Photocatalytic Cellulose-Paper: Deepening in the Sustainable and Synergic Combination of Sorption and Photodegradation

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ABSTRACT: Clean water is one of the sustainable development goals set by the United Nations for 2030. The development of effective but worldwide affordable strategies is essential to guarantee this achievement. Photocatalysis technology fulfills these criteria whenever the photocatalyst is sustainable and nontoxic. In this article, a cellulose-paper modified with a polyamide-titanium dioxide (TiO₂) nanocomposite by dip-coating is evaluated to degrade estrogens efficiently under solar light. The study deepens on the synergic combination of the sorptive capacity of the polyamide and the activity of TiO₂. The photocatalytic performance was studied under artificial and sunlight in a miniaturized experimental setup (batch of six reactors). Also, the effects of the dispersed/immobilized catalyst, irradiation time, and adsorption evaluation were studied under kinetic conditions. The photocatalyst composition, considering the immobilized catalyst, irradiation time, and adsorption evaluation were studied with a response surface methodology, and the reusability of the photocatalytic nanocomposite ingredients, and its performance under sunlight make the material attractive for in-field application.

INTRODUCTION

In 2010, the United Nations (UN) clearly stated the human right to clean water and sanitation.1 Although this issue is mostly solved in many nations, it is a recurrent health and economic concern in low-income countries. According to a joint World Health Organization (WHO) and United Nations Children’s Fund (UNICEF) report, 785 million people did not have access to a basic drinking water service in 2017.2 The UN has challenged the scientific community to design strategies that make possible the worldwide access to clean water by the definition of a specific sustainable goal for 2030.3 These strategies should be affordable to be implemented easily and at low cost. The removal of pollutants from water is one of the action areas, and in this context, photocatalysis is a very attractive strategy due to its performance and simplicity.4

Although different materials have been evaluated as photocatalysts,5–8 TiO₂ nanoparticles (NPs) are the most used due to their high efficiency, low price, and nontoxic character. They can be directly dispersed in the contaminated water as a (nano) powder, although this is not too practical in large-scale processes as the NPs are hard to be recovered after being deployed. Also, isolated TiO₂ NPs have a wide band gap (≈3.2 eV), which is only active in the UV region.5,10 This limitation can be overcome by the photosensitization of the inorganic semiconductors by tuning their bandgap response to the visible region. This process can be undertaken by doping it with nonmetals, incorporating or depositing noble metals (ions), and synthesizing nanocomposites.11 Polymer-TiO₂ nanocomposites have received growing attention for their applications in photocatalysis, sensing, and photoelectric applications. The immobilization of the nanocatalyst on a polymeric substrate/support can play several complementary roles, namely, mechanically stabilize the photocatalyst, eliminate the need of recovering the NPs suspended in the medium after the water treatment, and increase the interaction with organic compounds via selective adsorption.12,13 Several polymer-based TiO₂ photocatalysts have been developed for the visible-light degradation of pollutants, including polypropylene,14 aromatic polyamide dendrimer/polystyrene,15 polyamides such as nylon-6 (N6),16,17 polyurethane,18 polyethylene,19 poly(vinyl alcohol),20 polythio-
phene,\textsuperscript{12} and even recycled polymers.\textsuperscript{21} N6 is widely used in many fields because of its low price, favorable mechanical strength, and high thermal and chemical stability. Therefore, the hybrid material obtained from N6 and TiO\textsubscript{2} is a potential candidate for many applications.\textsuperscript{6,22,23}

Cellulose paper is an excellent substrate for the fabrication of functional materials as it is sustainable, porous, and presents a large superficial area.\textsuperscript{44–27} Also, it can be easily modified by covalent bonding or simple deposition of functional groups/ phases on its surface. The latter approach is simpler and reduces the solvents/reagents required. The synthesis of functional papers by dip coating, which has been recently reviewed,\textsuperscript{28} has allowed the preparation of papers covered with polymers,\textsuperscript{29–31} nanoparticles,\textsuperscript{32} and nanocomposites.\textsuperscript{33} In a previous communication,\textsuperscript{34} we proposed a photocatalytic paper, and the present article deepens the understanding of the synergic combination of sorption and photocatalysis using a relevant environmental problem, the removal of hormones from water, as a model.

