

Duplo Benefício Ambiental pela Remoção de Corantes Fotosensibilizadores da Água com Uso de Resíduo Sólido Particulado

Double Environmental Benefit by the Removal of Photosensitizing Dyes from the Water Using Particulate Solid Waste

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RESUMO

As indústrias têxteis estão entre os setores mais poluidores do mundo, principalmente pelo descarte de resíduos de corantes sintéticos nos efluentes. Alguns processos têm sido utilizados atualmente para a remoção de corantes dos efluentes, mas apresentam as desvantagens de baixa viabilidade econômica e dificuldade de reprodução em larga escala. Em paralelo, o descarte e a degradação de resíduos sólidos também constituem sérios problemas ambientais que colocam desafios às estratégias de reciclagem e degradação. O presente estudo descreve um eficiente mecanismo de remoção e degradação de corantes de efluentes com o uso de resíduos sólidos particulados. A justificativa desse processo é o uso de resíduo particulado sólido para adsorver corantes dissolvidos em água, tornando ambos os adsorventes e resíduos adsorvidos mais suscetíveis à fotodegradação. No presente estudo: uma porfirina sintética aniônica TPPS4 (meso-tetrakis (4-sulfonatofenil) porfirina) foi usada como um modelo de corante fotossensível a ser removido da água. Os modelos de resíduos sólidos foram poli (ácido láctico) (PLA) puro e misturado com 10% de amido termoplástico (TPS). As porfirinas livres e adsorvidas degradaram pela exposição de um dia à luz solar. O TPPS4 foi adsorvido de forma mais eficiente no PLA / TPS e degradado mais rapidamente no PLA. A adsorção da porfirina promoveu a fotodegradação de PLA e PLA/TPS.

Palavras-chave: resíduos sólidos, fotodegradação, amido termoplástico, PLA, porfirina.

ABSTRACT

Textile industries are among the most pollutant sectors in the world, mainly by the discard of synthetic dye residues in effluents. Some processes currently used for the removal of dyes from the effluents have the disadvantages of low economic viability and difficulty for reproducing on a large scale. In parallel, the disposal and the degradation of solid waste also constitute serious environmental problems that pose challenges for recycling and degradation strategies. Considering that some dyes have photosensitizing properties and some discarded solid materials are porous, the present study proposes a strategy for removal and concomitant degradation of effluent dyes and particulate solid wastes. The rationale of this process is the use of solid particulate residue to adsorb dyes dissolved in water making both the adsorbed residue and adsorbents more susceptible to photodegradation. In the present study: an anionic synthetic porphyrin TPPS4 (meso-tetrakis (4-sulfonatophenyl) porphyrin) was used as a model of photosensitizing dye to be removed from the water. The solid waste models were neat poly(lactic acid) (PLA) and mixed with 10 wt% of thermoplastic acid (TPS). The free and adsorbed porphyrins degraded by one-day exposure to sunlight. TPPS4 adsorbed more efficiently in PLA/TPS and degraded faster in neat PLA. Adsorption of the porphyrin promoted photodegradation of both PLA and PLA/TPS.

Keywords: solid waste, photodegradation, thermoplastic starch, PLA, porphyrin.

1. INTRODUCTION

The use of pigments for coloring tissues has been evolving over the centuries. Until the mid-nineteenth century, the dyes were derived from organic compounds extracted from plants or animals.[1] [2] Dyes extracted from biological tissues have low durability and to improve the industrial process, new types of synthetic dyes have been developed, with complex and varied aromatic structures, such as acids, basic, dispersed, azo, diazo, among others. [3][4][5] These structures are very stable and have as characteristics greater intensity of coloration and durability. [6] However, these dyes are more difficult to be degraded. The demand for synthetic dyes production increased after World War I and the use of synthetic dyes is predominant in the world.[7] The residual material of the pigmentation process can be retained by physical adsorption, the formation of salts or complexes with metals, mechanical retention or by the constitution of covalent chemical bridges.[8][9]

The study and development of new effluent treatment techniques for the textile industry are of great importance since it is estimated a loss of 10 to 15% of these synthetic dyes in the effluent after the staining process. [10][11] Because they are detected with the naked eye and are visible in some cases in very low concentrations, the discharge pattern of these effluents, often incorrectly discarded by industries in public waters, become an easy target for sanctions by the public power. In this way, standards have been stipulated for releases of effluents inspected by the public power. The color removal can be evaluated by a UV-visible spectrophotometry standard associated with other techniques. [12][13] By comparing the absorption spectra of the tailings with the effluent discharge pattern, it is possible to evaluate the degree of pre-established contamination. Despite the method used for detection, the discard of dyes in effluents cause great ecological effects due to their bioaccumulation.

