The Photocatalytical Properties of RGO/TiO$_2$ Coated Fabrics

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Abstract: The aim of this work was to immobilize reduced graphene oxide (RGO) and titanium dioxide (TiO$_2$) on the surface of selected fibrous structures. Textile fabrics made of cotton (CO) and polyamide (PA) were used as a carrier. The following modification methods were applied: coating for modification of PA and dip-coating for modification of CO. In the dip-coating method, no auxiliaries were used, which is a huge advantage. The RGO/TiO$_2$ coated fabrics were characterized using several techniques: ultraviolet–visible (UV–VIS) spectroscopy, scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The obtained results showed the immobilization of RGO and TiO$_2$ on the fabrics. Raw fabrics absorb much less radiation than coated ones, which is associated with strong absorption of radiation by applied modifiers (RGO and TiO$_2$). Photocatalytic activity of functionalized textiles was determined using aqueous phenol solutions. Phenol removal efficiency obtained for RGO/TiO$_2$ coated CO and RGO/TiO$_2$ coated PA was 51% and 46%, respectively. The hydroxyl radicals play a major role in the phenol photocatalytic degradation. The phenol removal efficiency in the fifth cycle was higher (about 14% and 8% for RGO/TiO$_2$ coated CO and RGO/TiO$_2$ coated PA, respectively) compared to the first cycle.

Keywords: RGO/TiO$_2$ coated fabrics; functionalized polyamide fabric; functionalized cotton fabric; photocatalysis; photocatalytic textiles; photodegradation of phenol

1. Introduction

In recent years, surface modification, including surface modification of various textile structures, has attracted the attention of scientists. Surface modification of textiles usually leads to changes in their properties. Mention should be made of multifunctional fabrics that have electroconductive properties [1–4], antibacterial properties [5–9], self-cleaning [10], flame retardant properties [11], ultraviolet blocking properties [3,4,9] and also photocatalytic properties [5,6,12]. The development of photocatalytic textiles is mainly associated with their covering with photocatalyst coatings. Due to the immobilization of photocatalysts on a proper carrier, the problem of their removal from the reaction solution after the photocatalytic process can be solved. One of the best known and most studied photocatalysts is titanium dioxide (TiO$_2$) which is characterized by relatively low toxicity, chemical stability and low cost [13–27]. Easy and fast recombination of photogenerated electron–hole pairs and limited photoactivity in the visible light range, which leads to lower photocatalytic performance, are the disadvantages of this catalyst. To increase the photocatalytic activity of TiO$_2$, doping with
various noble metals [13–17], as well as modification with nonmetallic chemical elements [18–20], including graphene and its derivatives (graphene oxide (GO), reduced graphene oxide (RGO)), can be done [21–26]. Graphene, defined as a single layer of carbon atoms densely packed in a benzene-ring structure, has a large specific surface area, high adsorption capacity and electrical conductivity [28]. Due to its unique properties, graphene and its derivatives can act as a conductive carrier, adsorbent, photosensitizer, photostabilizer, photocatalyst and co-catalyst in nanocomposites [28]. Pedrosa et al. applied GO materials, prepared by Hummers’ and Brodie’s method, as photocatalysts for phenol degradation under UV/VIS and visible irradiation [29]. These experiments showed that GO prepared by Brodie’s method has a much higher photocatalytic activity compared to GO prepared by Hummers’ method [29]. Moreover, GO prepared by Brodie’s method is active in visible light and stable in re-use cycles [29]. Hybrid graphene/TiO$_2$ nanocomposites have been used for photodegradation of pollutants and microorganisms, for the production of hydrogen, as well as in photoanodes of dye-sensitized solar cells [13–16,18–21,23–26,30–34].

The immobilization of the photocatalyst is a widely studied process [24,31,35–41]. Lin and coworkers synthesized the TiO$_2$-RGO coated side-glowing optical fibers and applied them for photocatalytic oxidation of pharmaceuticals [24]. Analysis of UV–VIS absorption spectra of the above nanocomposites indicated that mixing RGO into TiO$_2$ particles could reduce band gap energy, thereby enhancing utilization efficiency of visible light [24]. The sandwich structured GO-based membrane intercalated by TiO$_2$ was used in nanofiltration process [31]. Such a membrane showed a high water flux and maintained high organic dye rejection (99.36% and 99.85% for methyl orange and methylene blue, respectively) [31].

