

Article

Biopolymer Gellan-Gum-Based TiO₂: A Green Alternative Photocatalyst Approach for Removal of Pollutants

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Abstract: Titanium dioxide TiO₂/gellan gum (GG) in different compositions (1, 3, and 5% GG) was investigated to degrade methylene blue (MB) under UV light. XRD, SEM, and EDS confirmed the anatase phase. The textural properties demonstrated the formation of mesopores. The band gaps were 3.2 eV, 3.0 eV, and 2.9 eV. A photodegradation of MB of 95% was observed using the lowest gum concentration. It was attributed to the photogenerated radicals and the specific surface area. The FTIR spectra showed the photostability of the catalyst after successive cycles. The toxicity tests demonstrated no toxicity after dye degradation. Therefore, TiO₂/GG is promising for the treatment of water.

Keywords: polysaccharide; oxide; photocatalysis



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1. Introduction

Contamination from effluents has been identified as one of the main global problems, resulting from the massive development of the chemical, pharmaceutical, textile, agricultural, and food industries, which may discard chemical compounds in the aquatic environment that present risks to aquatic biota and the health of all living things [1,2]. Industrial effluents from using dyes are hazardous due to their mutagenic and carcinogenic characteristics and their difficult degradation.

The United Nations highlights the importance of achieving sustainable development goals (SDGs), prioritizing environmental issues and ecological technologies that prioritize sustainability and population well-being [3,4]. The number of treatment technologies is growing, and their combinations represent a major critical challenge toward their effective/feasible application in clean water policy [5]. Advanced oxidation technologies (AOTs) are effective in degrading organic and non-biodegradable pollutants, aiming to completely mineralize pollutants [6]. This is a process based on the generation of reactive oxygen species, such as the hydroxyl radical (OH), that exhibit a high standard redox potential ($E^0 = +2.80$ eV) and have a reaction constant of the order of $10^8 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$ [6,7]. Among the photochemical treatment methods, heterogeneous photocatalysis is an emerging approach to degrading and removing toxic pollutants in aquatic matrices [8].

Photocatalytic activation by semiconductors/photocatalysts uses light energy absorption to generate active species such as electrons and holes [9]. These are responsible for

forming active sites on the surface of the semiconductor that promote the formation of highly reactive radicals capable of degrading various contaminants [7,10].

The search for functional and efficient photocatalysts that combine politically correct and viable characteristics from a sustainable point of view to the environment has been discussed. TiO_2 -based photocatalysts exhibit excellent performance due to their attractive properties, such as non-toxicity, low cost, and chemical stability. However, there are several challenges concerning TiO_2 applications in the degradation of pollutants, being circumvented based on structural changes from strategies (polymeric support, doping, heterojunctions) that allow changes in the synthesis conditions in order to improve not only the quantum yield but also the absorption range of the photocatalysts from the modifications [11,12].

The research on synthesizing composites by combining oxides and natural polysaccharides has gained attention for producing biodegradable, stable compounds with high functional performance [13]. Gums contain many active groups that can interact with metal ions, resulting in a homogeneous dispersion of the cations present [13,14]. Manickam et al. [14] evaluated the synthesis of ZnO semiconductor nanoparticles capped in acacia gum to modify the surface and evaluate the photocatalytic capacity of methyl green dye, obtaining impressive efficiency. Araújo et al. [15] synthesized TiO_2 composites in the presence of gum Arabic and Karaya and investigated the photocatalytic activity of cationic blue dye, scavengers, recyclability, and the toxicity of photogenerated solutions.

Gellan gum (GG) is a polysaccharide produced by *Pseudomonas elodea*. It has the potential for application in several areas of study, such as the production of biodegradable packaging [16], antibacterial activity [17], tissue engineering [18], and the production of probiotics [19]. Recently, Razali et al. [20] reported GG as a stabilizer in TiO_2 nanoparticles for photocatalytic and biomedical applications.

The present study summarizes the synthesis of TiO_2 -based composites stabilized by gellan gum (TiO_2/GG), aiming at structural modification for photocatalytic tests. The study is characterized by structural, optical, and morphological properties and, therefore, aims to evaluate the effectiveness of the composites 1GGT (1% GG), 3GGT (3% GG), and 5GGT (5% GG) in the degradation of methylene blue cationic dye under UV light.

2. Materials and Methods

2.1. Materials

All the reagents used are analytical grade. For the synthesis of the composite and photocatalytic tests, the following reagents were used: Gellan gum (Sigma-Aldrich, St. Louis, MO, USA), methylene blue dye 97.0% (dynamic), ethyl alcohol 99.8%, and titanium isopropoxide 97% from Sigma-Aldrich. The water was distilled, and the reagents were used without prior purification. For the bioassay with brine shrimp, the reagents used were the following: calcium chloride 99.0% (Dynamic), magnesium chloride 99.0% (Dynamic), magnesium sulfate 98.0% (Isosfar), and sodium bicarbonate 99.4% (Sigma-Aldrich). The Gellan Gum is registered in SisGen number ABD61DA.

2.2. Synthesis of TiO_2

TiO_2 was obtained by the sol-gel method using titanium isopropoxide (TTIP) as a metallic precursor. Initially, 6.0 mL of TTIP was dropped into 100.00 mL of ethyl alcohol and kept in magnetic stirring for 30 min. After this period of agitation, 6.0 mL of ultrapure water was dropped into the system, which was maintained under the same agitation condition. Then, the system was kept at rest for 24 h, after which period it was dried in an oven at $\sim 75^\circ\text{C}$. The samples were calcined at 400°C in a muffle furnace for 2 h using a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

2.3. Synthesis of TiO_2/GG

The TiO_2 composites were obtained by the sol-gel method using titanium isopropoxide (TTIP) as a metallic precursor. Different gellan gum masses (1, 3, or 5% *w/v*) were initially

added to ethyl alcohol and under agitation for 30 min. Then, 6.0 mL of TTIP was dropped into 100.00 mL of the biopolymer solution, and the system was maintained under the same agitation conditions. After 30 min of stirring, 6.0 mL of ultrapure water was dropped into systems that were kept under the same stirring conditions for another 30 min. Then, the systems were kept at rest for 24 h and dried in an oven at 75 °C. The samples were calcined at 400 °C in a muffle furnace for 2 h using a heating rate of 10 °C min^{−1}. The composites obtained from the gellan gum were named 1GGT, 3GGT, and 5GGT according to the amount of gum used in the synthesis.