Endocrine disrupting compounds (EDCs) are dangerous pollutants that can be found at low concentrations in environmental waters.\textsuperscript{35} EDCs are pseudo-persistent substances and, therefore, a long-term environmental issue.\textsuperscript{36} EDCs interfere with the endocrine system at the molecular level, blocking natural hormones’ function or mimicking them, thus producing adverse effects on both humans and wildlife. EDCs are a broad term that includes hormones (natural or artificially administered) and chemicals of different nature.\textsuperscript{37} The presence of hormones in the environment has increased due to their extensive medical and veterinary uses.\textsuperscript{38,39} In this sense, estrone (E1), 17β-estradiol (E2), and estriol (E3) are potent biogenic estrogens that are usually detected in sewage\textsuperscript{40} and have been reported as the significant reason for estrogenicity in the effluents of sewage treatment plants.\textsuperscript{41,42}

Estrogens are resistant to biodegradation in conventional wastewater treatment processes making these substances a significant concern regarding the water quality\textsuperscript{43,44} and an excellent challenge to evaluate the performance of photocatalysis. This work describes a N6-TiO\textsubscript{2}–coated cellulose-paper photocatalyst for the efficient sorption/photodegradation of E1, E2, and E3. The ingredients of the photocatalytic cellulose-paper present low toxicity. In fact, the reported oral LD50 in rats for cellulose and TiO\textsubscript{2} nanoparticles is 5000 mg/kg.\textsuperscript{45,46} Nylon 6 can be considered nontoxic,\textsuperscript{47} while its monomer, ε-caprolactam, presents an oral LD50 in rats of 1200–1600 mg/kg.\textsuperscript{48} This aspect and the good performance of the photocatalytic cellulose-paper under sunlight make the material attractive for in-field application. Photocatalysis can be applied in two different scenarios: the treatment of a large volume of water for community sanitation or smaller volumes for individual or small groups. In the latter context, the use of the photocatalysts in water bottles is really interesting.\textsuperscript{49} Although plastic bottles are cheaper and their solar irradiation does not induce excessive leaching of hazardous compounds,\textsuperscript{50} the use of glass bottles can be an answer to the worldwide plastic environmental crisis.\textsuperscript{51} This study works in this scenario as the assays are performed in closed glass vials.

\section*{RESULTS AND DISCUSSION}

The UV–vis absorption spectrum for the photocatalytic paper (henceforth PCP for simplicity) presents a wider maximum absorption band with a sharper peak in the UV region (Figure S1). In the same Figure S1, the normalized emission spectrum of a visible LED source and sunlight is also presented for comparative purposes. Although, according to the overlapping curves, sunlight is clearly the best option to achieve a rapid degradation of the studied compounds, the photocatalytic performance of the material was initially evaluated under LED irradiation to understand more clearly the effect of pollutant sorption in the overall process.

The polymer plays a double role in this application. On the one hand, it stabilizes the NPs mechanically, avoiding their dispersion into the water. On the other hand, the polymer retains the hormones by a double mechanism,\textsuperscript{52} hydrophobic interaction with the polymeric backbone and H-bonding with the amide group, close to the photocatalytic hotspots. This aspect can be inferred from the results presented in Figure 1

![Figure 1](https://doi.org/10.1021/acsomega.1c00128)

Figure 1. Comparison between dispersed and immobilized TiO\textsubscript{2} in the degradation of estrogens. Membrane composed of 3% N6 and 4% TiO\textsubscript{2} dipped two times; 5 mL of a mixture of the analytes at 1 mg L\textsuperscript{−1} in ultrapure water; after irradiating the solutions for 4 and 7 h, the solutions were kept in contact with the PC in the dark for 30 min; constant agitation at 500 rpm.

where the activities of dispersed TiO\textsubscript{2} NPs and PCP are compared. Under the preliminary experimental conditions indicated in the figure caption, PCP always provided a higher removal of the estrogens at the two times studied. Another preliminary study was developed to evaluate the contribution of the sorption to this removal. Figure S2 shows the comparison between the removal efficiency of the paper containing only N6 and the photocatalytic paper containing a mixture of nylon and TiO\textsubscript{2}. The results demonstrated that both effects (sorption and photodegradation) were behind the removal of the hormones. However, a major contribution has been achieved using the PCP, which indicates its efficiency for the photodegradation of the compounds.