Gracic et al. used four series of supported photocatalysts based on TiO$_2$-chitosan composite (with or without the addition of triarylmethane dye) for photocatalytic treatment of a model solution of bisphenol A under visible irradiation, and household greywater effluent under sunlight [42]. As a carrier for the immobilization of photocatalysts, a polyester/wool blend fabric pre-treated with atmospheric and low pressure oxygen plasma was used. The authors observed the sensitizing effect of the dye during the first 180 min of photocatalytic treatment of greywater under solar irradiation. Whereas in the case of photocatalytic degradation of bisphenol A under visible light, the addition of dye caused a lower degradation rate [42]. Karimi and co-workers applied cotton fabric coated with graphene/TiO$_2$ nanocomposite for dye photodegradation [7]. The efficiency of photodegradation of methylene blue using of the above-mentioned photoactive cellulose textiles reached over 99% and 92% under UV irradiation and sunlight, respectively [7]. In addition, the cotton-coated nanocomposite had excellent antibacterial and antifungal properties and low cytotoxicity to human fibroblasts [7]. Research conducted by Molina et al. showed that photocatalytic potential of polyester fabrics based on RGO and TiO$_2$ coatings increased with the number of RGO coatings, due to the increased light absorption and better electrical properties [6]. A similar relationship occurred in the case of photocatalytic degradation of rhodamine B by using RGO and TiO$_2$ immobilized on cotton textile—the increase in the number of applied RGO layers caused an increase in photodegradation efficiency [43]. Touhid et al. used a semi-continuous dyeing process to immobilize RGO and TiO$_2$ on polyester fabric [41]. The functionalized fabric showed antibacterial properties. Overall efficiency of TiO$_2$-RGO against Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria was 99.5 and 98.0%, respectively [41]. Cao et al. showed that the use of neoprene as a binder in the production of TiO$_2$-coated fabrics improves the rate of photodegradation of dyes by the fabrics [44]. This binder simultaneously modifies the surface of the TiO$_2$ particles with Cl and dopes TiO$_2$ with Cl. The TiO$_2$ coated fabric exhibits excellent adsorption for two cationic dyes (rhodamine B and methylene blue), while the anionic dye (methyl orange) is very weakly adsorbed on the coated fabric [44]. After 50 min of photodegradation using TiO$_2$ coated fabric, the removal efficiency for rhodamine B and methylene blue was 95.2 and 96.0%, respectively. In the case of methyl orange, the photodegradation rate reached 95.4% after 180 min [44].
good recycling properties—the performance of this fabric has not been reduced after eight cycles of photodegradation of rhodamine B [44].

This paper describes research on the immobilization of RGO and TiO$_2$ on the surface of selected fibrous structures. The following modification methods were used: coating and dip-coating. As a result of the conducted experiments, RGO/TiO$_2$ coated fabrics were obtained. The RGO/TiO$_2$ coated fabrics were characterized by UV–VIS spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Photocatalytic activity of functionalized fabrics was determined using aqueous phenol solutions.

2. Materials and Methods

2.1. Materials

GO (water-based GO solution, oxygen content 45–52%) and RGO were purchased from Łukasiewicz Research Network—Institute of Electronic Materials Technology. TiO$_2$ (Aeroxide®P25, 21 nm primary particle size), hydrochloric acid (37%), acetonitrile (hypergrade for LC-MS LiChrosolv®, Supelco), phenol (≥99.0%) and tert-butyl alcohol (t-BuOH) (≥99.7%) were from Sigma-Aldrich (Taufkirchen, Germany). Binders (Helizarin® Binder TX 4738, Helizarin® Fixing Agent TX 4737) and thickeners (Lutexal TX 4733) were purchased from BASF (Berlin, Germany).

