Effects of ultraviolet irradiation and titanium(IV) oxide on greywater and domestic wastewater with a low propensity for bio-disintegration

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ABSTRACT

Current methods of treatment are often insufficient to purify greywater and household sewage; therefore, the presented study was aimed to assess the impact of ultraviolet irradiation and titanium(IV) oxide on the content level of organic substances and ammonium nitrogen, which are potential pollutants. The levels of organic contaminants were analyzed based on indicators used in the qualitative water and wastewater analyses. The chemical oxygen demand, the five-day biochemical oxygen demand, as well as ammonium nitrogen were all included in our determination. Two series of experiments on greywater and septic tank effluent were performed as a basis of the study. In each experiment, samples were irradiated with UV light in the presence or absence of various forms of TiO_2 as a photocatalyst. The results indicate that the use of UV light irradiation on its own and also in the presence of TiO_2 significantly influences the composition of greywater and domestic wastewater in relation to organic compounds and ammonium nitrogen. The decrease in N–NH4 was found in both experiments on septic tank effluents in the presence of TiO_2 with simultaneous UV irradiation.

Keywords: Domestic wastewater; Greywater; Remediation; Titanium(IV) oxide; UV light

1. Introduction

The socio-economic development of the world population has impacted the progressive increase in the environmental pollution in recent decades. Despite growing ecological awareness, a deterioration in soil and water quality is still observed. Many chemical substances from industrial plants, farms, and households end up in surface and groundwater. These compounds pose a potential threat not only to the environment but also to humans [1–3]. Routinely used wastewater treatment methods do not eliminate some substances, which are classified as so-called emerging contaminants [4]. Although many processes are suitable for laboratory scale applications, traditional chemical, physical, and biological waste removal techniques are not effective on an industrial scale. Therefore, removal of impurities or their degradation to less harmful derivatives requires the development of new methods, including those based on advanced oxidation processes (AOP) [5–7]. AOPs allow the degradation of compounds through the

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generation of reactive radicals and are considered highly effective and environmentally friendly [7–9]. One of the most popular AOPs used in photoremediation utilizes titanium(IV) oxide (TiO$_2$), which has been often chosen for photocatalysis studies as it is chemically stable, cheap, and easily manufactured. It occurs naturally in three polymorphic forms: anatase, brookite, and rutile. So far, TiO$_2$ has been studied to degrade pollutants from cosmetics and chemical products in daily use [10–12]. Due to its spectral properties, the exposure of this material to UV light leads to energy absorption, which results in TiO$_2$ undergoing a transition to its excited state. As a consequence, the induction of oxidoreductive processes on the catalyst surface is possible. The energy can be transferred to various molecules, including pollutants, either directly or through the formation of reactive oxygen species, which induce the decomposition process via oxidation reactions [9].

Although in principle the literature reports refer to wastewater, the studies that are described in them concern only selected compounds or specific groups of pollutants, for example, carbonyl derivatives (polycarboxylic benzoic acid (trimellitic acid)), alcohols, surfactants, pesticides, phenols, pesticides fungicides, herbicides, etc. [13,14], dyes from textile wastewaters and other dyes [15–17] as well as pharmaceutical wastewater [18]. These reports predominately focus on these compounds in isolation, with strictly controlled reaction conditions ignoring the possible presence of other pollutants. Thus, some important problems remain to be solved before the efficient application of heterogeneous photocatalysis in water and wastewater treatment [19].

Despite many studies carried out on the effect of photooxidation and catalytic photooxidation on polluted liquids, including wastewater, there is no comprehensive information in the literature. Furthermore, little data exists on wastewater treatment incorporating a mixture of many pollutants (which composition and origin are often not fully known). Domestic wastewater belongs to such a category, especially that containing a significant amount of gray wastewater. A substantial amount of greywater in domestic wastewater, as well as the relatively long retention time occurring under operating conditions (collection, processing, or treatment), may lead to low susceptibility to biological degradation, expressed by a high chemical oxygen demand (COD)/five-day biochemical oxygen demand (BOD$_5$) ratio – often above 3.0 (the value for biodegradable wastewater is assumed to be no more than 2).

Only a few studies, the results of which have been published, refer to wastewater of low biodegradability, including greywater [20–22]. There are practically no reports in the literature containing research on domestic wastewater of low biodegradability (including greywater).

There is a need for further research in this area due to a lack of clear results. Some of those encountered were related to the adsorption of pollutants by the photocatalyst. Another problem noted was with the differences in the removal efficiency for single substances compared to their mixtures [20], as well as low removal efficiency demonstrated by the organic substances indicators (e.g., total organic carbon) compared to others, for example, color [22].

The herein presented study was aimed to assess both the impact of ultraviolet irradiation and titanium(IV) oxide, as well as a pretreatment of wastewater (sedimentation, microfiltration) on the low susceptible to biodegradation organic matter present in greywater and domestic wastewater. The content of organic compounds was determined using indicators applied in the qualitative analyses of wastewater and water, namely the COD, BOD$_5$, and ammonium nitrogen (N–NH$_4$). The amount of suspended particles in the form of total suspended solids (TSS) and turbidity both in the raw state and after mechanical pretreatment were assessed.

Another goal of the research was to verify whether the efficiency of the photochemical reactions in a very complex mixture (wastewater) applied for the removal of pollutants could be demonstrated using conventional indicators. The simple statement was not obvious in this regard following literature data and initial study. It was mainly due to the instability and difficulties found in determining the initial conditions (COD variability up to 5%). In addition, the decomposition of easily degradable substances was determined as COD in a relatively short time (several minutes to several hours at room temperature). Moreover, the course of processes could also be significantly hampered by the presence of colloids and various compounds, which are common in natural and semi-natural wastewater.

2. Methods and description of experiments

2.1. Methods

Altogether, five experiments marked E1–E5 were performed and consisted of irradiation of greywater samples using two types of ultraviolet lamps (E1, E3, E4, E5 – Aquael UV AS lamp – 3.5 W (filament power), UV-C light – 254 nm; E2 – AquaNova NUVC lamp – 36 W (filament power), UV-C light – 254 nm, in several variants (36/12 W UV lamp: 55–90 W/m^2, 3.5/3 W UV lamp: 35–65 W/m^2, at 1–3 cm distance [23]). Samples of domestic wastewater (E6, E7) were irradiated using three diode lasers (10 W each, λ_{max} equal 365 nm), and the radiation intensity of each diode was assessed at the level of 200 W/m^2. Importantly, the measure of light intensity – DRI also allows calculating the total energy input ("J" unit), which can be converted to photocatalyst activity. Radiation intensity (dose) was calculated based on the lamp's filament power quotient and the area exposed to the UV radiation.