\textbf{Photocatalytic Cellulose-Paper Composition and Surface Characterization.} In this study, a Box–Behnken design was used as a chemometric tool to achieve the ideal proportion of N6/TiO\textsubscript{2} and the number of dips to provide the maximum removal of estrogens from the solution. The effects of N6 and TiO\textsubscript{2} percentages (0.5, 2.0, 3.5% w/v and 0, 2.5, 5.0% w/v, respectively) and dips (1, 2, and 3) on the withdrawal of estrogens were studied by a three-factor Box–Behnken design. The geometric means of the chromatographic peak areas for all the analytes were used as the signals. The response surfaces obtained with this optimization are shown in Figure 2.

Analyzing the results in Figure 2 obtained through a special cubic model with an $R^2$ of 0.9224, the best removal results
were obtained using 3.5% N6, 5% TiO2, and dipping three times the paper. This result corroborates the hypothesis that both N6 and TiO2 contribute to the estrogen removal in a synergic effect since poor results were obtained when values below 1% of each compound were used. Minimum quantities of both elements are required to guarantee an effective intermolecular interaction between the polymer and the hormones that bring them close to the photocatalytic hotspots. Also, three dips were considered sufficient to create a PCP with a satisfactory amount of nanocomposite material.

After the selection of the best PCP composition, surface characterization of the synthesized material was performed. Figure S3 shows the SEM image of the PCP where it is possible to observe the efficient nanocomposite deposition over the cellulose fibers.

The modified papers were subsequently studied by Raman spectroscopy and imaging (Figure S4). The Raman spectrum of cellulose paper (Figure S4d1) is dominated by the CCC and CCO vibrations of glucose rings at around 380 and 435 cm\(^{-1}\) and 435 and 458 cm\(^{-1}\), respectively.\(^53\) CH\(_2\) vibrations appear as a broad signal at about 2980 cm\(^{-1}\), and skeletal vibrations produce a band at ca. 1380 cm\(^{-1}\). Moreover, the band at about 520 cm\(^{-1}\) corresponds to the CCC vibration of the ring and glycoside bond, while the symmetric and symmetric vibrations of glycoside bonds can be observed at about 1096 and 1120 cm\(^{-1}\).\(^54\) The intensity of such bands is used to create the Raman image of Figure S4a, depicting the intensity of the cellulose substrate covering the surface of paper.

Figure S4d2 represents the Raman image of the cellulose paper modified with the nanocomposite obtained by monitoring the region 110.9–174.7 cm\(^{-1}\) corresponding to the Eg band of TiO2. As can be seen, TiO2 NPs are distributed along the cellulose substrate covering the surface of paper.

**Adsorption Kinetics Models.** To fully understand the E1, E2, and E3 adsorption mechanisms onto the PCP, the adsorption process was investigated at different times (0–420 min, \(C_0 = 1\) mg L\(^{-1}\)) under dark conditions, and the kinetic data were fitted to four models, namely, pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. The parameters are reported in Table 1.\(^56\) The adsorption kinetics of the estrogens by the PCP fitted the pseudo-second-order kinetic model (\(R^2 > 0.98892\)), indicating that the adsorption process was controlled by both estrogen concentration and adsorption sites on the PCP (Figure S5A).\(^56\) Similar results have been reported for the retention of E1, E2, and E3 onto N-propyl-modified mesoporous silica,\(^57\) few-layered BN nanosheets,\(^58\) and raw lotus seedpod biochar.\(^59\)

The model indicates that 60 min was the equilibrium time, as can be seen in the plot of \(q_c\) vs \(t\) demonstrated in Figure S5B. The adsorption amounts of E1, E2, and E3 at equilibrium were 0.637, 1.118, and 0.409 mg g\(^{-1}\), respectively. These values are in accordance with the logarithm of the octanol/water partition coefficients (log \(K_{ow}\)) for the compounds. In fact, the log \(K_{ow}\) values for E1, E2, and E3 are 3.13, 4.01, and 2.45, respectively. The results suggested a rapid adsorption rate at the beginning, which can be ascribed to the presence of a large number of available sites.\(^56\)

**Photocatalytic Studies.** The photocatalytic degradation of E1, E2, and E3 using the PCP has been carried out under visible LED light and sunlight irradiation. The experiments were also performed in dark conditions to study the sorption contribution. The removal efficiency (\(\eta\)) of these processes was calculated using the following equation

\[
\eta = \left(\frac{C_0 - C_t}{C_0}\right) \times 100
\]

where \(C_0\) and \(C_t\) are the initial and residual concentrations of the estrogens at various intervals of time, respectively.