However, the capacity of microorganisms to accumulate dyes can also be used for remediation. [14] Another important environmental problem is the discard and degradation of solid waste. [15–19] Therefore, research focused on the sustainable and biodegradable polymers and composites has gained impact. Poly(lactic acid) (PLA) is an aliphatic polyester that satisfies the physicochemical features that are appropriated for several common applications. In the state enantiomerically pure, D and L-lactic acid (PDLA and PLLA) are semicrystalline polymers. PLA composed by both the D and L lactic acid (PDLLA) is amorphous, and these characteristics allow the modulation of the properties of the polymer by varying the proportion of the enantiomers. [20] Another possibility for modulation of PLA properties is the use of additives such as thermoplastic starch (TPS), a biopolymer extracted from cereals and tuberous roots that is formed by a mixture of amylose and amylopectin. [21] In a previous study, it was demonstrated that the addition of TPS in PLA greatly favors the degradation of the material by oxidative mechanisms.[22]

In the present study, the objective was to investigate mechanisms to conciliate the cleaning of effluents with the degradation of particulate solid wastes. The modeling was done using triturated PLA and PLA/TPS to adsorb a model of effluent pollutant represented by an anionic porphyrin TPPS4 (meso-tetrakis (4-sulfonatophenyl) porphyrin) (Figure 1) for rendering adsorbent and adsorbent materials susceptible to the photochemical degradation process.

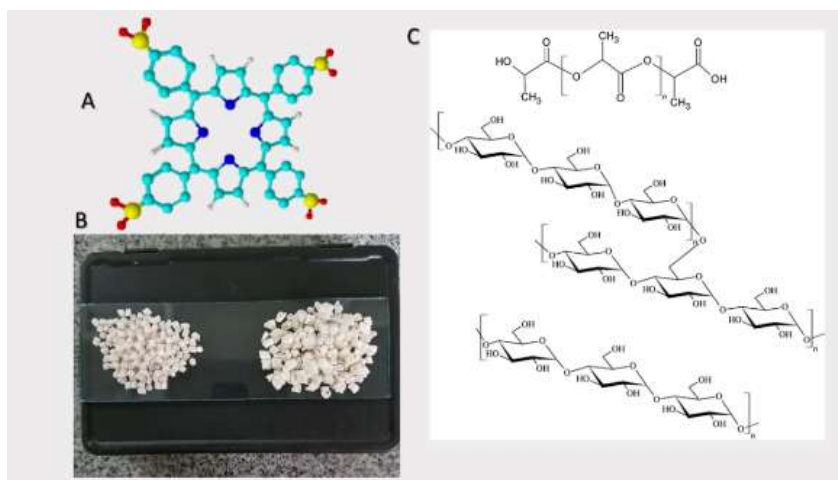


Figure 1: Photosensitizer and the adsorbent material for degradation. A) Ball and stick model of the TPPS4 structure, B) snapshot of PLA (left) and PLA/TPS (right) grains and C) PLA (upper) and TPS (down) structures.

2. MATERIALS AND METHODS

2.1 Chemicals and Materials

Anionic porphyrin TPPS4 (meso-tetrakis (4-sulfonatophenyl) porphyrin), methylene blue and TRIS buffer were obtained from Sigma-Aldrich Corp. (St. Louis, MO, USA). The modified starch, Penetrose 80 brand, was supplied by Corn Products Brasil Ingredientes Industriais Ltda. (Jundiaí, SP, Brazil) in the powdered form with 27% amylose and 73% amylopectin with a molar mass of $340,000 \text{ g}\cdot\text{mol}^{-1}$. Cargill Agricola S.A. (São Paulo, SP, Brazil) was the supplier of poly(lactic acid) (Ingeo 3801-X brand (lot 653-89-01)). Commercial glycerin was obtained from Cromoline Química Fina Ltda. (Diadema, SP, Brazil). All solutions and suspensions were prepared with deionized water (Millipore®).

2.2 Sample preparation

TPS was prepared by using a mechanical helix mixer. For the preparation, 2000 g of modified starch (Penetrose 80) and 500 g of glycerin were stirred for 8 minutes at a temperature of $70 \text{ }^\circ\text{C}$. The PLA composite with 10 wt% TPS was processed in a single screw extruder with a diameter of 25 mm and an $L/D = 25$ and with screens of 100 and 60 mesh on the headstock. In the process, it was used temperatures were $178 \text{ }^\circ\text{C}$ in zone 2, $183 \text{ }^\circ\text{C}$ in zone 2 and $174 \text{ }^\circ\text{C}$ in the headstock with a variation of $\pm 5 \text{ }^\circ\text{C}$. The extruded material was granulated and packed in bags to prevent moisture penetration. The samples submitted to the photochemical degradation were prepared in TRIS Buffer (10 mM, pH 8.5) in H_2O in the clear and amber glasses. These samples were exposed to sunlight and analyzed in the following after one and seven days of irradiation.

