

Article

Effect of Background Water Matrices on Pharmaceutical and Personal Care Product Removal by UV-LED/TiO₂

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Abstract: In this study, we evaluated the effectiveness of UV-LED-irradiated TiO₂ in removing 24 commonly detected PPCPs in two water matrices (municipal wastewater effluent and Suwannee River NOM–synthetic water) and compared their performance with that of ultrapure water. Relatively fast removal kinetics were observed for 29% and 12% of the PPCPs in ultrapure water and synthetic surface water, respectively (k_{app} of 1–2 min^{−1}). However, they all remained recalcitrant to photocatalysis when using wastewater effluent as the background matrix ($k_{app} < 0.1$ min^{−1}). We also observed that the pH-corrected octanol/water partition coefficient ($\log D_{ow}$) correlated well with PPCP degradation rate constants in ultrapure water, whereas molecular weight was strongly associated with the rate constants in both synthetic surface water and wastewater. The electrical energy per order (EEO) values calculated at the end of the experiments suggest that UV-LED/P25 can be an energy-efficient method for water treatment applications (2.96, 4.77, and 16.36 kW h m^{−3} in ultrapure water, synthetic surface water, and wastewater effluents, respectively). Although TiO₂ photocatalysis is a promising approach in removing PPCPs, our results indicate that additional challenges need to be overcome for PPCPs in more complex water matrices, including an assessment of photocatalytic removal under different background water matrices.



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Keywords: synthetic surface water; TiO₂ photocatalysis; pharmaceuticals and personal care products; UV-LED; wastewater effluents

1. Introduction

Currently existing water and wastewater treatment technologies can only partially remove emerging organic contaminants such as pharmaceuticals and personal care products (PPCPs). Therefore, innovative water treatment solutions are required for both water and wastewater purification [1,2]. Heterogenous photocatalysis, such as the use of titanium dioxide (TiO₂) nanomaterials, has been widely studied as a secondary and tertiary treatment option for the removal of PPCPs that remain recalcitrant [3,4]. TiO₂ can produce highly reactive and unselective oxidant species such as hydroxyl radicals (\bullet OH) upon UV irradiation, which can oxidize and mineralize organic contaminants at high reaction rates [5].

A total of 80 studies evaluated here, detailed in Table S1 in the Supplementary Materials (SI), including those from our lab [6–10], have intensively investigated the effect of parameters such as photocatalyst type and concentration, light intensity, pH, and organic and inorganic constituents in the background water (i.e., dissolved organic matter, suspended solids, and alkalinity) on PPCP degradation using TiO₂ treatment. Although these

studies have explored the photocatalytic removals of PPCPs in mixtures, approximately 70% of them investigated TiO₂ photocatalytic processes in a pure water matrix and only 30% of these studies have used surface water and wastewater effluents.

Industrial or municipal applications require careful consideration of the source water and effluent makeup as they are a complex mixture of chemicals that can influence the efficiency of the photocatalyst. For instance, inorganic ions such as NH₄⁺, NO₃⁻, and HCO₃⁻ simultaneously change the TiO₂ surface charge and adsorption of microcontaminants [11]. These major water constituents can further behave as scavengers or donors of the oxidative species produced during photocatalytic reactions [11]. Humic substances account for most of the natural organic matter (NOM) in the surface waters [12]. They may act as photosensitizers by generating additional oxidative species, which can then contribute to the indirect photodegradation of organic contaminants [13]. On the other hand, they may also scavenge the •OH produced during photocatalysis, slowing down the overall degradation of the target contaminant [14]. In addition, most of the studies restricted their experiments to a limited number of PPCPs (approximately three compounds on average, as shown in Table S1; please see Table S2 for the abbreviation expansions). However, pharmaceuticals are very structurally diverse and, therefore, have highly varied physicochemical properties, theoretically leading to large differences in removal kinetics under different conditions [9].

In this study, the photocatalytic degradation of 24 PPCPs (nominal concentration of 2 µg L⁻¹) in three different water matrices (ultrapure water; synthetic surface water using Suwannee River NOM; and the Waterloo Region wastewater effluent in Ontario, Canada) were investigated using UV-LED/P25. We further hypothesized a relationship between PPCP removal kinetics and their physicochemical parameters (isoelectric charge, pH-corrected octanol/water partition coefficient, solubility, and molecular weight). This can be useful in future photocatalytic optimization studies. Finally, we assessed the energy efficiency of UV-LED/P25 to remove PPCPs in different background matrices.

