Environment Protection Engineering

Vol. 44 2018 No. 4

DOI: 10.37190/epe180411

VOJTĚCH TROUSIL[1], JIŘÍ PALARČÍK[1], ZUZANA BLAŽKOVÁ[1], JAROSLAVA KOŘÍNKOVÁ[1], OLDŘICH MACHALICKÝ[2], JIŘÍ CAKL[1]

PARACETAMOL AND IBUPROFEN REMOVAL FROM AQUEOUS SOLUTIONS BY OZONATION AND PHOTOCHEMICAL PROCESSES

The comparative experimental study has been performed of removal of pharmaceuticals such as paracetamol and ibuprofen from aqueous solution by ozonation and photochemical degradation in several types of reactors. Ozone, oxygen, and hydrogen peroxide were used as oxidizing agents. Heterogeneous photocatalysis was carried out in the presence of anatase type TiO_2 catalyst. To determine the amount of radiation emitted by the UV lamps and transferred into the reactor, chemical feroxioxalate actinometric experiments were performed. The degree of the pollutant removal was monitored by HPLC, COD, BOD_5, and TOC. An ecotoxic biological test of process products with *Parachlorella kessleri* was also evaluated. The results indicate that the removal of both pharmaceuticals is most effective by heterogeneous photocatalysis. In the UV processes, the degradation rate increased considerably when H_2O_2 was added. However, the addition of peroxide into the ozonation system improved the ozonation only slightly. All products of the processes tested showed improved biodegradability according to the BOD_5/COD ratio and low toxicity to *Parachlorella kessleri*.

1. INTRODUCTION

Pharmaceuticals are substances that have inherently strong biological effects even at low doses. They are structurally stable so they are not activated prior to eliciting their therapeutic effect and easily penetrate biological membranes. After administration, the drug is excreted either unchanged or in the form of its metabolites. It has been frequently observed that pharmaceuticals and their metabolites cannot be easily subject to biological treatments in municipal water resource recovery facility because some of them are

[1]University of Pardubice, Faculty of Chemical Technology, Institute of Environmental and Chemical Engineering, Pardubice, 532 10, Czech Republic, corresponding author J. Palarčík, e-mail address: jiri.palarcik@upce.cz

[2]University of Pardubice, Faculty of Chemical Technology, Institute of Organic Chemistry and Technology, Pardubice, 532 10, Czech Republic.

non-biodegradable or toxic to either biological process or aquatic life and wastewater must be pre- or post-treated [1].

There are several approaches to remove drug micropollutants from wastewaters: (i) optimize existing technology in water resource recovery facility, (ii) upgrade these facilities with new technologies, (iii) improve source control, and (iv) prevent further environmental contamination. Research over the past few years has shown advanced oxidation processes (AOPs) to be very effective in the degradation of numerous organic and inorganic compounds, including pharmaceuticals. Although they make use of different reaction systems, all AOPs are characterized by the same chemical feature, i.e., production of highly reactive oxidant species, like hydroxyl radicals ($^{\bullet}OH$) produced in situ in reaction media. As a result, AOPs can mineralize all organics to final mineral products, such as CO_2 and H_2O. Considerable research interest has recently been shown in this area, predominantly in the investigation of ozonation, photolysis, Fenton processes (including Fenton-like and photo-assisted Fenton), photocatalysis, and various their combinations, such as O_3/H_2O_2, UV/O_3, UV/H_2O_2, $UV/TiO_2/H_2O_2$, and UV/ultra-
sound systems. Developing a better understanding of removal mechanisms, limitations, and effectiveness of different treatment AOPs is vital in preventing downstream contamination of water resources [2, 3].