Titanium(IV) oxide was applied in two forms: (i) a commercially available material Plastoperm KP0188-75IR (Permedia Ltd., Lublin, Poland) in the form of beads with a diameter of 2–3 mm, containing an LDPE (Low Density Polyethylene) carrier and 75% of TiO$_2$, and (ii) bulk TiO$_2$ microparticles, anatase crystalline phase (Sigma-Aldrich, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) with a particle size of 325 mesh (<44 μm).

2.2. Description of the experiments

The conditions of E1–E7 experiments are summarized in Table 1. In experiments E1–E5, greywater was prepared in the manner described previously [24].

There are two attempts to the control experiment; one is to simultaneously conduct the experiment at the same conditions as the research experiment. Another assumption is to

consider the initial state at time "0" as the "control" state. Such attempts have been applied by the study of Sanchez et al. [25].

Greywater was used as both naturally occurring (E1) and mechanically pretreated (E2 – 10 min sedimentation, E3 – filtration <2.5 μm) (Fig. 1). Semi-natural greywater was also used. The proportions of grey wastewater used were: 31%, 62%, and 7% for laundry, shower/bath, and washbasin, respectively [26]. The semi-natural greywater consisted of 12 dm^3 of natural greywater collected from the washing machine after the completion of washing 3–5 kg of clothes (20 g washing powder, Ariel, Procter & Gamble, Warsaw, Poland). Another component was artificial greywater imitating greywater originating from the shower/bath, prepared by using: 3.6 g of shampoo (Head & Shoulders, Procter & Gamble, Warsaw, Poland), 5.7 g shower gel (Colgate-Palmolive, Warsaw, Poland), 0.42 g liquid soap (Serpol-Cosmetics Ltd., Poland) and 27 dm^3 tap water.

Although the samples in E1 came from the same source, they constituted non-pretreated wastewater with a high

content of suspended solids and colloids. Lack of thorough mixing (unifying) and rapid sedimentation of some of the suspended solids could result in significant differences between E1 "time 0" and E1 control "time 0". Appropriate actions have been taken for these methodological reasons and those presented in the literature and related to the raw wastewater features, like hindered UV light penetration due to increased turbidity. Namely, in all subsequent experiments with greywater or wastewater, a preliminary (mechanical) treatment step was performed to improve the clarity of the liquid and allow to obtain more homogeneous and comparable samples for the experiments.

In E2–E5 experiments (Figs. 1 and 2), greywater was subjected to pretreatment processes (Table 1) by sedimentation or filtration. The sedimentation was performed for 10 min (E2) or 90 min (E4 and E5). In E1 and E5 experiments, UV radiation and Plastoperm were used.

In the E4 experiment, three UV lamps (3 W power) of the same type as in E1 were applied but using only a light bulb (without housing) (Fig. 3). Before irradiation, greywater was subjected to 90 min of sedimentation and then homogenized. For this purpose, a blender with a rotation speed of 11,000/min was applied for 1 min. The sedimentation process preceding irradiation was aimed to mimic the primary sedimentation, which often occurs in technical conditions in greywater treatment plants. The light bulbs (lamps without housing) were immersed in one tank holding 6 L of the greywater. The E4 was carried out in two parts using the same experimental conditions. The first part

Table 1
Conditions of the performed experiments

Experiment	Pretreatment/treatment	TiO$_2$ presence
	Greywater	
E1	No pretreatment	0.24 g/L[a]
E2	Sedimentation (10 min)	–
E3	Filtration <2.5 μm	–
E4	Sedimentation (90 min)	–
E5		0.4 g/L[a]
	Wastewater	
E6	Pretreated in a septic tank	1.0 g/L[b]
E7	Pretreated in a septic tank and treated on the textile filter	1.2 g/L[b]

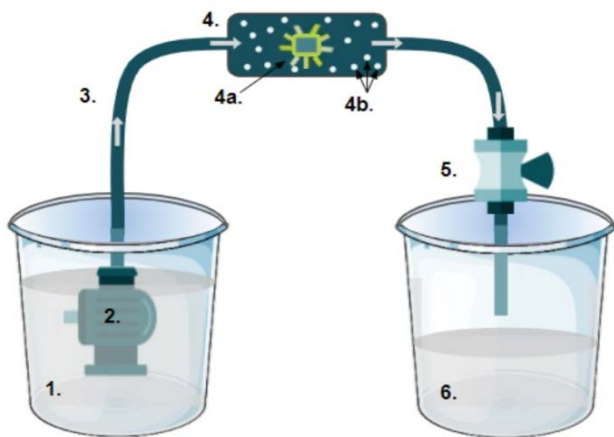[a]Plastoperm;
[b]Anatase microparticles.

Fig. 1. E1 and E3 experimental set-up (1) greywater before UV radiation, (2) pump, (3) tube, (4) UV lamp, (4a) UV filament, (4b) Plastoperm beads (E1), (5) valve, (6) greywater after UV radiation.
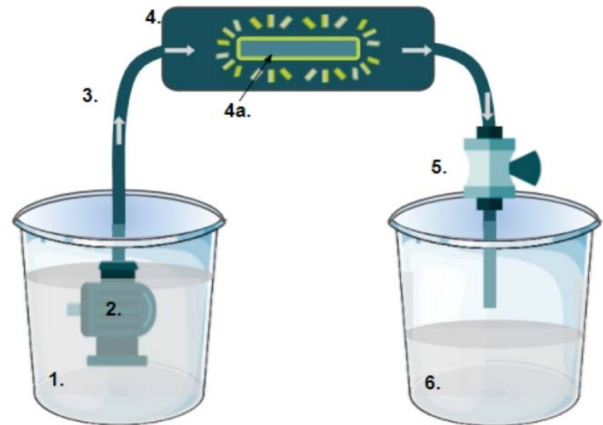

Fig. 2. E2 experimental set-up (1) greywater before UV radiation, (2) pump, (3) tube, (4) UV lamp, (4a) UV filament, (5) valve, (6) greywater after UV radiation.
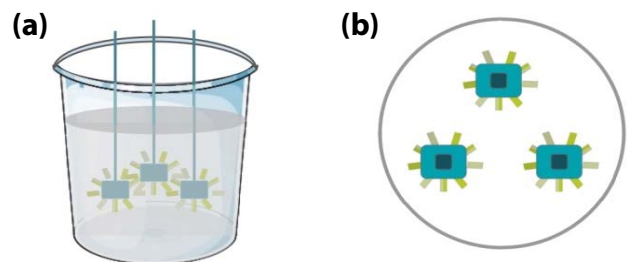

Fig. 3. E4 experimental set-up: (a) side view and (b) top view.

was conducted as a pilot study to evaluate the methodology applied. Upon receiving the results, the second part was conducted with more repetitions and in which more samples were collected at the initial and final time points (0 and 120 min, respectively).