2. Results and Discussion

2.1. Adsorption and Photolysis Control

The PPCP removal through adsorption during the equilibration period (i.e., 60 min dark treatment before irradiation starts) was calculated by dividing the difference between initial and final concentrations during the dark period by the initial concentration (Equation (S1) in SI). Although most compounds showed minimal removal (0–10%) in three water matrices via adsorption (Figure 1), removal of o-hydroxy atorvastatin (63%), p-hydroxy atorvastatin (43%), bisphenol (2%), diclofenac (18%), and monensin (15%) were significantly different in ultrapure water vs. synthetic surface water and wastewater (one-way ANOVA, $\alpha = 0.05$, *p*-values in Table S3). Water characteristics such as pH can have an impact on PPCP removal [15]. The acidity and alkalinity of the water matrix change the isoelectric point of both the photocatalyst and the organic compounds and can influence the electrostatic interaction between them [16]. TiOH, TiOH₂⁺, and TiO⁻ are the primary TiO₂ surface functional groups and their distribution is determined by the pH at the point with zero charge (pH_{ZPC}). At pH < pH_{ZPC}, TiOH₂⁺ is the predominant species, while at pH > pH_{ZPC}, the P25 surface becomes negative through reactions with hydroxyl compounds that produce TiO⁻ [17]. At pH conditions above the dissociation constant (pK_a) of organic compounds, the functional groups become negatively charged and will likely facilitate interactions with oppositely charged photocatalysts [18]. As illustrated in Figure 2, charged PPCPs were attracted to oppositely charged P25 nanoparticles but were repelled from a surface that is similarly charged. The P25 surface is slightly positive in ultrapure water (pH_{ZPC} for P25 is 5.5 or 6 at pH_{UPW} = 6) [19], while it is more negative in wastewater effluents and synthetic surface water (pH_{WWE} = 7 and pH_{SSW} = 8), as shown in Table 1. Therefore, the interaction between anionic compounds such as atorvastatin, monensin, and diclofenac is favored in ultrapure water.

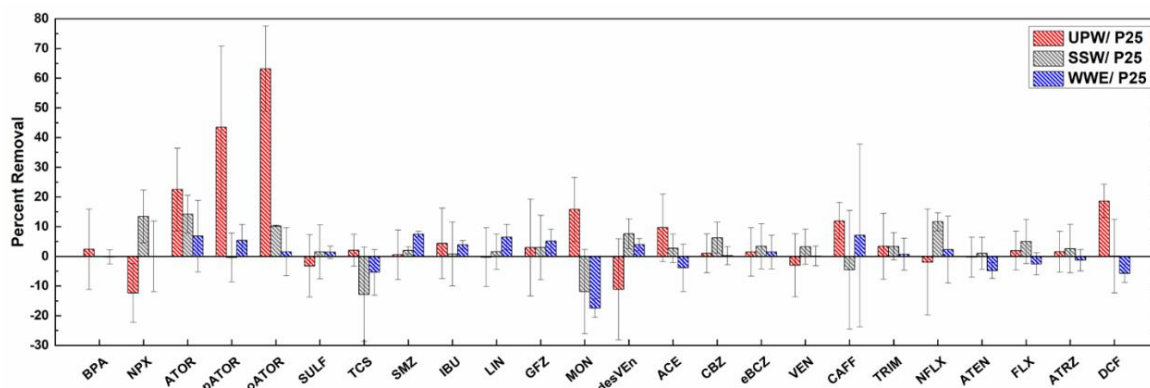


Figure 1. Removal of PPCP in ultrapure water (UPW), synthetic surface water (SSW), and wastewater effluent (WWE) during the equilibration period (60 min in the dark and at room temperature). Negative values are within the 15% acceptable experimental error.

