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Influence of substrate on the activity of composite film of TiO_2 and chitosan for photodecolorization of a reactive dye solution

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Abstract

Reactive dyes are refractory organic pollutants that should be eliminated from colored effluents before the disposing and photocatalytic processes using TiO_2 are very studied to treatment of this type of waste. However, the investigation of the performance of this semiconductor as a composite film with chitosan to decolorization of reactive dyes was not yet performed. In this work, composite films of TiO_2 and chitosan were successfully synthesized and immobilized on glass and stainless-steel substrates by a simple molding method (drop casting). The materials were tested on decolorization of Reactive Black 5 aqueous solution (RB5) as a model organic reactive dye under UV irradiation at mild conditions. Photocatalytic process was carried out by irradiating RB5 aqueous solution (100 mg L^{-1}) with 125 W mercury vapor lamp, at 25 °C, for 2 h. Under these conditions, films presented high activity, stability and reproducibility. Their surface morphology, thermal behavior, optical properties and structure were investigated by scanning electron microscopy (SEM), TG/DTG, diffuse reflectance spectroscopy in the UV–Vis region (DRS) and absorption spectroscopy of infrared radiation (FTIR). The non-immobilized composite film was preliminarily evaluated and exhibited a good photocatalytic activity, with 98% of RB5 discoloration. Regarding the immobilized ones, the removal efficiencies ranged between 22 and 49%, depending on the used substrate. The results showed that films are well adhered on the glass, as a substrate, but on stainless steel is necessary to apply commercial primer, by a method cost-effective and easy to perform method. The catalytic film immobilized on 304 stainless-steel presented the highest discoloration result, which opens the perspective of applying this system to textile wastewater treatment by photoelectrocatalysis process, since this substrate has high electrical conductivity.

Keywords Photocatalytic treatment · Industrial waste · Titania · Films · Reactive black 5

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Introduction

Catalytic applications are highly diversified in the chemical industry, contributing significantly to processes aimed at sustainable development and environmental protection. One important aspect that should be considered on the catalytic system design is the efficiency improvement by low generation of contaminants and by-products [1–3]. Regarding the environmental impact of industrial waste, both the textile and dye manufactures have a great pollutant power arising from the quantity and recalcitrant nature of the effluents. As environmental protection becomes a global problem, new solutions emerge for the development of technologies capable to reduce this damage, such as photodegradation processes [4–10].

An improvement of the photocatalytic process may be the use of immobilized heterogeneous catalysts, which facilitate their recovery and reuse, since the non-removal of such nanoparticles in the treated wastewater may cause serious genotoxicity and cytotoxicity to aquatic and human lives [11–15]. Several photocatalysts have been studied, but undoubtedly, TiO_2 is one of the most used semiconductors for the treatment of aqueous textile wastes because it is efficient, nontoxic and it has a high specific surface area [16–21].

The immobilization of photocatalysts into a matrix to a film generation could certainly improve this process for industrial application because dismisses separation step of catalyst from the reaction medium. Moreover, the development of immobilized photocatalytic films allows the fabrication of pipes, tanks or reactors internally coated with these materials, as well as to confectioner electrodes for electrocatalytic use [15]. In this case, the effluents could be treated during flow, storage or at the reaction step.

TiO_2 pure films could be obtained by MOCVD, sol–gel dip coating, electrophoretic deposition and titanium oxidation, at controlled condition, for example, but the chosen technique depends on the substrate used and the characteristics of the final material obtained [15, 22, 23]. Other important aspect is the, and while dip coating is simple and not expensive, CVD and electrophoretic deposition could be costly. However, many authors have reported the feasibility of using inorganic catalysts blended to natural polymeric matrices, as chitosan, immobilized in different materials such as glass, activated carbon and metal substrates [15, 24–30].

Chitosan is a polymer particularly attractive to produce composite films due to its interesting properties [31, 32]. This deacetylated product from chitin is permeable and moldable, besides being obtained from waste (crustacean shells), which adds environmental interest and low cost to its qualities [33]. This material is a linear hydrophilic copolymer with large glucosamine and acetylglucosamine units. It is insoluble in water, alkaline solutions or organic solvents, nevertheless, it is diluted on organic acids, such as acetic acid, formic acid and some inorganic acids, since the free amino groups are protonated in acid medium [33, 34]. Chitosan has amino and hydroxyl groups in its polymer chain that are able to act as adsorption sites for pollutants removal or as reactive sites for several chemical processes [35]. This material can be a potential and versatile biopolymer for use in the catalyst's composition for the textile wastewater treatment, apart its contribution in the reduction of solid wastes [36].

Titania-chitosan composites have been used by several groups, with different purposes. It is possible highlight the use of this type of composites in medical implants, due to the biocompatibility of chitosan for allowing the cell proliferation on surface and improving implant fixation [37–39]. The antimicrobial and anti-fungal action of chitosan also favors its use for medical and food industry purposes and, combined with the photoactivity of titania, increases the possibility to use this system to eliminate microorganisms under radiation [37, 40–42]. Titania nanoparticle could be obtained using chitosan, as structure template, but the polymer is eliminated from the final photocatalyst [43, 44].

This organic–inorganic composite film can also be used to mitigate corrosion [45], but it is worth mentioning that the main applications of films or nanoparticles of this catalytic system is to photodecomposition of organic substances, especially pollutants [42, 46–48]. However, the performance of this catalytic composite depends on the synthesis parameters and the reaction system. In this context, different dyes could be more or less refractory to degradation, for example, methyl orange and methylene blue are entirely degraded, but reactive azo dyes used in the textile industry are more resistant and pollutant, consequently it is necessary the development of more efficient technologies to treatment of this type of waste [49–51]. In this case, the oxidative reaction condition could be severe enough to degrade the dye molecules or oxidation condition or an electrical stimulation could also be applied, typically in a photoelectrocatalysis process. Elimination of Reactive Black 5 from wastewater, specifically, could be performed by adsorption, although this strategy generates a residue loaded to the organic pollutant [52–54]. In this perspective, photocatalysts immobilized represent an environmentally friendly system to treatment of colored effluent.