Woven fabrics made of cotton (CO) (surface mass of 150 g·m$^{-2}$, Andropol S.A., Poland) and polyamide (PA) (surface mass of 294 g·m$^{-2}$, Pabiantex Wojtas Tomaszewski Sp. J., Poland) were used as a carrier.

2.2. Methods

The applied modification methods included coating and dip-coating. Modification of CO was made by dip-coating method using a water dispersion containing GO (5 cm$^{-3}$ water-based GO solution at the concentration of 10 g·dm$^{-3}$) and TiO$_2$ (10 g). The dispersion was acidified with hydrochloric acid (0.2 cm$^{-3}$ HCl solution with concentration of 37%), next mechanically mixed (60 min) and sonicated (60–90 min). The fabric samples were placed in the water dispersion, and then were squeezed (automatic padding machine, Ernst Benz Textilmaschinen, Rumlang-Zurich, Switzerland) at a nip pressure of 30 kg·cm$^{-2}$. Three padding cycles were applied. Then the samples were dried (20 min, 60 °C) and heated (3 h, 200 °C) in a KTF-350 S coating-heating machine (Mathis) which caused a thermal reduction of GO. The deposition of the TiO$_2$ and GO on CO by using the dip-coating method gave satisfactory results (data presented in the results and discussion), therefore the coating method was not applied for CO. As the melting point of polyamide is in the range 200–230 °C [45,46], it makes the application of the above described dip-coating method followed by thermal reduction of GO for PA modification difficult. Therefore, for modification of PA only coating method was applied.

The PA was modified by the coating method using a KTF-350 S coating-heating machine (Mathis, Oberhasli, Switzerland). The water-based paste (100 cm$^{-3}$) consisting of TiO$_2$ (5 g), RGO (0.025 g), binding agents (12 g of Helizarin® Binder TX 4738, 2 g of Helizarin® Fixing Agent TX 4737) and a thickener (5 g of Lutexal TX 4733) was used. The coated PA samples were dried (4 min, 100 °C) and heated (30 s, 160 °C) in a KTF-350 S coating-heating machine (Mathis).

XPS/AES Microlab 350 spectrometer (Thermo Electron, Waltham, MA, USA) was used to analyze the chemical composition of the surface of the obtained materials. Non-monochromated X-ray source (Al K$_a$) with excitation energy at 1486.6 eV and 300 W of power was used for XPS analysis. For determination of the chemical state of the individual elements and quantitative chemical composition, the high-resolution XPS spectra were recorded in narrow binding energy ranges with a resolution of 0.1 eV. For deconvolution of the recorded XPS spectra, an Avantage software (ver. 5.9911, Thermo Fisher Scientific, Waltham, MA, USA) was used.

SEM-EDX analyses were performed using a scanning electron microscope equipped with a BSE detector (backscattered electrons signal detection) (LEO Electron Microscopy Ltd., Cambridge, UK).
FTIR spectra were obtained using Fourier-transform infrared spectrophotometer (Jasco 4200 series) equipped with an ATR attachment (Pike Gladi ATR, Fitchburg, WI, USA). The study was carried out in the range of 400–4000 cm$^{-1}$.

UV–VIS spectra were assessed using a double beam Jasco V-550 UV/VIS spectrophotometer (Tokyo, Japan) with integrating sphere attachment in the range of 200–800 nm.

The photocatalytic efficiency of the prepared fabric-based composites was investigated by phenol degradation. The experiments were carried out in a 400 cm$^{-3}$ quartz photoreactor placed in a merry-go-round device located between UV lamps. Three UV A (11 W, Philips, Eindhoven, The Netherlands) and one UV ABC (125 W, Philips, Eindhoven, The Netherlands) lamps were used as a source of ultraviolet light. A roll of rectangular RGO/TiO$_2$ coated fabric (dimensions 14 cm $\times$ 22 cm) was immersed in a photoreactor filled with an aqueous phenol solution. The content of the photoreactor was irradiated for 6 h and 2 cm$^{-3}$ samples were taken continuously. The photolysis experiment was carried out in a similar way, but without a coated fabric placed in the photoreactor. The adsorption experiment was also carried out in the above-mentioned equipment, but without irradiation. In case of scavenger test, t-BuOH in concentration of 0.1 mol dm$^{-3}$ was added to the aqueous phenol solution. After the experiments, the coated fabrics were rinsed with demineralized water and dried at ambient temperature.