2.3 UV-Visible Spectrophotometry

Absorption spectra of the samples were measured before and after the reactions using a 220 UV-Vis Spectrophotometer from Thermo Fisher (Waltham, Massachusetts, EUA). For the solid material spectral analysis, it was used as an integrator sphere.

2.4 Scanning Electron Microscopy (SEM)

The images of the control and degraded polymer plates were obtained with a FEI Quanta 250 microscope from Thermo Fisher (Waltham, Massachusetts, EUA) to study the surface morphology of the samples before and after photo-oxidative degradation. The samples were previously coated with gold by using a sputtering Leica ACE200 and used voltage of 5-10 kV.

3. RESULTS

Considering that the photosensitizing property of TPPS4 should promote the degradation of PLA and PLA/TPS, it was determined the spectral region of sunlight that could be absorbed by the porphyrin in the transparent and amber glasses. The absorbance spectrum of TPPS4 in solution was determined and overlapped with the transmittance spectra of transparent and amber glasses (Figure 2). The spectral analysis of TPPS4 and the two types of glass shows that the transparent vial allows the absorption of light in the region of 350-800 nm, while the use of the amber glass allows only the absorption of red light.

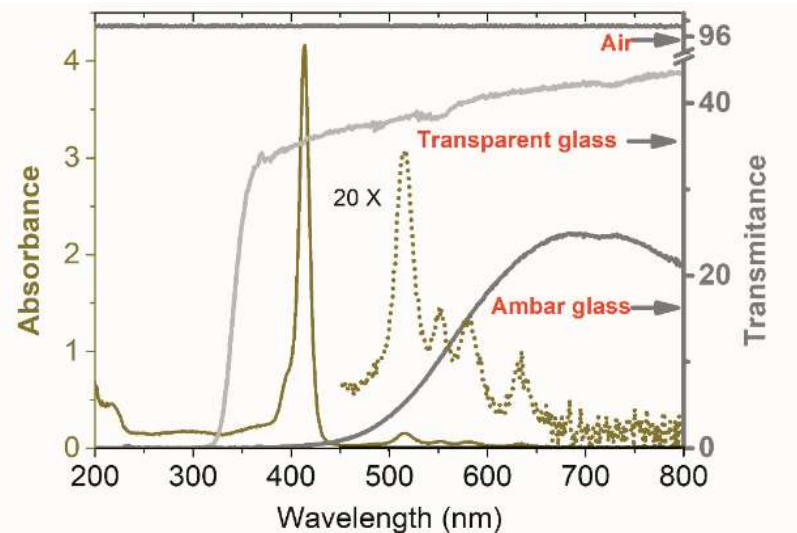


Figure 2: UV-visible absorbance spectrum of porphyrin TPPS4 (scale on the left axis) and transmittance of the transparent and amber glasses as indicated in the Figure.

Considering that the photodegradation capacity of TPPS4 on neat PLA and PLA/TPS is related to the adsorption capacity of the polymers, this property was investigated in the dark. Figure 3 4 A shows the spectra of the porphyrin solution before and after one day of incubation in the dark with the neat PLA and PLA/TPS. TPPS4 presented quantitative and qualitative spectral changes after one day of incubation with neat PLA and PLA/TPS that are consistent with adsorption and chemical modifications of the photosensitizer. The incubation with PLA/TPS promoted the higher decrease of Soret band intensity.

In fact, the presence of TPS increases the porosity of the material favoring the adsorption of the porphyrin. In the presence of PLA/TPS, it was also observed redshift of the Soret band from 414 to 420 nm as well as changes in the visible region of the spectrum (inset of Fig. 3-4). The spectrum of TPPS4 incubated one day with neat PLA featured as a composite spectrum with contributions of species peaking at 414 and ~420 nm that was corroborated by spectral decomposition (Figure 3-4-B). In Fig. 3-4, the experimental spectrum is reproduced as gray line and overlapped by the spectral components, i.e., two Soret bands and N band (black dotted line). The sum of spectral components fitted to the experimental spectrum (cyan line). The results suggest that neat PLA adsorb TPPS4 and possibly liberates ions in solution that coordinate with the porphyrin ring leading to the redshift of the Soret band. [23]

The presence of metal ions in PLA is expected as contaminant resulting from the synthesis by ROP (ring-opening polymerization). [24] In Figure 3-4 A the spectrum of TPPS4 incubated with PLA/TPS overlap the shoulder of the TPPS4 spectrum after incubation with PLA. This result suggests that metal-coordinated TPPS4 gained additional charge and partitioned preferentially in solution both in the presence of neat PLA and PLA/TPS. On the other hand, the higher porosity present in PLA/TPS allows the adsorption of a higher amount of TPPS4 free base relative to PLA, and consequently, the spectral contribution of TPPS4 free base is lower in the supernatant of PLA/TPS.

