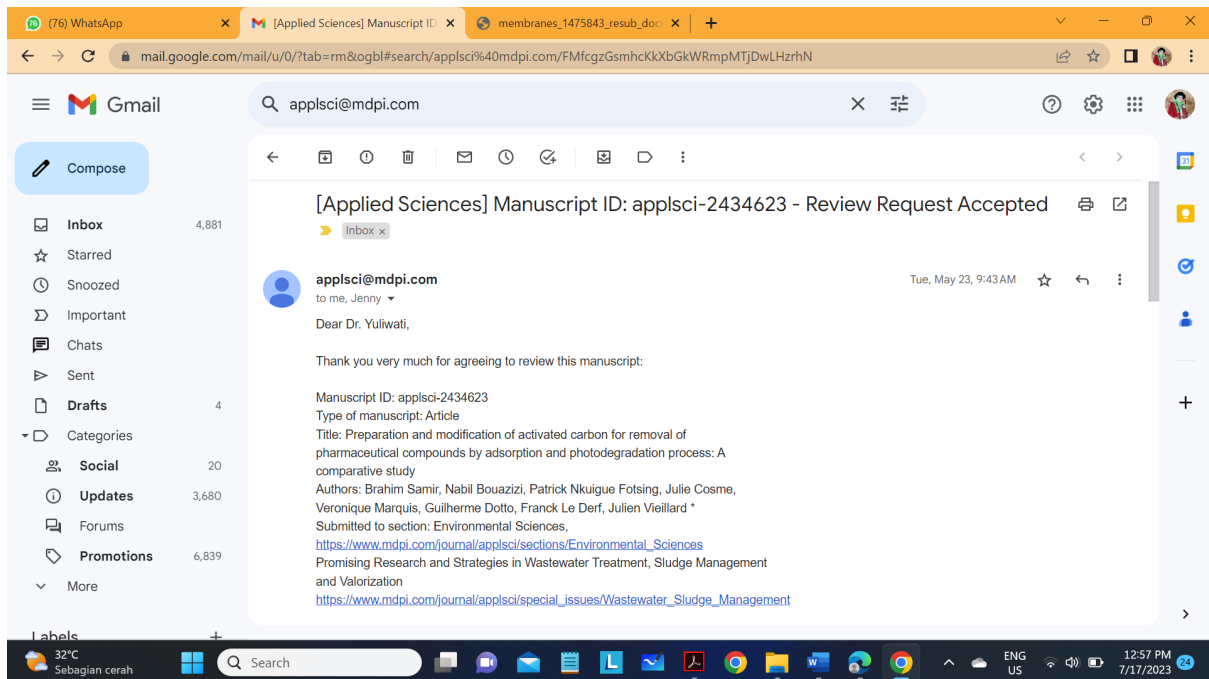
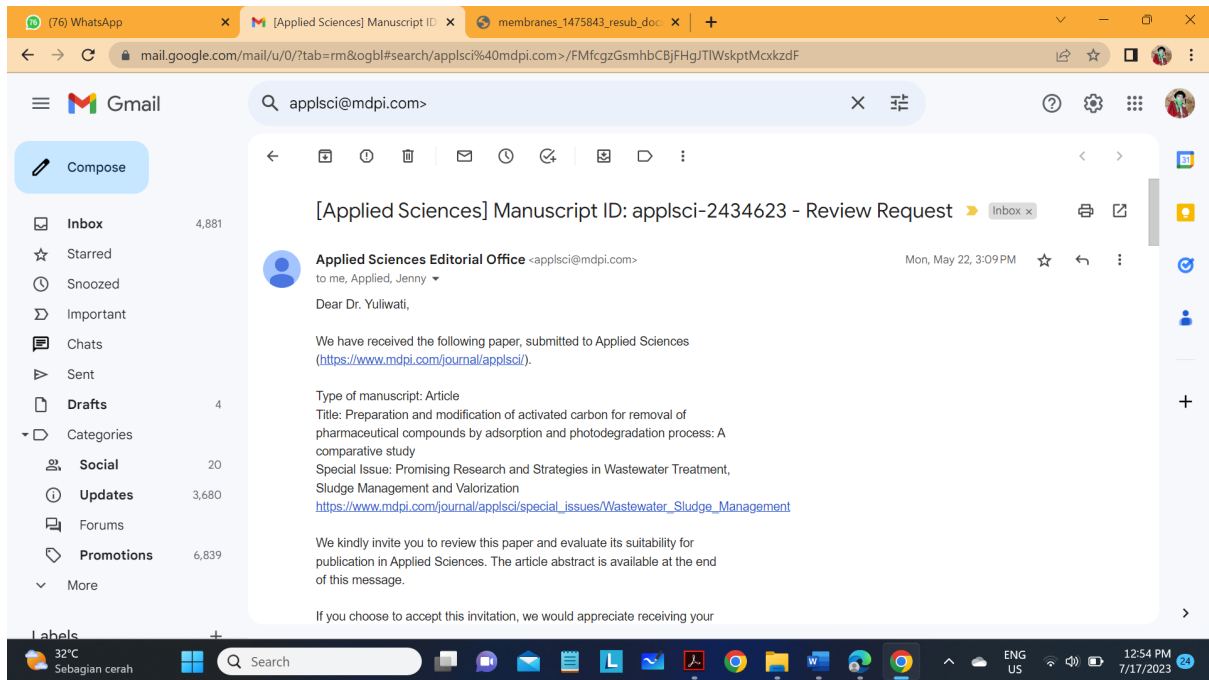


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Article

Preparation and Modification of Activated Carbon for the Removal of Pharmaceutical Compounds via Adsorption and Photodegradation Processes: A Comparative Study

Brahim Samir, Nabil Bouazizi, Patrick Nkuigwe Fotsing, Julie Cosme, Veronique Marquis, Guilherme Luiz Dotto, Franck Le Derf and Julien Vieillard

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Article

Preparation and Modification of Activated Carbon for the Removal of Pharmaceutical Compounds via Adsorption and Photodegradation Processes: A Comparative Study

Brahim Samir ¹, Nabil Bouazizi ¹, Patrick Nkuigwe Fotsing ¹, Julie Cosme ¹, Veronique Marquis ¹,
Guilherme Luiz Dotto ^{1,2}, Franck Le Derf ¹ and Julien Vieillard ^{1,*}

