SELF-CLEANING PROPERTIES OF COTTON GAUZES IMPREGNATED WITH CALCIUM ALGinate/TiO₂-Ag/REDUCED GRAPHENE OXIDE COMPOSITE

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Nano-modified fabrics using photocatalytic materials have a vast potential for the development of new products from self-cleaning fabrics for consumer to filter membranes for separation field and/or photocatalytic degradation of various dyes from wastewater. The aim of this study was to obtain TiO₂-Ag/reduced graphene oxide-treated cotton gauzes impregnated in calcium alginate matrix with self-cleaning properties. The morphological and structural properties of prepared materials were investigated by X-ray diffraction, FTIR spectroscopy and SEM analysis. Self-cleaning tests were performed by evaluation of the photodegradation of amaranth dye solution. Samples were exposed to sun light in March at Cluj-Napoca, Romania (latitude: 47°N; longitude: 24°E; altitude: 354 m) for 2 hours. No noticeable discoloration of dye was observed when the untreated cotton sample was used. TiO₂-Ag composite-treated cotton gauzes display self-cleaning properties. By using TiO₂-Ag/reduced graphene oxide composite, an increase in self-cleaning efficiency based on the photocatalytic amaranth degradation was obtained. The photocatalytic activity under natural environmental conditions indicates that the prepared composite has practical application to develop textile materials with self-cleaning properties.

Keywords: TiO₂-Ag/reduced graphene oxide, photocatalytic materials, amaranth degradation

INTRODUCTION

Treatment of fabrics with various additives (organic or inorganic nano-structured materials) shows a growing interest for domestic and industrial use due to self-cleaning, antimicrobial and anti-pollution characteristics (Wang *et al.*, 2014). TiO₂-based materials are a reliable choice to provide photocatalytic properties considering the special properties of TiO₂ (such as, chemical and photo stability, non-toxicity, lower cost, etc.) (Katoueizadeh *et al.*, 2017). An interesting perspective is created by using graphene derivatives for uniform coating the cotton fibers that confer them special properties, such as good electric conductivity, tensile strength, flexibility etc. As a result, smart multifunctional fabrics could appear on market making life safer, healthier, and more comfortable (Kowalczyk *et al.*, 2017; Karim *et al.*, 2017).

In this study, TiO₂-Ag and TiO₂-Ag/reduced graphene oxide (TiO₂-Ag/RGO) composites were prepared and coated over cotton gauzes specimens impregnated in calcium alginate matrix in order to develop fabrics with self-cleaning properties.

EXPERIMENTAL

Materials

Sodium alginate was purchased from Sigma Aldrich, United Kingdom, calcium chloride (CaCl₂) was obtained from Alfa Aesar, Germany. Conventional cotton gauze fabric was used. TiO₂-Ag and TiO₂-Ag/reduced graphene oxide (TiO₂-Ag/RGO) composites were prepared according to the previously described procedure (Rosu *et al.*, 2016).

Preparation of Composite-Treated Cotton Gauzes

The composite powders (TiO₂-Ag and TiO₂-Ag/RGO) were dispersed into a 2% aqueous solution of sodium alginate (8 mg/ml) and were sonicated for 15 min. The cotton gauze specimens (2cm x 3cm 6-fold 1 sheets) were impregnated with these two prepared dispersions (4 ml/each piece of cotton gauze). Thereafter, the specimens were immersed in 4% CaCl₂ aqueous solution for cross-linking and thus, obtaining insoluble Ca-alginate with TiO₂ immobilized on them. After one day, all gauze cotton specimens were removed from CaCl₂ aqueous solution and were dried at 25°C in an oven for 24 h. The resulting materials were denoted as CaAlg/TiO₂-Ag/CG and CaAlg/TiO₂-Ag/RGO/CG. A cotton gauze specimen impregnated with calcium alginate matrix without composites was prepared as control specimen (CaAlg/CG).

Characterization of Composite-Treated Cotton Gauzes

The X-ray diffraction (XRD) patterns of the specimens were measured with a BRUKER D8 Advance X-ray diffractometer using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). The functional groups of the specimens were investigated with a JASCO FTIR-6100 Instrument. The morphology of the composite-treated cotton gauzes was studied by scanning electron microscope (SEM) using an SU-8230 operated at 30 kV (Hitachi, Japan). Energy dispersive X-ray (EDX) spectroscopy was used for elemental analysis. An UV-VIS Jasco Spectrophotometer (Japan) was used for recording the absorbance spectrum of amaranth dye solutions.