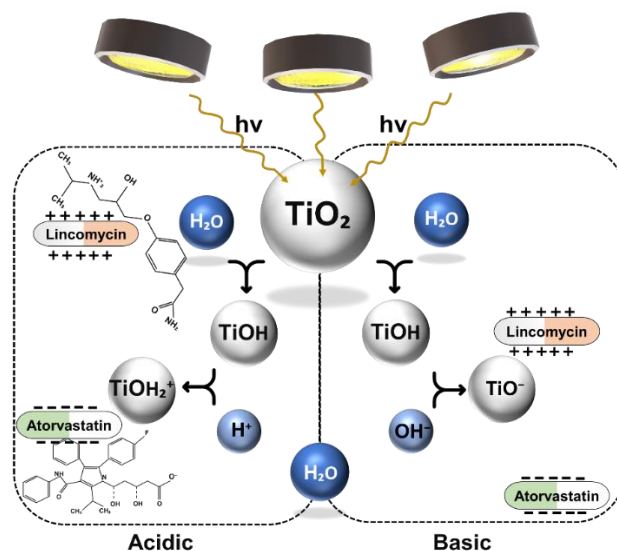


Figure 2. TiO₂ functional groups and their adsorption tendency toward PPCPs in acidic and basic environments. In acidic conditions, negatively charged PPCPs tend to sorb to TiOH₂⁺ (e.g., atorvastatin), whereas in basic conditions, positively charged PPCPs tend to interact with TiO⁻. See Figure 1 for the adsorption results of other target compounds.

Table 1. Average water-quality characteristics of synthetic surface water and wastewater effluent.

Parameters	Units	Synthetic Surface Water	Wastewater Effluent
pH		8–8.5	7–7.5
TOC	mg L ⁻¹	6.12	9.37
Dissolved Chloride	mg L ⁻¹	40	490
Hardness	mg L ⁻¹ as CaCO ₃	114	N/A
Alkalinity	mg L ⁻¹ as CaCO ₃	117	N/A
Nitrate	mg L ⁻¹	3	36.53
Nitrite	mg L ⁻¹	N/A	0.53
Sulfate	mg L ⁻¹	241	N/A

N/A: Not available.

Preferential adsorption of synthetic surface water or wastewater constituents can also occupy the adsorption sites for microcontaminants, reducing the adsorption capacity of TiO₂ [20]. It was also observed in our study that the overall removal during the dark period was higher in ultrapure water compared to surface water and wastewater (23%, 10%, and 1%, respectively). Since most studies have explored photocatalysis in ultrapure water,

photocatalyst-related adsorption (Figure 2) may not be achieved in complex water matrices due to additional water constituents.

The results of photolysis treatments in ultrapure water and wastewater effluents indicated that there was no statistical difference in removal under UV irradiation alone except for atorvastatin metabolites (o-hydroxy atorvastatin and p-hydroxy atorvastatin) and diclofenac (Figure S1 and Table S3). This result is not surprising as some of these compounds have been found to be susceptible to photodegradation [7]. However, their removals via photolysis remained lower compared to photocatalysis, as described subsequently below.

2.2. Removal of PPCPs during Photocatalytic Treatment

2.2.1. Effect of Water Matrices

To investigate the effects of background water matrices on PPCP photocatalytic degradation, the rate constant (k_{app}) of PPCPs in water matrices were calculated using the Langmuir–Hinshelwood kinetics model (Equation (S2) in the SI). Of the 24 compounds, 7 of the PPCPs were removed quickly in ultrapure water including bisphenol A, naproxen, atorvastatin, and its metabolites. However, only three were removed at this rate in surface water (i.e., atorvastatin and its metabolites), and all of them showed little to no removal in wastewater effluent (Figure 3). The rate constants of caffeine and carbamazepine were not impacted by any water matrices (Table S3), suggesting that they are either recalcitrant to treatment or the background matrices simply do not affect their behaviour.