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Abstract: In the present research, the removal of pharmaceutical contaminants based on atenolol (AT) and propranolol (PR) using modified activated carbon (AC) in a liquid solution was studied. Two methods, adsorption and photodegradation, were used to eliminate AT and PR. First, AC was prepared from date stems and then modified via hydroxylation (AC-OH) and impregnated into titanium dioxide (AC-TiO₂) separately. The removal of AT and PR was investigated in terms of experimental parameters, such as pH, concentration, temperature, and the effectiveness of the processes. The results show that the removal of AT and PR reached 92% for the adsorption method, while 94% was registered for the photodegradation process. Likewise, in optimal experimental conditions, the adsorption of AT and PR over AC-OH showed good stability and recyclability, achieving five cycles without a visible decrease in the removal capacity. The results obtained in this work suggest that the low-cost and environmentally friendly synthesis of AC-OH is suitable to be considered for wastewater treatment at the industrial scale. Interestingly, the above results open a potential pathway to determine whether adsorption or photodegradation is more suitable for eliminating wastewater-related pharmaceutical pollutants. Accordingly, the experimental results recommend adsorption as a promising, durable, eco-friendly wastewater treatment method.

Keywords: hydroxylation; titanium dioxide; adsorption; photodegradation; atenolol; propranolol



Citation: Samir, B.; Bouazizi, N.; Nkuigwe Fotsing, P.; Cosme, J.; Marquis, V.; Dotto, G.L.; Le Derf, F.; Vieillard, J. Preparation and Modification of Activated Carbon for the Removal of Pharmaceutical Compounds via Adsorption and Photodegradation Processes: A Comparative Study. *Appl. Sci.* **2023**, *13*, 8074. <https://doi.org/10.3390/app13148074>

Academic Editors: Amanda Laca Pérez and Yolanda Patiño

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1. Introduction

In recent years, the concentrations of toxic pharmaceutical products in the global environment have increased substantially [1,2]. Pharmaceutical and chemical personal care products are widely used in daily life. Unfortunately, more than 50% of these hazardous products are discharged into the environment, such as in rivers, which can cause danger to fauna and flora [3]. Therefore, their destruction of ecological processes and functions in freshwater ecosystems is often called to be limited or reduced, as the continuous input of these pharmaceutical molecules in the water environment affects water safety, resulting in chronic toxic effects on organisms [4–7] and has potential impacts on human health through the food chain [8]. Numerous pharmaceutical products are discharged into the water environment, and atenolol (AT) and propranolol (PR) are the most used medicaments. PR and AT are medications called beta-blockers and are used to treat cardiovascular diseases, such as hypertension, tachycardia, and acute myocardial infarction [9]. In recent research studies, AT and PR were detected at high concentration levels in urban wastewater treatment plant effluents [10–13]. In addition, AT and PR were widely detected in hospital

sewage and wastewater treatments in concentrations ranging from about 0.78 to 6.6 µg/L in Greece [14]. Regarding the above problems, water quality is in danger, and alternative reserves or crucial solutions are requested to alleviate this issue. Wastewater treatments via biological, filtration, settling, adsorption, coagulation, and many other processes displayed interesting results in removing these toxic products. However, almost all these processes showed a real weakness due to the lack of continuous properties and the high energy consumption. Adsorption is a very useful method for wastewater treatments, representing an eco-friendly and low-cost option. While adsorption is suitable for water treatment, it can only be considered an effective process if the adsorbent has complementary properties that ensure its eco-friendly and high adsorption capacities during its utilization.

Numerous adsorbents have been developed with the above aims, such as metallic oxide, biomass, activated carbon, graphene oxide, metal–organic frameworks, and zeolites [15–19]. To produce eco-friendly and low-cost properties, researchers focused on biomass and its derivatives as potential adsorbents and effective candidates for wastewater treatments. Up to now, activated carbon has been considered one of the best materials for water treatment due to its surface properties, low cost, and high capacity to remove pollutants from water. However, the rapid saturation of these adsorbents means they must be changed or recycled frequently; heterogeneous photocatalysts can be a good alternative to adsorption. This chemical process of photocatalysis involves reactive radical species, such as hydroxyl radicals (HO·), in the presence of a semiconductor catalyst based on a metal oxide to degrade the pharmaceutical molecules. Titanium dioxide (TiO₂) is a good catalyst due to its photochemical stability. Lu et al. and many other researchers investigated the immobilization of TiO₂ nanoparticles on an activated carbon surface to improve the photocatalytic activity and make the separation of treated effluent more effective [20–23]. The results obtained toward this goal are of great importance and, up to now, have not been developed. The coating of surfaces with TiO₂ produces a relatively low improvement regarding the photocatalytic reaction because of the particles' low dispersion and limited mass transfer between the pollutant molecules and the catalyst [24,25]. Catalysts can be more effective and easily separated from the effluent [26–28].

In this regard, activated carbon covered with TiO₂ semiconductors is active since it enhances the photocatalytic reaction between TiO₂ and the contaminants due to the adsorption of pollutants on its surface [29,30]. Increased adsorption contributes to a higher concentration of contaminants around the TiO₂ active sites [31]. Therefore, this study was designed to examine removing AT and GT pharmaceutical products from the water via adsorption and photodegradation with activated carbon and activated carbon covered with TiO₂. This first study focused on treating products with environmentally activated carbon and TiO₂. The results of this study could be used as a solution for water treatments, which is considered the most important environmental pollution issue to be resolved. In detail, this study evaluated the removal of AT and PR via an adsorption process using agro-waste (date stems) as a source of activated carbon (AC). At first, the adsorption of AT and PR was evaluated on AC and AC-OH, and then, their photodegradation in the presence of a heterogenous photocatalyst (AC-TiO₂) was tested.

2. Materials and Methods

2.1. Materials

Zinc chloride (ZnCl₂), hydrochloric acid (HCl) 37%, titanium (IV) isopropoxide (TTIP) 97%, atenolol (AT), propranolol (PR), acid nitric (HNO₃), hydrogen peroxide (H₂O₂), iron (III) nitrate nanohydrate (Fe(NO₃)₃·9H₂O), and commercial activated carbon (AC) were purchased from Sigma-Aldrich, St. Louis, MI, USA. The chemical formulas and descriptions of AT and PR are presented in Table S1 and Figure S1.