The progress of phenol degradation was monitored by liquid chromatographic analysis using a chromatograph (Nexera-I LC-2040C, 3D Plus, LCMS-8045, Shimadzu, Kyoto, Japan) equipped with a Kinetex C18 column (100 mm $\times$ 3.0 mm, 1.7 µm) (Phenomenex, Aschaffenburg, Germany). A linear H$_2$O/acetonitrile gradient (10% acetonitrile at 1 min to 100% at 4 min) was used during the analysis. The analyses were performed at a constant temperature of 30 °C. The injection volume of the samples was 20 µL. Phenol was detected at 272 nm.

### 3. Results and Discussion

#### 3.1. Physicochemical Properties of Coated Fabrics

##### 3.1.1. UV–VIS Analysis

At the beginning, the light-absorbance properties of the raw and coated fabrics were analyzed by UV–VIS spectroscopy. The results of this analysis are presented in Figure 1. It can be clearly seen that both coated and raw fabrics absorb UV–VIS radiation. Raw fabrics, however, absorb much less radiation than coated ones, which is associated with strong absorption of radiation by the applied modifiers (RGO and TiO$_2$). In general, TiO$_2$ absorbs radiation in the UV region, which can be assigned to the intrinsic band gap absorption of this photocatalyst resulting from the electron transitions from the valence band to the conduction band (O2p $\rightarrow$ Ti3d) [22]. GO absorbs the UV and VIS radiation, which leads to changing of its physicochemical properties and the toxicity [47]. GO shows characteristic absorbance peaks at 230 and 300 nm due to $\pi$-$\pi^*$ transitions of C=O and n-$\pi^*$ transitions of C=O, O–C=O and C–OH, respectively [47]. According to the studies performed by Chen et al., the transmittance of the RGO/water nanofluids is quite less than of the GO/water one, what indicate that the change from GO to RGO enhanced optical absorption [48]. UV–VIS diffuse reflectance spectra measurement performed by Landi Jr. et al. [43] showed that the addition of more RGO coatings onto the cotton fabric induce the increase of absorbance in the UV region. Moreover, the above studies confirmed the strong absorption of radiation in the visible region by RGO [43].
3.1.2. SEM-EDX Analysis

RGO/TiO$_2$ coated fabrics were examined using SEM. This analysis confirmed the immobilization of RGO/TiO$_2$ onto fabrics (Figure 2). The energy-dispersive X-ray spectroscopy (EDX) mapping showed the aggregation of TiO$_2$ (Figures 3 and 4), which is particularly evident in RGO/TiO$_2$ coated PA (Figure 4). The aggregation of TiO$_2$ nanoparticles on the RGO coatings was also noticed by Molina et al. during the modification of polyester fabrics [6]. Cai et al. observed the laminar GO layers on the SEM image of the cotton fabric treated with GO [4]. These laminar structures were also seen on the cotton fabrics surface coated with GO after thermal treatment [4]. SEM analysis performed by Zulan et al. showed that the morphology of RGO coated silk fabric was similar to the morphology of GO coated silk fabric, what suggests that the thermal GO reduction did not change the surface conformation [49]. The modification of cotton fabric by graphene and TiO$_2$ performed by Karimi et al. lead to achieving the cotton surface completely coated by graphene/TiO$_2$ nanocomposite layer [7]. The similar observation was made by Landi Jr. et al. [43].

Figure 1. Absorption spectra of raw and reduced graphene oxide (RGO)/TiO$_2$ coated fabrics.

Figure 2. Cont.
Figure 2. SEM images of (a) raw CO, (c) raw PA, (b) RGO/TiO$_2$ coated CO and (d) RGO/TiO$_2$ coated PA fibrous structures.

