



Production of propolis/TiO₂ (P-TiO₂) nano composites for degradation of food dyes

Melek Koç Keşir¹ , Münevver Sökmen^{2*} 

¹Karadeniz Technical University, Faculty of Science, Department of Chemistry, 61080, Trabzon, Turkey

²Konya Food and Agriculture University, Faculty of Engineering and Architecture, Department of Bioengineering, 42080, Konya, Turkey

Abstract

The aim of this study is to produce highly active hybrid propolis-TiO₂ nanocomposites using the sol-gel method and to use it in remediation of food industry waste. Propolis solution was prepared in ethanol and added to the sol-gel mixture at increasing volume (0.25, 0.50, 0.75, 1.00 mL) to prepare propolis-TiO₂ (P-TiO₂) hybrid catalyst. Neat TiO₂ was also prepared by the same sol-gel technique and its action was compared to propolis doped ones. Catalysts were calcinated at 300°C to obtain the desired anatase form. After production the catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and FTIR. Sunset Yellow (SY), Allura red (AR) and Tartrazine (TT) were used as model compounds ([C]₀=10 mg L⁻¹, catalyst mass=1 g L⁻¹). The concentration of dyes was monitored by UV-vis spectrometry. P-TiO₂ catalyst prepared with 1.00 mL propolis solution was extremely effective for removal of all dyes studies for both 254 nm and 365 nm light exposure. LED light exposure provided lower removal rate (approx. 25%) but it was still significant for dye removal.

Keywords: Photocatalysis, propolis-TiO₂, food dye

1. Introduction

TiO₂ is a well-known photocatalyst and surface modification is done to obtain more effective nanoparticles. The modification can be accomplished by either direct wet deposition or sol-gel methods. Sol-gel methods have some advantages due to controllable stoichiometry and homogenous dispersion of both dopant and TiO₂. The main photocatalytic material is usually TiO₂ and dopants are immobilized on its surface or its inner layers. TiO₂ shows relatively high reactivity (anatase crystalline phase) and chemical stability under ultraviolet light is lower than 387 nm. There are many doping materials to develop photocatalysts exhibiting high reactivity under visible light ($\lambda > 400$ nm). Visible light-activated TiO₂ could be prepared by metal-ion implantation, metal or non-metal immobilization, dye sensitization [1,2]. On the contrary, TiO₂ was immobilized on several support

matrices such as silica, zeolite, clay, and activated carbons [3].

Doping of TiO₂ with the compounds such as activated carbon adds some superior properties such as increased adsorption capacity, higher surface area, robust and stable structures and compositions [4]. Additionally, carbon doping can significantly stabilize the anatase TiO₂ and improve the adsorption of organic pollutant molecules on the catalyst surface as well as shifting its absorption band to longer wavelength. Carbonaceous doping promotes the interaction and facilitates the interphase transfer of the target compounds to the TiO₂ phase. Some studies have been reported for the C-doping of TiO₂ [4,5]. Propolis immobilized TiO₂ hybrid nanocomposites might be a good choice for the removal of food dye effluents. A proper immobilization of this biocompatible material on

photocatalyst is a new approach in photocatalytic studies. Especially sol-gel production might be a good alternative to produce propolis-TiO₂ nanostructures (P-TiO₂) to increase the effectiveness of this valuable photocatalyst. The aim of this study is to produce highly active hybrid propolis-TiO₂ nanocomposites using the sol-gel method and to use its remediation of food industry waste. After the production of the catalyst P-TiO₂ hybrid catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and FTIR. In the current literature, there are a few reported studies related to photocatalytic removal of food colouring dye effluents. Photocatalytic Tartrazine degradation using ZnO as photocatalyst has been reported by Rahman et al. [6]. Another work was published by Zazouli et al. [7] for photocatalytic removal of food dye Brilliant Blue FCF using Fe₃O₄-TiO₂ hybrid catalyst. The catalyst was effective and degraded the dye using UVC and LED (Light Emitting Diodes) light. In the present study Sunset Yellow (SY), Allura red (AR) and Tartrazine (TT) were used as model compounds (Figure 1). The concentration of dyes was monitored by UV-vis spectrometry before and after treatment. Dye removal percentages were calculated from the remaining dye concentration after a certain treatment period.