2.2. Materials Synthesis

According to our previously published work, activated carbon was obtained from agro-waste, specifically from date stems [32,33]. The date stems were washed with distilled

water, dried at 105 °C for 24 h, and cut at around 0.2 cm. For activation, 48 g of date stems were stirred with 96 g of ZnCl₂ ($m(\text{ZnCl}_2) = 2 \times m(\text{AC})$) for 4 h and carbonized at 600 °C for 2 h under dried air. Afterward, the obtained product was washed with HCl 37% and dried at 80 °C overnight. The product obtained was identified as AC. To increase the number of the hydroxyl group (-OH) at the surface of activated carbon (AC), AC was impregnated into a solution of hydrogen peroxide, nitric acid, and deionized water (1:1:5 v/v/v, respectively) at 70 °C for 4 h. The obtained powder was filtrated, washed with deionized water, and dried at 80 °C overnight. The resulting material is denoted as AC-OH a refers to OH-enriched activated carbon. In parallel, activated carbon was coated with a TiO₂ solution via an in situ impregnation method, according to a method described elsewhere [34]. Briefly, 0.1 g of AC is added to different quantities of TTIP (30, 50, and 70%) and dissolved in 20 mL of isopropanol. The mixture was stirred for 1 h, washed with isopropanol, and dried at 70 °C for 6 h. The final obtained powder is identified as activated carbon over titanium dioxide (AC-TiO₂).

2.3. Materials Characterization

The prepared products were characterized by scanning electron microscopy (SEM) using a JCM-6000 electron microscope (JEOL, Rueil Malmaison, France) to observe the surface morphology of AC and AC-OH. The chemical composition of AC before and after adsorption and AC-OH were characterized through Fourier transform IR spectroscopy (FTIR) using a Tensor 27 (Bruker, Wissembourg, France) spectrometer with a ZnSe ATR crystal device. For each spectrum, 20 scans were accumulated with a resolution of 4 cm⁻¹. The thermal stability of AC and AC-OH was analyzed by differential scanning calorimetry (DSC) using a DSC-92 (Setaram, Caluire et Cuire, France) device at a heating rate of 5 °C min⁻¹ from room temperature to 550 °C. The zeta potential of each sample dispersion was measured in phase analysis light scattering (PALS) mode using a Zeta sizer nanoZS setup (Malvern, Palaiseau). For the zeta measurements, nanoparticle suspension was obtained by adding 100 mg of each sample to 10 mL of ultrapure water.

2.4. Adsorption Experiments

The batch adsorption experiments were carried out using 50 mL of the solution containing a 50 mg L⁻¹ concentration of the pharmaceutical molecules. The effect of pH was studied in the range from 2 to 10, where HCl and NaOH solution adjusts pH. Afterward, a predetermined amount of the adsorbent (0.010–0.8 g) was mixed into the solution before sonication at ambient temperature for 5–180 min. The supernatant was centrifuged at 2000 rpm for 3 min. Then, the absorbance was measured using a UV-vis spectrophotometer (Shimadzu Uv-1900) at λ_{max} of each molecule at 224 and 288 nm for AT and PR, respectively. The results are averages of a minimum of 3 experiments.

The percent removal of contaminant and the adsorption capacity was calculated using Equations (1) and (2).

$$\text{Contaminant removal \%} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$\text{The capacity for adsorption} = (C_0 - C_t) \times \frac{V}{M} \quad (2)$$

C₀ mg/L and C_t mg/L are the initial concentration and concentration at time “t”, respectively. “V” (mL) is the volume of (PR, AT), and “m” (mg) is the mass of the adsorbent.

2.5. Photocatalytic Experiments

The UV chamber (Model, 2000), 12.7 cm × 12.7 cm, was purchased from DYMAX, Germany. A UV lamp (DYMAX, Wiesbaden, Germany) that had a 400 W UV-mercury lamp. It generated a continuous spectrum of 320–400 nm with a measuring intensity of 225 mW/cm². Batch experiments were carried out in 500 mL quartz beakers, where the

light source was held perpendicular to the batch reactor. Both catalytic and noncatalytic degradation was measured under identical conditions. Before absorption analysis, samples were collected at regular intervals and centrifuged (5000 rpm, 10 min). Then, the concentration of AT and PR were determined by measuring the absorbance (spectrophotometer UV-1900 Shimadzu, Marne La Vallée, France) at 224 and 288 nm, respectively.

3. Results

3.1. Morphological Properties

Figure 1 shows SEM analysis of AC (activated carbon), AC-OH (OH-enriched activated carbon), and AC-TiO₂ (activated carbon over titanium dioxide) samples. A smooth and nonuniform surface is registered for AC and its modified counterpart. The average particle size is around 50 µm. The presence of many cavities on the material's surface designs the morphology of AC. However, the addition of TiO₂ nanoparticles is confirmed by the high distribution of TiO₂ particles on the AC surface. A visible change is observed by the cavity displayed in Figure 1g, explaining the successful coating of TiO₂ particles onto the AC surface. The TiO₂ particles are spherical and distributed uniformly at the AC surface. It should be noted that the in situ synthesis of metallic particles presents a weak aggregation. Herein, immobilizing a high amount of TiO₂ over AC could be baneful for surface reactivity and the adsorption of pollutants. The morphology changes of AC and AC-TiO₂ are shown by the fewer cavities than AC, which suppose that TiO₂ occupied the majority of the surface.