2.4. Characterization

The prepared composites were analyzed using an X-ray diffractometer from Shimadzu Labx-XRD 600. The infrared spectra were obtained using the FTIR equipment, Vertex 70v from Bruker, with 120 scans of 400 to 4000 cm^{−1} and a resolution of 4 cm^{−1}. The measurements were performed by transmission using potassium bromide (KBr) pellets. The UV-visible spectrometer (Ocean View Optics DH-2000-BAL <https://www.oceaninsight.com/contact-us/> (accessed on 22 October 2023)) was used to study the optical absorption of the samples in the range of 200–800 nm. Scanning electron microscopy (SEM) images were obtained using a field emission electron microscope JEOL JSM-7401F at an acceleration tension of 5.0 kV, an SEI secondary electron detector, a working distance ranging from 3.0 mm, and a resolution of 1.5 nm, with EDS. The sample was sputtered with Au.

2.5. Dye Degradation via Photocatalysis

The photocatalytic evaluation was analyzed by the degradation of the methylene blue (MB) dye with a concentration of 1.2×10^{-5} mol L^{−1} under UV light (tungsten lamp without bulb–125 W), in which the emission peaks in the range between 350–450 nm. The radiation intensity was monitored with a Luxmeter (Hanna) measuring 2.56 Klx. A concentration of 0.5 g L^{−1} of photocatalyst was used in a borosilicate reactor with a volume of 100 mL coupled to a thermostatic bath maintaining the system temperature at 25 °C. Then, the suspension was allowed to reach adsorption–desorption equilibrium under a dark atmosphere and stirring for 30 min. The samples were collected at different times. The samples were centrifuged at a rotation of 5000 rpm, and subsequently, the change in absorbance at the maximum wavelength ($\lambda_{\text{max}} = 664$ nm) of the dye was monitored using an Agilent Technologies–Cary 60 spectrophotometer.

$$\% \text{ Degradation} = \frac{([C_0] - [C])}{[C_0]} \times 100 \quad (1)$$

where $[C_0]$ corresponds to the initial concentration, and $[C]$ corresponds to the final concentration of MB. The total irradiation time was 120 min.

2.5.1. Reuse and Photostability of Photocatalyst

Photocatalyst recycling was evaluated as previously reported [21–23]. The material was used, washed, and dried for reuse during three consecutive cycles of photocatalysis. After reuse, the photocatalyst used in the recycling was dried and submitted for analysis to verify its photostability. The characterization procedure was the same as previously described.

2.5.2. Artemia Saline Bioassays

Microcrustaceans were cultivated for 48 h in synthetic saline solution under lighting and oxygenation, as described in Araujo et al. [24]. The seawater solution, with a concentration of 38.0 g L^{−1}, was prepared with the salts: calcium chloride, magnesium chloride, magnesium sulfate, and sodium bicarbonate. The ten nauplii were added to a solution containing irradiated MB (used in reuse test) and synthetic saline in a ratio (1:1), and their mortality rate was evaluated after 24 h and 48 h. The control solution was only the synthetic saline solution to evaluate its quality.

3. Results and Discussion

3.1. X-ray Diffraction Studies

Figure 1 shows the X-ray diffractograms of the (TiO₂)/gellan gum (GG) 1GGT, 3GGT, 5GGT, and pristine TiO₂. Analyzing the diffractograms using the crystallographic Search-match program, we observed reflections at $2\theta = 25.4, 38.1, 48.1, 53.9, 55.1, 62.7$, and 68.6 that correspond to the planes (101), (004), (200), (105), (211), (204), and (116), respectively, based on reference code 01-084-1286. These planes are typical of the anatase phase of TiO₂ with tetragonal geometry, which is formed due to calcination at 400 °C, as observed in several studies [25–27]. TiO₂ has three mineral forms: anatase, rutile, and brookite, with the anatase phase having the best photocatalytic performance [26].

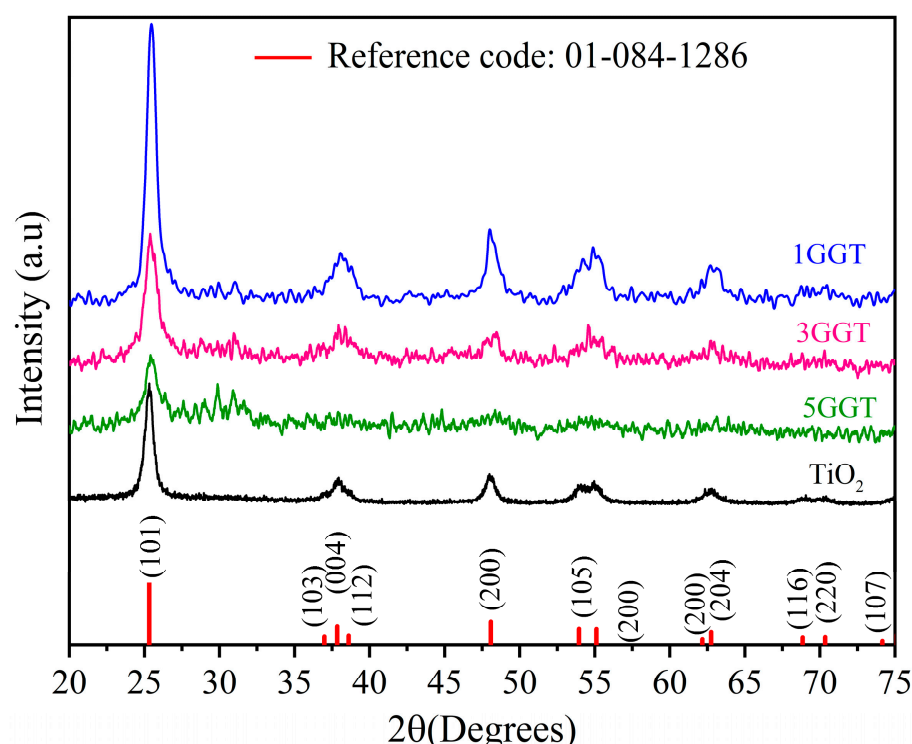


Figure 1. X-ray diffraction diagram of the composites 1GGT, 3GGT, 5GGT, and pristine TiO₂.