Under dark conditions, the adsorption process corresponds (at 420 min) to 54, 60, and 36% of the E1, E2, and E3 removal, respectively. In addition to the removal of the pollutants by adsorption, their photocatalytic degradation was observed for...
Table 1. Different Types of Kinetic Models for the Adsorption of E3, E2, and E1 at C0 = 1 mg L⁻¹

| Model                           | E1     | E2     | E3     |
|--------------------------------|--------|--------|--------|
| Pseudo-first order             |        |        |        |
| *k₁* (min⁻¹)                  | 0.00794| 0.00832| 0.01215|
| qₐ (mg g⁻¹)                   | 0.37751| 0.38038| 0.37576|
| *R²*                          | 0.97720| 0.97200| 0.97200|
| Pseudo-second order            |        |        |        |
| *k₂* (min⁻¹)                  | 0.04994| 0.05561| 0.05561|
| qₐ (mg g⁻¹)                   | 0.04994| 0.05561| 0.05561|
| *R²*                          | 0.98926| 0.99881| 0.99881|
| Interparticle diffusion        |        |        |        |
| *k₃* (min⁻¹)                  | 0.1089 | 0.06258| 0.06258|
| qₐ (mg g⁻¹)                   | 0.01443| 0.03536| 0.03536|
| *R²*                          | 0.98720| 0.98720| 0.98720|

Both visible LED light and sunlight treatments. The degradation efficiency was 99.5% of E1 and 98.5% of E3 after 180 min of sunlight exposure. For the visible LED lamp, removal efficiencies of 65, 62, and 52% for E1, E2, and E3 were reached after 420 min of visible LED exposure.

Also, a competitive effect for the active sites was observed for both the adsorption and photodegradation processes. Figure S6 describes the competition study evaluating each compound individually and into a mixture under dark and LED light conditions. Differences in the removal efficiencies for E3, E2, and E1 were 7, 13, and 10% greater under dark conditions and 17, 25 and 15% greater under visible LED conditions when studying each compound individually and the mixture, respectively.

Figure 3 depicts the chromatograms obtained by analyzing an aqueous mixture of E1, E2, and E3 being irradiated by sunlight and visible LED at different times. E1, E2, and E3 peaks decreased apparently with increasing irradiation time, implying the degradation/removal of the compounds from the solution with consequent formation/decay of by-products and intermediates. Different by-product peaks were found in the chromatograms. These differences can be ascribed to different pathways or different snapshots of the degradation process. Further investigations will be carried out, using high-resolution mass spectrometry, to elucidate the chemical identity of the unknown peaks.

Kinetics of E1, E2, and E3 Degradation. To further understand the kinetics of E1, E2, and E3 degradation under visible LED light and sunlight irradiation, the data were adjusted to a pseudo-first-order equation

\[ \frac{-dC}{dt} = kC \]  

where \( C \) is the concentration of the estrogens, \( t \) is the reaction time (min), and \( k \) is the pseudo-first-order rate constant (min⁻¹). If the initial concentration of estrogens is \( C₀ \), eq 2 can be simplified as

\[ \ln C - \ln C₀ = -kt \]  

The arrangement of eq 3 leads to eq 4

\[ \frac{C}{C₀} = e^{-kt} \]  

Figure 4 presents the kinetics of E1, E2, and E3 degradation fitted to this model, and the kinetic parameters for E1, E2, and E3 photodegradation under different light sources were determined and can be seen in Table 2. These results indicate a good fitting, with \( R² \) higher than 0.98260 and 0.99066 for the visible LED light and sunlight, respectively. The good fitting suggests that the reaction depends only on the estrogen concentration, as the hydroxyl radical concentration at the PCP surface is high, and it can be considered almost constant. The proposed model is in agreement with others from the literature for the photodegradation of E1, E2, and E3 promoted by immobilized and dispersed TiO₂ under several radiation sources.4,41,43,62

The \( k \) values for the estrogen degradation under sunlight were slightly higher than those obtained for the visible LED light with \( k_{\text{sunlight}} = 0.02126, 0.02521 \), and 0.01059 min⁻¹ vs \( k_{\text{LED}} = 0.01992, 0.01724 \), and 0.00832 min⁻¹ for E1, E2, and E3, respectively. Interestingly, despite similar \( k \) values under LED and sunlight conditions, the mixture of E1, E2, and E3
was completely removed after only 180 min under sunlight whereas only 60% of the estrogens was removed after 420 min of LED light irradiation treatment. This aspect is ascribed to the different intensity of the sources.