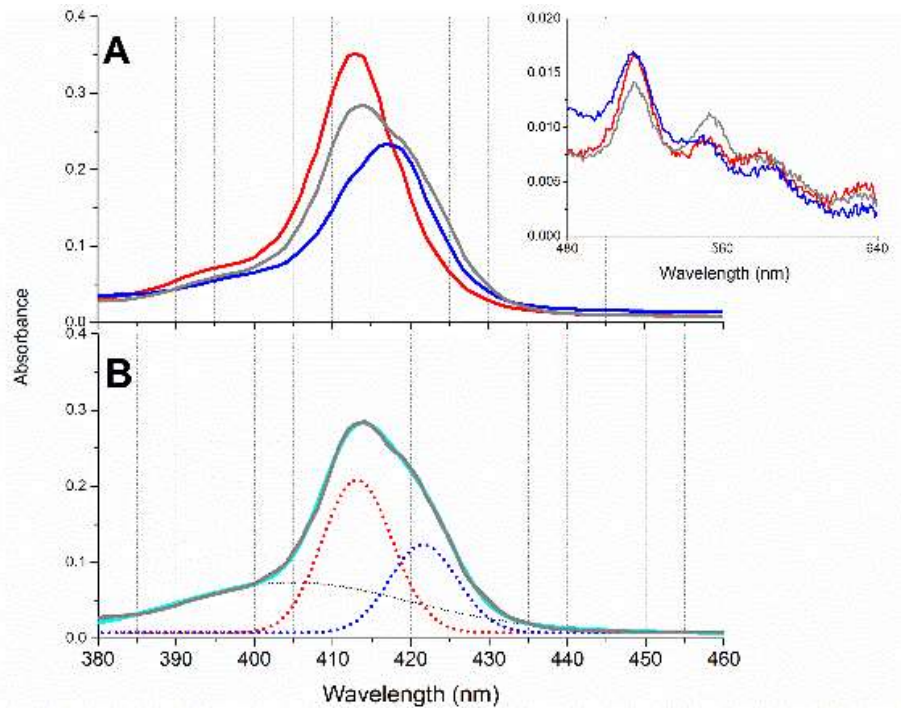


Figure 3: Spectral changes of TPPS4 incubated with neat PLA and PLA/TPS in the dark. A) The spectrum of the initial aqueous solution of the porphyrin (red line) and after one day of incubation in the dark with the neat PLA (gray line) and with the PLA/TPS (blue line). The inset shows the spectra at the visible region above 480 nm. B) The spectrum of TPPS4 after one day of incubation with the neat PLA in the dark (gray line) overlapped by its spectral components (black, red and blue dotted lines) and the sum (cyan line) that fitted the experimental spectrum. Spectral decomposition was obtained using multipeak fit in Origin 9.0 software. Black dotted line is the contribution of N band.

The samples of the TPPS4 solution, TPPS4 solution with PLA pellets and TPPS4 solution with PLA/TPS pellets were placed in transparent and amber glasses and exposed to the sun. Aliquots of the porphyrin solution and the supernatant of PLA and PLA/TPS were analyzed after one day, seven days and fifteen days of exposure to the sun (Figure 4). Figure 4 shows that TPPS4, in the presence and absence of PLA (not shown) and PLA/TPS, undergoes photodegradation in amber glass, but in the presence of the polymers, the degradation was faster.