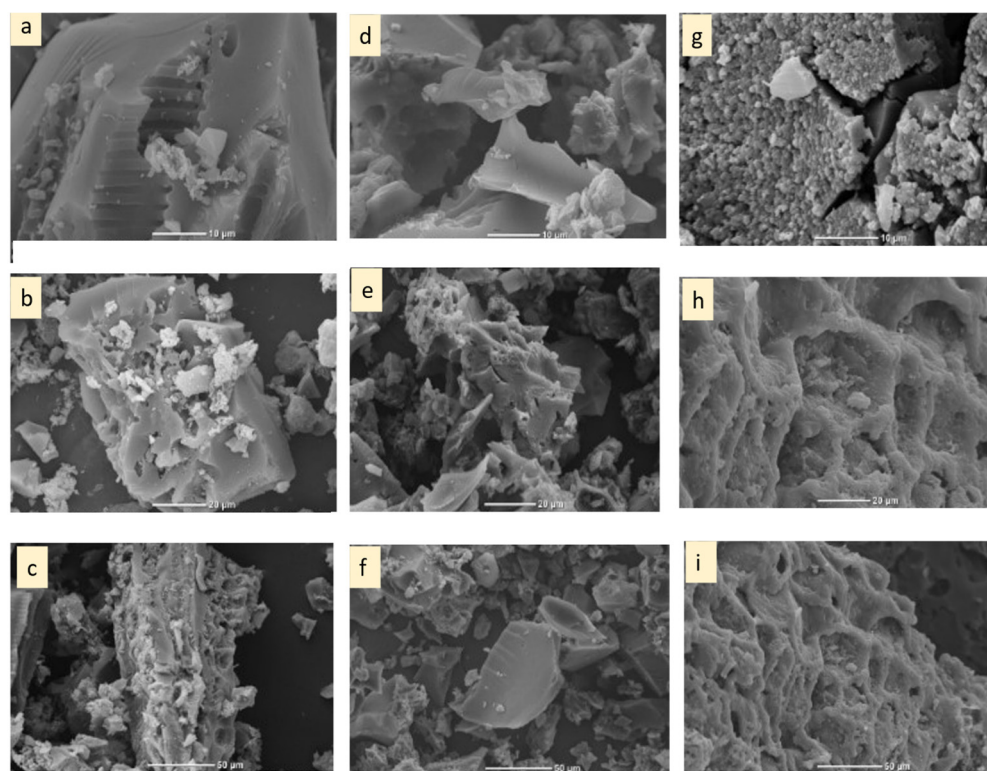


Figure 1. SEM images of AC (a–c), AC-OH (d–f), and AC-TiO₂ (g–i).

3.2. Surface Properties

Figures 2 and 3 show the FTIR analysis for all samples to investigate the surface properties and the stability of synthesized samples in liquid media. Starting by measuring the ZP values of all samples, it was found that the ZP of AC-OH is less than 20 mV, suggesting the good stability of the materials. Although, ZP results confirmed the successful addition of hydroxyl groups at the AC surface, as supported by noticeable decreases in ZP. The surface charge of the particles has a potential effect on catalytic activity, as it

could involve such interaction with pharmaceutical pollutants. The results on the AC-TiO₂ surface displayed a marked decrease in the zeta potential from 8 mV for AC to −14 mV for AC-TiO₂. The negative surface charge could play a key role in the adsorption of pollutants from the water.

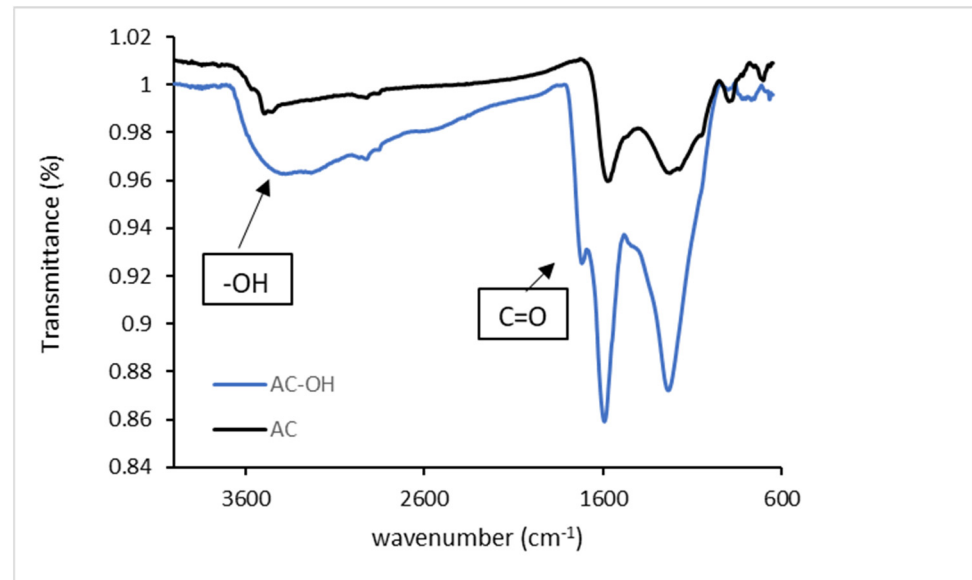


Figure 2. FTIR spectra of AC and AC-OH.

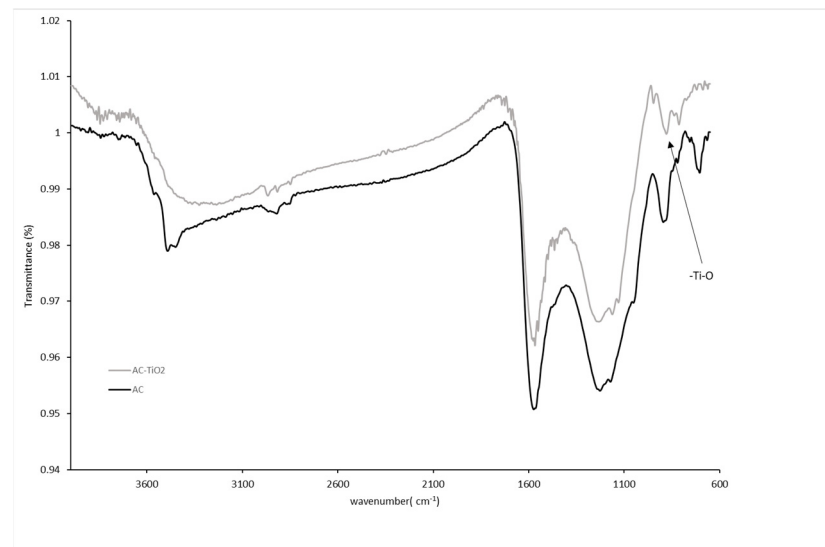


Figure 3. FTIR spectra of AC and AC-TiO₂.

According to the Fourier transform infrared spectrum shown in Figure 2, the peaks of the AC surface before and after hydroxylation treatment are different from one sample to another. For AC, the peak located at 1579 cm^{-1} is assigned to the stretching vibration of C=C, whereas the band observed at 1259 cm^{-1} is attributed to the bending vibration of C-H in the methylene group. At the same time, the spectrum of AC-OH displayed a visible change due to the hydroxylation steps. The new band that appeared at 3415 cm^{-1} is associated with hydroxyl groups' stretching vibration (-OH). Accordingly, the chemical structure of the synthesized samples, the bands centered at around 1720 cm^{-1} and 1105 cm^{-1} , are attributed to the presence of the C=O and C-O groups, respectively.

A comparison between the FTIR spectra of AC and AC-TiO₂ is shown in Figure 3. The stretching vibration of the hydroxyl group registered at 3400 cm⁻¹ is assigned to the physisorbed surface water [34]. A slight shift to a lower wavenumber is observed and explained by the presence of TiO₂ on the AC surface. According to Loo et al., the peak that appeared at 768 cm⁻¹ is assigned to the stretching vibration of Ti-O [34].