2. Experimental

2.1. Materials and reagents

Propolis is a resinous natural substance that is produced by bees to protect the hive against external threats such as bacteria and viruses. Raw propolis sample was collected from local bee producers in the 2018 season (Trabzon, Turkey) and was stored at +4°C. Propolis samples (each 5 g) were weighed and added to 100 mL of methanol. The samples were continuously stirred with a shaker at room temperature for 24 h before the suspension was centrifuged at 10,000 G for 15 min. The supernatant was concentrated in a rotary evaporator under reduced pressure at 40°C. Then, the residue resolved in a minimal volume of 98% absolute ethanol. The ethanolic extract was directly used in the sol-gel process. All chemicals were analytical grade and purchased from Sigma-Aldrich. The chemical structures of dye molecules are given in Figure 1. Dye solutions were prepared in deionized at 10 mg L⁻¹ concentration.

2.2. Sol-Gel synthesis of propolis/TiO₂ (P-TiO₂) hybrid catalysts

Sol-gel synthesis leads to the excellent distribution of large molecules in ethanolic titanium isopropoxide (TiP) solution and eases the homogenous hydrolysis to produce (P-TiO₂) composite. The general procedure is given in Figure 2.

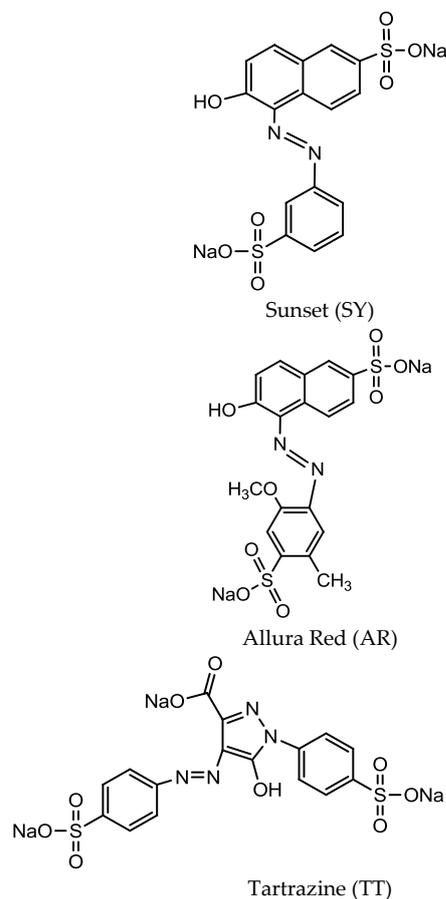


Figure 1. Chemical structures of each dye molecules.

As given above 8.4 mL of titanium (IV) isopropoxide (TiP) was dissolved in 20 mL absolute ethanol and ethanolic propolis solution was added (0.25, 0.50, 0.75, 1.00 mL). To a solution of acidic ethanol containing 9 mL of absolute ethanol and 1 mL of concentrated HNO₃ was added 1 mL of distilled water and slowly added to the first solution before the mixture was left stirring overnight. Then, the mixture was dried at 76°C for 12 h. The obtained powder was calcined for 4 h at 300°C and cooled down to room temperature. The product was kept in dark bottles until use. The same procedure was employed to prepare neat TiO₂ powder.