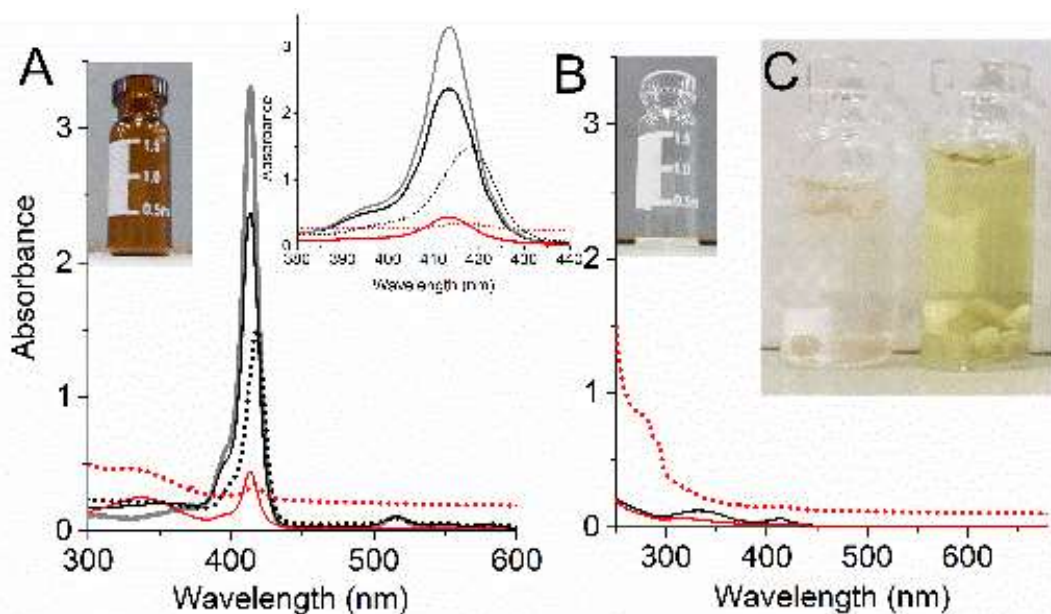


Figure 4: A) Samples incubated in amber glasses (snapshot inset). The solid lines show the spectra of a TPPS4 aqueous solution of the porphyrin before exposure to sunlight (gray line), after one day (black line) and seven days (red line) of exposure to sunlight. The dotted lines show the spectra after one day (black line) and seven days (red line) of exposure to sunlight in the presence of PLA/TPS. The inset of A shows a zoom of the Soret bands at the corresponding conditions. B) Samples incubated in transparent glasses (snapshot inset). The solid lines show the spectra of TPPS4 obtained after one day (black line) and seven days (red line) of exposure to sunlight. The dotted line is the spectrum obtained after seven days of exposure to sunlight in the presence of PLA/TPS. C) Snapshot of TPPS4 before (right) and one day after (left) the exposure to sunlight in the presence of PLA/TPS in transparent glass.

The photobleaching of the porphyrin adsorbed in neat PLA and PLA/TPS was also analyzed (Figure 5). This result is significant because the photobleaching of the porphyrin indicates the generation of oxidative species that could also target the adsorbent materials, neat PLA and PLA/TPS. The intensity of the porphyrin spectra in these materials depends on the amount adsorbed and the degree of degradation. The intensity of the Soret band of TPPS4 adsorbed in neat PLA decreased from the first to the seventh day of irradiation. In PLA/TPS, the photobleaching of TPPS4 was also more intense in transparent than in amber glass.