The E5 experiment was carried out using light bulbs (UV lamps without housing, 3 W power) with a Plastoperm addition (20 mL) in each beaker containing 100 mL of greywater (Fig. 4), which was subjected to sedimentation prior to the test for 90 min. As reaction vessels, three 250 mL beakers were implemented, wrapped in aluminum foil, and covered with black cardboard. The contents of the beakers were mixed using a WTW OxiTop mixing platform.

The layout of the experimental set-up for E6 and E7 is presented in Figs. 5 and 6, respectively. In E6 and E7 experiments, domestic wastewater was applied. This wastewater was collected from a septic tank effluent (in the form of a single chamber of 3.0 m³) placed in a four-people family household. In the E7 experiment, it was additionally treated using a nonwoven filter (technical and technological details

were presented in the article [27]). In both these experiments, titanium(IV) oxide was applied in the form of pure anatase microparticles. A constant temperature of 20°C was maintained using an incubator. A magnetic stirrer (WTW OxiTop) was used for mixing at a constant speed. Different conditions were evaluated: (i) without the presence of light, (ii) with UV irradiation, and (iii) with UV irradiation upon the addition of anatase microparticles at the concentration of 0.1%. Experiments were carried out for 210 min, the samples were filtered with syringe filters (0.45 μm) and subjected to COD, and $N-NH_4$ analyzes.

For the analysis of the remediation experiments results, three main indicators were applied:

- COD, which was performed following the bichromate method (oxidation of organic compounds using chromosulfuric acid, determination as chromate) using a Merck spectrophotometer Spectroquant® NOVA 60A (Merck KGaA, Darmstadt, Germany).
- The BOD_5, which was performed using the respirometric method (OxiTop, WTW).
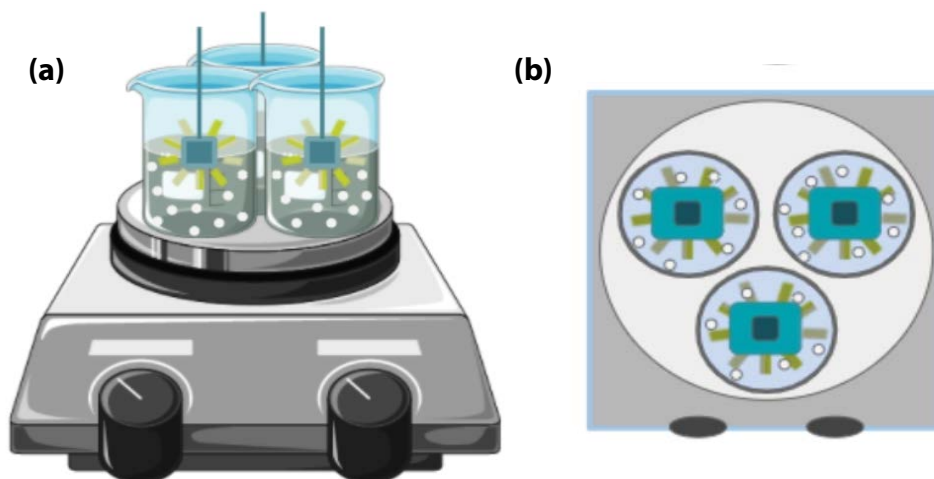

Fig. 4. E5 experimental set-up: (a) side view and (b) top view; white spheres inside the beakers are the Plastoperm beads.
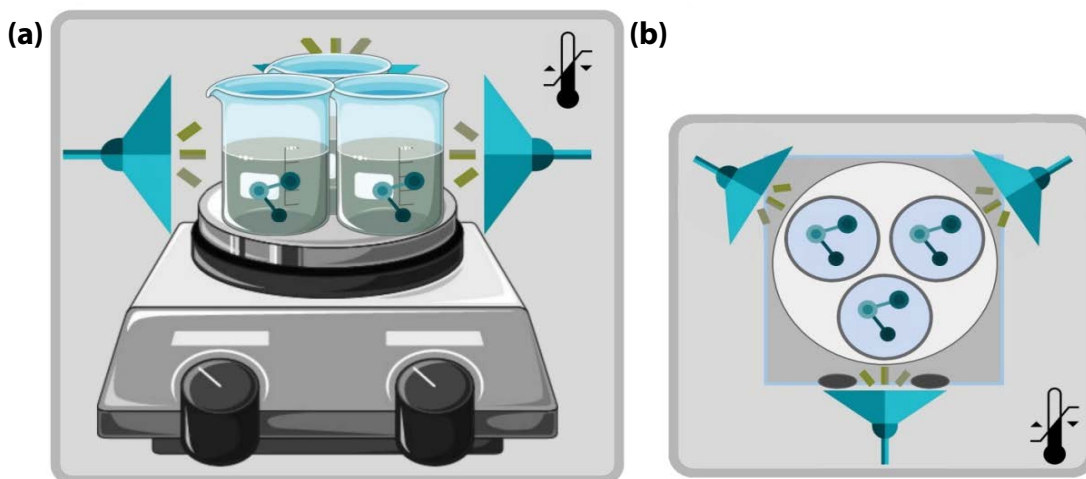

Fig. 5. E6 experimental set-up: (a) side view and (b) top view.

- Ammonium nitrogen (ammonium ions) N–NH$_4$ was rated by the indophenol method using a Merck Spectroquant® NOVA 60A spectrophotometer (Merck KGaA, Darmstadt, Germany).