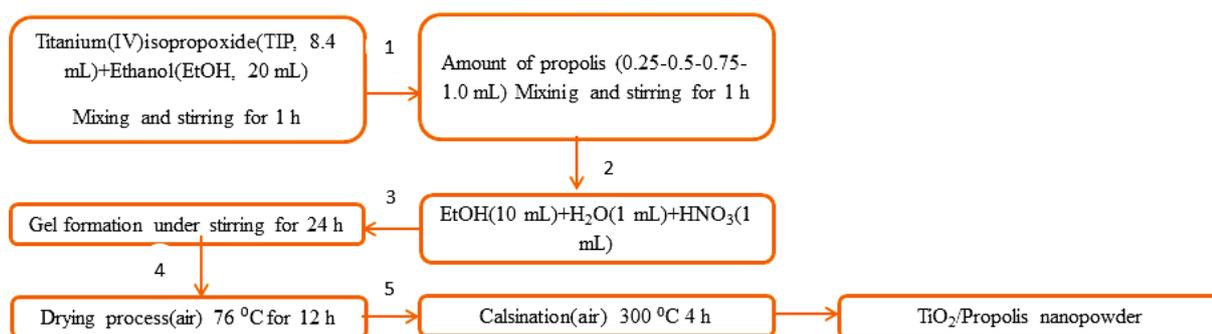


Figure 2. General procedure for sol-gel preparation.

2.3. Characterization

After preparation and calcination of (P-TiO₂) composite the structural properties of solid matter were determined. XRD analysis of the catalysts was carried out by a Rigaku Smartlab diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) over the range $2\theta=20^\circ-60^\circ$ at room temperature. The surface morphology of the catalysts was determined by SEM analysis (JEOL, JSM 6610). Infrared spectra were obtained with a PerkinElmer 1600 FTIR (4000–400 cm^{-1}) spectrometer.

2.4. Photocatalytic studies and analysis

Dye solution (100 mL) was placed into photoreactor and hybrid photocatalyst (1.0 g L^{-1}) was added to test solution under magnetic stirring. Remaining dye concentration in the presence and absence of light was monitored for 90 and 150 minutes treatment periods.

In the case of photocatalytic experiments, the suspension was illuminated with a UV lamp emitting 254 nm and 365 nm light (6 W, Spectroline ENF-260). Additionally, a LED lamp was used for visible region studies (LED: $300 \mu\text{W}/\text{cm}^2$). A 2.0 mL of the test solution was withdrawn after 150 minutes exposure period. To separate the solid catalyst the sample was centrifuged for 5 min at 3000 rpm by using Eppendorf Centrifuge 5180. The supernatant was used for the determination of the remaining concentration of the dye after filtration with a $0.45 \mu\text{m}$ membrane filter.

The photodegradation of each dye solution (without catalyst) was also measured. Photocatalytic tests were carried out with neat TiO₂ nanoparticles preparing by the same sol-gel procedure. The concentration of each dye was monitored spectrophotometrically at their specific wavelength (Unicam UV-2 spectrometer).

3. Results and discussion

3.1. Structural analysis of the photocatalysts

TiO₂ exists in several polymorphic forms but anatase is being the most active photocatalyst. Sol-gel synthesis and heat treatment at high temperatures dominate the crystal structure [8,9].

Propolis is a heat-sensitive compound and burns out at high-temperature treatment. Calcination at 300°C is a relatively low but enough temperature treatment to obtain anatase structure [10,11]. This temperature is preferred to avoid the thermal degradation of propolis and obtain the desired anatase structure. The XRD pattern of each catalyst is given in Figure 3. The diffraction peak 101 at $2\theta=25.50^\circ$, originate from anatase TiO₂ indicating that the hybrid photocatalysts consist of the pure crystalline anatase phase.

The SEM images are given in Figure 4. The crystalline structure was observed. Smaller nanoparticles distribute over larger crystals due to calcination and aggregation. Small propolis islands are located on larger TiO₂ crystals.

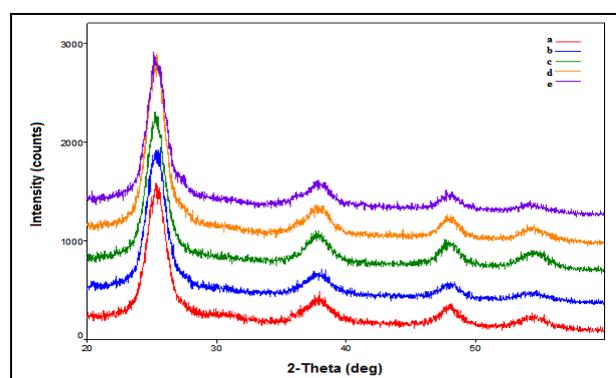


Figure 3. XRD patterns for a) TiO₂, b) TiO₂-0.5 mL propolis solution, c) TiO₂-0.25 mL propolis solution, d) TiO₂-0.75 mL propolis solution, e) TiO₂-1.0 mL propolis solution.