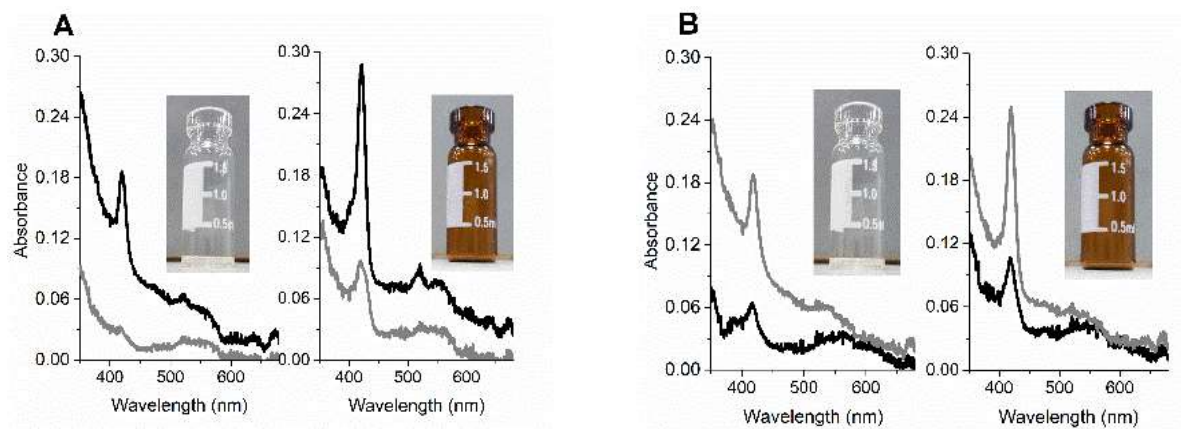
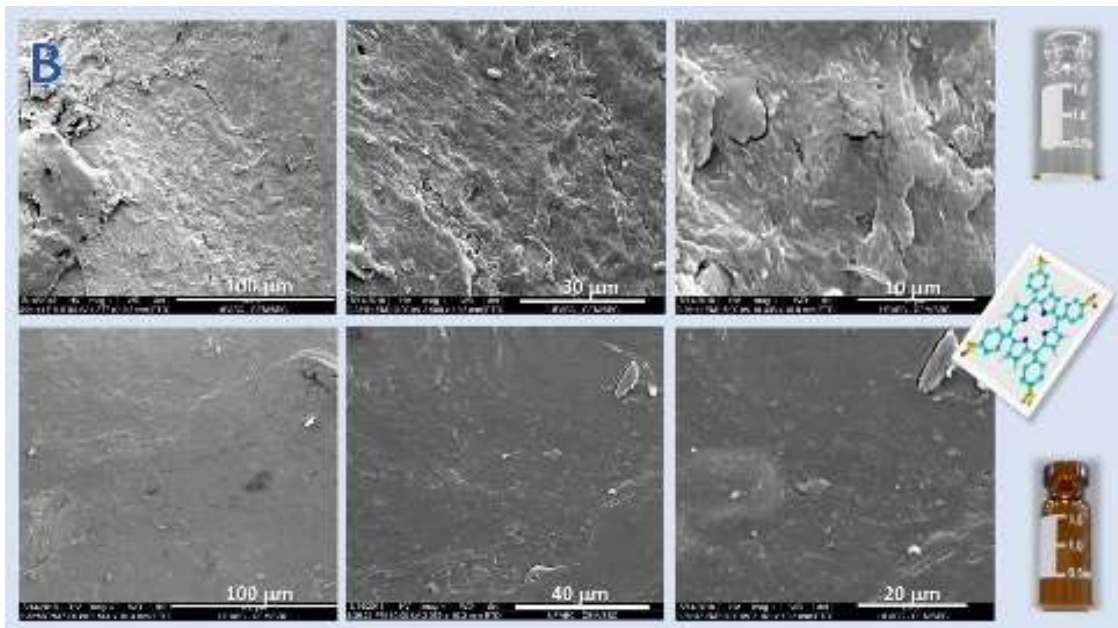
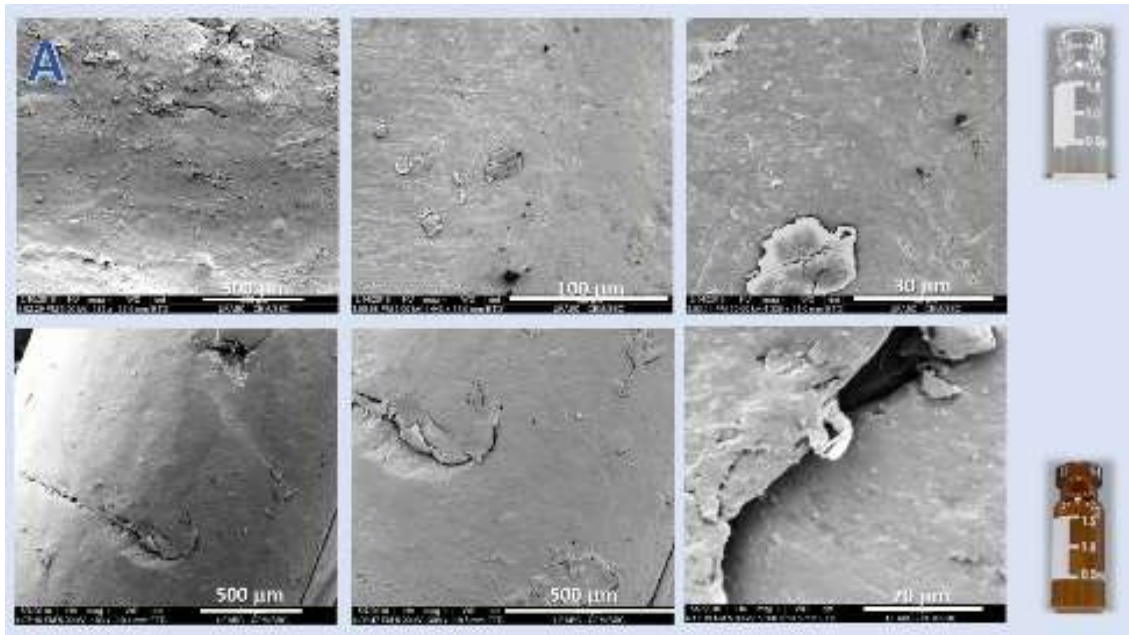


Figure 5: UV-visible absorbance spectrum of TPPS4 adsorbed in PLA and PLA/TPS. A) The spectra TPPS4 adsorbed in PLA after one day (black line) and seven days (gray line) of exposure to the sun (black line) in transparent and amber glasses, as indicated in the Figure insets. B) The spectra TPPS4 adsorbed in PLA/TPS after one day (black line) and seven days (gray line) of exposure to the sun (black line) in transparent and amber glasses, as indicated in the Figure insets.

The result obtained for TPPS4 adsorbed in PLA/TPS was seemingly paradoxical since the intensity of the Soret band increased at the seventh day of irradiation. However, the rationale for this result is that electronically excited TPPS4 generates pro-oxidant species that promoted degradation of the porphyrin and the adsorbent material. The photodegradation of PLA/TPS increased the material porosity leading to increased adsorption of porphyrin. This result was suggestive of the degradation of PLA and PLA/TPS by the photodynamic action of TPPS4 that was corroborated by SEM images. Figure 6 (A) shows representative SEM images of PLA samples dipped in deionized water after seven days of exposure to sunlight inside transparent (upper panels) and amber (lower panels) glasses.