3.3. Thermal Properties

DSC analysis was performed to investigate the thermal properties of AC and AC-OH. AC samples produced a higher endothermic peak. This peak detected around 90 °C corresponds to the dehydration of the adsorbents. In addition, AC displayed an exothermic peak from 410 to 500 °C associated with the degradation of cellulose, lignin, and hemicellulose. DSC thermograms of AC-OH (Figure 4) display two endothermic peaks around 90 and 400 °C associated with the dehydration and dihydroxylations of the date stem. All of these results correspond to the literature as well as SEM and IR data.

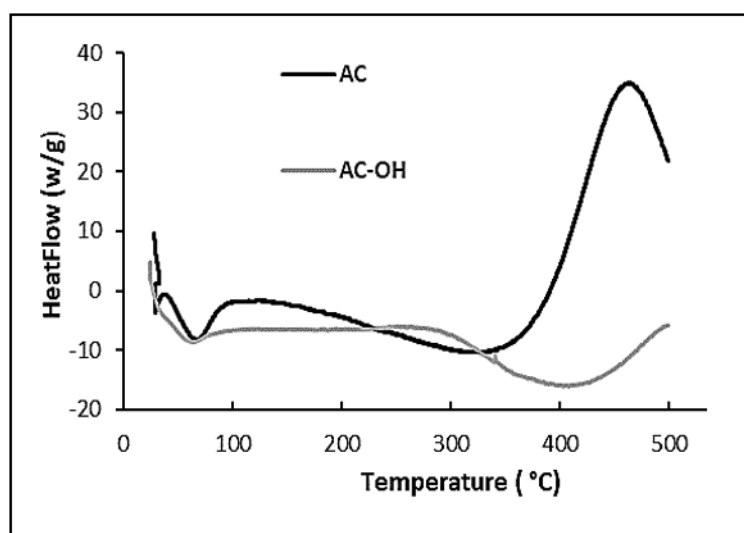


Figure 4. DSC analysis of AC and AC-OH.

3.4. Adsorption of Atenolol and Propranolol

The adsorption of AT and PR was carried out in the presence of AC and AC-OH. A commercial activated carbon (AC) was also evaluated for removing AT and PR from contaminated water. To investigate the parameter effects on the adsorption of pharmaceutical products, temperature, initial concentration, and pH were studied in terms of adsorption capacity. The results are shown in detail in the Supplementary File. As seen in Figures S2–S4, the high temperature was not suitable for the adsorption of AT nor PR molecules due to their limited temperature stability. The adsorption capacity increased as the concentration of pollutants increased to achieve the equilibrium phase, indicating its saturation [14,26,35]. Measurements on the effect of pH displayed that the adsorption of pharmaceutical molecules could have been performant in basic media, while the acidic solution avoided competition with a proton. The removal capacities of the samples, which had the same experimental conditions, i.e., the synthetic and the commercial AC, are reported in Figure 5. The results show that both samples adsorbed the pharmaceutical products in two distinct phases. A rapid adsorption process describes the first phase, while equilibrium steps characterize the second phase. The large number of active sites available at the AC surface for the adsorption of AT and PR explains this result. Meanwhile, over 60 min, the main part of these active sites became saturated by adsorbate, resulting in limited access to more molecules in the solution. Therefore, the second step was reached to achieve the adsorption equilibrium [14].

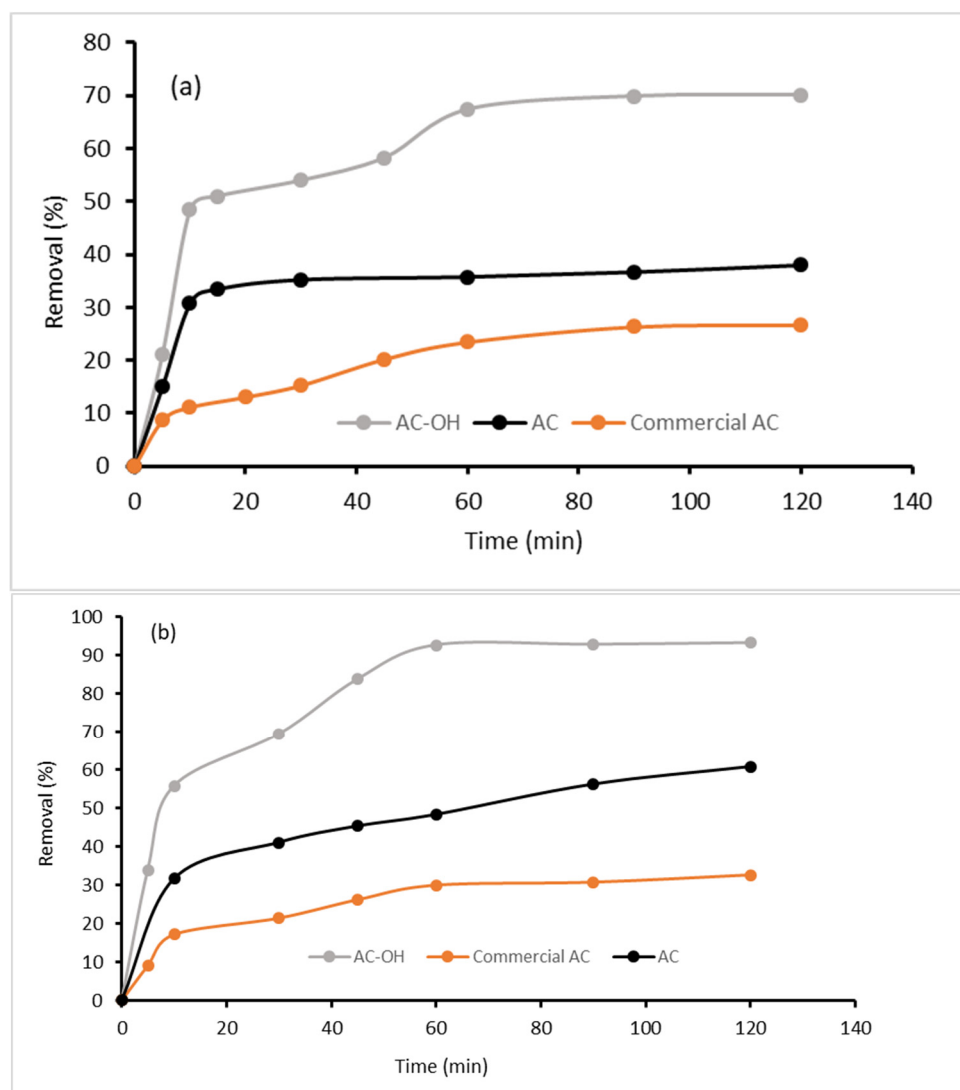


Figure 5. Removal capacity of (a) AT and (b) PR over AC, AC-OH and commercial AC.