Additionally, specific parameters and experiment conditions were monitored, as follows:

- Total suspended solids (measured using a dry-weight method with filtration on paper filters of a 2.5 μm pore size).
- Dry residue assessment (performed by evaporation of water at 105°C until a constant weight was reached).
- Turbidity (evaluated using a turbidity meter and a spectrophotometer).
- Temperature.

2.3. Statistical analysis

Statistical analyses were conducted using program R (version 3.5.1). Significant differences in the results were evaluated with analysis of variance (ANOVA) test and Tukey-HSD test ($p \leq 0.05$) (at least two comparisons). The significant difference ($p \leq 0.05$) between the two results was tested by the *t*-test (normal distribution of population values) or the Wilcoxon signed-rank test (non-normal distribution of population values).

3. Results and discussion

The concentrations of pollutants in the studied greywater fluctuated within a typical range [28–31], and the obtained values for pretreated domestic wastewater did not differ from the average (Table 2). The COD values varied from 209 to 553 mg O$_2$/L in the greywater series experiments and from 70.7 to 139 mg O$_2$/L in the septic tank effluent (domestic wastewater) series experiments. The COD values were comparable to the concentrations observed by Sanchez et al. [25] in low-strength laundry greywater. BOD$_5$ ranged 90–130 mg O$_2$/L in the greywater series experiments and equaled 37 mg O$_2$/L in the septic tank effluent. In turn, N–NH$_4$ concentration in domestic wastewater pretreated in a septic tank was determined at an average of 57.3 mg/L, while additional treatment on a nonwoven filter reduced this value to 0.43 mg/L.
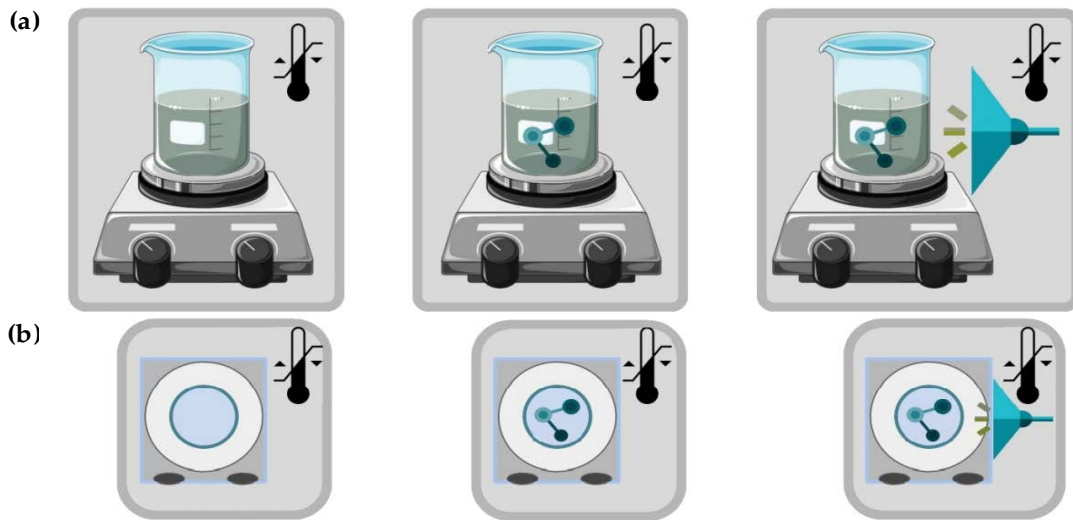
Fig. 6. E7 experimental set-up: (a) side view and (b) top view.

Table 2
Concentrations of pollutants in the studied greywater and wastewater

Experiment	COD, mg O$_2$/L	BOD$_5$, mg O$_2$/L	N–NH$_4$, mg/L	Medium	COD/BOD$_5$
E1 (control)	553	110	n.d.		5.0
E1	356	110			3.2
E2	351	105			3.3
E3	209	n.d.		Greywater	
E4 (pilot)	226 (377)[a]	130[a]			1.7 (2.9)
E4	(427)[a]	116			3.7
E5	338	90			3.8
E6	139	37	57.3	wastewater	3.8
E7	70.7	n.d.	0.43		

[a]homogenized

The COD/BOD$_5$ ratio was relatively high for most experiments (1.7 to 5.0, with a 3.5 mean value), which is comparable to literature data for greywater (1.4–4.0) [32]. The non-specificity of the COD and the BOD$_5$ indicators did not permit the direct identification of specific chemical compounds and substances responsible for low suscepti-bility to biochemical degradation. The presence of mineral washing powder and detergents constituted a significant obstacle due to alkaline substances, significantly increas-ing the pH of greywater [32]. Domestic wastewater pre-treated in the septic tank did not differ from greywater in terms of the COD/BOD$_5$ ratio (3.8). The long retention time of the wastewater, both in the septic tank and in the labora-tory before applying in the experiment, could cause anaer-obic biochemical decomposition of readily biodegradable organic compounds, which were detected as BOD$_5$.

3.1. Greywater experiments

3.1.1. Experiment 1 (E1)

The goal of the E1 experiment was to assess the poten-tial effect of using Plastoperm addition in photoremedia-tion of raw (not pretreated) greywater. The results showed the reduction of both the COD (24.7% and 24.2% for 22 and 33 s of exposure, respectively) and the BOD$_5$ (13.6% and 27.3% for 22 and 33 s of exposure, respectively). In the con-trol experiment of E1 (in the absence of the Plastoperm), after 49 s of UV-light exposure, the COD parameter decreased by 30.6%, whereas the BOD$_5$ indicator increased by 18.2% as compared to the initial values (Table 3).

The interpretation of the results in this experiment was difficult, as obtained values were highly scattered. This was most probably because of the retention of particles or colloids on the surface or in the spaces between the used Plastoperm material beads.

3.1.2. Experiment 2 (E2)

UV light cannot pass through the whole volume of untreated greywater as it is too opaque. For this reason, an additional experiment was proposed to increase the per-meability of light. In the first part of E2 experiment, the suspended solids of the highest density were removed by sedimentation within 10 min, and after decantation, the resulting solution was subsequently irradiated (Table 4). An average COD decrease of just over 12% was found. In contrast, the BOD$_5$ values increased by an average of 22%, which can be explained by the possible decomposition of substances during photooxidation reactions. Similar obser-vations have also been noted in other studies on the photoo-xidation of persistent pollutants, including pharmaceuticals [33], pesticides [34], and others [35].