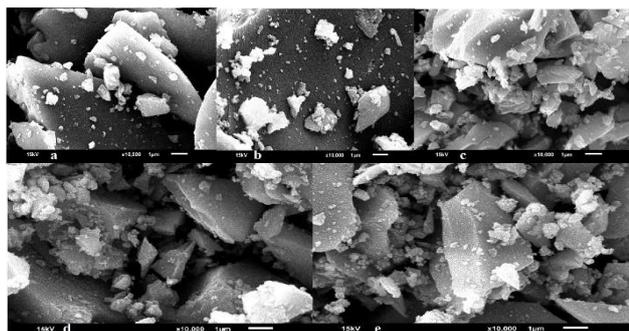


Figure 4. SEM image of prepared photocatalysts a) TiO₂, b) TiO₂-0.5 mL propolis solution, c) TiO₂-0.25 mL propolis solution, d) TiO₂-0.75 mL propolis solution, e) TiO₂-1.0 mL propolis solution.

FTIR spectra of the catalysts are given in Figure 5. Characteristic peaks at 1700-2000 cm⁻¹ and 2300-2500 cm⁻¹ region belong to propolis doped catalysts represent the organic structure.

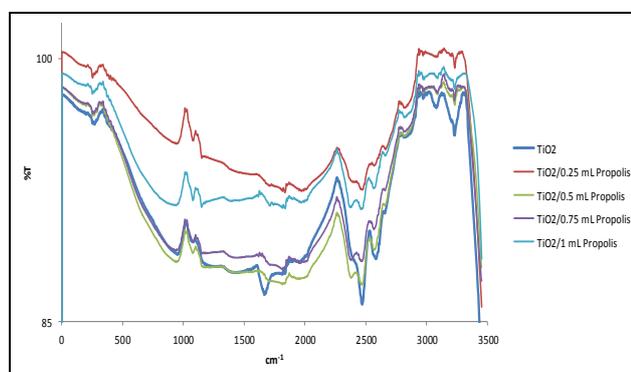


Figure 5. FTIR spectra of propolis/TiO₂ catalysts.

Propolis contains various organic molecules and the main components are resin (50%-70%), oil and wax (30%-50%), pollen (5%-10%) and other chemical compounds. Additionally, other compounds such as amino acids, minerals, sugars, vitamins B, C and E, flavonoids, phenol are present in this massive structure.

3.2. Photocatalytic removal of food dyes

The spectral characters of studied dyes are given in Figure 6. TiO₂ itself or propolis doped hybrid catalyst are good adsorbent and can remove pollutants from aqueous medium by using direct adsorption processes. So, the dark adsorption experiments were carried out before photocatalytic treatment.

A set of experiments were designed for dark adsorption measurements and photocatalytic treatments (at $\lambda=254$ nm; 365 nm and LED-visible light) were carried out as discussed above. Removal rates are given in Figure 7-9 for each dye.

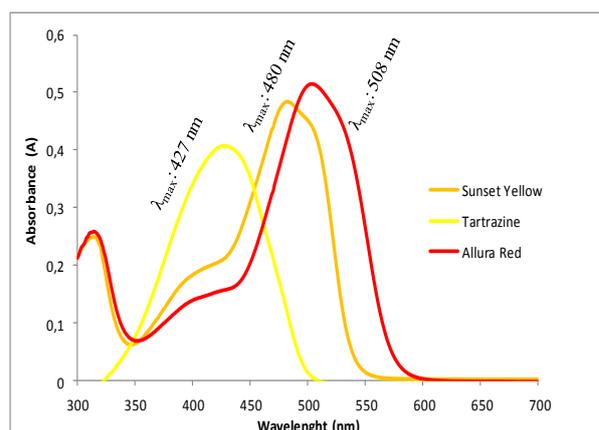


Figure 6. UV-vis. spectra of studied food dyes in water ($[C]=10$ mg L⁻¹).