A comparison of the adsorption capacity of commercial and prepared AC shows that AC synthesized from date stems produced a higher adsorption uptake (60%) than commercial AC (32%). This trend can be explained by the key role of treatment and carbonization in this work. It was found that our prepared AC's equilibrium time is longer than the commercial AC's. Interestingly, the best performance is observed for the AC-OH sample, where the adsorption capacity is over 93% for the removal of PR in 120 min. The adsorption kinetic is also faster with AC-OH because the equilibrium was reached after 60 min, and only 10 min is required to adsorb 56% of the PR. This result can be explained by the negative charge surface of AC-OH, as supported by the Zeta potential measurement. For the atenolol molecule, the performance of AC and AC-OH is still higher than that of commercial AC, but the adsorption was more difficult than for propranolol. Indeed, 67% of the AT was adsorbed on AC-OH compared to 36% and 23% for AC (from date stem) and commercial AC, respectively.

3.5. Photocatalytic Degradation of Atenolol and Propranolol

The effect of TiO_2 concentration is considered the first parameter that can affect the removal efficiency of the catalyst. The photocatalytic activity of AC- TiO_2 was measured for various concentrations of TiO_2 (30%, 50%, and 70%); the results are shown in Figure S6. The results show that AT and PR's photocatalytic degradation depends on the TiO_2 quantity.

While the TiO_2 concentration increased, photocatalytic degradation increased. The rise of photocatalyst radicals can explain this. The degradation continued until reaching an optimum close to 50%. Measurements on the AC-OH-supported TiO_2 were investigated regarding adsorption capacity for both molecules AT and PR. Figure 6 depicts the results obtained for the photocatalytic efficiency of AC-OH/ TiO_2 and AC- TiO_2 .

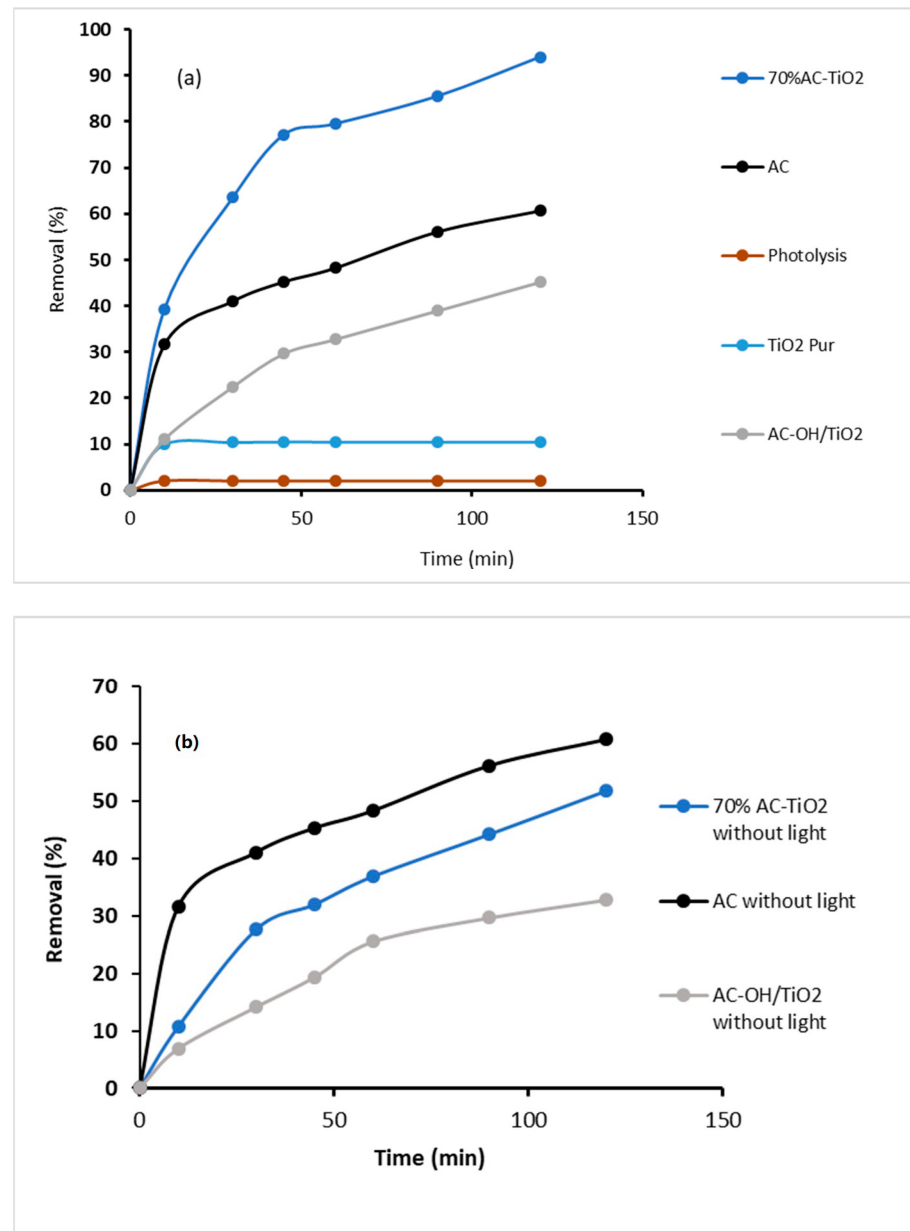


Figure 6. Removal of PR (a) with and (b) without light using AC, TiO_2 , AC-OH, AC-OH-/ TiO_2 , and AC- TiO_2 catalysts.

According to the obtained results, it is clear that AC-OH/ TiO_2 can eliminate more than 45% of PR, while AC- TiO_2 achieves 94% degradation. Photolysis and pure TiO_2 are tested separately to understand the high degradation capacity. Only 10% PR removal is obtained for the materials, suggesting the potential role of the coating process for AC-OH and TiO_2 .

