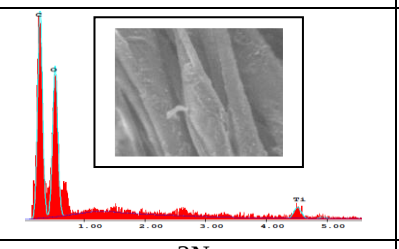
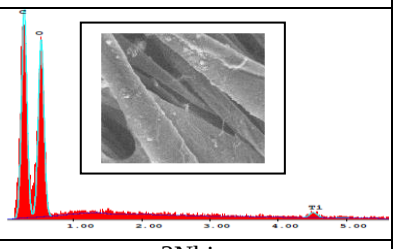
		
1Na	1Nb	2N
		
2Nbis	3N	3Nbis

***Table 3**: EDAX elemental microanalysis of N-TiO_2 deposited on knit*

Element, %Wt/ Knit	1Na	1Nb	2N	2Nbis	3N	3Nbis
C K	51.96	48.69	52.92	48.40	45.13	47.03
O K	43.96	47.58	35.39	45.18	40.89	45.92
Ti K	**4.08**	3.73	**11.69**	6.42	**13.99**	7.05

As results demonstrate the treatment with the 1Nb re-used dispersion, containing less than 0.5g/L N-TiO_2 lowers the %TiK deposited on fabric by only 8.57% compared to the treatment with 1Na dispersion containing 1 g/L N-TiO_2.

The amount of N-TiO_2 deposited on 2Nbis fabric represents more than half from the amount deposited using 2N dispersion even the TiO_2 concentration is lower than that of 2N solution due to the dilution and the use of a wetting agent (Biowet PB) which causes more intense particle wetting and cotton fabric swelling. By diluting the dispersion with ethanol and wetting agent, a higher number of particles are deposited on fabrics than by using water.

Also, the amount of TiO_2 deposited using dispersion 3Nbis represents ~ 50% of that deposited by treating the fabric with dispersion 3N and is slightly higher than that deposited by using the 2Nbis dispersion although the compositions of the 2Nbis and 3Nbis dispersions and the parameters of fabrics are basically similar. The only difference is represented by higher temperature treatment of 3Nbis fabric, which causes a more pronounced swelling of the fabric, and consequently the deposition of larger quantities of TiO_2.

The stability of aqueous N-TiO_2 dispersion is improved by addition of polyethylene glycols probably due to their absorption on particles which decreases the nanoparticles ability to agglomerate. The main disadvantage of PEG is its hydrophobicity, prolongation the time necessary for textiles drying. Also, even used in very low quantity, PEG 20000 remains on textile surface making them damp and waxy. To avoid these disadvantages, the re-used N-TiO_2 dispersions were diluted with water, organic solvents (ethanol) and wetting agents (Biowet PB). The dilution favors a better dispersion of particles which migrate much easier on the material.

Concluding, the use of a wetting agent and a higher treatment temperature favors the deposition of a higher amount of N-TiO_2 particles existing in the dispersions remained after the first treatment of the fabric.

4. CONCLUSIONS

The stability of aqueous N-TiO_2 dispersion is improved by addition of small amounts of polyethylene glycols and wetting agents. The use of a wetting agent and a higher treatment temperature favors the deposition of a higher amount of N-TiO_2 particles existing in the dispersions remained after the first treatment of the fabrics due to a better nanoparticles wetting and swelling of the cotton fabric.

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