# Alkaline treatment of PETG 3D printed structures for $TiO_2$ thin films adhesion aiming the p-toluic Acid photodegradation

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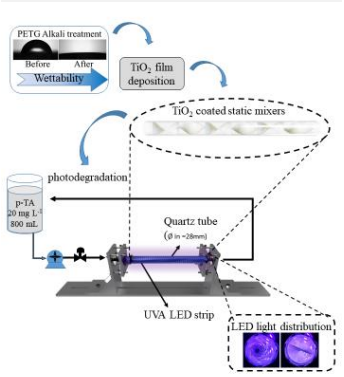


This study evaluated the surface modification of 3D printed PETG structures via alkaline treatment to enhance the adhesion of $TiO_2$ thin films deposited by dip-coating method. The influence of NaOH concentration and treatment time on the wettability was evaluated using response surface methodology. The results indicated that the increase of the NaOH concentration and the treatment time promoted the increased wettability and fixation of $TiO_2$ nanoparticles to the substrate. Therefore, Kenics-type static mixers made of PETG were subjected to alkaline treatment under the best obtained condition (3 mol $L^{-1}$ of NaOH, 60 min treatment), coated with $TiO_2$, and used in the photodegradation of the petrochemical pollutant p-TA, achieving 23% degradation in 480 min of UVA LED light irradiation. The film exhibited high stability, maintaining degradation efficiency for 5 reuse cycles.

## Introduction

The petrochemical pollutant p-toluic acid (p-TA) is toxic and exhibits resistance to conventional effluent treatment processes, such as biological treatments. Advanced oxidative processes, such as heterogeneous photocatalysis with $TiO_2$, offer a viable alternative for p-TA degradation [1]. Although $TiO_2$ suspension exhibits high efficiency, its recovery from the reaction medium is challenging. Thus, $TiO_2$ thin films eliminates additional recovery steps. Various substrates, including polymers, can support $TiO_2$ thin films due to their cost-effectiveness and high chemical and mechanical resistance. Polyethylene terephthalate glycol (PETG), widely used in 3D printing for its mechanical strength and chemical stability, can be limited in its ability to deposit $TiO_2$ nanoparticle thin films due to its low wettability. However, surface modifications in polymers can enhance interaction by forming surface organic groups, increasing roughness and wettability, for which alkaline treatment can be employed [2]. Static mixers, which increase mixing by enhancing medium turbulence, have been used as supports for $TiO_2$ thin films to reduce mass transfer limitations in the heterogeneous photocatalysis process, thereby increasing process efficiency [3]. This work aims to evaluate the surface modification of the PETG polymer regarding its wettability to facilitate the formation of $TiO_2$ thin films. The optimal condition obtained will be applied to a set of static mixers made by 3D printing and used in the photocatalytic degradation of the petrochemical pollutant p-TA to assess its efficiency and practical applicability.

## Material and Methods

p-TA (Sigma Aldrich, ≥98.0%). $TiO_2$ (Evonik, P25), with a particle size of 21 ± 10 nm. NaOH (Neon, ≥99.20%). PETG translucent polymer filament (Voolt 3D), with a diameter of 1.75 mm..

The design software Autodesk Fusion 360 (v2.0) was employed for the modeling of the fabricated 3D structures. Flat plates (20mm x 20mm x 1.6mm) and Kenics-type static mixers (28mm x 56mm x 1.6mm, α=90°) were manufactured from PETG filament using a Creality Ender 3 Pro 3D printer. The printing temperature for the PETG was set to 217°C, while the printing platform was maintained at 70°C.

The surface of 3D printed polymer plates was chemically modified using an alkaline treatment with NaOH. Prior to treatment, the PETG plates were dried in an oven at 60°C for 4 hours, then vacuum-dried for 24 hours. Subsequently, the plates were immersed in 100 mL of aqueous NaOH solution, heated to 70°C for a interval time. Afterwards, the plates were washed with ultrapure water to eliminate residual NaOH, dried at 60°C, and desiccated under vacuum for 24 hours. The effect of the alikaline treatment on the surface modification was evaluated using a $2^2$ factorial design, with NaOH concentration (1(–1), 2(0) and 3(+1) mol $L^{-1}$) and treatment time (20(–1), 40(0) and 60(+1) min) as variables, and the contact angle as the response. The statistical evaluation was performed using Statistica 8 software. The wettability of the plates was assessed by determining the contact angle using a Biolin Attension Theta Optical Tensiometer, with a 7 µL droplet of water.

Both untreated and NaOH-treated PETG plates underwent a dip-coating process, with a descent speed of 3 cm $min^{-1}$, an immersion duration of 60 seconds, and a withdrawal speed of 3 cm $min^{-1}$. For the coating, a suspension of $TiO_2$ 10% (m/V) in water:ethanol (90:10), pH 4, was used. The detachment evaluation tests were carried out by immersing the $TiO_2$-coated PETG plates in 80 mL of ultrapure water under ultrasonication (40 kHz) by 5 min.