The XRD results suggest the formation of the crystalline structure due to the well-defined formation and intensity of the peaks, suggesting that TiO₂ was incorporated into the gellan gum satisfactorily, as previously reported [17,26,28]. The sharper peaks in 1GGT indicate the high crystallinity of the material, mainly observing the greater intensity of the peak (101). The lower intensity of the 3GGT and 5GGT materials indicates the lower crystallinity of the material synthesized. The Scherrer Equation (2) was used to measure the crystallite size:

$$T_c = K \cdot \lambda / \beta \cdot \cos \theta \quad (2)$$

The values of K , λ are constant, where K is the shape factor and λ the wavelength of the $k\text{-}\alpha\text{Cu } \beta$ radiation, which is the width at half height of the highest intensity peak. The values found were 12.23 nm for 1GGT, 8.01 nm for 3GGT, and 5.28 nm for 5GGT. These values confirm that the 3GGT and 5GGT materials have low crystallinity, and this decrease may be due to a decrease in lattice tension during synthesis [29]. Therefore, when we increase the amount of gellan gum, there is a decrease in crystallinity observed in the reduction of peaks, mainly at 25.40, possibly due to less oxide formation in 3GGT and 5GGT. No other peaks were identified in the diffractograms, indicating that the formation of precipitates or other phases did not occur.

3.2. UV-Vis Spectra and Band Gap Energy

The optical properties of materials 1GGT, 3GGT, and 5GGT were evaluated by UV-vis diffuse reflectance. The band gap of the material is a vital factor in understanding what type of radiation is absorbed in the photocatalysis process [30,31]. The reflectance spectrum $\times$ wavelength was transformed into the Kubelka–Munk function (K) $\times$ Photon energy ($h\nu$) or $(\alpha h\nu)^{1/2} \times h\nu$ [32]. The gap was determined by extrapolating the spectrum's linear region, and the Tauc graph is shown in Figure 2 [33]. The values found were 3.29 eV for 1GGT, 3.08 eV for 3GGT, 2.99 eV for 5GGT, and 3.24 eV for pristine TiO_2 . It is well known that TiO_2 has a band gap equal to 3.2 eV, as in the literature [32,34,35], that requires radiation with a wavelength shorter than 380 nm. The gum combined with TiO_2 generates a difference in the band gap and consequently improves the photocatalytic performance of TiO_2 , reducing the high rate of combination of electrons and holes in pure TiO_2 [32,36,37]; similar results were observed with Karaya and Arabica gum and zinc oxide [15].

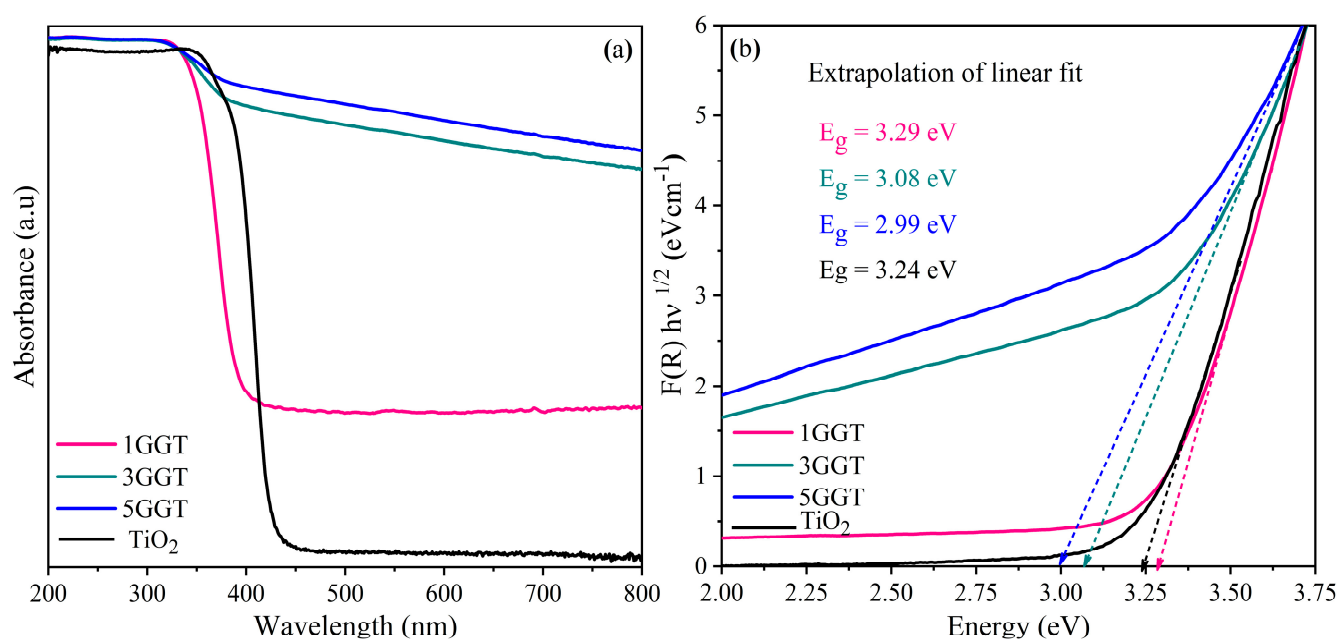


Figure 2. (a) UV-VIS spectra of the samples obtained with different concentrations of GG polysaccharide and (b) band gap energy determined from the UV–VIS reflectance spectra using Tauc's plot method.

3.3. Electron Microscopic Studies

The evaluation of the material's morphology was carried out using scanning electron microscopy (SEM). Figure 3 shows the material's morphology; the TiO_2 is distributed uniformly and in scales [38,39] and the EDS results. The granules can be attributed to the formation of TiO_2 nanoparticles, characteristic of the anatase phase [40,41]. 1GGT presented a more excellent distribution of TiO_2 particles and a larger crystalline size, a fact that is related to the greater surface area according to the BET and XRD results. The titanium (Ti) peaks demonstrate that the composite was successfully synthesized because the Ti element is present in all synthesized materials.