Experiments were carried out in the presence of and without light to demonstrate the beneficial effect of irradiation light combined with AC-OH- TiO_2 and AC- TiO_2 . Figure 7 demonstrates that light is combined with AC- TiO_2 to obtain high adsorption uptake. The

removal of PR and AT by AC-OH-TiO₂ and AC-TiO₂ without light is mainly due to their adsorption on the active surface. Results showed that the photocatalytic degradation efficiency increased significantly for all AC-TiO₂ composites compared to pure TiO₂. When (PR and AT) are adsorbed on the AC surface, they react with reactive radicals by an oxidation reaction; this improves the catalyst activity. Hayati et al. [36] confirmed that AC is very important because it could act as an electron sink, which allows for the interfacial transfer of photo-induced electrons from TiO₂ to AC and the inhibition of the electron recombination rate.

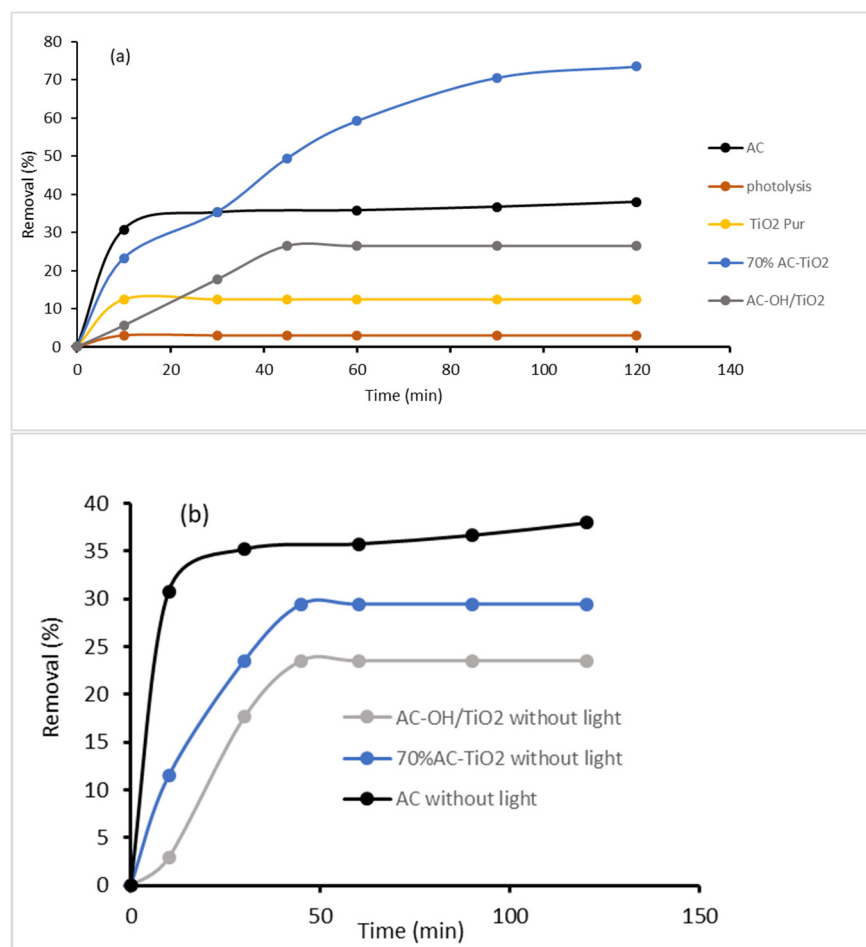


Figure 7. Removal of AT (a) with and (b) without light using AC, TiO₂, AC-OH, AC-OH/TiO₂, and AC-TiO₂ catalysts.

3.6. Stability and Reusability of the Prepared Materials

The reusability of the prepared materials is investigated and evaluated. The AC-based adsorbent is tested for various adsorption cycles, and the results are displayed in Figure 8.

From the recyclability test, it was established that the system could work with a removal efficiency close to 50% for the studied molecules (AT, 46%; PR, 58%) for a minimum of four cycles. After each adsorption cycle, the adsorbent AC-OH is used for the desorption system, in which the leaching solvent is methanol. The histogram of the removal of AT and PR after each cycle is represented in Figure 8. As seen, for the PR removal, in the first cycle, percent recovery rates of 92% were reached in 2 h, while the second cycle shifted to 87%, which can be considered appreciable results for the recycled adsorbent. The same trend was observed for the removal of AT, which presents a slight decrease from 70% to 65%. Importantly, the developed materials had good recyclability, reaching 52% of PR removal

over the fourth cycle. Accordingly, the obtained results could be considered a suitable and stable adsorbent for removing pharmaceutical products.

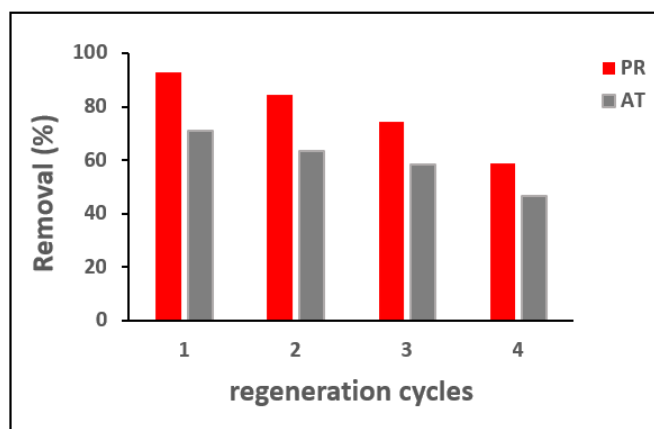


Figure 8. Effect of regeneration cycle on adsorption removal for PR and AT pharmaceutical contaminants.

The adsorption capacities of the pharmaceutical molecules were compared with data already published using other adsorbents. Table 1 summarizes the maximum adsorption capacity over various adsorbents for treating AT and PR. Comparatively, it was found that AC-OH showed a better adsorption capacity for AT (288 mg/g) and PR (339 mg/g) compared to the other adsorbents, such as granular activated carbon, hematite nanoparticles, and activated carbon fiber. Interestingly, this finding can open a new prospect to evaluate the prepared materials for other toxic molecules on a large scale, like the industrial scale.

In addition, it will be important to evaluate the efficiency of AC-TiO₂ on the photodegradation uptake. It was clear that AC-TiO₂ performs well on the photodegradation of AT and PR in liquid solution. Table 2 reports the photocatalytic degradation capacity using AC-TiO₂ compared to other commercial photocatalysts reported in the literature. However, the photocatalytic degradation of pollutants by TiO₂ has been extensively studied, while there are few reports of utilizing AC-TiO₂ to degrade atenolol and propranolol (Table 2). It can be observed that AC-TiO₂ is an efficient candidate to eliminate AT and PR, as compared to the other catalysts. It is interesting to note that AC-TiO₂ is efficient in treating concentrated solutions of AT and PR in a short time compared to data already published in the literature. It should also be reminded that AC-TiO₂ is inexpensive as it is prepared from a lignocellulosic agro-waste.