Thus, the main goal of this paper is the confection of TiO_2 and chitosan films by a simple and reproductive method on three substrates for photodecolorization of Reactive Black 5 (RB5) under UV-light. The study reports the characterization and photocatalytic activity of the obtained composite films.

Experimental section

Chemicals

Reactive Black 5 dye (RB5; $C_{22}H_{21}N_5Na_4O_{19}S_6$; Yorkshire Americas) was selected as a model organic contaminant. Commercial chitosan (87.4% degree of deacetylation; POLYMAR Indústria e Comércio Ltda) and titanium dioxide P25 powder (TiO_2; 80% anatase; 20% rutile; purity greater than 99.5%; EVONIK INDUSTRIES) were selected as raw materials. Acetic acid solution (HAc) 5% (v/v) were prepared.

Substrates

Substrate is the material used for the films immobilization and its surface must be cleaned, for contaminant removal and better adhesion, before usage. Dishes made by stainless steel 304 (2.4 ohms), 316 (2.6 ohms) and glass, with 6.25 cm^2 area (25 mm × 25 mm), were the investigated substrates. Stainless steels were firstly sanding with sandpaper and then sonicated for 1 h in acetone bath, with the solvent replacement every 20 min. Then, they were dried at room temperature and weighed before coating, followed by recovering with commercial Primer, drying and weighting. The glass slides were sonicated for 20 min successively with extran solution, distilled water and ethanol and then for 1 h in acetone, changing the solvent every 20 min, to remove impurities from substrates. Finally, they were dried and weighted.

Films

The methodology for the synthesis of the films is an adaptation of works from the open literature [55]. Commercial chitosan was dissolved in 5% v/v acetic acid by stirring for 24 h, followed by dispersion of an amount of TiO_2 and stirring for 2 h. About 1 mL of this dispersion was dropped at the center of the substrate and molded to its surface. Drying was performed at room temperature (25 °C) for three days and the film as one layer was formed. The final weight ration TiO_2:chitosan was 1:1, and the total dried mass is 0.0140 g.

Characterization

The surface morphology of the composite films was analyzed by scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) using JEOL, JSM-6510LV. Thermogravimetric analysis (TG/DTG) and differential scanning calorimetry (DSC) were used to analyze the thermal behavior of the materials. The curves were performed on a simultaneous TA model instrument SDT 600 and obtained from approximately 12 mg of sample by subjecting them to a temperature range of 20–800 °C under synthetic air atmosphere (20 mL min^{-1}) and heating rate of 10 °C min^{-1}. Diffuse reflectance spectroscopy in the UV–Vis region (DRS) was used to investigate the optical properties of the films in different proportions, using a spectrophotometer UV-2600, from Shimadzu. FTIR ATR spectra were obtained in the wavelength range from 4000 to 650 cm^{-1} during 16 scans, with a resolution of 2 cm^{-1} (Shimadzu Iraffinity-1). FTIR spectra with the pellet samples were obtained in the wavelength range of 4000 to 500 cm^{-1} during 16 scans (Nicolet6700-FTIR).

Photocatalytic tests

Photocatalytic activity of the composite films was performed in a batch reactor using 50 mL of RB5 aqueous solution (100 mg L^{-1}), at 25 °C, aeration of

200 mL min^{-1} and UV irradiation by a 125 W mercury vapor lamp (Osram), 13 cm above the solution level, inside a dark chamber, as shown schematically in Fig. 1S.

The catalytic tests with the films on the substrates were performed with them completely immersed in the solution and fixed with a connection, to stay in a normal position related to the surface of the solution. Preliminary test with non-immobilized film was also carried out.

The concentration of RB5 was measured by absorbance of the solution at the maximum wavelength, using a UV–Vis Spectrophotometer (DR/5000, HACH). The discoloration percentage (% D) was evaluated by Eq. 1.

$$\%\mathrm{D} = \frac{\mathrm{Abs}_0 - \mathrm{Abs}_t}{\mathrm{Abs}_0} \times 100, \tag{1}$$

where Abs_o and Abs_t are the absorbance of the dye solution, at 597 nm, before and after the photochemical treatment.

The total organic carbon (TOC) of the samples after 2 h of reaction was determined using a Shimadzu TOC-L CSN apparatus.

Results and discussion

Materials characterization

The thermal stability of the composite film was evaluated by TG experiments and compared to the weight lost events of chitosan and titania individually. The obtained thermogravimetric curves are presented in Fig. 1.

It is verified that pure titania practically does not suffer loss of mass in the temperature range investigated, while the materials containing chitosan decompose when the temperature is high, which is expected to an organic material.

The pure chitosan film (QTF) presents three stages of decomposition. With titania incorporation, the decomposition temperature decreases, so it is possible that titania promoted the decomposition of chitosan. The final weight loss was 50%, as expected if the organic material was almost completely decomposed, because the ratio 1:1 was used, and thermal stability was achieved around 530 °C. The first weight loss is due to dehydration, then, this result indicated that it is possible to heat the films at a temperature up to 200 °C.

The UV–Vis diffuse reflectance spectroscopy technique was used to investigate the optical properties of TiO_2 and composite film. The spectra of the materials are characterized by a broadband between 200 and 350 nm (Fig. 2), typical of TiO_2-based materials and corresponds to the electron transition of the O^{2-}antiligant (valence band) 2p orbitals to the Ti^{4+} low energy empty 3d orbital (conduction band).