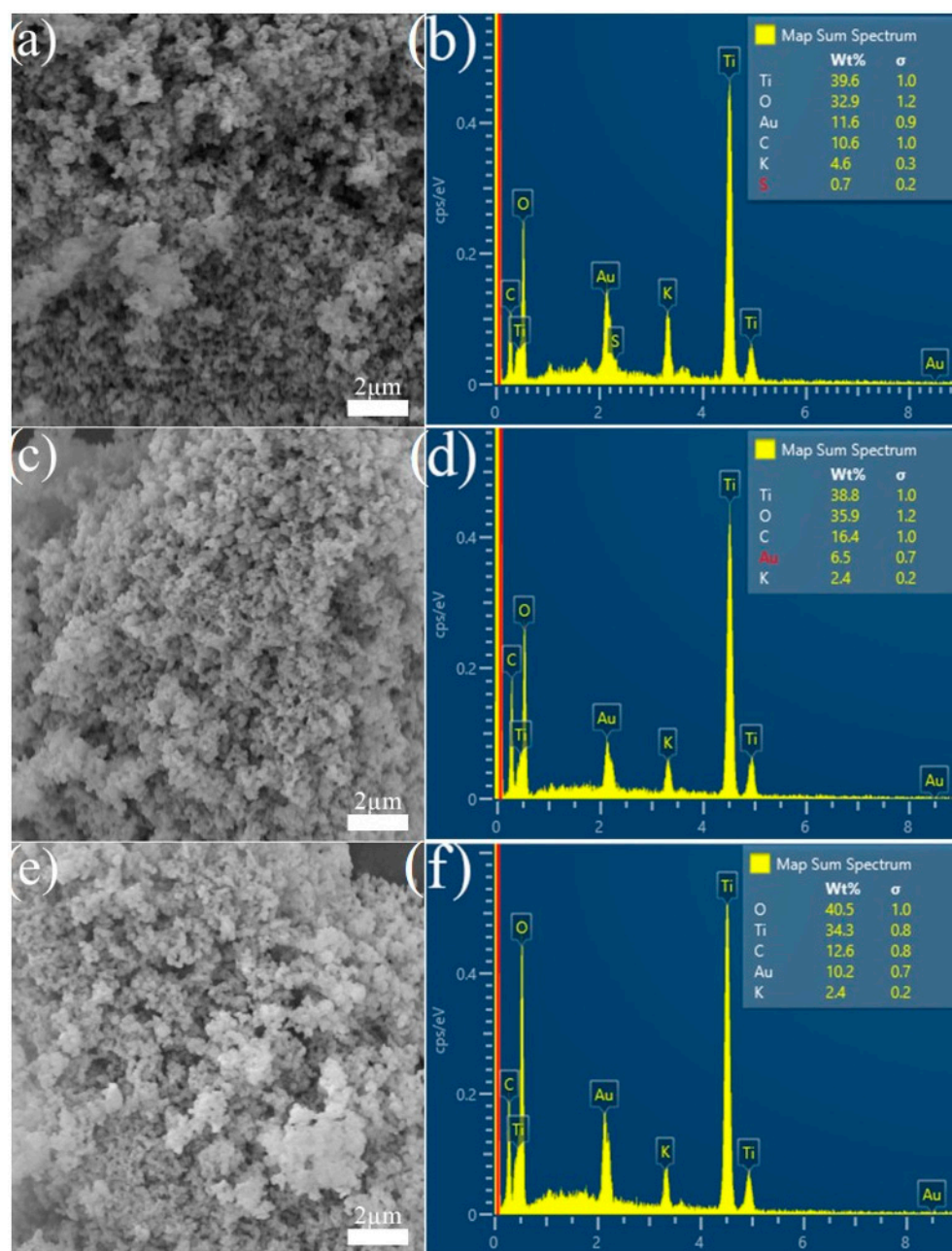


Figure 3. SEM images and EDS spectra of (a,b) 1GGT, (c,d) 3GGT, and (e,f) 5GGT samples.

3.4. Adsorption–Desorption of N_2

N_2 adsorption–desorption was used to evaluate the textural properties such as porosity, surface area, and pore size distribution. Based on the isotherms, specific surface area (SBET), average pore diameter, and pore volume were calculated and are presented in Table 1.

Table 1. Specific surface area, pore volume, and pore diameter distribution of nanocomposites.

Catalyst	Specific Surface Area ($m^2 \cdot g^{-1}$)	Pore Volume ($cm^3 \cdot g^{-1}$)	Average Pore Diameter (nm)
1GGT	80.59	0.1199	5.949
3GGT	69.72	0.06847	3.928
5GGT	28.71	0.03395	4.730
TiO ₂ pristine	2.8	0.0013	3.2

The 1GGT sample has a larger surface area, pore volume, and diameter. The best distribution of titanium polycations on the clay surface results in the formation of more porous structures and greater N_2 absorption [32,42]. The result can promote more excellent photocatalytic activity because there is an increase in reactive sites due to the greater surface area, where chemical reactions occur [43]. In Table 1, even with different surface areas, the particle sizes differ based on the synthesis method and solvation temperature, as these are parameters that influence the structure and physicochemical properties [44,45]. For example, in XRD, the decrease in crystallinity affects the effectiveness of increasing the surface area and tends to be decreased through surface factors during the synthesis process [46]. For Lin et al. [47], when synthesizing TiO_2 nanoparticles of different sizes, they related the band gap as a function of the size of the primary particle. They pointed out that as the size of the primary particle increases, the photocatalytic rate decreases exponentially, and this same observation was verified in our experimental study. In another study, Cheng et al. [48] pointed out that AgI/BiOI photocatalysts exhibit size-dependent photocatalytic activity, with the increase in activity being inversely proportional to the smaller particle size. The explanation is based on the more significant number of surface-active sites and the mobility of charge carriers. Therefore, the ideal balance between crystallinity, specific surface area increase, pore volume, and particle size reduction ratio are variables that affect the electro-optical properties of photocatalysts [45,49], explaining how one of the samples has the highest photoactivity among the others.

Analyzing the isotherm in Figure 4a, 1GGT presents classification type IV, according to the International Union of Pure and Applied Chemistry (IUPAC). The existence of a mesoporous structure with pores between 2 and 50 nm [50], confined by Figure 4b, shows the distribution of pores and their diameter between 2.9 nm and 23.9 nm. The adsorption process in solid and mesopore substances is generally accompanied by a hysteresis loop, so for all materials, this loop would be type H3 with slit-type pores [38,51]. The 3GGT and 5GGT also have type IV classification, but they have almost no hysteresis loop, which may be related to the smaller pore size [17,38].