Figure 3. EDX mapping of RGO/TiO$_2$ coated CO ((a)- map of the C element, (b)- map of the O element, (c)- map of the Ti element).

Figure 4. Cont.
Table 1 provides the results of the EDX analysis. Raw fibrous structures consisted mainly of C, O and in the case of PA also of the N element, while coated fabrics additionally contained Ti with mass percentages of 50.27% and 72.67% (Table 1) for RGO/TiO$_2$ coated CO and RGO/TiO$_2$ coated PA, respectively.

**Table 1. Results of EDX analysis.**

| Sample                  | Mass Percentage, % | C   | O   | Ti  | N   |
|-------------------------|--------------------|-----|-----|-----|-----|
| CO                      | 46.15              | 53.85| -   | -   | -   |
| RGO/TiO$_2$ coated CO   | 19.84              | 29.88| 50.27| -   | -   |
| PA                      | 74.49              | 13.42| 0.36| 11.73|
| RGO/TiO$_2$ coated PA   | 19.96              | 7.19 | 72.67| 0.19|

3.1.3. XPS Analysis

Figures 5 and 6 show the results of the XPS analysis of RGO/TiO$_2$ coated fabrics. The XPS wide scans revealed the presence of C 1s and O 1s peaks, which are related to RGO deposits and fabrics. Whereas the presence of Ti 2p signals was associated with the TiO$_2$ nanoparticles deposits. Additionally, in case of RGO/TiO$_2$ coated PA the N 1s peak appears, what is associated with nitrogen functional groups being part of this fabric. In Figures 5b and 6b it can be observed that C 1s, O 1s and Ti 2p spectra can be deconvoluted respectively into few peaks, which correspond to characteristics bonds of analyzed materials like: C–C, C–O, C=O, C–N, C–F, Ti–O (TiO$_2$). The XPS results are summarized in Table 2, which show the most probable origin of the peaks with their binding energies and atomic percentage of each group. Our XPS results are consistent with the literature data [4,6,32]. The reduction of GO should be indicated by the decrease in oxygen to carbon (O/C) ratio of XPS spectra. Gao et al. obtained the O/C ratio equal to 0.4 and 0.59 for GO irradiated under UV and Vis light, respectively [47]. Chen et al. performed the reduction of GO under UV irradiation [48]. After irradiation of GO by UV light, they observed the decrease in area percentage of C=O group and the increase in area percentage of the C-C group [48]. The calculated O/C ratio for RGO/TiO$_2$ coated CO is higher (0.69) than O/C ratio for RGO/TiO$_2$ coated PA (0.44) which may suggest that the RGO/TiO$_2$ coated CO contains more oxygen functional groups than RGO/TiO$_2$ coated PA.
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**Figure 5.** XPS (a) and C 1s, O 1s and Ti 2p XPS (b) spectra of RGO/TiO2 coated CO.

**Table 2.** Deconvoluted XPS data of coated fabrics (A smart-type background subtraction model was used to obtain the XPS signal intensity of each individual peaks. Subsequently, an asymmetric Gaussian/Lorentzian function at a constant ratio G/L = 0.35 was used for the deconvolution procedure. All measured BEs were calibrated to the position of C 1s peak at 285.0 eV).

|                | RGO/TiO2 Coated CO | RGO/TiO2 Coated PA |
|----------------|--------------------|--------------------|
| **Name**       | **Peak BE**        | **Atomic %**       | **Bond**            |
| Ti2p3 459      | 8                  | Ti–O (TiO2)        |
| Ti2p3 461.4    | 0.3                | Ti–O (TiOx)        |
| O1s 530.3      | 18.8               | Ti–O (oxide)       |
| O1s 533.4      | 14.7               | C–O                |
| O1s 532.4      | 3.7                | C=O                |
| O1s 535.1      | 0.5                | CO ads or H2O      |
| C1s 285        | 24.9               | C–C/C–H            |
| C1s 286.8      | 22.6               | C–OH, C–O, C–N     |
| C1s 288.7      | 5.7                | O–C–O, O=C–OH      |
| C1s 282.7      | 0.9                | carbide            |
|                |                    |                    |
|                | **Name**           | **Peak BE**        | **Atomic %**       | **Bond**            |
|                | Ti2p3 458.7        | 7.9                | Ti–O (TiO2)        |
|                | Ti2p3 460.2        | 0.5                | Ti–O (TiOx)        |
|                | O1s 530            | 16.6               | Ti–O (oxide)       |
|                | O1s 531.6          | 3.5                | C=O                |