The obtained values of E_g (Fig. 2b) show a slight decrease in the E_g value of the film related to pure titania. This decrease should occur due to the irregular surface of the composite film, that act as traps and is able to form localized energy states in

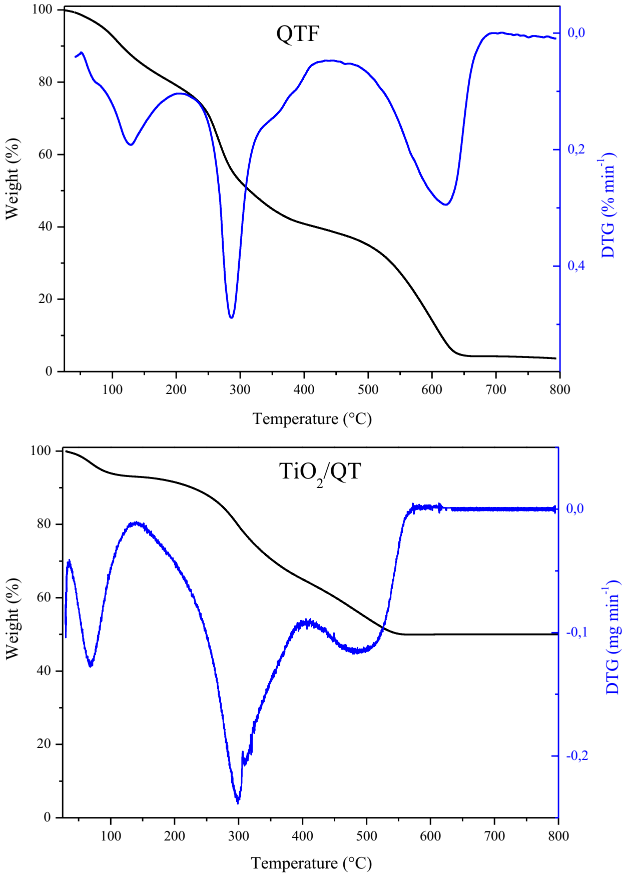

Fig. 1 TG/DTG curves of chitosan film (QTF) and TiO_2 chitosan film, under 20 mL min^{-1} of synthetic air and heating rate of 10 °C

the forbidden band, where the electrons of band valence can be excised by the UV incident radiation, as observed for nanoparticles [56].

Fig. 3 shows the SEM images and EDS results of the two stainless steel substrates used and commercial chitosan powder surface. Both substrates were polished before the film immobilization and the images indicate that the surfaces are smooth but present some grooves. Commercial chitosan powder surface reveals irregular shape and size, with pores.

Table 1 highlights the elements percentage of the two stainless steel substrates used and commercial chitosan. As expected, the iron content is high for both substrates. The absence of carbon indicates that they can be classified as low carbon content steel. The small oxygen percentage is natural, since the samples are exposed to the air. Although traces of molybdenum in 304 stainless steel are detected, the elements atomic percentages of both steels are consistent with the Brazilian Association of Technical Standards (Associação Brasileira de Normas Técnicas, ABNT).

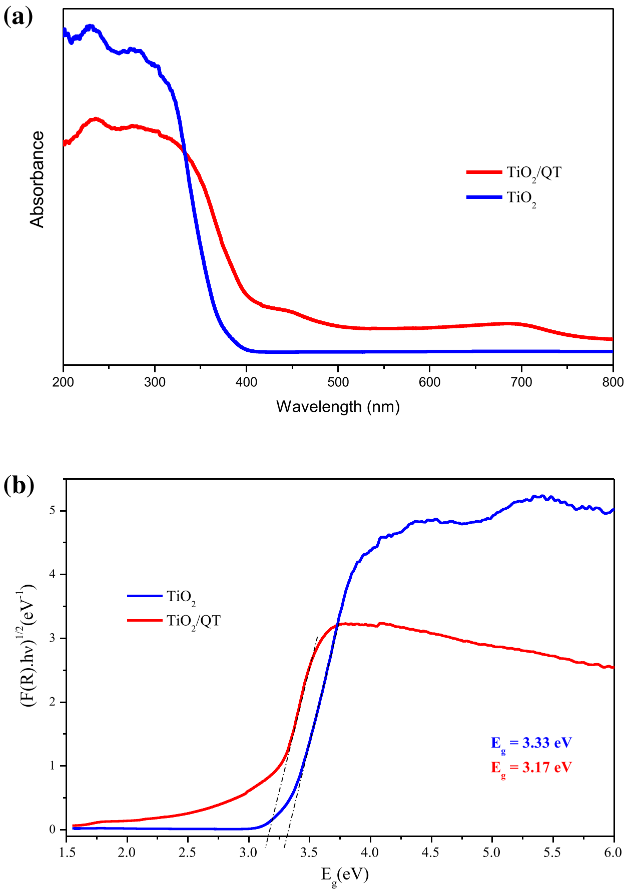

Fig. 2 **a** UV–Vis absorbance spectra of composite film and pure titania; **b** graph of $[(F(R_\infty)h\nu)]^{1/2}$ vs hν of composite film and pure titania for band gap (E_g) determination

Chitosan EDS analysis (Table 1) indicates the major presence of carbon, oxygen and nitrogen, as expected for polysaccharide, whose general chemical formulae is $[C_xH_yO_zN_w]_n$. The presence of trace elements is due to the chitosan source and the method used to obtain it. In general, demineralization is performed by treatment with HCl solution and its efficiency depends on the reaction parameters used.

SEM micrograph of immobilized films showed homogeneous surfaces and the thickness are about 400 µm. EDS results indicates that titanium is homogeneously distributed through the films, as titania particles.