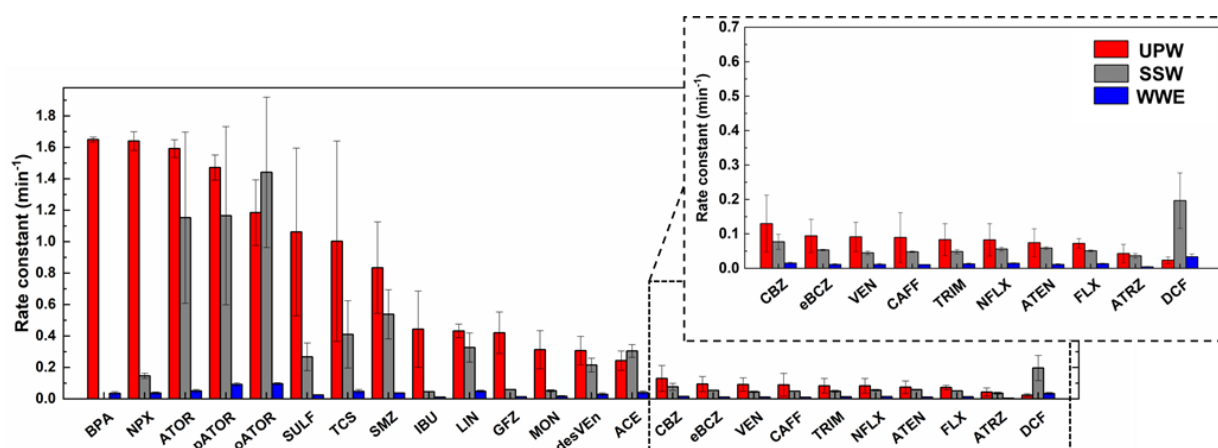


Figure 3. Pseudo first order rate constants for all target compounds during 120 min P25 photocatalysis in ultrapure water (UPW), synthetic surface water (SSW), and wastewater effluent (WWE). Inset magnifies the PPCPs with low k_{app} .

As expected, poor removal was observed with the increasing complexity of the background matrix (Table 1). Reactive oxygen species (ROS) (i.e., $\bullet\text{OH}$, $\text{O}_2\bullet^-$, and h\nu_B^+) produced by UV-LED/P25 photocatalysis reactions allow for the degradation of the wide range of organic contaminants, including PPCP [21]. However, parallel reactions between the oxidizing agents and water constituents, such as Cl^- , NO_3^- , organic carbon, and carbonate ions (HCO_3^- and CO_3^{2-}), may consume the oxidizing species required for the degradation of contaminants [20]. For instance, the presence of Cl^- ions in the water matrix can have multiple effects on photocatalysis: (i) when TiOH_2^+ is the main functional group (low pH), Cl^- ions can compete with organic contaminants for active sites on the catalyst surface and can decrease the reaction rate [22]; (ii) in the presence of oxygen molecules, Cl^- ions compete for scavenging photoinduced electrons and block the chain reactions of $\bullet\text{OH}$ [23]; and (iii) possible reactions between Cl^- ions and free radicals can impede the degradation process [24]. In our experiments, the amounts of dissolved chloride were 40 and 490 mg L^{-1} in synthetic surface water and wastewater effluents (Table 1) and a range of 100–1000 mg L^{-1} was found to produce some of these effects [22,24–26].

Carbonate ions in wastewater effluents and surface waters (normally found in the ranges of 38–575 and 61–183 mg L⁻¹, respectively) have been reported to have contrasting outcomes in TiO₂ photocatalysis, i.e., by either inhibiting or enhancing the degradation of PPCPs [11,27–29]. For instance, HCO₃⁻ ions may scavenge ROS and decrease the photocatalytic efficiency, or react with them and produce carbonate radicals (•CO₃⁻) [30]. •CO₃⁻ is an oxidant (E₀ = 1.78 at pH = 7) with high selectivity toward organic compounds (with a second-order rate constant 10²–10⁹ M⁻¹ s⁻¹) [31,32], and it can preferentially react with electron-rich compounds such as aromatic anilines, amino acids, and sulfur or nitrogen-containing compounds such as oxytetracycline and sulfamethoxazole through electron transfer of hydrogen abstraction [31,33–35].

The average PPCP rate constants in synthetic surface water were 10 times higher than that in wastewater effluents. This result may be related to the photosensitization effect of NOM. As indicated by prior studies, NOM can also have two contrasting effects on TiO₂ photocatalysis [36–38]. It can either inhibit the photodegradation by scavenging the photoinduced holes, attenuate the light, compete for active sites, deactivate the photocatalyst surface [39], or act as precursor for reactive radical species in water matrices [40]. Humic substances contribute to photocatalytic degradation of organic compounds by producing reactive oxidant such as solvated electrons (e⁻_{aq}), singlet oxygen (¹O₂), •OH, •O₂⁻, and H₂O₂ [41]. Doll and Frimmel, in 2003, related the high degradation rate of carbamazepine in Hohloh Lake NOM to NOM-induced reactions [40].