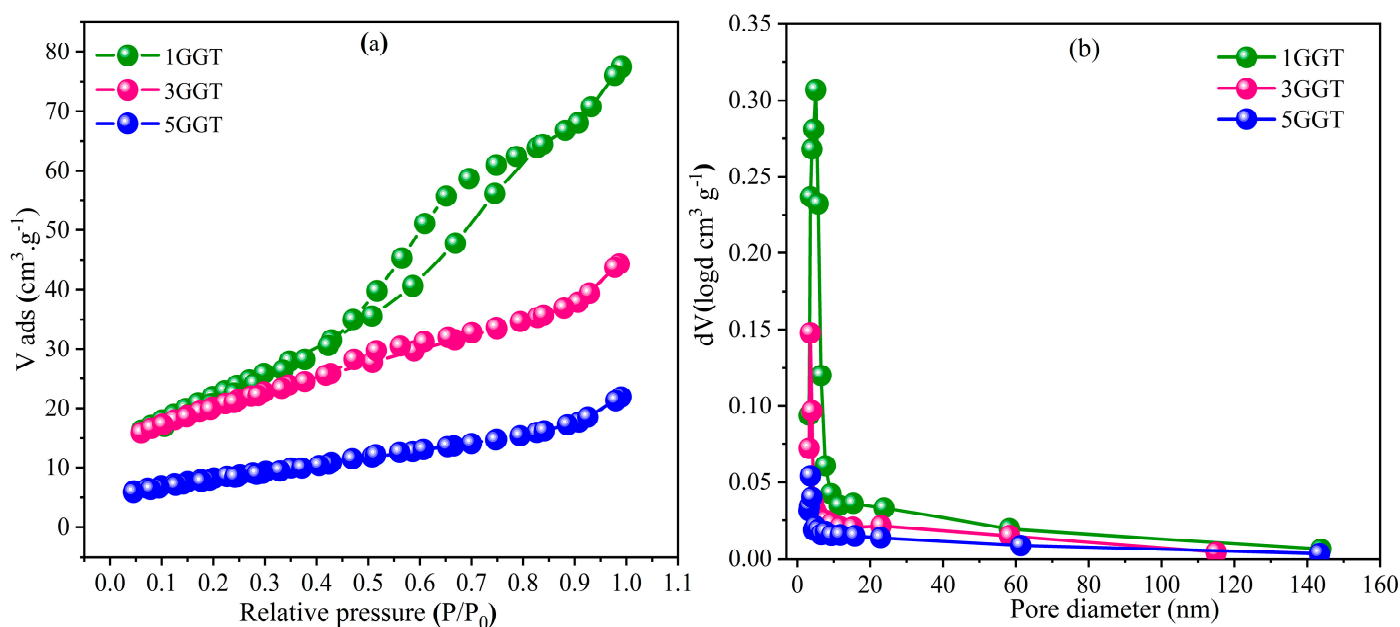


Figure 4. (a) Adsorption-desorption isotherm and (b) pore size distribution of 1GGT, 3GGT, and 5GGT composites.

3.5. Performance Photocatalytic

Figure 5 shows the MB removal under UV irradiation using the different samples obtained in this study. According to the results, it was evident that using GG in TiO_2 improves the photocatalytic activity of the 1GGT, 3GGT, and 5GGT composites. There is a decrease

in absorbance values with the increased irradiation time (for example, 1GGT—Figure 5a). The effect of the interaction of light with the surface of the composites promotes the generation of reactive oxidizing species (ROS), such as the $\bullet\text{OH}$ capable of breaking down MB molecules adsorbed on the surface of the composites to degrade and produce less toxic species and/or by-products [52].

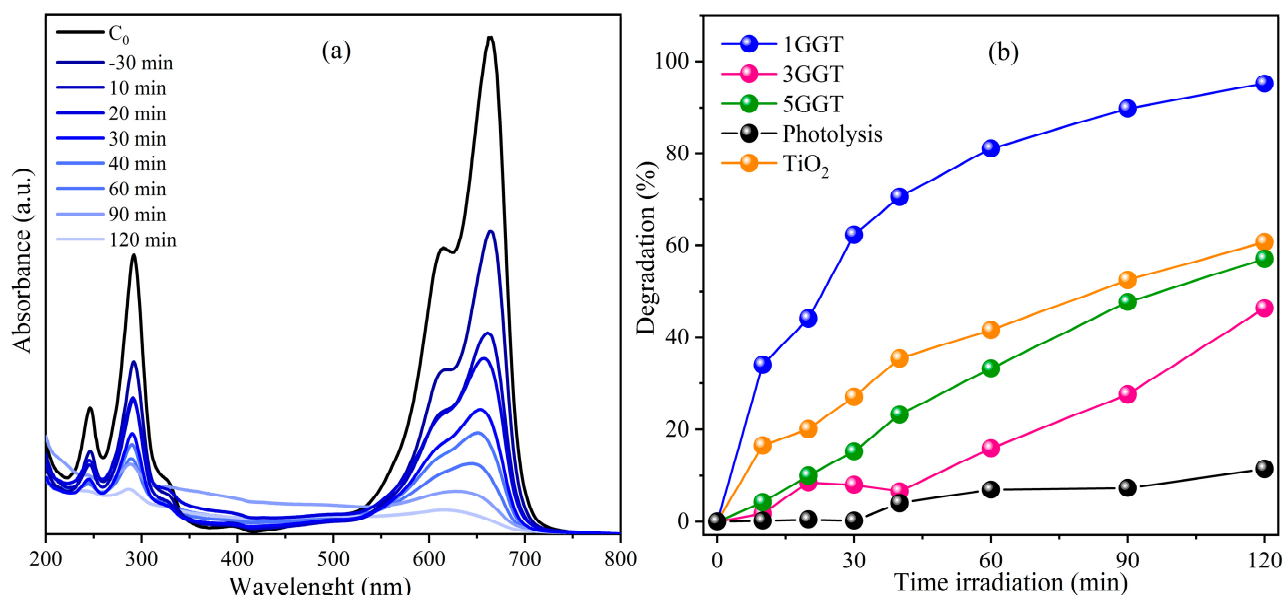


Figure 5. (a) Spectral variation in MB dye irradiated with 1GGT sample and (b) degradation kinetic curves of the MB solution irradiated using 1GGT, 3GGT, and 5GGT solutions under UV light.