Fourier Transform Infrared spectroscopy (FTIR) for the chitosan film was performed by ATR mode and the spectrum is shown in Fig. 4. The bands observed in the chitosan film spectrum are close to those of the powder sample. For this film, two bands corresponding to the deformation vibrations of the typical amine groups at 1637 cm^{-1} and 1562 cm^{-1} can be observed. The characteristic stretch

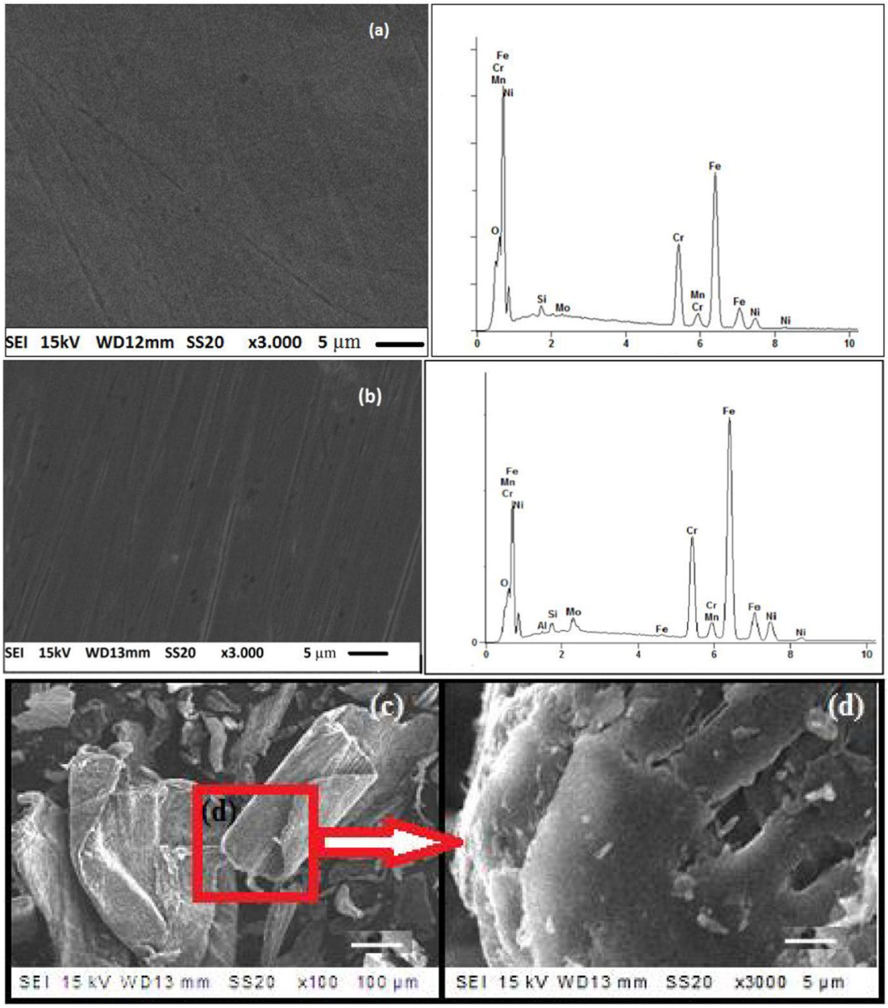

Fig. 3 SEM images (left) and EDS results (right) of: **a** 304 stainless-steel substrate and **b** 316 stainless-steel substrate. SEM images of: **c** commercial chitosan surfaces micrograph; and **d** amplification of the detached part

band of the amide C=O bond is observed at approximately 1409 cm^{-1}. This band is inherent to acetamide groups from chitin, since commercial chitosan, obtained by deacetylation of chitin, does not have a 100% deacetylation. Bands found at 1383 and 1317 cm^{-1} correspond to the angular deformation of the C-H present in the glycosidic ring. The asymmetric stretch band due to the β (1–4) glycosidic bond in the polymer chain occurs at 1155 cm^{-1} [55, 57].

Table 1 Elementary compositions indicated by EDS

316		304		QT	
Element	at.%	Element	at.%	Element	at.%
O K	5.90	O K	7.31	C	10.09
Al K	0.18			N	7.59
Si K	1.44	Si K	1.21	O	77.99
Cr K	19.06	Cr K	19.93	Na	1.43
Mn K	1.43	Mn K	1.50	Mg	0.63
Fe K	62.74	Fe K	63.55	Al	0.99
Ni K	7.93	Ni K	6.31	Si	0.22
Mo L	1.32	Mo L	0.18	Cl	0.19
				Ca	0.14
				Cu	0.42
				Zn	0.30

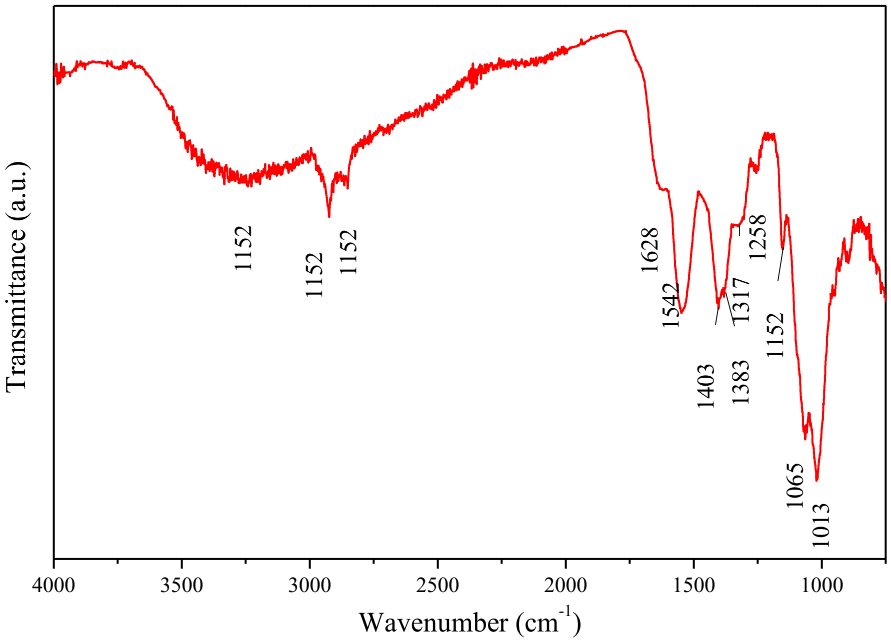

Fig. 4 Chitosan film FTIR ATR spectrum

Preliminary studies on model dye degradation

A 5% acetic acid solution (HAc) promoted a good dispersion of titanium dioxide, under the conditions used. The first probing test performed was to obtain a film of the Chitosan-Titania composite (TiO_2/QT), with enough mass to be tested, without being immobilized in the substrate. It was obtained by using 5 mL of the