TiO₂ photocatalysis can increase the biodegradability of persistent PPCPs. In most cases, complete degradation of the parent compounds does not correspond directly to the mineralization rate, generating more stable by-products during the treatment. TOC reduction indicates breaking larger molecules into smaller ones and the decomposition of aromatic compounds, which can then increase the aliphatic hydrocarbon fraction. A high aliphatic fraction suggests a larger breakdown of organic compounds by •OH [42,43]. In our experiments, we observed 26% and 30% reductions in TOC during 120 min photocatalytic reaction times in wastewater effluent and surface water, respectively. Limited removal of the background TOC was observed in previous studies as well (less than 20%) [44,45]. However, UV absorbance at λ = 254 nm (77% in synthetic surface water) suggested that the parent TOC molecules were oxidized, forming by-products that can also scavenge •OH [46].

It should be noted that •OH oxidation is not the only pathway for degrading PPCPs via TiO₂ photocatalysis. Electrons and holes on the TiO₂ surface can initiate PPCP degradation, alternatively referred to as the single electron transfer (SET) pathway. Both •OH oxidation and SET pathways contribute to ring-opening reactions, but SET is attributed to the ring-opening reactions of hydroxylated aromatic compounds, particularly orthodihydroxylated ones. •OH participates in OH substitution, alkyl group degradation, and ring hydroxylation [47–49]. Understanding the mechanistic pathway is beyond the scope of the current study since it involves comprehensive analysis of by-product formation during photocatalytic reactions.

2.2.2. Effect of Physicochemical Characteristics

Physicochemical properties such as charge, molecular weight, hydrophobicity, and molecular structure can affect photocatalytic degradation. Previous studies, including ours, show that the chemical structure of PPCPs can be correlated with their photocatalytic degradation [6,9]. Arlos et al. [9] studied the degradation of 16 PPCPs using TiO₂ immobilized on porous support in ultrapure water under UV-LED exposure and indicated that ionic interactions can determine PPCP degradation. Cationic and anionic PPCPs interact well with oppositely charged membranes, while neutral compounds were found to be recalcitrant under any treatment. Liang et al. [6] studied the kinetic rate constants of degradation of the 18 PPCPs with different net charges, molecular weights, and solubilities on the PPCPs' degradation rates and concluded that charge was the main factor determining the degradation rate constant among the other three parameters. Other studies focused

on the correlation between chemical bonding and photodegradation under UV irradiation (photolysis) and suggested that chemicals with amide bonds ($R-CO-NR_2$) are poorly degraded via TiO_2 photocatalysis [50,51] whereas PPCPs with amine bonds (R_xNH_{3-x}) such as sulfamethoxazole showed higher degradation rate constants [50]. In another study, varying rate constants for trace organics with amine groups have been observed, but further concluded that this is not the main bond affected by UV irradiation during photocatalytic reaction [52]. In our study, we did not find consistent relationships between the PPCPs' functional groups or the number of aromatic rings with degradation rate constants in any of the matrices (Table S4). However, our analysis showed that $\log D_{ow}$ is well correlated with TiO_2 photocatalysis in ultrapure water but that this was not the case for synthetic and wastewaters (Figure 4; Tables S4–S6). Instead, molecular weight may be more predictive of TiO_2 photocatalysis in these background water matrices. Our result was unexpected, and we recognize that additional studies on several other matrices are needed to validate this finding.