3.7. Comparison between the Adsorption and the Photocatalysis Methods

As mentioned in the introduction, this work comprehensively compared two methods for the water treatment, i.e., adsorption and photodegradation techniques, using the same support like AC-OH and AC-TiO₂ for adsorption and photodegradation, respectively. Despite the interesting results obtained in the above section for both processes, a distinguishing difference can be illustrated in many aspects, particularly the reusability and the cost. Accordingly, the most useful and more suitable methods for wastewater treatment can be selected. On the one hand, the photocatalytic degradation of pharmaceutical products is based on utilizing TiO₂ nanoparticles, which represents one of the most promising methods to decontaminate water containing organic pollutants, such as AT and PR. In its nanometric form, titanium dioxide is considered the first interesting catalyst for photocatalytic wastewater treatments, as it presents high stability. Also, in light of the results obtained in this work, it was found that TiO₂ incorporated over AC is attractive due to its highly reactive surfaces, which make them a good photocatalyst of pollutants. Unlike the high energy consumption caused by the UV light during the sorbent activation, nanoparticle powders can be released in treated water, contaminating the environment. As the toxicity of the environment is not accepted to any degree, photodegradation via AC-TiO₂ is limited

and cannot be developed on a large scale, including any industrialization of the process. However, the adsorption process represents an appreciable removal capacity of up to 89% of AT and PR pharmaceutical pollutants. Likewise, the adsorption methods are widely employed since it provides many advantages, such as low energy consumption, strong reusability, cost-effectiveness, and easy handling.

Table 1. Comparison of the adsorption capacity of AT and PR over various adsorbents.

| Pharmaceutical Molecules | Adsorbent | Maximum Adsorption Capacity (mg/g) | References |
|--------------------------|--|------------------------------------|------------|
| Atenolol | Waste-biomass-derived activated carbon | 183.7 | [37] |
| | Graphene oxide | 93.0 | [35] |
| | Granular activated carbon | 1.2 | [14] |
| | Activated palm kernel shell | 0.2 | [37] |
| | Multiwalled carbon nanotube | 5.1 | [38] |
| | Corncob biochar-Mt | 90.0 | [39] |
| | AC | 119.7 | This work |
| | AC-OH | 288.0 | This work |
| Propranolol | Graphene oxide | 68.0 | [35] |
| | Activated carbon fiber | 0.3 | [40] |
| | Smectite clay mineral montmorillonite | 161 | [41] |
| | AC | 202 | This work |
| | AC-OH | 339.0 | This work |

Table 2. Comparison between photocatalytic degradation of (AT and PR) in this study with other catalysts reported in the literature.

| | Catalyst | Light Source | Concentration (mg/L) | Time (h) to Reach Maximal Degradation | References |
|-------------|--|----------------------------|----------------------|---------------------------------------|------------|
| Propranolol | Aeroxide TiO ₂ P25 | Low-pressure mercury lamp | 26 | 3 h (92%) | [9] |
| | AC-TiO ₂ | UV-lamp | 50 | 2 h (94%) | This work |
| | Degussa P25 TiO ₂ | Xe lamp | 15 | 1 h (100%) | [42] |
| | Ag-TiO ₂ | High-pressure mercury lamp | 20 | 0.5 h (92%) | [43] |
| Atenolol | TiO ₂ /Salicylaldehyde-NH ₂ -MIL-101 | Xe lamp | 10 | 1 h (82%) | [44] |
| | Quartz fiber-TiO ₂ | High-pressure mercury lamp | 0.002 | 6 h (50%) | [45] |
| | Aeroxide TiO ₂ P25 | Low-pressure mercury lamp | 80 | 3 h (87%) | [9] |
| | AC-TiO ₂ | UV-lamp | 50 | 2 h (73%) | This work |

Interestingly, no secondary contamination can be caused by this eco-friendly adsorption during water treatment. To date, wastewater treatment by adsorption can be used in full-scale applications, and very effective results are obtained using this method [15,16,46,47]. On the other, to assess the possible environmental impact and the safety of the whole process, the absence of toxic effects of the process effluents must be guaranteed. Accordingly, the adsorption process is more efficient than photodegradation methods.

4. Conclusions

We have compared the adsorption and the photodegradation methods in wastewater treatment, particularly the removal of pharmaceutical products (AT and PR). In this regard, biomasses based on date stem were activated and calcinated to prepare an activated carbon (AC). The AC materials were modified by a hydroxylation strategy to increase the hydroxyl

groups over the AC surface, resulting in AC-OH. In addition, to ensure the photodegradation methods, AC was impregnated into TiO₂ solution to produce AC-TiO₂. The prepared materials were characterized and tested for the removal of AT and PR. The results show that the obtained adsorbent exhibited high adsorption capacity for both molecules. The core of the adsorption mechanism involved interactions such as an electrostatic attraction between adsorbate pharmaceutical molecules and AC-OH adsorbent in the aqueous medium. AC-OH regeneration was studied through four adsorption–desorption cycles and found to have a recovery rate of more than 50% after adsorption. A comparison between the treatment methods proved that adsorption is more suitable for removing pollutants from water, as it presents low energy consumption. The study facilitates the preparation of recyclable and stable adsorbent material for wastewater treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app13148074/s1>, Table S1: Properties of atenolol and propranolol; Figure S1: Chemical structure of propranolol and atenolol; Figure S2: The effect of temperature on the adsorption capacity of AT and PR; Figure S3: Effect of concentration variation in the adsorption capacity of AT and PR; Figure S4: The effect of pH variation in the removal of (a) atenolol and (b) propranolol; Table S2: Thermodynamic parameters for Langmuir and Freundlich models; Figure S5: Thermodynamic adsorption of AT and PR on AC-OH; Table S3: Thermodynamic adsorption parameters for AT and PR; Figure S6: Removal capacity of (a) PR and (b) AT by AC doped with various % TiO₂.

Author Contributions: B.S., P.N.F., J.C. and V.M. were involved in the investigation. B.S., N.B., J.V. and G.L.D. were involved in the writing, supervision, and funding acquisition. F.L.D. was involved in the supervision. All authors have read and agreed to the published version of the manuscript.

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