Direct adsorption of SY on either neat TiO₂ or P-TiO₂ was extremely low. However, light exposure for 150 minutes dramatically increased the removal/degradation of SY. As expected, 254 nm light was effective on dye degradation. Neat TiO₂ removed 47.07% of SY and SY itself degraded 15.99% without catalyst but with UV light (254 nm). All propolis doped TiO₂ catalysts were significantly provided higher removal rates. P-TiO₂ produced using 0.75 mL and a 1.00 mL propolis solution was so effective that it removed 91.96% and 86.83%, respectively. It is clear that propolis doping was good strategy for remediation of water contaminated with these dye molecules. More interestingly, 365 nm exposure was effective and 88.01% removal was obtained with P-TiO₂ prepared with 1.00 mL propolis solution. This catalyst removed 28.71% of SY concentration after 150 minutes exposure with LED lamp which is producing visible light.

Similar results were obtained for AR dye. Dark adsorption of AR molecules on propolis doped TiO₂ catalysts was high (Figure 8). Total removal of the dye was achieved for both 254 nm and 365 nm light exposure after 90 and 150 minutes. Catalysts were able to degrade almost 25% of AR when illuminated with a LED light. Propolis doping resulted in a good catalyst for the effective removal of AR.

Tartrazine (TT) is a common dye for the food industry and has a specific yellow colour. Removal rates are given in Figure 9.

Direct absorption of TT on the catalyst was negligible but photocatalytic removal is quite high for both 254 nm and 365 nm with P-TiO₂ 1.00 mL propolis solution. Visible light removal percentages are also significant.