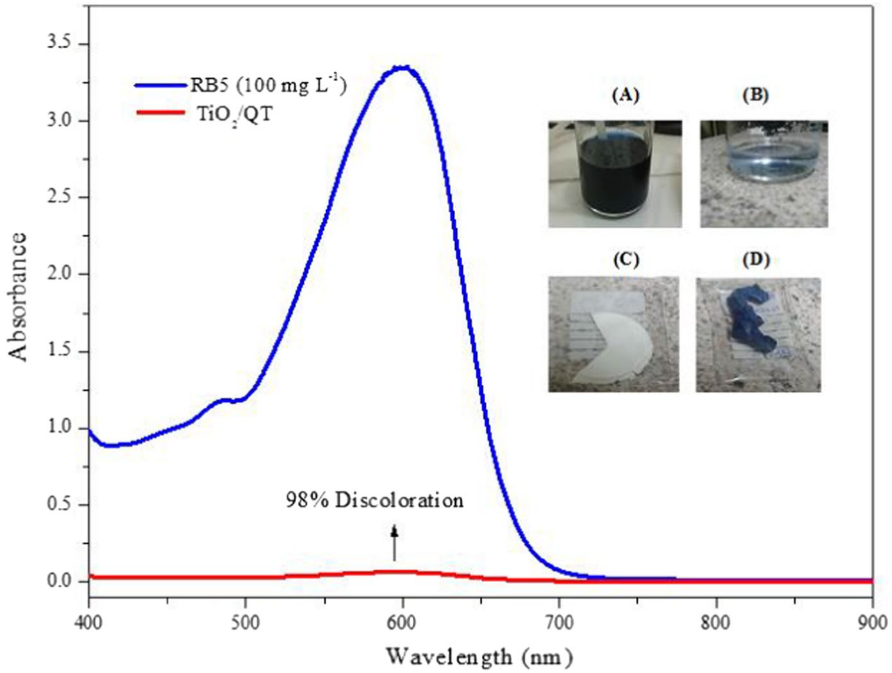

Fig. 5 RB5 solution absorbance before and after the photocatalytic test at 25 °C for 2 h under UV and aeration (200 mL min^{-1}) with the non-immobilized composite film: **a** Dye solution appearance before the reaction; **b** after the reaction; **c** a part (3/4) of Titania-Chitosan (TiO_2/QT) non-immobilized composite film before the test; **d** 1/3 of TiO_2/QT after the test

Chitosan suspension—5% HAc—Titania in a small previously cleaned petri dish, as described in the methodology, and dried at ambient air for 5 days. After all solvent evaporation, one uniform composite film was formed, resistant and malleable, whose total mass was 145.9 mg (Fig. 5c).

About 1/3 of this film was tested in the PC system, in a proportion of 25 mg of titania to 50 mL of the dye solution. Fig. 5 shows the film before (c) and after (d) the photocatalytic test. Clearly, part of the dye was adsorbed in the composite film, since it turned blue. The composite film also presented physical stability, not being dissolved in the performed condition. It is noteworthy that a few days after the catalytic test, the blue film coloration intensity decreased, showing that the titania present in the film maintained its activity in removing the color of the adsorbed dye, even into dry medium. It is worth mentioning that the RB5 photolysis test under UV–Vis light demonstrated no visible decolorization after 2 h of reaction in absence of catalyst.

Fig. 5 shows RB5 solution spectrophotometric profile before and after the test, in the range of 400 to 900 nm, highlighting the percentage of discoloration obtained and the appearance of the dye solution before (Fig. 5a) and after (Fig. 5b) 2 h of reaction. Clearly there was an accentuated discoloration, a result that corresponds to 98% of color removal in relation to the original solution.

This result indicates that titania is photocatalytically active to decolorate RG5 dye even into a composite film. Chitosan associated to TiO_2 has been exhibited some interesting characteristics, as capacity to decompose ethylene photocatalytic and antimicrobial activity against bacteria and fungi [42], UV protection and antimicrobial activity of cotton fabric [58] and as component of a Biosensor for Phenolic Compounds [59], but there are no studies to decolorate refractory reactive dyes. Consequently, this first investigation is relevant to the development of technologies to textile waste treatment.

The used film was analyzed by FTIR and UV–Vis, but the dye remained absorbs radiation strongly in both of spectra, and its bands are dominant.

The result of TOC of the RB5 solution indicated a carbon content of 27 ppm, but after 2 h of discoloration, this value raised to 193 ppm. This observation is compatible to a partial dissolution or leaching of the chitosan, but after drying, the used film has presented no significant weight loss (less than 5%). As the film proved to be highly active in the reaction medium, the composite was immobilized on the glass and steel substrates to investigate the influence of this parameter on the film performance. About 1 mL of the titania-chitosan dispersion was used, which represented approximately 0.014 g of composite film.

Photocatalytic activity of immobilized composite films

The syntheses of the composites and the immobilized films were reproducible and presented a good adherence. Adhesion on the glass substrate was high, but the adhesion of the film to the stainless-steel substrates was only possible with the prior application of a commercial primer coat on its surface. Primer, normally used as background paint, is responsible for the anticorrosion protection and adherence of the paint system to the metallic substrate, for this reason this substance was chosen and applied before application of the films on both stainless-steel [60].

The adhesion of the three films was very good and they remained adhered to the three substrates after the 2 h of the catalytic test. Jbeli et al. studied films of chitosan, TiO_2 and ZnO coated on glass substrates for photodegradation of some organic compounds [46]. Their materials presented high activity to aromatic amines and carboxylic acids, and the films were stable, in agreement with our observation to this substrate, despite the difference between the used methodologies. Thin films based on titania and silver were immobilized on carbon steel using chitosan as template, for corrosion mitigation in HCl, with good adhesion without primer, but carbon steel has a higher roughness than steel-stainless, that favor the linkage [45].

The obtained composite films presented good activity, so that on steel 316 promoted a discoloration of 33%, while with the film on steel 304 the result was 49% and on glass is 25%. These results are shown in Fig. 6.