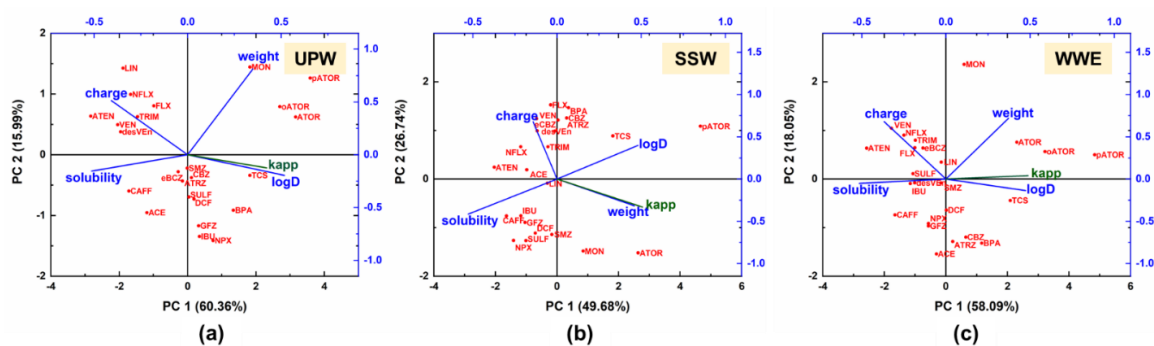


Figure 4. Principal component analysis (PCA) biplot showing the multivariate variation among 24 PPCPs in terms of physicochemical properties (net charge, weight, solubility, and $\log D_{ow}$) in (a) ultrapure water (b) synthetic surface water (c) wastewater effluents. Blue vectors indicate the direction and strength of each variable (physicochemical properties) and their correlation to k_{app} (green vector).

2.3. Electrical Energy per Order Required for Removal

Energy efficiency of UV-based reactions is commonly reported using electrical energy per order (EEO), which is defined as the kilowatt hours of electrical energy needed to decrease contaminant concentration by the first order of magnitude in 1 m^3 of polluted water [53] (Equation (S3) in the SI).

On average, we found that the energy required to remove the mixture of PPCPs in wastewater effluents (16.36 kW h m^{-3}) was higher than that for synthetic surface water and ultrapure water (4.77 and 2.96 kW h m^{-3} , respectively) (Figure 5). The energy required for removing individual PPCPs in ultrapure water and synthetic surface water was not significantly different except for atorvastatin, bisphenol A, naproxen, and sulfamethoxazole (p -values in Table S8). Among our target PPCPs, atrazine consumed the highest energy required to remove in wastewater effluents (76.37 kW h m^{-3}). It was completely removed in ultrapure water and synthetic surface water in 2 h treatment, but complete removal of atrazine in wastewater effluents required prolonged photocatalytic treatment. In synthetic surface water, removal of bisphenol A required the highest EEO value of 32.84 kW h m^{-3} . Bisphenol A has been reported to degrade at a higher rate in acidic conditions ($\text{pH} < 6.5$). The higher pH in synthetic surface water ($\text{pH}_{SSW} = 8$) may affect the photocatalytic degradation of BPA, increasing the EEO value [54].

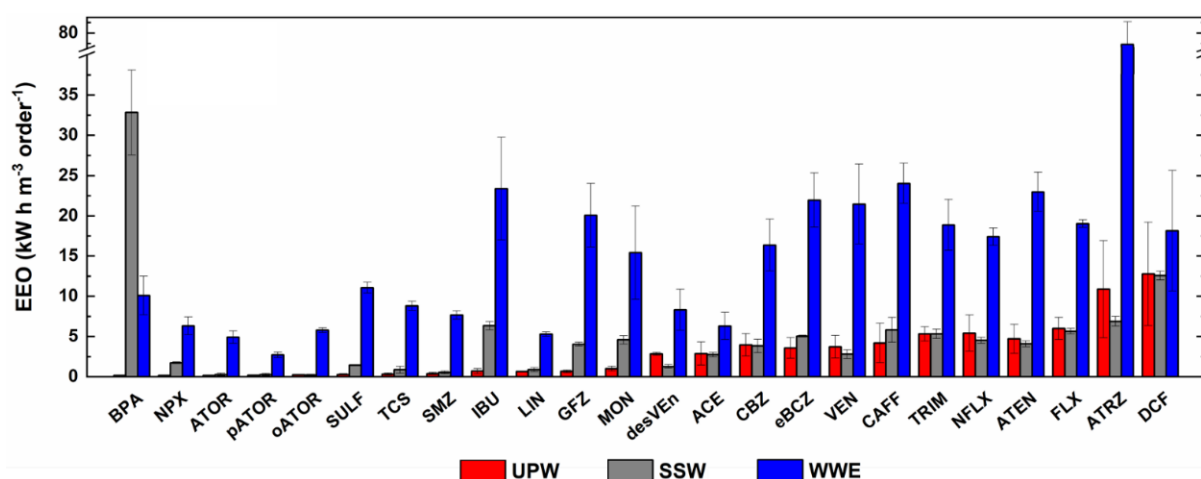


Figure 5. Values of electrical energy per order (EEO) required for removing PPCPs in ultrapure water (UPW), synthetic surface water (SSW), and wastewater effluent (WWE).