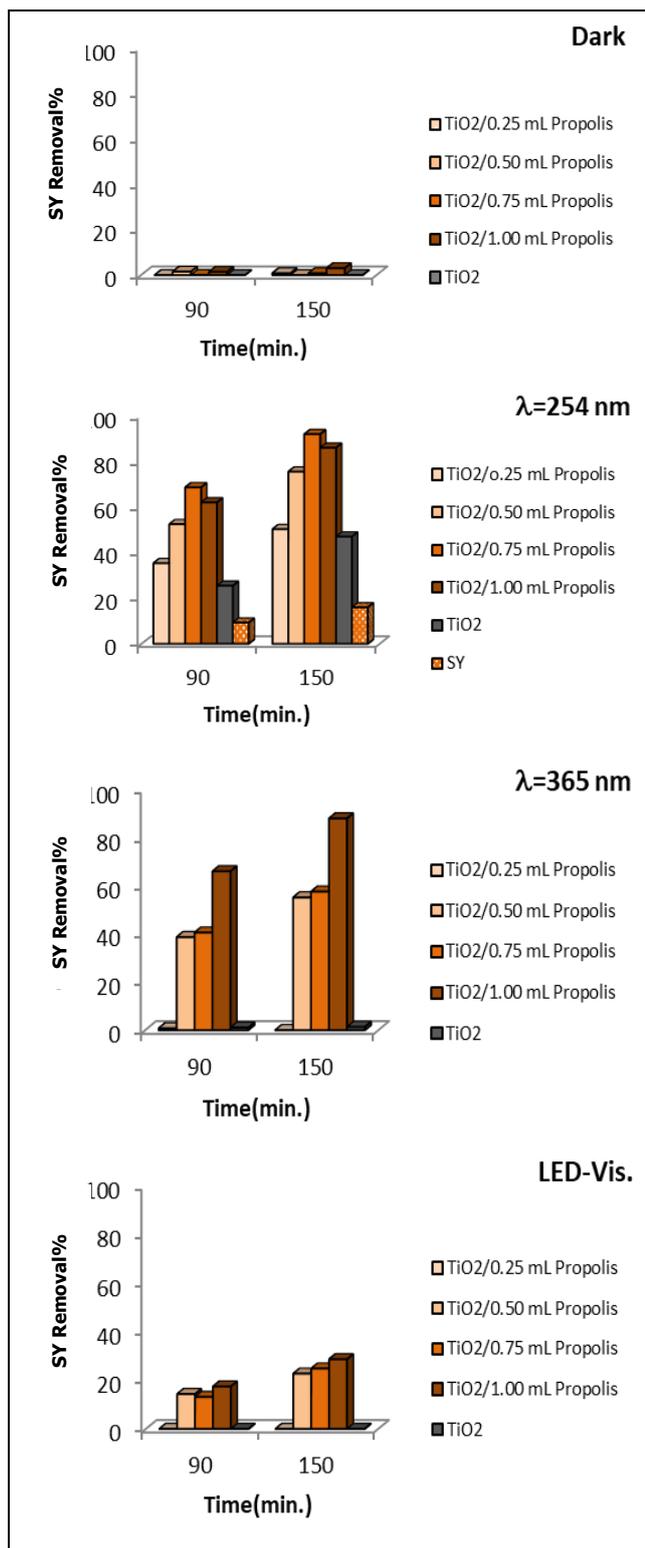


Figure 7. The photocatalytic removal of SY ($[C]_0 = 10 \text{ mg L}^{-1}$, catalyst mass = 1 g L^{-1} , light 254 nm, 365 nm and LED-vis).

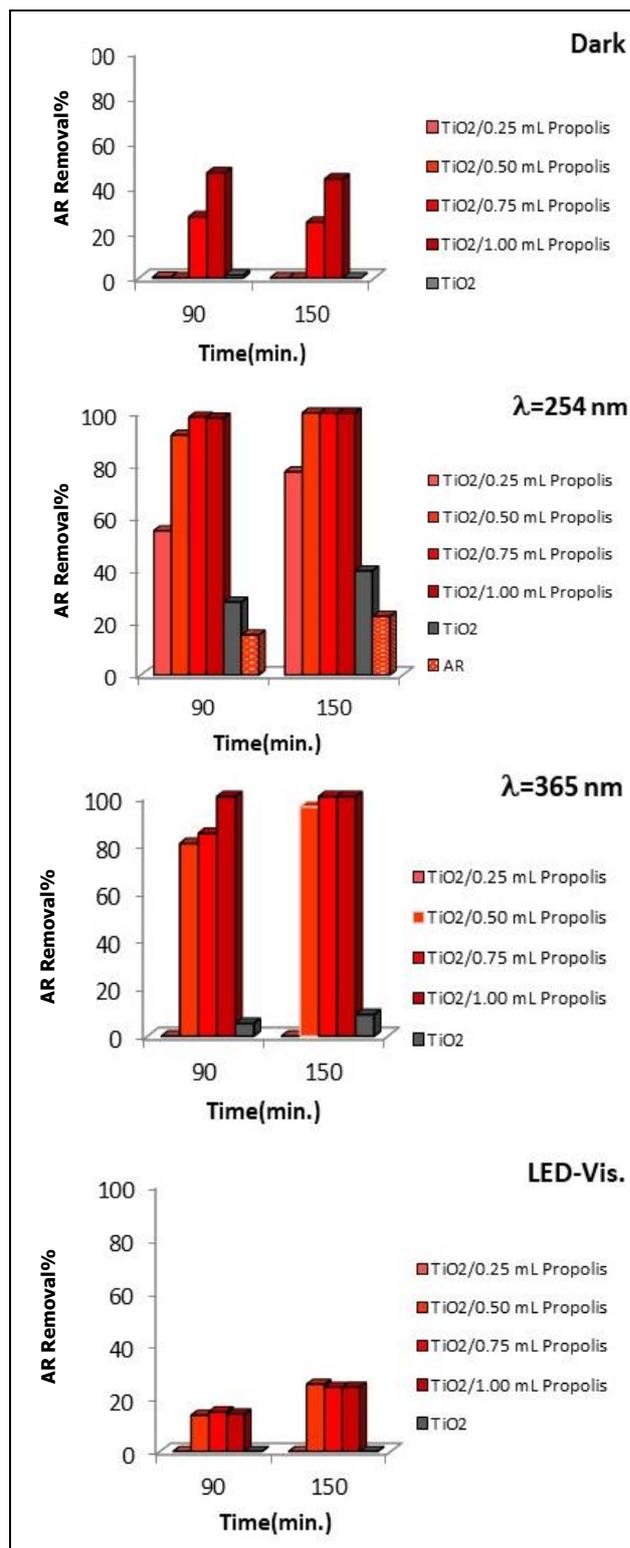


Figure 8. The photocatalytic removal of AR ($[C]_0 = 10 \text{ mg L}^{-1}$, catalyst mass = 1 g L^{-1} , light 254 nm, 365 nm and LED-vis).