Apparently, the film deposited on steels were more active than on glass, and both presented stability during all photocatalytic reaction time. Commercial primer presents titania in its formulation and therefore could contribute to the increase of the activity of the films immobilized on steels. However, a blank experiment of photolysis performed in absence of catalyst generated the same low discoloration that reaction over substrate

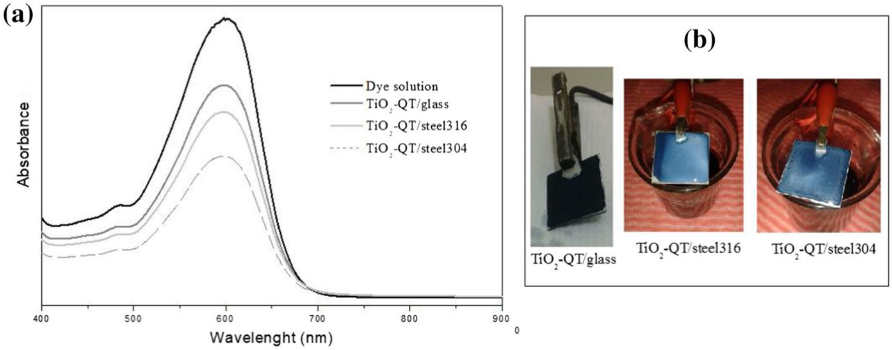

Fig. 6 Absorbance of the reaction media before and after the photocatalytic test at 25 °C for 2 h under UV and aeration (200 mL min^{-1}) with the composite film immobilized on the three substrates (**a**) and the used films (**b**)

covered by primer, less than 2% and could not be responsible for these high activities. This behavior is probably related to electronic effects between the metallic substrate and the composite film at the reaction condition.

The TOC results of these samples after 2 h of reaction presented a carbon content about 30 ppm, which means 10% more carbon than the initial carbon concentration. This behavior indicates that probably the films were partially solubilized into the reaction medium, nevertheless, the immobilization on the substrates increased its stabilization, once the sample obtained after catalytic test with the non-immobilized film have increased more the carbon amount of the reaction medium. However, the films have remained linked to the substrates, with weight loss less than 1% after drying at 80 °C, and this partial dissolution of chitosan do not increase the toxicity of the waste, once this organic matter could be edible. Unfortunately, as the films were partially dissolved, it was not possible evaluate if the discoloration was associated to mineralization but making textile effluents colorless is an important step of treatment.

The adsorption experiment was performed with the pure chitosan film on steel 304, presenting 34% of discoloration and TOC of 42 ppm. This behavior demonstrates the high adsorption capacity of chitosan, as observed by other works [53, 54], and the partial dissolution of the biopolymer, due the increase of carbon amount. Consequently, a fraction of discoloration capacity of the composite films could be attributed to adsorption, but titania plays an important role in the performance of photocatalysts, increasing the remotion of color and decreasing the chitosan dissolution.

The confection of the specimens is reproductible, once several samples with the same film were obtained and presented similar performance.

Conclusion

TiO_2/QT composite films have been successfully obtained from the use of acetic acid solution as a solvent and have exhibited good adhesion when immobilized by the proposed methodology, allowing them to be easily removed from reaction medium.

Preliminary study figured that discoloration could reach 98% after 2 h reaction with 0.0546 g of TiO_2/QT non-immobilized film, a relevant result to technological development of efficient treatment of textile wastewater rich in recalcitrant dyes as RB5.

Regarding the film immobilized on glass, about 0.0140 g promoted around 25% of the dye discoloration, while on stainless steel, there was a limitation on the attraction force between the composite and the metal surface, requiring an application of a commercial primer coat to improve adhesion. In this case, the same amount of immobilized film on 316 and 304 stainless steel achieved 33 and 49% of discoloration, respectively.

The discoloration of composite films could be attributed partially to adsorption on chitosan, but titania increases their performance under UV radiation. The biopolymer was partially dissolved in the reaction medium, that is acid, but both immobilization on substrates and titania decrease this phenomenon.

The methodology used to obtain TiO_2/QT composite films is cost-effective and easy to make, moreover, the immobilization on substrates produces a way to use a photocatalyst without necessity to separation. Using steel as substrate open the possibility to apply the film in a photoelectrocatalysis process, since this material is a good electrical conductor, and the electrical stimulation could increase the catalyst activity of titania.

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References

1. Sheldon RA (2012) Fundamentals of green chemistry: efficiency in reaction design. Chem Soc Rev 41:1437–1451
2. Anastas PT, Warner J (1998) Green chemistry: theory and practice. Oxford University Press, Oxford
3. Guan Q, Jiang M, Wu J, Zhai Y, Wu Y, Bao K, Zhang W (2016) Direct cycle between co-product and reactant: an approach to improve the atom economy and its application in the synthesis and protection of primary amines. Green Chem 18:5794–5799
4. Verma AK, Dash RR, Bhunia P (2011) A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J Environ Manage 93:154–168
5. Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM (2016) A critical review on textile wastewater treatments: possible approaches. J Environ Manage 182:351–366
6. Bilal M, Asgher M, Iqbal M, Hua H, Zhang X (2016) Chitosan beads immobilized manganese peroxidase catalytic potential for detoxification and decolorization of textile effluent. Int J Biol Macromol 89:181–189