It should be noted that EEO values for PPCP removal in this study are comparatively lower than that for previous publications, suggesting that UV-LED/TiO₂ is an energy efficient process. For instance, the EEO values of 50–70 kW h m⁻³ were reported by Paredes et al. [55] for degradation of gemfibrozil, carbamazepine, metoprolol, trimethoprim, and warfarin in secondary wastewater effluents using P25 and a low-pressure UV lamp (40 W). Pouloupoulos et al. [56] also reported the EEO values of 121–250 kW h m⁻³ for degradations of phenol, 2-chlorophenol, 2,4 dichlorophenol, 2,4,6, trichlorophenol, and 4-nitrophenol in synthetic wastewater using P25 and a UV lamp (6 W).

3. Materials and Methods

3.1. Water Matrices

Three different water matrices were used as the test matrix for the experiments: (i) ultrapure water (UPW) (resistivity of 18.2 mΩ·cm at 25 °C, Milli-Q Advantage A10 Water Purification System, EMD Millipore, Burlington, MA, USA); (ii) synthetic surface water (SSW) that was produced in the lab using Suwannee River NOM reverse osmosis isolate (International Humic Substances Society, City and County of Denver, CO, USA), alginic acid, and inorganic ions, published previously in our study [7,46] (purchased from Sigma Aldrich, St. Louis, MO, USA; purity ≥ 99%); and (iii) wastewater effluent (WWE) collected from the Waterloo Regional Wastewater Treatment Plant, stored in ice, and then filtered using a 2 μm glass fiber filter (Whatman, Maidstone, UK) to remove large suspended particulate matter. Maxxam Analytics (Mississauga, ON, Canada) analyzed the wastewater effluent characteristics including total organic carbon (TOC), conductivity, dissolved chloride, ammonia, nitrite, and nitrate. The TOC of the synthetic surface water was measured in filtered (polyether sulfone membrane filters; 0.45 μm) samples using a Shimadzu TOC-L total organic carbon analyzer supplied with 680 °C combustion catalytic oxidation, NDIR detection method, and a Shimadzu ASI-L autosampler.

3.2. Photocatalytic Degradation of PPCPs

Commercially available TiO₂ (P25 Aeroxide™) was used as the model photocatalyst nanomaterial. Twenty-four pharmaceutical and personal care products with different properties and applications were selected as target compounds for the photocatalytic experiments (Table S9). PPCPs and isotopically labeled standards were purchased from different suppliers as detailed in Table S10, dissolved in methanol stock solution (1 g L⁻¹), and stored at −20 °C.

Three glass beakers covered with aluminum foil were spiked from PPCP stock solution to create a nominal concentration of 2 μg L⁻¹ of each compound. The compounds in methanol were first evaporated to dryness to reduce carrier solution concentration by

Arlos et al. [10] and then 300 mL of the desired water matrix (ultrapure, synthetic surface water, or wastewater effluent) was added to the beakers followed by 30 mg of P25 and stirred at 600 rpm. The experimental setup was similar to previous work by Arlos et al. [9]. Briefly, the multi-positioned magnetic stir plate was placed 10.5 cm below the in-house assembled UV-LED beam ($\theta_{\text{beam}} = 4 \text{ cm}$, $\lambda = 365 \text{ nm}$) setup. The rated power of UV-LED lights was 2060 at 1000 mA (measured using Mouser Electronics, Mansfield, TX, Canada). The average power output of the UV-LEDs was 0.390 mW cm^{-2} determined by Thorlabs power and energy meter (PM100-USB). A 60 min equilibration period in the absence of UV light was used followed by 120 min UV-LED light irradiation. Aliquots of beakers (4.5 mL) were taken at several time points from -60 to 120 min.