The SEM images of PLA sample exposed to sunlight for seven days in transparent are like those that have been irradiated in amber glasses. The PLA sample irradiated in the absence of TPPS4 presented large areas with low roughness and some protrusions and pinholes. Figure 6 (B) shows the representative SEM images of PLA grain surface after seven days of irradiation with sunlight in transparent (upper panel) and amber (lower panel) glasses in the presence of 10 μM TPPS4. In this condition, the higher efficiency of TPPS4 for degrading PLA in the transparent glass is clear. The SEM images of PLA grain surface irradiated in transparent glass reveal a highly rough fibrous surface while the sample incubated in amber glass conserved the features of the controls. Considering the transmittance spectra of transparent and amber glasses showed in Figure 2, the exclusive efficiency of TPPS4 in transparent glass can be assigned to the high absorbance of the porphyrin in the spectral region of 400 nm (Soret band) that was filtered by the amber glass.



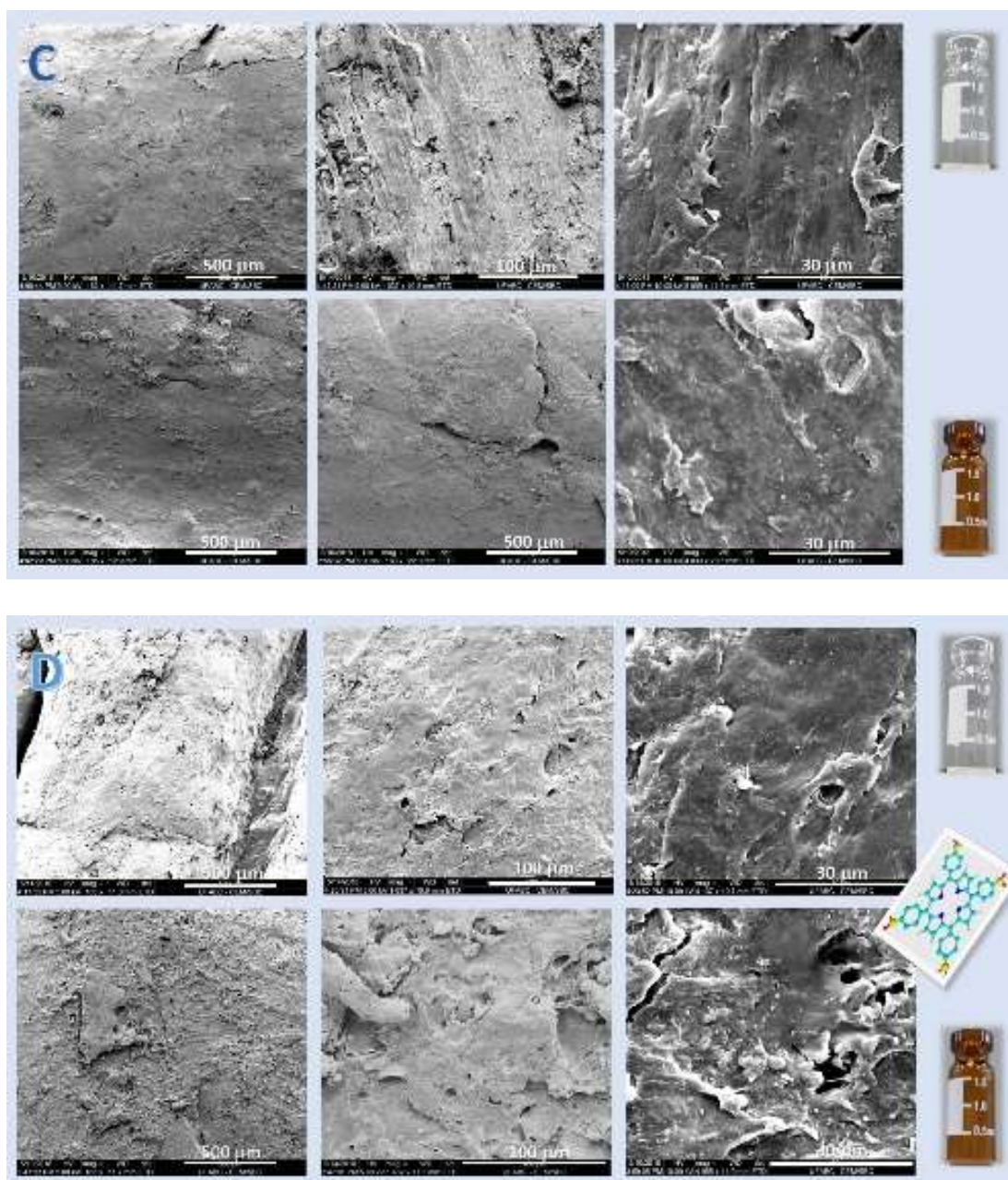


Figure 6: Changes in PLA and PLA/TPS surfaces associated with exposure to sunlight in transparent and amber glasses in the absence and presence of TPPS4 as indicated in the Figure. Panel A shows images of PLA in the absence of TPPS4, panel B shows the images of PLA in the presence of TPPS4, panel C shows images of PLA/TPS in the absence of TPPS4, panel D shows the images of PLA/TPS in the presence of TPPS4.