Figure 5 shows that an enhanced photo response was observed using 1GGT and the strong synergistic interaction between TiO_2 /gum molecules and the cationic surface of the dye, leading to maximum degradation [45,53,54]. Furthermore, the active sites are the atoms or faces of the crystal where the reaction occurs, so the number of photocatalytically active surface sites does not necessarily increase with the increasing surface area. However, under certain conditions, a large surface area facilitates the dispersion of sites, improving photocatalytic activity independent of other factors [55]. It is believed that values above the mass ratio (3 and 5% GG) may result in a shortage of reactive sites and an increase in the agglomeration rate, thus, generating unavailability and, consequently, a decrease in degradation efficiency [45,53,54,56]. Therefore, the surface area is a crucial factor affecting the photocatalytic material performance [45]. However, this is not a logical trend of greater gum concentration, greater surface area, and greater quantum yield but rather the combination of several factors that interfere in the photodegradation rate associated with the ionization state of the photocatalyst surface, the valence and conduction of the photocatalyst, the ability to agglomerate particles and the dynamics of charge carriers for the formation of radicals that act directly on the process, and reaction kinetics [54,56]. Recently, the different approaches discussed have been a significant challenge in photocatalytic studies, especially in synthesizing inorganic nanoparticles in an economical and environmentally friendly way by applying gums as a stabilizing agent [15,57].

The absorbance data vs. irradiation time show that the decrease in the concentration of GG in the composites presents with a lower absorbance value, which is reflected in the increase in the photocatalytic efficiency of the material, i.e., 1GGT (95%), 3GGT (46%), 5GGT (53%), and TiO_2 (60%), as presented in Figure 6.

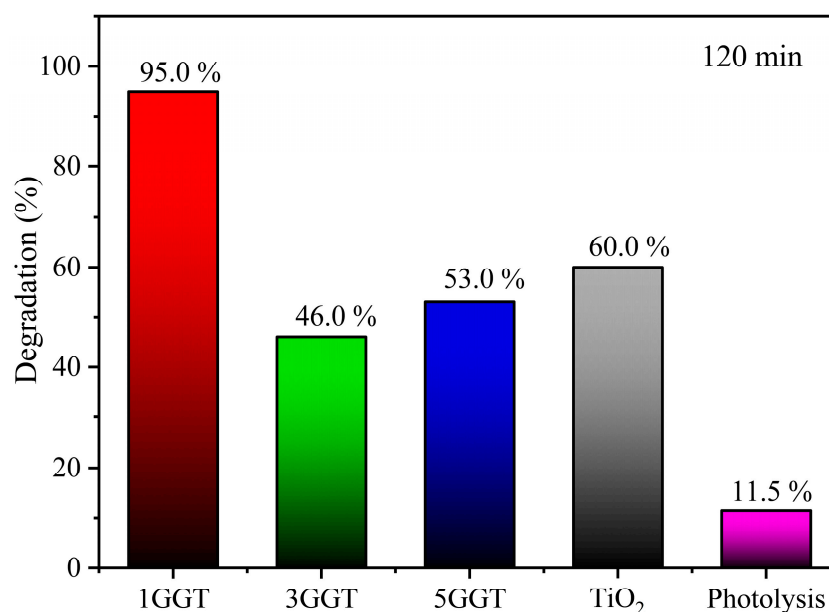
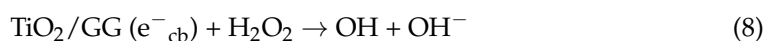
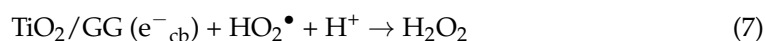
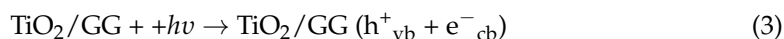
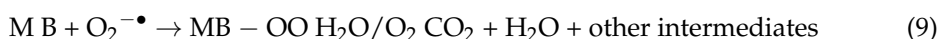


Figure 6. Percentage of decomposition of MB by 1GGT, 3GGT, and 5GGT over 120 min under UV light.

The photoactivity at a lower concentration of GG may be related to the greater surface area of the 1GGT material. It facilitates adsorption and better distribution of TiO₂ crystals, providing a greater distribution of active sites that promote the photocatalytic process [58,59]. Additionally, a shielding effect is generated by the layer of MB molecules that can prevent the irradiation process on the surface of the photocatalysts, therefore, interfering with the oxidation yield. On the other hand, the high photodegradation of MB by 1GGT is due to the stability of the anatase phase of the photocatalyst. Anatase crystals create several oxidizing species upon UV irradiation, which attack the structure of the dye, and it is quickly fractionated into smaller intermediate molecules [37]. The •OH acts kinetically in photocatalytic oxidation, causing excellent activity.

According to the activity percentages, 1GGT exhibits a minimum recombination of charge carriers (e^-/h^+) given the high efficiency concerning pure TiO₂ [32,36]. Given the TiO₂/GG combination, it is considered that the bond formed between TiO₂ and the polysaccharide facilitates the transfer of charge carriers and reduces the concentration of the recombinant species of pure TiO₂ [42,60]. This favors the formation of ROS that attack and cleave the thiazine group of MB [61–64], breaking the chromophore ring structure and causing the subsequent degradation process [14]. The scheme of possible reactions for MB degradation that occur on the surface of the photocatalyst is described in Equations (3)–(9) [52,64].





The path of a catalytic photoreaction is summarized in the following steps: (i) photoexcitation with UV light under TiO_2 /GG to generate charge carriers in the CB and VB bands, (ii) production of reactive oxygen species responsible for MB degradation, and (iii) oxidation-reduction reactions involving the $\bullet OH$ in the breakdown of the dye and possible mineralization of the pollutant [4,10]. Figure 7 simplifies the degradation mechanism involving the TiO_2 /GG/dye system.