**Figure 6.** XPS (a) and C 1s, O 1s and Ti 2p XPS (b) spectra of RGO/TiO2 coated PA.
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| RGO/TiO\(_2\) Coated CO | Name | Peak BE | Atomic % | Bond               |
|--------------------------|------|---------|-----------|--------------------|
| Ti2p3                    | 459  | 8       | Ti–O (TiO\(_2\)) |
| Ti2p3                    | 461.4| 0.3     | Ti–O (TiO\(_x\)) |
| O1s                      | 530.3| 18.8    | Ti–O (oxide)    |
| O1s                      | 533.4| 14.7    | C=O            |
| O1s                      | 532.4| 3.7     | C=O            |
| O1s                      | 535.1| 0.5     | CO ads or H\(_2\)O |
| C1s                      | 285  | 24.9    | C–C/C=H        |
| C1s                      | 286.8| 22.6    | C=OH, C–O, C=N |
| C1s                      | 288.7| 5.7     | O–C–O, O=C=OH  |
| C1s                      | 282.7| 0.9     | carbide        |

| RGO/TiO\(_2\) Coated PA | Name | Peak BE | Atomic % | Bond               |
|--------------------------|------|---------|-----------|--------------------|
| Ti2p3                    | 458.7| 7.9     | Ti–O (TiO\(_2\)) |
| Ti2p3                    | 460.2| 0.5     | Ti–O (TiO\(_x\)) |
| O1s                      | 530  | 16.6    | Ti–O (oxide)    |
| O1s                      | 531.6| 3.5     | C=O            |
| O1s                      | 533  | 5.6     | C=O            |
| O1s                      | 534.2| 0.8     | CO ads or H\(_2\)O |
| C1s                      | 285  | 40.7    | C=C           |
| C1s                      | 286.6| 18.2    | C=O/C=N       |
| C1s                      | 288.4| 1.8     | C=O/C=O–F    |
| F1s                      | 689  | 0.7     | C–F           |
| N1s                      | 399.6| 3.8     | C–N           |

3.1.4. FTIR Analysis

Figure 7 presents FTIR spectra of modifiers as well as raw and coated fabrics. The FTIR spectra of raw and coated fabrics displayed a broad absorption band of around 3280 cm\(^{-1}\), which is attributed to the O–H stretching vibration of C–OH groups [4]. The presence of peaks at 1640 and at 1514 cm\(^{-1}\) is related to C=O stretching of COOH groups and C=C groups, respectively [4,43]. The broad absorption band in the range of 100–400 cm\(^{-1}\) is attributed to Ti–O and Ti–O–Ti vibrations [42,50]. In addition, for cotton fabrics there is a peak of around 1057 cm\(^{-1}\) corresponding to C–O stretching [4]. For coated fabrics, a decrease in the intensity of characteristic peaks can be observed compared to the raw fabrics. Cai et al. did not observe any significant changes in the FTIR spectrum of GO coated CO fabric. However, in the case of CO fabric coated with RGO, in the FTIR spectrum the peak related to C=O stretching was absent and the peaks associated with O–H stretching and asymmetrical C-H stretching became relatively weak [4].
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3.1.5. Photocatalytic Activity

The photocatalytic activity of RGO/TiO₂ coated fabric was evaluated for the photodegradation of phenol under UV light irradiation. Figure 8a shows the results of phenol degradation using various processes: photocatalytic degradation as well as adsorption and photolysis. In the case of RGO/TiO₂ coated CO, after 6 h of degradation process, the removal efficiency reached 4% and 51% for adsorption and photocatalysis, respectively. The application of RGO/TiO₂ coated PA leads to the phenol removal efficiency of 8% and 46% for adsorption and photocatalysis, respectively. The photolysis efficiency after the same time was 30% which indicates that this process plays an important role in phenol degradation during photocatalytic degradation using RGO/TiO₂ coated fabrics, while the adsorption process has a small effect. The studies of photocatalytic degradation of phenol under visible light irradiation and using AgBr/BiOBr/graphene as a photocatalyst showed that photolysis had no effect on phenol removal, and the adsorption process remarkably influenced degradation of this compound. In these studies, simultaneous adsorption and photocatalysis led to complete mineralization of phenol within 6 h [51].