These findings are in accordance with literature data, as UV light irradiation is known to have little effect on total organic carbon values of the greywater but simulta-neously may induce serious changes in the chemical struc-tures of the present compounds, thus affecting the COD and BOD$_5$ values [36].

The second part of experiment E2 (Table 5) was car-ried out in similar conditions as indicated in the first part.

Table 3
Conditions and results of E1

	TiO$_2$, g/L	Time, s	COD		BOD$_5$	
			mg/L	Change of initial value (%)	mg/L	Change of initial value (%)
E1	0.24	0	356	0.0	110	0.0
		11	296	−16.9	120	+9.1
		22	268	−24.7	95	−13.6
		33	270	−24.2	80	−27.3
Without TiO$_2$ (Control)	0	0	553	0.0	110	0.0
		49	384	−30.6	130	+18.2

Table 4
Conditions and results of the first part of E2

Time, s	Dose, J/m^2	COD		BOD$_5$	
		mg/L	Change of initial value (%)	mg/L	Change of initial value (%)
0 (Control sample)	–	351	0.0	105	0.0
1	388	288	−17.9	140	+33.3
3	1,163	304	−13.4	130	+23.8
13	5,039	293	−16.5	120	+14.3
26	10,078	297	−15.4	115	+9.5
39	15,117	344	−2.0	150	+42.9
52	20,155	296	−15.7	140	+33.3
65	25,194	334	−4.8	–	–

However, a constant temperature of 20°C was maintained by using a thermostatic box. The BOD_5 parameter was not measured due to the lack of reduction of this indicator in the first part of the E2 experiment.

Some variations in the COD parameter levels were observed in the control sample (2–6%). However, significant reductions in the COD parameter level under UV irradiation were found both after 65 s and 1 h of reaction with decreases by 4.9% and 20.4%, respectively. Samples irradiated with UV light in the presence of TiO_2 (Plastoperm) in the initial phase, after 65 s, revealed a slight decrease in COD by 8.9% (samples did not become turbid), whereas, after 1 h, an increase in COD by 43.9% and an evident increase in turbidity was noted.

A statistical difference for the COD parameter was also confirmed between the control sample and the UV irradiated sample, both – respectively after 65 s and 60 min of the process (variances statistically not different, t-test, $p < 0.05$).

In the short-term experiments – up to about 1 min (E1, first measurement of second part of E2) with TiO_2 (Plastoperm) a decrease of COD and BOD_5 were observed, which could be a result of short-term adsorption. However, in experiments with longer reaction times in the presence of TiO_2, the COD value increased, possibly due to the mechanical abrasion of LDPE and its decomposition under UV influence. An increase in turbidity of samples with TiO_2 (Plastoperm) subjected to mixing (E2–2, E5) was also observed. Hence the effect of COD increase was noted with longer reaction times.

A control measurement was performed to verify this hypothesis. The amount of 100 cm^3 of greywater was mixed with 24 mg TiO_2 (in Plastoperm) on a platform with an electromagnetic stirrer (180–450 rpm) for 1 and 2 h. Intensive turbidity of the sample after 1 h and even more intense after 2 h was noted. A greywater sample that was mixed at the same time – but without Plastoperm – revealed no change in turbidity.

Due to the initial decrease (adsorption) and then increase (LDPE release) of COD in the presence of Plastoperm material, it was difficult to identify a trend and to determine the reaction kinetics (not one but at least two reactions in the process).

It was assumed that radiation times of the order of tens of seconds could significantly reduce the content of organic compounds determined as COD and BOD_5, so relatively short time intervals were applied to identify the period

of time with the most significant impact on organic compound decomposition. It turned out, however, despite literature reports on relatively short times of decomposition of organic compounds in wastewater by photocatalytic reactions [37], which the authors considered planning this experiment, no significant reductions in the concentrations of these substances were noted. It is worth mentioning that there are also contradictory reports in the literature raising the effect of decomposition of these compounds at very long reaction times (not of the order of several minutes, but of several hours) [38]. According to the authors, this confirms the insufficient understanding of the processes in such complex solutions and suspensions, such as domestic or greywater.

3.1.3. Experiment 3 (E3)

E3 was proposed to assess the effect of filtering the greywater before irradiation. Interestingly, despite the initial removal of suspended solids from the wastewater by filtration (2.5 μm) followed by a long exposure time of 120 min, the COD value remained almost unchanged (Table 6). However, a significant temperature increase of about 20°C (from 18.0°C to 38.5°C) was observed for the most extended irradiation times of 60 and 120 min, as a result of heat generation by the UV light source.

Although the temperature has a significant effect on the photocatalytic reaction rate [39] – even up to 6 times when the temperature is increased from 38°C to 100°C, the

Table 6
Conditions and results of E3

Time, s	Dose, J/m²	COD	
		mg/L	Change of initial value (%)
0 (Control sample)	–	209	0.0
1	476	218	+4.3
10	4,757	217	+3.8
60	28,544	206	−1.4
600	285,444	210	+0.5
3,600	1,712,665	209	0.0
7,200	3,425,330	210	+0.5

Table 5
Conditions and results of the second part of E2

Reaction time	Control sample (COD, mg/L)	TiO₂+UV (COD, mg/L)	UV (COD, mg/L)
0	379.7 ± 0.3	–	–
65 s	404.3 ± 9.2	368.3 ± 0.9	384.3 ± 0.7
Difference between means (concerning the control sample) – 65 s			
–	–	−8.9	−4.9
1 h	385.3 ± 0.3	554.3 ± 3.0	321.7 ± 1.7
Difference between means (concerning the control sample) – 1 h			
–	–	+43.9	−20.4

difference in temperature of about 15°C–20°C for about 1–2 h is relatively low – only several percent. Therefore at these conditions (temperature/time), the question of the range is probably insignificant. A similar, relatively low effect of temperature difference in the range of about 20°C, was found by Meng et al. [40] for the degradation of Congo red in the presence of TiO_2 at very high irradiation intensities (irradiation: artificial sunlight, light source: 300 W Xenon lamp). They obtained a reduction in Congo red concentration with a temperature increase from 25°C to 45°C of about only a few percent for reaction (photocatalysis) times from 20 to 80 min.