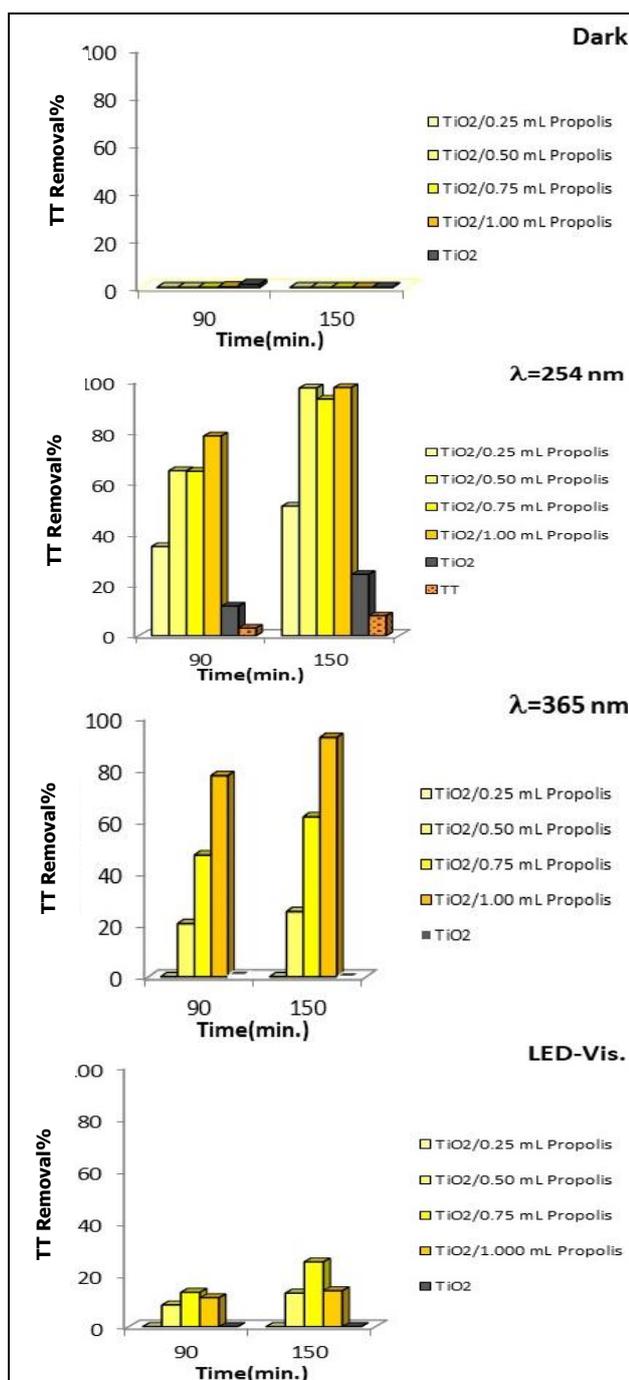


Figure 9. The photocatalytic removal of TT ($[C]_0 = 10 \text{ mg L}^{-1}$, catalyst mass = 1 g L^{-1} , light 254 nm, 365 nm and LED-vis).

4. Conclusions

It is shown that propolis doping promotes the electron transfer of titanium dioxide for effective photodegradation of food dye effluents. The catalysts were successfully prepared and characterized the first time and tested for photocatalytic removal of dye pollutants used in the food industry. Catalysts were anatase form and doped propolis amount was quite low. Propolis

related carbon doping does not have an enhancing effect on direct absorption of the dye on catalyst but certainly, have an excellent promoting effect on photocatalysis. Surface properties and the form of propolis on the TiO_2 surface need more detailed work to explain the mechanistic side of this doping effect.

Acknowledgments

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