7. Su CX, Low LW, Teng TT, Wong YS (2016) Combination and hybridization of treatments in dye wastewater treatment: a review. J Environ Chem Eng 4:3618–3631
8. Yaseen DA, Scholz M (2019) Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. Int J Environ Sci Technol 16:1193–1226
9. Abdi J, Yahyanezhad M, Sakhaie S, Vossoughi M, Alemzadeh I (2019) Synthesis of porous TiO_2/ZrO_2 photocatalyst derived from zirconium metal organic framework for degradation of organic pollutants under visible light irradiation. J Environ Chem Eng 7:103096
10. Answer H, Mahmood A, Lee J, Kim K-H, Park J-W, Yip ACK (2019) Photocatalysts for degradation of dyes in industrial effluents: opportunities and challenges. Nano Res 12:955–972
11. Srikanth B, Goutham R, Narayan RB, Ramprasath A, Gopinah KP, Sankaranarayanan AR (2017) Recent advancements in supporting materials for immobilized photocatalytic applications in wastewater treatment. J Environ Manage 200:60–78
12. Das S, Mahalingam H (2020) Novel immobilized ternary photocatalytic polymer film based airlift reactor for efficient degradation of complex phthalocyanine dye wastewater. J Hazard Mater 383:121219
13. Srikantha B, Gouthama R, Narayana RB, Ramprasatha A, Gopinatha KP, Sankaranarayanan AR (2017) Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment. J Environ Manage 200:60–78
14. Das TK, Ganguly S, Ghosh S, Remanan S, Ghosh SK, Das NC (2019) In-situ synthesis of magnetic nanoparticle immobilized heterogeneous catalyst through mussel mimetic approach for the efficient removal of water pollutants. Colloid Int Sci Commun 33:100218
15. Alhaji MH, Sanaullah K, Khan A, Hamza A, Muhammad A, Ishola MS, Rigit ARH, Bhawani SA (2017) Recent developments in immobilizing titanium dioxide on supports for degradation of organic pollutants in wastewater—a review. Int J Environ Sci Technol 14:2039–2052
16. Bouarioua A, Zerdaoui M (2017) Photocatalytic activities of TiO_2 layers immobilized on glass substrates by dip-coating technique toward the decolorization of methyl orange as a model organic pollutant. J Environ Chem Eng 5:1565–1574
17. Baccaro ALB, Cordon LD, Nishimura FG, Gutz IGR (2019) Fotocatálise mediada por TiO_2 no estado nanoparticulado: revisão da reatividade pelo conceito de traps e algumas aplicações em química analítica. Quim Nova 42:329–345
18. Al-Mamuna MR, Kader S, Islam MS, Khan MZH (2019) Photocatalytic activity improvement and application of UV-TiO_2 photocatalysis in textile wastewater treatment: a review. J Environ Chem Eng 7:103248
19. Jamila A, Bokharia TH, Javed T, Mustafa R, Sajid M, Noreene S, Zuber M, Nazir A, Iqbal M, Jilani MI (2020) Photocatalytic degradation of disperse dye Violet-26 using TiO_2 and ZnO nanomaterials and process variable optimization. J Mater Res Technol 9:1119–1128
20. Talaiekhozani A, Mosayebi MR, Fulazzaky MA, Eskandari Z, Sanayeee R (2020) Combination of TiO_2 microreactor and electroflotation for organic pollutant removal from textile dyeing industry wastewater. Alexandria Eng J 59:549–563
21. Singh J, Kumar S, Manna AK, Soni RK (2020) Fabrication of ZnO–TiO_2 nanohybrids for rapid sunlight driven photodegradation of textile dyes and antibiotic residue molecules. Opt Mater 107:110138
22. Lozano NM, Castro MA, Ramírez AM, Muñoz EMR, Castillo RV, González CA, Antuñano MZ (2020) Morphological study of TiO_2 thin films doped with cobalt by metal organic chemical vapor deposition. Results Phys 16(102891):1–5
23. Cui X, Kim H-M, Kawashita M, Wang L, Xiong T, Kokubo T, Nakamura T (2009) Preparation of bioactive titania films on titanium metal via anodic oxidation. Dent Mater 25:80–86
24. Zhai Y, Feng W, Wang Q, Ning X (2014) Study of properties and synthesis of sulfonated coal supported nanostructure TiO_2 photocatalyst. Catal Commun 58:103–107
25. Lucas MS, Tavares PB, Peres JA, Faria JL, Rocha M, Pereira C, Freire C (2012) Photocatalytic degradation of Reactive Black 5 with TiO_2-coated magnetic nanoparticle. Catal Today 209:116–121
26. Nawi MA, Sabar S, Jawad AH, Sheilatina W-N (2010) Adsorption of Reactive red 4 by immobilized chitosan on glass plates: toward the design of immobilized TiO_2-chitosan synergistic photocatalyst-adsorption bilayer system. Biochem Eng J 49:317–325
27. Wu C, Lee Y, Lo T, Lin C, Wu C (2013) Thickness-dependent photocatalytic performance of nanocrystalline TiO_2 thin films prepared by sol-gel spin coating. Appl Surf Sci 208:737–744
28. Hardy JJE, Hubert S, Macquarrie DJ, Wilson AJ (2004) Chitosan-based heterogeneous catalysts for Suzuki and Heck reactions. Green Chem 6:53–56