3.1.4. Experiment 4 (E4)

Changes in the content of organic compounds in the first part of this experiment were determined using the COD indicator for wastewater samples with or without homogenization (Table 7). There were no significant differences in the COD values for irradiation times up to 60 min, varying from 0.8% for an increase to 2.1% for a decrease in the values. For the longest exposure time of 120 min, a 34% decrease in COD from 376.5 ± 1.5 mg O_2/L to 248.5 ± 1.5 mg O_2/L was noted. However, in the case of the COD values for non-homogenized samples exposed for no longer than 60 min, a significant increase was observed, ranging from 16.8% to 18.1%, whereas it is only 1.3% for the exposure time of 120 min. In the beginning, the BOD_5 value slightly increased and subsequently decreased compared to the initial sample with the difference of the initial and final samples decreasing by 19.2%, from 130 to 105 mg O_2/L. The turbidity parameter, determined as nephelometric turbidity units (NTU), did not change significantly for the first 60 min of the experiment (117–119 NTU), but increased considerably after 120 min (134 NTU).

On the one hand, using natural or semi-natural wastewater (septic tank effluent or greywater) results in less likely repetitive results and makes this discussion more difficult, but on the other hand, it does reveal the complexity of wastewater processes and its changeability.

A statistically significant difference was found between the average COD value (homogenized samples) for the time "0 min" and the exposure time of 120 min (*t*-test, $p < 0.05$) and between the average BOD_5 value for the time "0 min" and the exposure time of 120 min (*t*-test, $p < 0.05$). Encouraging results of the E4 experiment prompted us to carry out the second part of this experiment with more repetitions and improved methodology for sediment removal from the test vessel walls before collecting samples for physicochemical analyses. The 120 min exposure time resulted in a reduction of the COD parameter by an average of 2.8% in homogenized wastewater samples (Table 8). However, an average increase for the BOD_5 values of 33.6% was found (from 116.0 ± 15.8 mg O_2/L to 155.0 ± 8.2 mg O_2/L). Such observation is interesting in the light of another study by Liu et al. [41], wherein the authors noted an 80% decrease of dissolved organic carbon content after 150 min of exposure in the UV/TiO_2 system. However, the literature experiment was conducted for much lower concentrations of initially dissolved organic carbon and turbidity, similar to distilled water (on average 1.32 NTU). Additionally, the authors observed an average reduction in TSS concentration by 45% from an average of 86 to 47 mg/L and a slight decrease in dry residue concentration by 2.8%. Some data also indicate that the effects of UV radiation alone are negligible [42].

Statistical analysis indicated a significant difference between the average COD value (homogenized samples) for the samples at a time "0 min" and the samples after 2 h of exposure (ANOVA, Tukey-HSD test, $p < 0.05$). In contrast to the COD value, which decreased during UV irradiation, the BOD_5 value increased (*t*-test, $p < 0.05$).

The results of E4 indicate the COD and BOD_5 decrease in the first instance. However, in the second instance, the decrease in COD was lower than in the first, and the BOD_5

Table 7
Conditions and results of the first part of E4

| Time, min | Dose, J/m² | COD homogenized | | COD | | BOD_5 | |
		mg/L	Change of initial value (%)	mg/L	Change of initial value (%)	mg/L	Change of initial value (%)
0 (Control sample)	0	376.5 ± 1.5	0.0	226	0.0	130 ± 0	0.0
1	3,666	379.5 ± 0.5	+0.8	264	+16.8	135 ± 15	+3.8
10	38,701	369.5 ± 0.5	–1.9	265	+17.3	115 ± 5	–11.5
60	246,160	368.5 ± 0.5	–2.1	267	+18.1	115 ± 5	–11.5
120	512,661	248.5 ± 1.5	–34.0	229	+1.3	105 ± 5	–19.2

Table 8
Conditions and results of the second part of E4

| Time, min | Dose, J/m² | COD homogenized | | BOD_5 | |
		mg/L	Change of initial value (%)	mg/L	Change of initial value (%)
0 (Control sample)	0	427.0 ± 4.2	0.0	116.0 ± 15.8	0.0
120	460,413	415.2 ± 1.5	–2.8	155.0 ± 8.2	+33.6

value increased. The organic compounds indicated as the BOD_5, due to their relative accessibility to biological biodegradation, can undergo processes related to the activity of the microorganisms independently from photocatalytic processes.

3.1.5. Experiment 5 (E5)

During the E5 experiment, no change was noted in the COD value despite the presence of the TiO_2-containing Plastoperm (Table 9). Also, the content of organic compounds determined as BOD_5 increased by 51.8% on average, with a maximum of 85.2%. The concentration of the TSS in subsequent series decreased, although the values demonstrated considerable variability. It is necessary to note that for the longest exposure time of 180 min, a significant temperature increase from 18°C to 31°C was observed due to the light bulb heating the liquid.

A statistical difference was found between the COD values, especially the measurement at "0 min" and after 60 or 180 min of light exposure (t-test, $p < 0.05$). A statistical difference in the TSS concentration was also confirmed between the control sample and the sample after 180 min of the process (t-test, $p < 0.05$).

Although the titania-based pigments used in an industry usually exhibit larger particle sizes due to the extent to which they enable the coloring of other materials [43], the composition of Plastoperm prompted us to test it as a potential photocatalyst (experiments E1 and E5). Plastoperm is composed of polymer (polyethylene) and titania. Literature data indicate that titania, regardless of its size, exhibits photocatalytic activity unless its surface is treated, usually with oxyhydrates of aluminum or silicon [44]. Moreover, the photoactivity decreases with the increase of the particle size but is never reduced to zero. As the manufacturer does not specify the particle size of TiO_2 used in Plastoperm, our goal was to assess the possibility of using cheap and commercially available material that could be easily removed from the mixture after the photoremediation experiment.

It was used in this study in order to unambiguously verify whether or not there is any significant impact of this material in photodegradation processes. The premise for the use of this pigment was a very high TiO_2 content, reaching 75%. The photocatalytic activity was already demonstrated at much lower contents - 1%–3% for pigments being a mixture of TiO_2 and PP [45] and for TiO_2 on polyethylene films [46]. The disadvantage of the Plastoperm application was its relatively low bulk density. Although the TiO_2 content in the concentrate was relatively high

(70%/75%), the concentration of TiO_2 (pure) was low. Due to the obstruction of (irradiation) access to light by the relatively large diameter of solid particles of Plastoperm, the applied amount of concentrate was determined to be no more than 25% of liquid volume.