The $k$ values for the estrogen degradation followed the tendency $k_{E1} > k_{E2} > k_{E3}$ for LED light and $k_{E2} > k_{E1} > k_{E3}$ for sunlight, which was consistent with the previous $E1$, $E2$, and $E3$ photocatalytic behaviors.

Reusability of the Photocatalytic Cellulose-Paper. Finally, to investigate the photochemical stability and reusability of the synthesized PCP, repeated experiments were carried out for the photodegradation of $E1$, $E2$, and $E3$ under sunlight using the same PCP. The cleaning procedure between cycles was adopted as being 1 mL of a mixture of acetonitrile/methanol (50:50) for 15 min. After the cleaning step, the supernatant was injected, and no signal of the analytes was detected, indicating that all the adsorbed compounds were photodegraded by the material. As can be seen in Figure S7, after three cycles, the photocatalytic activity was maintained higher than 95% for all the compounds, indicating that the developed PCP is considered fairly stable under the studied experimental conditions and the same PCP can be used at least three times maintaining the efficiency.

Photocatalytic Cellulose-Paper in Context. The performance of the PCP must be done externally (compared with other counterparts) and internally (evaluating the pros
Table 3. Comparison of the Performance of Some Reported Methods for the Removal of E1, E2, and E3

| analyte | C0 (mg L⁻¹) | kinetics (min⁻¹) | removal (%) | light source | catalyst | ref |
|---------|-------------|------------------|-------------|--------------|----------|-----|
| E1, E2, E3 | 1.0 | pseudo-first order, k = 0.02126, 0.00221, and 0.01059 min⁻¹ | 99.5, 99.5, and 98.5% in 180 min | sunlight 14.5 mW cm⁻² | paper-based nylon-TiO₂, 0.0222 g | this work |
| E1, E2 | 0.05 | k = 0.068 and 0.012 min⁻¹ | 97.0 and 49.2% in 50 min | UV lamp, λ = 253.7 nm, 350 μW cm⁻² | UV/H₂O₂, 10 mg L⁻¹ | 63 |
| E1 | 1.0 | pseudo-first order, k = 0.01 min⁻¹ | 100% in 18 min to UVA and 93% in 60 min to white LED | UVA (λ = 365 nm) and cool white (λ > 420 nm) | 4% Au-TiO₂ nanocomposite, 50 mg L⁻¹ | 41 |
| E3 | 2.88 | pseudo 1st order, k = 0.021 min⁻¹ | 100% in 180 min | two black light lamps, λ = 365 nm, 15 W, 1500 μW cm⁻² | TiO₂ P25, 20 mg L⁻¹ | 64 |
| E2 | 1.0 | k = 0.043 min⁻¹ | 99% in 240 min | solar simulator, λ = 280–400 nm, 450 W | nanocrystalline TiO₂, 20 mg L⁻¹ | 65 |
| E2 | 2.0 μM | pseudo-first order, k = 0.0025 min⁻¹ | 50.86% in 300 min | sunlight, 1910 μW cm⁻² | nanotubular TiO₂ | 4 |
| E2 | 3.0 | pseudo-first order, k = 0.0983 min⁻¹ | 99.5% in 60 min | mercury lamp, 20 W | 5% Fe/β₂SiO₅, 500 mg L⁻¹ | 39 |

and cons). Table 3 compares the main features of different methods described in the literature⁵⁻⁹,⁴¹,⁶³⁻⁶⁵ for the photocatalytic degradation of E1, E2, and E3 mostly through TiO₂-based nanomaterials with the PCP described in this work. The data suggest very interesting photoactivity, particularly regarding the high removal efficiency achieved using the sunlight as the radiation source. The synergic combination of the paper substrate and the polymer containing TiO₂ NPs allowed a photocatalytic activity in the visible region comparable to studies performed under UV conditions.¹¹,⁶⁴ In addition, this study evaluated an equimolar mixture of the estrogenic hormones, which resembles the real conditions usually found in the environment. Besides being the only study combining a polymer and TiO₂ NPs for the removal of estrogens, the k values obtained by the kinetics studies are very similar to the others. These formidable features make the proposed photocatalyst paper a very promising tool to be explored for photodegradation purposes.

An honest internal evaluation of the PCP, indicating the pros and cons, is essential to present a realistic view of the material and a route for future improvements.

The PCP is simple to synthesize, and the components are relatively cheap and nontoxic, but the dip-coating technique requires a solvent. A procedure to recover (by evaporation/condensation) this solvent would be interesting to reduce the price of the material and the environmental impact of the synthesis in potential large-scale production.