Photocatalytic Experiments

The photocatalytic experiments were carried outside the laboratory based on the degradation of amaranth dye (AM) in an aqueous solution under sun light radiation. The composite-treated cotton gauzes were placed in 20 ml of $2 \times 10^{-5} \text{ M}$ amaranth aqueous solution. After irradiation of sun light at fixed intervals of time, the dye concentration was determined based on UV-VIS spectroscopy measurements and AM calibration curve ($\lambda_{\text{max}} = 520 \text{ nm}$). The AM degradation percentage was calculated as:

$$\text{degradation efficiency (\%)} = (1 - C_0/C_t) \times 100, \quad (1)$$

where C_0 and C_t are the concentrations of the dye at the initial time and at time t , respectively.

RESULTS AND DISCUSSION

The morpho-structural characterization of TiO_2 -Ag and TiO_2 -Ag/RGO composites was previously reported (Rosu *et al.*, 2016). The XRD patterns of composite-treated cotton gauzes were presented in Figure 1. X-ray diffraction studies showed the typical of cellulosic materials peaks at $2\theta = 14.8^\circ$, 16.2° , 22.5° , and 34.0° related to (101), (101), (002) and (040) reflections of cellulose I (natural cellulose) (Liu *et al.*, 2012; Mikhalovska *et al.*, 2012). The peaks at $2\theta = 25.1^\circ$, 37.5° , 47.8° , 53.8° , 54.8° correspond to crystal planes (011), (004), (020), (015), (121) of tetragonal TiO_2 anatase phase (PDF Form 99-100-9413). No TiO_2 rutile phase was detected. No typical peaks of silver were found. The broad and low intensity XRD peak of (002) reduced graphene oxide at $2\theta \approx 25^\circ$ was not observed.

Figure 1. X-ray diffraction profiles of $\text{CaAlg/TiO}_2\text{-Ag/CG}$ and $\text{CaAlg/TiO}_2\text{-Ag/RGO/CG}$

Infrared spectra of composite-treated cotton gauzes (Figure 2) are typical of natural cellulosic fibres. The main absorption bands were noted at 3400 cm^{-1} , 2900 cm^{-1} , 1650 cm^{-1} , 1151 cm^{-1} , 1100 cm^{-1} attributed to vibration of functional groups of cellulose: -OH stretching, -CH stretching, HOH bending of adsorbed water/C=O stretching, C-O-C stretching and C-O stretching (Liu *et al.*, 2012; Mikhalovska *et al.*, 2012).

Figure 2. FTIR spectra of $\text{CaAlg/TiO}_2\text{-Ag/CG}$ and $\text{CaAlg/TiO}_2\text{-Ag/RGO/CG}$

The SEM images (Figure 3) showed a surface discontinuity of cotton gauze coated with CaAlg/TiO₂-Ag. On the other hand, the treatment of cotton gauze using CaAlg/TiO₂-Ag/RGO resulted in a smoother and more homogeneous surface than that CaAlg/TiO₂-Ag-treated one suggesting a good adhesion bonding between composite and cotton fibers.

Figure 3. SEM image of composite-treated cotton gauzes

EDX analysis (Figure 4) reveals the presence of C, O, Ti, Ag, Ca and Cl elements in the CaAlg/TiO₂-Ag/RGO/CG specimen. The presence of Cl element is caused by cotton gauze immersion into CaCl₂ aqueous solution for cross-linking. The EDX mapping image of CaAlg/TiO₂-Ag/CG is not shown.

Figure 4. Elements mapping of CaAlg/TiO₂-Ag/RGO/CG specimen surface

The photocatalytic behavior of the composite-treated cotton gauzes was evaluated by photodegradation of amaranth dye solution under sun light exposure. Figure 5 shows the UV-VIS spectra of composite-treated cotton gauzes in comparison with amaranth

dye solution spectrum. The intensity of the adsorption peaks diminished in order: CaAlg/CG > CaAlg/TiO₂-Ag/CG > CaAlg/TiO₂-Ag/RGO/CG.

Figure 5. Comparative UV-VIS spectra of composite-treated cotton gauzes after 2 h of sun light exposure

As can be seen from Figure 6, the CaAlg/TiO₂-Ag/CG and CaAlg/TiO₂-Ag/RGO/CG rapidly degrade AM under sun light irradiation with a slight increasing degradation efficiency of specimens containing reduced graphene oxide.

Figure 6. Comparative degradation efficiency of composite-treated cotton gauzes after 2 h of sun light exposure

CONCLUSION

The TiO₂-Ag and TiO₂-Ag/RGO-treated cotton gauzes impregnated in calcium alginate matrix have been prepared to compare their photodegradation efficiencies. The photodegradation of amaranth dye over TiO₂-based composite treated cotton gauzes is improved under exposure of sun light. This result highlights the potential of obtained composites to use in the development of self-cleaning photocatalytic cotton fabrics. Further experimental studies will be considered in order to determine the optimum conditions for maximizing amaranth dye degradation using the TiO₂-Ag/RGO based composites.

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