Mercury UV lamps were abandoned in favor of diodes and samples that were placed in a greenhouse to eliminate temperature effects. Despite the small source of thermal radiation, temperature conditions could change due to insulation by aluminum foil and covering with a blackboard.

As previously mentioned, this study was designed to assess the influence of ultraviolet irradiation and titanium dioxide, in the role of a catalyst, on greywater. For this purpose, common indicators, usually applied in the qualitative analyses of wastewater and water, were used. Nevertheless, the intermediates and products that may be formed during the photodegradation process need further investigation. Noteworthy, the composition of greywater may vary in different households due to the large variety of laundry detergents and personal care products used [47]. Therefore, it is difficult to predict the direction of certain photocatalytic processes, which in fact, could lead to various products. To date, many studies have revealed the application of photocatalytic reactions, also with the use of different catalysts, in the treatment of greywater [48–51], but little is known about the degradation products. Mechanistic considerations can be based on experiments consisting of the degradation of a single component. For example, such an approach was undertaken by Hegedűs et al., who investigated the photodegradation of Triton X-100, a widely-applied non-ionic surfactant with a hydrophilic polyethylene oxide chain and an aromatic hydrocarbon lipophilic group in its structure [51]. In this case, UV spectral studies and GC-MS analysis indicated ring-opening of the treated compound, and the intermediate for the most abundant fragment ion was defined as a short-chain hydroxycarboxylic acid or its ester.

3.2. Septic tank effluent experiments

Considering the results of experiments E1-E5 and literature reports [52], it was decided to run experiments E6-E7 for a sufficiently long time (210 min) to obtain the removal effect by photocatalysis.

Despite lower nominal power (power consumption), UV-LED diodes are characterized by higher radiation intensity (200 W/m²) than UV-C (254 nm) lamps (36/12 W UV lamp: 55–90 W/m², 3.5/3 W UV lamp: 35–65 W/m², at 1–3 cm distance [23]).

Table 9
Conditions and results of E5

TiO$_2$, g/L	Time, min	Dose, J/m²	COD		BOD$_5$	
			mg/L	Change of initial value (%)	mg/L	Change of initial value (%)
– (Control sample)	0	–	338.0 ± 1.5	0.0	90.0 ± 8.2	0.0
	10	87,059	346.3 ± 2.7	+2.5	110.0 ± 8.2	+22.2
0.4	60	522,355	402.7 ± 1.9	+19.1	133.3 ± 6.7	+48.1
	180	1,567,064	406.3 ± 3.2	+20.2	166.7 ± 6.7	+85.2

Literature data indicate higher efficiency of photooxidative processes in media with relatively low decomposition concentrations and low turbidity substances [53]. Therefore, E6 and E7 experiments aimed to decompose organic compounds and ammonium nitrogen (ammonium ions) in mechanically and mechanically-biologically treated wastewater. In these experiments, the additional ammonium nitrogen (N–NH$_4$) parameter was assessed, which is an indirect indicator of transformations of organic compounds that are quickly convertible into ammonium compounds. As BOD$_5$ could undergo processes related to the activity of the microorganisms independently from photocatalytic processes, the determination of this indicator was abandoned in the experiments (E6 and E7) on septic tank effluent, which is more susceptible to these changes.

3.2.1. Experiment 6 (E6)

Due to the ineffective irradiation of greywater with the UV-C (254 nm), in experiments performed on domestic wastewater (septic tank effluent), the radiation source was changed to emit light of a range still optimal for TiO$_2$ photo-activity (three diode lasers, λ_{max} equal 365 nm) but offering a slightly more penetration depth [54].

Despite the relatively large particle size and a small surface area compared to nanometric TiO$_2$ (P25), the material used in E6 and E7 experiments showed significant efficiency in removing pollutants [53].

Due to the ambiguous results of the E5 study, the irradiation of the samples was extended up to 210 min. The obtained results are summarized in Table 10. The concentration of ammonium nitrogen decreased in the samples with the addition of TiO$_2$ by 10.5%, and by 27.6% in the samples with the addition of TiO$_2$ and the UV-irradiated. Similar efficiencies of N–NH$_4$ removal (16%–17%) were obtained by Marszałek and Puszczało [22] for wastewater from the confectionery industry affected by the photooxidation process. In turn, the addition of TiO$_2$ induced an increase of the COD values by 2.9%, whereas the addition of TiO$_2$ and the UV irradiation by 4.8%.

A statistical difference was found in the concentration of ammonium nitrogen, both between the samples from the control experiment and the experiment with TiO$_2$, as well as between the samples from the control and the experiment with TiO$_2$ with UV irradiation. However, the observed changes in COD values in the E6 experiment were negligible (1%–5%) and statistically insignificant.

3.2.2. Experiment 7 (E7)

Experiment 7 was a modification of E6, with additional filtration of the wastewater and an increase of the catalyst addition. The concentration of ammonium ions decreased by 2.3% for the samples with the addition of TiO$_2$, and by 22.7% for the samples subjected to the treatment of TiO$_2$ and irradiation (Table 11). The latter value is comparable to the N–NH$_4$ removal efficiency obtained by Marszałek and Puszczało [22]. The COD values decreased upon mixing with TiO$_2$ by 17.0% compared to the control samples, while the use of TiO$_2$ and UV irradiation light caused only a 15.8% decrease.

A statistically significant difference was found for the COD values of the control and the TiO$_2$ sample (*t*-test, $p < 0.05$).

Although there are numerous indications in the literature that to ensure a fast rate of the photocatalytic reaction, the turbidity should be relatively low, even below 5 NTU [53], the wastewater treatment technologies often don't provide highly transparent effluents, so looking for the processes effective at higher turbidity is still reasonable. One of the main problems related to the high contamination of the medium is the deactivation of the titanium dioxide catalyst, which can be caused by its surface saturation [13].