For photocatalytic efficiency evaluation, a set of six

Kenics-type static mixers fabricated from PETG were subjected to alkaline treatment under the optimal condition obtained from the aforementioned evaluation and coated under the same conditions as the PETG plates. The mixers were arranged in a quartz tubular reactor (L= 36 cm, $D_{in}$ = 28mm, $D_{ex}$ = 32mm). An 800 mL solution of p-TA (20 mg $L^{-1}$), was introduced into the recirculation tank. The flow rate was adjusted to 14.4 L $h^{-1}$ (Re = 203). The irradiation source used was a 5 m LED strip containing 60 LEDs emitting in the wavelength range of 385 to 410 nm and power of 0.05 mW $cm^{-2}$. The LED strip was wrapped along the length of the tube to promote uniform light distribution. The system was kept under recirculation for 30 min for the dark adsorption. Aliquots of 5 mL were collected over the reaction time and analyzed in a UV-vis spectrophotometer (Agilent, Cary 100) at the wavelength of 236 nm, characteristic of p-TA. Reuse tests were carried out sequentially, without removing the static mixers from the reactor tube, only recharging the p-TA solution.

## Results and discussion

The Pareto chart (Figure 1a) shows that the concentration of NaOH exerted an effect approximately 2.2 times greater than that of the interaction variable. The response surface (Figure 1b) suggests a decrease in the contact angle corresponding to an increase in the levels of NaOH concentration and reaction time, thereby enhancing wettability. This observation could be attributed to the formation of chemical groups on the polymer surface during the process of alkaline hydrolysis [2]. Higher NaOH concentrations resulted in more efficient initial interaction with the polymer surface, promoting steeper degradation. The lowest contact angle measured was 27.69°, achieved with a treatment condition of 3 mol $L^{-1}$ and 60 min.

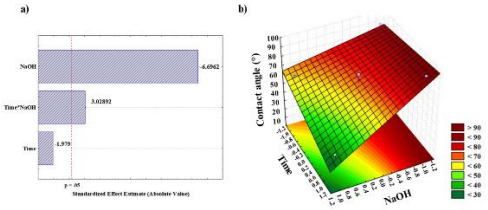


**Figure 1.** a) Pareto chart and b) response surface for experimental design

Figure 2 shows water droplets on PETG polymer surface before and after the alkaline treatment demonstrating the enhance of the wettability of the PETG.

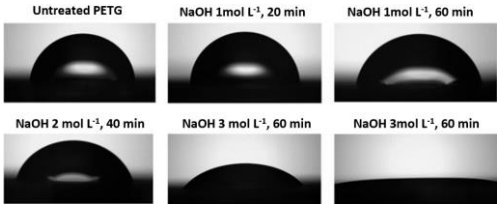


**Figure 2.** Images of the representative static water contact angles measured untreated and treated PETG polymer surface.

The PETG polymer plate, treated with 3 mol $L^{-1}$ NaOH for 60 min, exhibited a $TiO_2$ load of 3082 ± 307µg, while the average $TiO_2$ deposited on untreated plates was 2049 ± 134µg. This indicates that the surface treatment increased the $TiO_2$ loading capacity by approximately 33.5%. This could be related to increased wettability, promoting greater interaction between the surface polymer groups and $TiO_2$. The detachment test revealed a $TiO_2$ detachment of 50.50 ± 2.07% for plates treated with 1 mol $L^{-1}$ NaOH for 20 min and 18.26 ± 1.61% for plates treated with 3 mol $L^{-1}$ NaOH for 60 min. These results suggest that increased wettability enhances the fixation of $TiO_2$ particles.

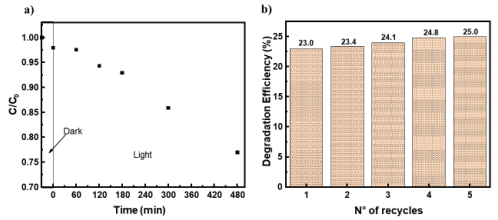


**Figure 3**. a) p-toluic acid degradation using 3D printed PETG static mixers coated with $TiO_2$ film and b) results of reuse tests.

The photoactivity and stability of the $TiO_2$ film on the PETG polymer were evaluated in a quartz tubular reactor containing a set of six static Kenics-type mixers, treated with NaOH (3 mol $L^{-1}$) for 60 min and coated with $TiO_2$. The measured $TiO_2$ load was 36100 µg, resulting in a distribution of 176.7 µg·$cm^{-2}$. The efficiency of a 23% was achieved after 480 min of irradiation (Figure 3a). The reuse evaluation (Figure 3b), demonstrated the high stability of the photocatalytic film. The average reuse efficiency was 24.06 ± 0.86, which attests to the system's high reusability. After the completion of the reuse cycles, no variation in the mass of $TiO_2$ was observed.

## Conclusions

The alkaline treatment proved effective in promoting the surface modification of the PETG polymer, as evidenced by the increase in wettability. The alkaline treatment led to an increase in the $TiO_2$ load by approximately 33.5% compared to the untreated polymer, and a noticeable improvement in the fixation of the $TiO_2$ film. Photocatalytic tests confirmed the system's high reusability and efficiency in degrading the p-toluic acid contaminant.

***Acknowledgments***
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***References***

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