The PCP is mechanically stable at the macroscopic level, and its components are nontoxic. A deep study of the potential leaching of the polymer and the NPs and the evaluation of the effect of the photocatalysis on the N6 degradation would be also interesting for investigation.

**CONCLUSIONS**

In this study, a PCP was successfully synthesized and characterized and its photocatalytic effectiveness was properly evaluated toward E1, E2, and E3 visible-driven degradation. The PCP combines the sorption capacity of a polyamide with the photocatalytic activity of TiO₂ NPs. Under the optimized experimental conditions, the PCP exhibited a high degradation performance to the sunlight, having a range of 98.5–99.5% of the estrogenic hormones E1, E2, and E3 removed from the solution after 180 min of irradiation. Also, the PCP was stable, and it can be reused. The facile synthesis via simple dipping of the cellulose paper in a nanocomposite medium paves the way for novel solar-driven photocatalytic applications using several polymer/semiconductor ensembles. The analysis of the degradation product by high-resolution mass spectrometry (HRMS) will be considered in the next projects. Due to the higher polarity of the compounds, which presents retention times shorter than the parent compounds, LC-HRMS or direct infusion HRMS can be a better option for these studies.

The developed PCP is cheap and has low toxicity. Further work will be focused on its in-field application for the removal of contaminants as its small design is fully compatible with individual water bottles.

**EXPERIMENTAL SECTION**

**Chemicals and Materials.** With a few exceptions, the reagents were purchased from Sigma-Aldrich (Madrid, Spain). Stock (1 g L⁻¹) and working standards (1 mg L⁻¹) of estrone (E1), 17β-estradiol (E2), and estriol (E3) were built in formic acid. After each dip, the paper was dried entirely. The PCPs were prepared by immersing three times a paper substrate and the polymer containing TiO₂ NPs prepared in formic acid. After each dip, the paper was dried entirely. The
The dipping position was changed after each material deposition to achieve a more homogeneous coating. The physical/chemical characterization of the nanocomposite paper-based films was carried out by microscopy and Raman spectroscopy as indicated in the Supporting Information.

**Adsorption/Photocatalytic Studies.** The activity of PCP was studied by the photodegradation of E1, E2, and E3 under visible LED light and sunlight irradiation. A diagram describing the overall procedure is shown in Figure 5. A visible LED light (10 W Agostar LED lamp, 3000 K, 90 mA, 230 V/50 Hz, 800 lm), positioned above an orbital agitator containing six glass vessels (10 mL headspace vials) used as photoreactors, was used as the light source. The experimental apparatus was placed inside a dark chamber to ensure any interference from other light sources. The as-prepared PCP in a ring format with an area of 2 cm² of each side was placed in a vial with 5 mL of an aqueous solution of each analyte (starting concentration of 1 mg L⁻¹). During the photoreaction, the vial was stirred at 500 rpm while irradiated by the radiation source. The vials were positioned face down for better irradiation. Supernatant aliquots of 50 μL were taken at different times and analyzed by LC. For studies under sunlight, the same procedure was adopted, but the experimental apparatus was placed directly exposed to the sunlight. The procedure was also performed at room temperature under dark conditions to evaluate the adsorption kinetics.

The PCP composition was evaluated through a Box–Behnken design consisting of 15 experiments, according to Table S2. The studied variables were N6 amount (0.5, 2, and 3.5% w/v), TiO₂ percentage (0, 2.5, and 5% w/v), and total dips (1, 2, and 3). StatSoft Statistic 8.0 and Microsoft Excel were used for the statistical study.

For the adsorption process, four different kinetics models were evaluated as it is indicated in the Supporting Information.

**ASSOCIATED CONTENT**

[Supporting Information](https://pubs.acs.org/doi/10.1021/acsomega.1c00128)

UV–vis absorption spectrum of the photocatalytic paper and emission spectra of the light sources; removal efficiency of the photocatalytic paper compared with an N6-coated paper without TiO₂; scanning electron microscopy of the photocatalytic paper; Raman spectroscopy studies; adsorption kinetics of the estrogens by the photocatalytic paper; study of competition for the active sites of the photocatalytic paper; photocatalytic paper reusability under sunlight irradiation; calibration of the direct injection LC-UV method; experimental design of the optimization of the photocatalytic paper; kinetics studies (PDF)

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**Figure 5.** Schematic description of the experimental photodegradation procedure.
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Notes

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