The PPCP degradation experiments were conducted under six conditions with three replicates per treatment: (i) dark test in ultrapure water; (ii) photolysis in ultrapure water; (iii) photolysis in wastewater effluents; and P25 photocatalysis in (iv) ultrapure water, (v) wastewater effluents, and (vi) synthetic surface water. Sample preparation and analysis are explained in detail by Arlos et al. [9]. Data processing and principal component analysis were completed using Origin Pro (version 8). Statistical analysis was performed using one-way ANOVA, Tukey tests, and $\alpha = 0.05$ Sigma Plot (version 13).

4. Conclusions

This study focused on the impact of the background water matrix on TiO_2 photocatalytic treatment of 24 target PPCPs. Specifically, the photocatalytic degradation of PPCPs were compared in ultrapure water, synthetic surface water, and wastewater effluents. The results showed a substantial decrease in PPCP removal kinetics in synthetic surface water and wastewater effluent matrices. Out of the 24 PPCPs, 29% and 12% were removed quickly in ultrapure water and surface water, while all of the PPCPs were removed poorly ($<0.1 \text{ min}^{-1}$) in wastewater effluents. In addition, caffeine and carbamazepine removal kinetics via photocatalysis were not influenced by the background water matrix. Low rate constants of PPCPs in complex water matrices highlight the importance of the background water on photocatalytic degradation, which is usually neglected by many previous studies (we examined 80 in total). Furthermore, 26% and 30% TOC reductions in wastewater effluents and surface water were observed, suggesting that complete degradation did not occur during the 120 min irradiation.

Among the PPCP physicochemical characteristics that we evaluated, the pH-corrected n-octanol/water partition coefficient ($\log D_{\text{ow}}$) was correlated with the PPCP degradation rate constants in ultrapure water, and molecular weight was strongly associated with the rate constants in synthetic surface water and wastewater. As expected, the average electrical energy consumption for removing PPCPs in wastewater effluents were higher than that for synthetic water and ultrapure water (16.36 vs. 4.77 and 2.96 kW h m^{-3} , respectively). Low EEO values in our study suggest that UV-LED-irradiated TiO_2 is a promising energy-efficient technology for PPCP degradation in water.

Finally, since there is an increasing trend in the synthesis of novel nanomaterials for photocatalytic applications, we highly recommend that researchers closely investigate the impact of water matrices, especially during the “proof-of-concept” stage of nanomaterials development for the technology, to become more applicable in the future.

Supplementary Materials: The supplementary materials are available online at <https://www.mdpi.com/article/10.3390/catal11050576/s1>. Figure S1: Removal of targeted PPCPs in ultrapure water (UPW), wastewater effluent (WWE), and synthetic surface water (SSW) under dark (120 min dark irradiation using P25), photolysis (120 min under UV-LED irradiation without P25) and photocatalysis (120 min under UV-LED irradiation and using P25) treatments; Figure S2: Removal of targeted PPCPs in ultrapure water (UPW), wastewater effluent (WWE), and synthetic surface water (SSW) under dark (120 min dark irradiation using P25), photolysis (120 min under UV-LED irradiation without P25) and photocatalysis (120 min under UV-LED irradiation and using P25) treatments. Table S1: Studies in photocatalytic degradation of pharmaceuticals and personal care compounds in different water matrices; Table S2: Pharmaceuticals and personal care products (PPCP) and their abbreviations;

Table S3: *p*-values for One-Way ANOVA tests (SigmaPlot, $\alpha = 0.05$) during 60 min equilibrium period, photolysis and photocatalysis. Tukey tests (multiple comparisons) were conducted when a statistical significance was detected with overall statistical significance level of 0.05; Table S4: PPCPs types and number of bonds; Table S5: Correlation coefficient in PCA matrix; Table S6: Extracted Eigenvectors in three water matrices; Table S7: Total organic carbon for wastewater effluent upon collection from the Waterloo treatment plant and after photocatalytic tests were performed on the matrix; Table S8: *p*-values for One-Way ANOVA tests (SigmaPlot, $\alpha = 0.05$) for EEO. Tukey tests (multiple comparisons) were conducted when a statistical significance was detected with overall statistical significance level of 0.05; Table S9: Chemical and physical properties of targeted PPCPs in three water matrices and their concentrations UPW = ultrapure water; SSW = synthetic surface water; WWE = wastewater effluent; Table S10. List of PPCPs, isotopically labeled standard and suppliers.

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Conflicts of Interest: The authors declare no conflict of interest.

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