29. El-banna FS, Mahfouz ME, Leporatti S, El-Kemary M, Hanafy NAN (2019) Chitosan as a natural copolymer with unique properties for the development of hydrogels. Appl Sci 9:2193
30. Pokhrel S, Yadav PN (2019) Functionalization of chitosan polymer and their applications. J Macromol Sci Part A 56:450–475
31. Verma ML, Kumar S, Das A, Randhawa JS, Chamundeeswari M (2020) Chitin and chitosan-based support materials for enzyme immobilization and biotechnological applications. Environ Chem Lett 18:315–323
32. Olivera S, Muralidhara HB, Venkatesh K, Guna VK, Gopalakrishna K, Kumar KY (2016) Potential applications of cellulose and chitosan nanoparticles/composites in wastewater treatment: a review. Carbohydr Polym 153:600–618
33. Renault F, Sancey B, Badot PM, Crini BG (2008) Chitosan for coagulation/flocculation processes—an eco-friendly approach. Eur Polym J 45:1337–1348
34. Szygula A, Guibal E, Palacín MA, Ruiz M, Sastre AM (2009) Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan. J Environ Manage 90:2279–2286
35. Nawi MA, Sabar S, Jawad AH, Sheilatina W-N (2011) Immobilized bilayer TiO_2/chitosan system for the removal of phenol under irradiation by a 45 watt compact fluorescent lamp. Desalination 280:288–296
36. Etshindo LA, Martinhon PT, Rocha AS, Araujo LRR, Silva CRS (2018) Potencialidades e uso da quitosana no tratamento de rejeitos têxteis. Braz App Sci Rev 2:2010–2020
37. Benea L, Celis JP (2018) Reactivity of porous titanium oxide film and chitosan layer electrochemically formed on Ti-6Al-4V alloy in biological solution. Surf Coat Technol 354:145–152
38. Shukla SK, Mishra AK, Arotiba OA, Mamba BB (2013) Chitosan-based nanomaterials: a state-of-the-art review. Int J Biol Macromol 59:46–58
39. Mohan I, Anandan C, Rajendran N (2015) Electrochemical behaviour and bioactivity of self-organized TiO_2 nanotube arrays on Ti-6Al-4V in Hanks' solution for biomedical applications. Electrochim Acta 155:411–420
40. Qian T, Su H, Tan T (2011) The bactericidal and mildew-proof activity of a TiO_2–chitosan composite. J Photochem Photobiol A Chem 218:130–136
41. Wei X, Li Q, Hao H, Yang H, Li Y, Sun T (2020) Li X (2020) Preparation, physicochemical and preservation properties of Ti/ZnO/in situ SiOx chitosan composite coatings. J Sci Food Agric 100:570–577
42. Siripatrawan U, Kaewklin P (2018) Fabrication and characterization of chitosan-titanium dioxide nanocomposite film as ethylene scavenging and antimicrobial active food packaging. Food Hydrocolloids 84:125–134
43. Hamden Z, Bouattour S, Ferraria AM, Ferreira DP, Ferreira LFV, Do Rego AMB, Boufi S (2016) In situ generation of TiO_2 nanoparticles using chitosan as a template and their photocatalytic activity. J Photochem Photobiol A 321:211–222
44. Joshi MM, Labhsetwar NK, Mangrulkar PA, Tijare SN, Kamble SP, Rayalu SS (2009) Visible light induced photoreduction of methyl orange by N-doped mesoporous titania. Appl Catal A Gen 357:26–33
45. El-Katori EE, Al Angari YM, Abousalem AS (2019) Corrosion mitigation of carbon steel by spin coating with Ag–TiO_2 gel films in acidic solution: fabrication, characterization, electrochemical and quantum chemical approaches. Surf Coat Technol 374:852–867
46. Jbeli A, Ferraria AM, do Rego AMB, Boufi S, Bouattour S (2018) Hybrid chitosan-TiO2/ZnS prepared under mild conditions with visible-light driven photocatalytic activity. Int J Biol Macromol 116:1098–1104
47. Wu S, Kan J, Dai X, Shen X, Zhang K, Zhu M (2017) Ternary carboxymethyl chitosan-hemicellulose-nanosized TiO_2 composite as effective adsorbent for removal of heavy metal contaminants from water. Fibers Polym 18:22–32
48. Miller SM, Zimmerman JB (2010) Novel, bio-based, photoactive arsenic sorbent: TiO_2-impregnated chitosan bead. Water Res 44:5722–5729
49. Norranattrakul P, Siralertmukul K, Nuisin R (2013) Fabrication of chitosan/titanium dioxide composites film for the photocatalytic degradation of dye. J Met Mater Min 23:9–22
50. Dhanya A, Aparana K (2016) Synthesis and evaluation of TiO_2/chitosan based hydrogel for the adsorptional photocatalytic degradation of Azo and Anthraquinone dye under UV light irradiation. Procedia Technol 24:611–618

51. Zhu H, Jiang R, Fu Y, Guan Y, Yao J, Xiao L, Zeng GE (2012) Effective photocatalytic decolorization of methyl orange utilizing TiO_2/ZnO/chitosan nanocomposite films under simulated solar irradiation. Desalination 286:41–48
52. Shaheed MA, Hussein FH (2014) Adsorption of Reactive Black 5 on synthesized titanium dioxide nanoparticles: equilibrium isotherm and kinetic studies. J Nanomater. https://doi.org/10.1155/2014/198561
53. Dotto GL, Ocampo-Pérez R, Moura JM, Cadaval TRS Jr, Pinto LAA (2016) Adsorption rate of Reactive Black 5 on chitosan based materials: geometry and swelling effects. Adsorption 22:973–983
54. Eren Z, Acar FN (2006) Adsorption of Reactive Black 5 from an aqueous solution: equilibrium and kinetic studies. Desalination 194:1–10
55. Dinga W, Lian Q, Samuel RJ, Polka MB (2003) Synthesis and characterization of a novel derivative of chitosan. Polymer 44:547–556
56. Yoshihara T, Katoh R, Furube A, Tamaki Y, Murai M, Hara K, Murata S, Arakawa H, Tachiya M (2004) Identification of reactive species in photoexcited nanocrystalline TiO_2 films by wide-wavelength-range (400–2500 nm) transient absorption spectroscopy. J Phys Chem B 108:3817–3823
57. Brugnerotto J, Lizardi J, Goycoolea FM, Argüelles-Monal W, Desbrières J, Rinaudo M (2001) An infrared investigation in relation with chitin and chitosan characterization. Polymer 42:3569–3580
58. Goyal N, Rastogi D, Jassal M, Agrawal AK (2016) Chitosan as a potential stabilizing agent for titania nanoparticle dispersions for preparation of multifunctional cotton fabric. Carbohydr Polym 154:167–175
59. Laranjo MT, Morawski FM, Dias SLP, Benvenutti EV, Arenas LT, Costa TMH (2019) Silica/titania graphite composite modified with chitosan and tyrosinase employed as a sensitive biosensor for phenolic compounds. J Braz Chem Soc 30:2660–2671
60. Josua YD, Damron M, Tang G, Zheng H, Chu C-J, Osborne JH (2001) Inorganic/organic hybrid coatings for aircraft aluminum alloy substrates. Prog Org Coat 41:226–232

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