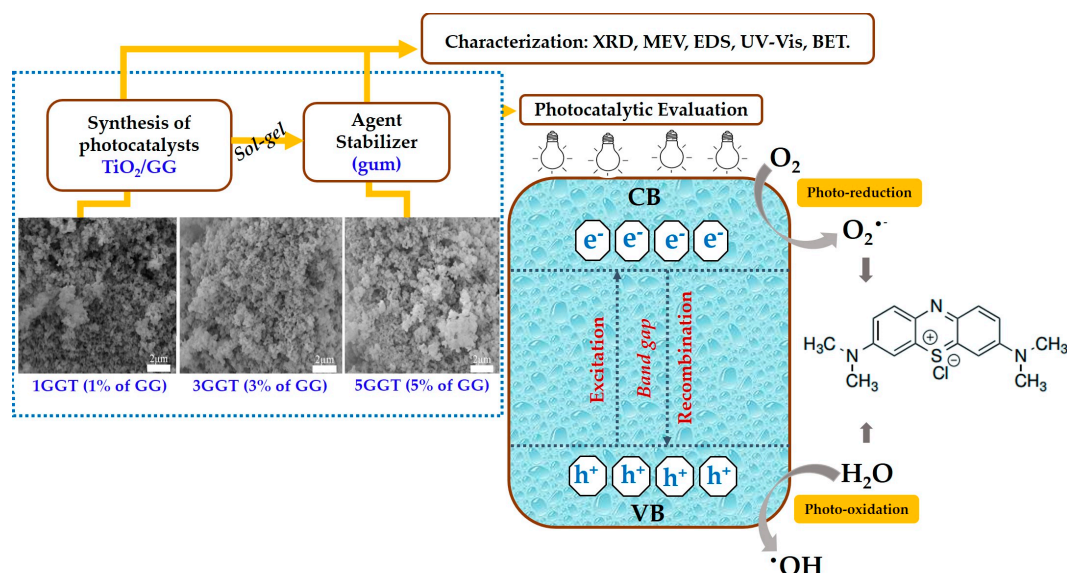


Figure 7. Schematic of the photocatalytic mechanism using TiO_2 /GG.

Several works have used gum composites to immobilize different oxides [17,57,65]. Based on parameters from different approaches and applications, gums, in combination with other compounds and metals, have obtained favorable results in photocatalytic performance [15,66] and efficiency in antibacterial treatment [67]. Araújo et al. [24] used flower-shaped ZnO structures obtained from karaya gums and evaluated the performance in the photodegradation of methylene blue under visible light irradiation. The authors demonstrated that photophysical processes and photocatalytic activity were decisive in interpreting the dynamic separation behavior of photoinduced charge carriers to promote the degradation of the MB dye. Among the photocatalysts, KGZnO achieved 77% degradation. Table 2 summarizes gellan-gum-based catalysts as stabilizers/supports for environmental applications.

Table 2. Research carried out with modified gellan gum and different applications.

Composites	Application	Ref.
TiO_2 -NTs/gellan gum	Actividad antibacterial	[17]
Gellan gum/graphene oxide aerogels	MB adsorption	[68]
Gellan gum–tiossemicarbazida	Cadmium removal	[69]
Xanthan gum/ZnO	Removal of MB	[65]
Xanthan gum/Agar@ZnO	Mineralization of malachite	[52]
Guar gum/ TiO_2 / Fe_3O_4	Photocatalysis of methyl	[57]
(3D) nanostructured gellan gum (GG) and TiO_2	Photodegradation of methyl orange	[20]

In addition to the photocatalytic performance, the reusability of the photocatalyst was also evaluated. The 1GGT sample was selected for the reuse experiment, and the stability of the photocatalyst was verified by MB degradation—Figure 8.

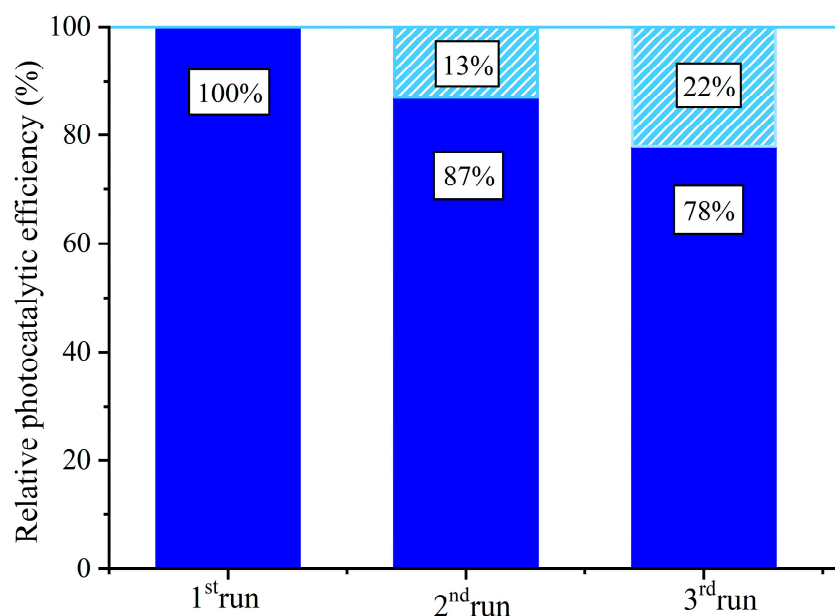


Figure 8. Relative photocatalytic efficiency using 1 GGT under UV irradiation in the reuse test. Unhatched blue column represents relative photocatalytic efficiency, while Light blue hatched column represents the relative loss of efficiency during reuse tests.

A total of three cycles were investigated. In terms of relative photocatalytic efficiency, 100% (equivalent to 95% degradation), 87% (equivalent to 83% degradation), and 78% (equivalent to 74% degradation) were obtained, respectively, for the three consecutive cycles. Surprisingly, the degradation rate maintained by 1GGT after the cyclic degradation was significant. TiO_2 was on the gum structure, effectively restricting aggregation by the proportionality of the polymer composition, thus, ensuring better dispersion of active material in the 1GGT composite. Therefore, the efficiency of the photocatalyst was maintained, varying by a percentage of 22% between the first and third cycles, thus, reinforcing the stability of the photocatalyst. The degradation rate decreased after the recovery and consecutive use of 1GGT. This behavior was also observed in other studies reported in the literature [70–72]. The reuse capacity is an essential characteristic of materials used in environmental remediation. However, the recyclability of photocatalysts has some technical challenges that cause a decrease in pollutant removal efficiency. In general, factors such as the accumulation of photocatalysis byproducts on the surface of the photocatalyst and the formation of species with greater adsorption capacity than the reactants are associated with a reduction in the rate of degradation [73,74].