Figure 6 C shows the SEM images of PLA blended with 10 wt% of TPS after seven days of exposure to sunlight inside transparent (upper panels) and amber (lower panels) glasses. Like previous studies, the presence of 10% of TPS intensified the grooves and roughness of the sample surface (Fig. 6D). The irradiation of these samples in TPPS4 solution leached the fibrous feature, increased the roughness and the presence of large craters in the surface of both the samples, i.e., those incubated in transparent and amber glasses.

4. CONCLUSIONS

Neat PLA and PLA blended with 10 wt% TPS were triturated and used as a model of solid waste and the porphyrin in an aqueous solution that modeled an effluent residue with photodynamic activity. The photosensitizing agents produce pro-oxidant species such as singlet molecular oxygen and free radicals (Fig. 7). The pellets of neat PLA and PLA/TPS were able to adsorb TPPS4 partially, but the blended material adsorbed the porphyrin more efficiently. TPPS4 adsorbed in PLA/TPS promoted photodegradation of the mate-

rial that contributed to the increasing material porosity. The increase of the PLA/TPS porosity contributes to late additional adsorption of porphyrin. The contribution of TPPS4 for the degradation of neat PLA was dependent on the absorption at the spectral region of 400 nm. TPPS4 was similarly efficient to promote superficial erosion of PLA/TPS under irradiation with both visible and red light. The present study shows that is viable exploitation of some solid waste for the removal of effluent contaminants and if the adsorbed compound is a photosensitizing the process could result in double beneficial: the water cleaning and solid waste degradation.

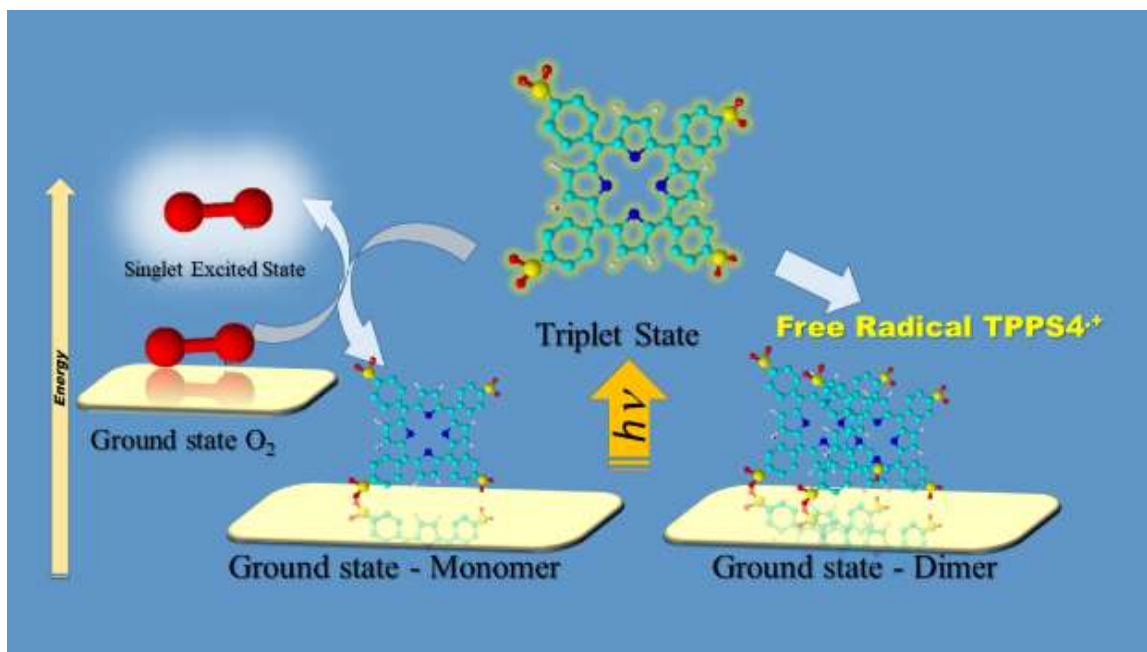


Figure 7: Reactive species produced by TPPS4 modulated by the aggregation state of the porphyrin. In the monomeric form, triplet excited porphyrin transfers the excitation energy to molecular oxygen that is converted to singlet molecular oxygen. In the aggregated form triplet excited porphyrin oxidizes the ground state counterpart and produces free radicals.

5. ACKNOWLEDGMENTS

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