In order to better understand the mechanism of the phenol photodegradation, the scavenger tests were performed. In these studies, the well-known hydroxyl radical scavenger—t-BuOH [52] was applied. The obtained results (Figure 8a) suggested that hydroxyl radicals (OH•) play a major role in the phenol photocatalytic degradation. The phenol removal efficiencies in the presence of t-BuOH
(about 25% and 29%, respectively for CO and PA) were slightly lower than efficiency of the photolysis process, which indicates that radicals take part in the phenol photolysis process. According to the literature, absorption of UV radiation by phenol leads to its excitation [53]. The excited state of phenol can undergo relaxation to the ground state or transformation to the phenoxy radicals and solvated electrons. Then, the phenoxy radicals can react with oxygen leading to the formation of benzoquinone. While solvated electrons can undergo a few reactions leading to the hydroxyl radicals formation, which can then react with phenol [53].

Figure 8. Phenol removal from aqueous solution by various methods (a) and multiple applications of RGO/TiO$_2$ coated fabrics (b) in photocatalytic degradation of phenol.

The disadvantage of this work is low phenol removal efficiency; therefore, our future work will be focused on the improvement and optimization of the photodegradation efficiency. The removal efficiency can be improved by the addition of a higher amount of TiO$_2$ to the dispersion or paste used in the dip-coating and coating process, respectively, which may increase the absorption of the UV light by this photocatalyst. According to the Chun et al. studies, an appropriate catalyst dosage can avoid direct photolysis of phenol and possibly other compounds, as well as increase the mineralization rate of phenol [54]. On the other hand, the amount of RGO can also influence the photodegradation. The experiments performed by Lin et al. indicated that the photocatalytic activity increased with increasing concentration of RGO in composites from 0% to 2.7%, but the degradation was inhibited when the RGO concentration was larger than 2.7% [24]. The increasing of RGO amount in the composite may be achieved by application of another GO reduction method after dip-coating process. There are several methods of GO reduction: thermal reduction applied in this and other works [4,49,55], hydrothermal [32,56], UV photoreduction [28,48,57], chemical reduction [1,6,7,43],...
Moreover, the application of GO prepared by Brodie’s method instead of the GO prepared by Hummers’ method can increase the photodegradation efficiency. According to the literature, GO prepared by Brodie’s method has a much higher photocatalytic activity compared to GO prepared by Hummers’ method.

4. Conclusions

Textile fabrics made of cotton and polyamide have been modified by RGO and TiO$_2$. The following two methods were used for modification: coating for modification of PA and dip-coating for modification of CO. In the dip-coating method, no auxiliaries were used, which is a huge advantage. The physicochemical studies (UV–VIS, SEM, XPS, FTIR) confirmed immobilization of RGO/TiO$_2$ on fibrous structures. The raw fabrics absorb much less radiation than coated ones, which is associated with strong absorption of radiation by the applied modifiers (RGO and TiO$_2$). The photocatalytic activity of functionalized textiles using aqueous solutions of phenol was determined. The 51% and 46% efficiency of phenol removal was obtained for RGO/TiO$_2$ coated CO and RGO/TiO$_2$ coated PA, respectively. The hydroxyl radicals play a major role in the phenol photocatalytic degradation. Phenol removal efficiency in the fifth cycle was higher (about 14 and 8% for RGO/TiO$_2$ coated CO and RGO/TiO$_2$ coated PA, respectively) compared to the first cycle. In summary, very promising results have been obtained, but more research is needed, particularly related to improvement of the photocatalytic efficiency.

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