Ammonium nitrogen occurs as ammonia and in the form of ammonium ions. Between the two forms exists a pH-dependent equilibrium. Under natural conditions for

Table 10
Conditions and results of E6

N–NH$_4$, mg/L			COD, mg/L		
Control sample	TiO$_2$	TiO$_2$+UV	Control sample	TiO$_2$	TiO$_2$+UV
57.3 ± 0.5	51.3 ± 4.7	41.5 ± 4.7	139.3 ± 11.4	143.3 ± 11.7	146.0 ± 6.4
Difference between means (concerning control sample)					
–	–10.52	–27.62	–	+2.87	+4.78

Table 11
Conditions and results of E7

N–NH$_4$, mg/L			COD, mg/L		
Control sample	TiO$_2$	TiO$_2$+UV	Control sample	TiO$_2$	TiO$_2$+UV
0.43 ± 0.04	0.42 ± 0.01	0.34 ± 0.01	70.7 ± 3.5	58.7 ± 4.9	59.5 ± 11.5
Difference between means (concerning the control sample)					
–	–2.31	–22.69	–	–16.98	–15.80

the complete removal of total nitrogen from wastewater, it is necessary to oxidize ammonium ions in phase I by nitrifying bacteria or ANAMMOX (anaerobic ammonia oxidation) bacteria. Removal of ammonium ions from wastewater is essential mainly to the need for the protection of receivers (surface water and groundwater) from eutrophication, which is caused by the supply of nitrogen and phosphorus compounds. The source of ammonium ions in greywater can also be surfactants [32].

One of the most likely processes leading to mineral nitrogen compounds in septic tank effluent is the photocatalytic decomposition of nitrogen-containing organic compounds via transformation processes to NH_4^+ due to the reactive radicals or intermediate species. Photodegradation of the $-N=N-$ double bond molecule leads to N_2 generation [55].

To sum up, the performed study results indicate that UV irradiation and titanium dioxide's presence affect ammonium nitrogen concentration. The BOD_5 measurements allowed to determine the susceptibility of greywater to biochemical decomposition following the calculated COD/BOD_5 ratio. The indicator reveals a relatively small range of applicability for transformations involving UV irradiation and photocatalysis because it relies on an indirect method and, under certain conditions, depends on the concentration of microorganisms in the sample. COD is also an indirect indicator, but much more explicit, and is applied primarily for water and wastewater analysis and the assessment of the efficiency of their oxidation measurements concerning organic compounds. Quintana et al. [56] reported that this method's relative standard deviation was about 8.8%. However, in the presence of chlorides at 100 mg/L, it can increase up to 9.4%. The necessity to use expensive and toxic reagents and the relatively long analyses time remain this method's main disadvantages [57]. Worthy of further study is the use of AOP/TiO_2 as an alternative to the COD indicator of content in the solution of substances susceptible to oxidation [57].

In our study, no correlation was found between the light exposure dose and organic compounds' degradation level. Despite the same preparation procedure, the wastewater or greywater did not reveal the exact composition every time. However, in other studies, it was also presented that some substances may undergo photocatalytic decomposition while others remain unchanged, indicating that the degradation of certain substances often occurs only under particular conditions [58]. Thus, in this way, diverse results obtained in our study and other authors indicate the complexity of the raised issues.

For obvious reasons, the observed increase in temperature may accelerate the rate of chemical reactions, including photocatalytic [59]. The determination of the temperature effect on the photodegradation seems to be necessary for practical reasons. Due to the long exposure time, this effect was minimized [60]. On the other hand, one should look for the shortest possible reaction times with relatively high efficiency for economic reasons. Unfortunately, attempts to use the Plastoperm KP0188-75IR material did not yield satisfactory results, probably due in part to the TiO_2 occlusion inside the polymer (LLDPE) and additionally its low surface diminishing the possible amount of active sites. Moreover, the lack of material transparency and the immense 2–3 mm size of the beads in diameter presumably prevented them from irradiation and led to insufficient catalytic photoactivation.

4. Conclusions

Some statistically significant changes in COD of the homogenized greywater. As BOD_5 could undergo differentiated and complex processes related to the activity of the microorganisms independently from photocatalytic processes, the changes of this indicator in the greywater were difficult to explain. The decrease in $N-NH_4$ was found in both experiments on septic tank effluents, inconsiderable in the presence of TiO_2 alone (by adsorption) and statistically significant – in the presence of TiO_2 with simultaneous UV irradiation. These changes were identified indirectly using non-selective pollution indicators, such as COD, BOD_5 and $N-NH_4$. The analyses with the use of these indicators suggest that changes appearing in the reaction content are only related to the decomposition of specific substances with the simultaneous formation of by-products, influencing the obtained results.

Although greywater for each experiment was prepared according to the same procedure, the values of COD and BOD_5 differed in the range of several percent, the greatest deviation was found for greywater up to E4 part I – not only in the COD range, but also due to a very low COD value – as well as in terms of the COD/BOD_5 ratio, being the biochemical degradability index. The results of this experiment should therefore be treated with great caution. It is also because that it was the only experiment with greywater and UV irradiation (without TiO_2-Plastoperm), where a reduction in COD was observed only for the homogenized sample but not for the non-homogenized sample.

Therefore, experiments using greywater can be summarized by stating that a reaction time of 1–2 h at UV radiation results in a COD reduction of 3%–34% (homogenized samples). It is sufficient to treat this wastewater mechanically. Plastoperm in the presence of UV radiation did not reveal any positive effect on the removal of pollutants (even an increase of COD and BOD_5 was found) due to the embedding of TiO_2 in LDPE, and in case of mixing due to the release of fine particles of this material.

The results of our study on the decomposition of ammonium nitrogen in pretreated domestic wastewater with relatively long exposure times to 210 min, both on its own and in the presence of TiO_2 anatase microparticles, seem to be the most promising. Nevertheless, it seems advisable to study further the optimization of the catalytic conditions. Application of the wastewater process on a technical scale should in fact be made possible by minimization of the thickness of the liquid film. Due to the irradiated wastewater's relatively high turbidity, it seems expedient to use a thin layer of not more than a few millimeters to ensure proper irradiation throughout the liquid. This is consistent with observations made by the study of Parsons [61]. Such a significant reduction of the layer thickness would, unfortunately, be an obstacle on a technical scale. Such obstacles would include reduced flow rates or hydraulic losses and increased investment and unit costs. Even though promising results have been obtained, it

also seems reasonable to test "pure" TiO$_2$ in different forms, for example, a plate covered with a thin film of liquid.

There is a need for further research to obtain higher removal efficiencies. Therefore, the research will be continued using synthetic wastewater with a strictly defined composition, which should result in better repeatability of replication for individual samples determined for identical experimental conditions.

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