3.5.1. Photostability of Photocatalyst

The structural stability after the third reuse cycle of the 1GGT photocatalyst was investigated using the XRD technique, and the results are shown in Figure 9a. Comparing the 1GGT data before and after reuse, it is evident that there was no change in the diffractogram profile of the samples, indicating that the photocatalytic tests, under the conditions studied, do not cause structural changes in the TiO_2 network. The same behavior was observed in the FTIR spectrum of the 1GGT material before photocatalysis and after three cycles of the material (Figure 9b). This result corroborates the photocatalytic efficiency demonstrated by 1GGT in removing MB dye in three consecutive cycles.

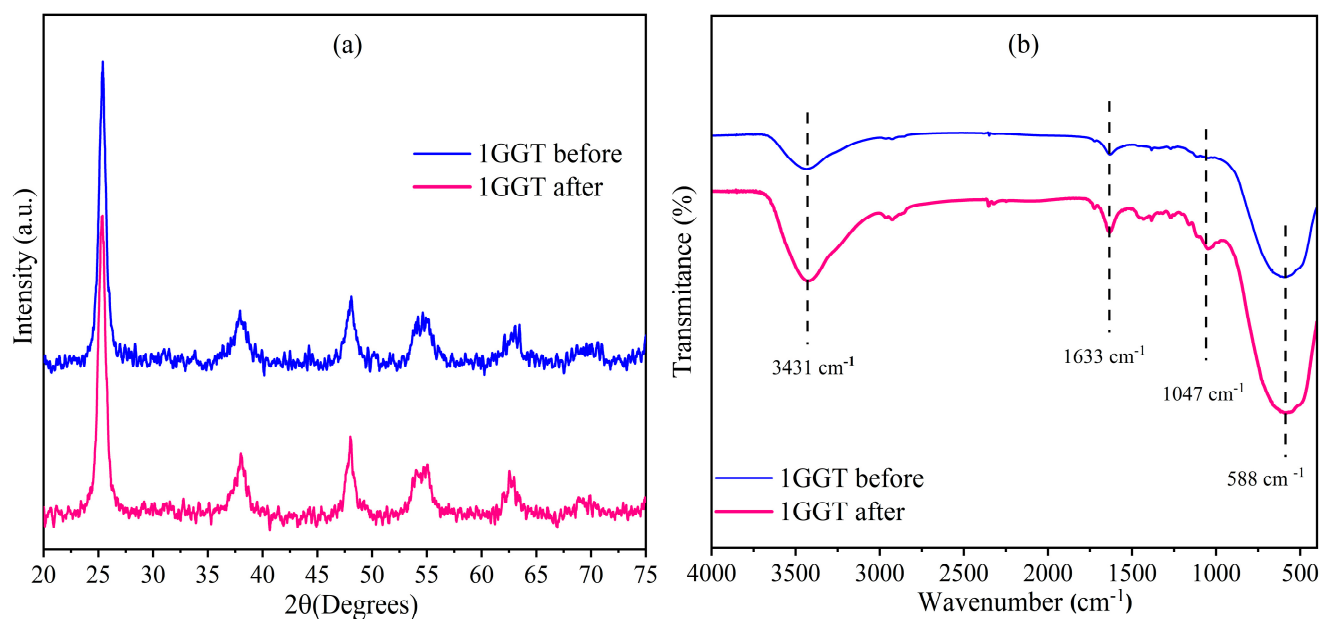


Figure 9. (a) XRD diffractogram and (b) FTIR spectra of the 1GGT photocatalyst before the photocatalyst test and after the third cycle of MB degradation.

3.5.2. Artemia Saline Bioassay

The results obtained for the toxicity parameter evaluated using *Artemia saline* were expressed as a percentage and compared with the control solution. Values that cause brine shrimp mortality equal to or less than 50% of the control solution were considered toxic. Figure 10 shows the results of testing the 1GGT solutions in the three photogenerated cycles.

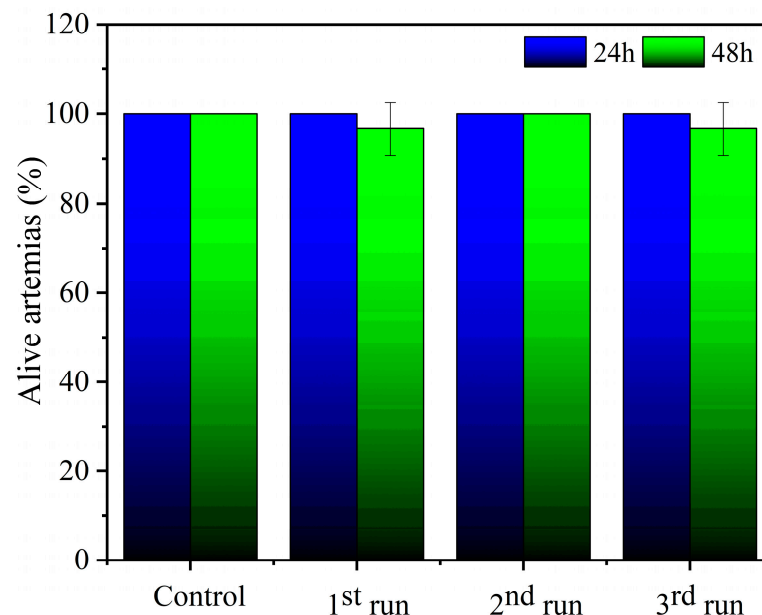


Figure 10. Bioassay test on *A. salina*, where the control corresponds to microcrustaceans cultivated in synthetic saline solution and the effluent of photocatalysis performed using 1 GGT.

Insignificant percentages of mortality were noted. None of the solutions treated resulted in toxic effects. This result infers that the photoproducts generated after irradiation have low toxicity as the mortality of nauplii was practically similar to that found in the control sample, which kept 100% of the brine shrimp alive for 24 h and 48 h. Therefore, it was found that brine shrimp, a test bioindicator, were not sensitive under the conditions investigated.

4. Conclusions

The biopolymer TiO₂/GG was synthesized satisfactorily, with the formation of TiO₂ nanoparticles in the anatase phase, as confirmed by XRD, SEM, and EDS. The textural property evaluation demonstrated mesopore formation characteristic of TiO₂ hybrid materials. The photocatalytic capacity evaluated under UV light showed that the 1GGT material, with lower gum contraction, presented a better performance for application in the photodegradation of organic pollutants. The stability assessment also showed promising results after successive cycles and the toxicity tests of the effluents after photodegradation, demonstrating that no treated solution did not present toxicity. Therefore, biopolymer is an excellent option for application in environmental remediation.

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