The most prevalent pharmaceuticals in treated wastewater are typically those that are most frequently prescribed or purchased over the counter, such as paracetamol (PCA) and ibuprofen (IBP). The compound 2-[3-(2-methylpropyl)phenyl] propanoic acid, commercially available as ibuprofen (IBP), is extensively used worldwide, primarily in musculoskeletal treatments and secondarily as a broad spectrum analgesic. It is a moderately toxic compound; its EC_{50} value according to the Microtox® luminescent bacteria test is reported to be 3.85 mg/dm^3 [4]. The EC_{50} value for *Lemna minor* (growth inhibition) test was 22 mg/dm^3 [5]. The solubility of IBP in water at 25 °C is limited to about 21 mg/dm^3, but the solubility of its sodium salt is 100 g/dm^3 [6]. Concentrations of IBP in the environment have been reported between 10 ng/dm^3 and several hundred μg/dm^3 [7]. Some degree of removal efficiency of IBP was reached by biological oxidation, in some cases more than 70% [8]. In spite of its apparently high biodegradation, the ecological risk remains high owing to the main by-products generated during the biological oxidation, such as hydroxyl-IBP and carboxy-IBP, which have shown quite similar toxicological consequences in the aquatic environment to those of the original drug [9]. The degradation of IBP by several oxidation processes has already been reported.

The ozone process is always based on the effect of direct and indirect reaction mechanisms. Also, the effect of H_2O_2 addition is favorable due to hydroxyl radicals formation. The reaction is affected by other factors such as the temperature or chemical composition of the wastewater. The degradation of IBP solely by irradiation is very slow and only secondary reactions with radicals can lead to slight transformations. Low

pressure mercury vapor lamps with different electric powers (8, 11, 15 W) have been used in batch reactors for the degradation of IBP of different initial concentrations [10]. Medium-pressure lamps have been applied in batch and circulation reactors [11]. Generally, the presence of dissolved molecular oxygen at increased initial concentration of IBP positively affected the degradation kinetics. In addition, vacuum ultraviolet (VUV) irradiation decreased the time required for the complete degradation of IBP. Among the AOPs, heterogeneous photocatalysis employing TiO_2 catalyst demonstrated its efficiency in degrading IBP. The catalyst can be suspended in the treated water or fixed on a carrier material. Compared to the fixed catalyst, the suspended one is more efficient because it has a larger surface area and, consequently, active area. Nevertheless, the key challenge of the photocatalytic process is the recycling of the catalyst used. For the purpose of recycling, the suspended catalyst, membrane separation processes such as microfiltration (MF) have been successfully used. Photocatalytic degradation of IBP was also studied. It was suggested that post-biological treatment of the reaction mixture was possible based on the biodegradability test of the treated IBP solutions [12, 13].

Paracetamol (N-(4-hydroxyphenyl) acetamide or acetaminophen (PCA) is widely used as an analgesic and antipyretic drug. At therapeutic levels, paracetamol is considered to be safe for humans upon normal drug use. The low therapeutic doses are usually rapidly metabolized (the plasma half-life being about 75% at 1.5 to 2.5 h), but part of the therapeutic dose is excreted as its conjugates. Its presence in the environment has been confirmed at the outlets of water resource recovery facilities as well as in rivers. The highest concentrations were found in hospital and pharmaceutical plant wastewater. In raw wastewater, paracetamol was detected at a median concentration of 48±75 μg/dm^3. In sewage water resource recovery facilities, the content was in the range from tens ng/dm^3 to tens μg/dm^3 and in surface waters the concentration of PCA was detected in the range from tens to hundreds ng/dm^3 [14–17].

The widespread use of PCA raises the concern of whether or not the compound persists during treatment of wastewater and drinking water. Nowadays, paracetamol wastewater is also treated by advanced chemical oxidation processes, such as ozonation and H_2O_2/UV oxidation, TiO_2 photocatalysis [18, 19]. Systems of ozonation, often coupled with hydrogen peroxide, were capable of achieving 100% conversion of the PCA but mineralization (indicated by dissolved organic compounds) occurred in 30% only. The intermediates such as benzoquinone, hydroquinone, 4-aminophenol and 4-nitrophenol formed were more toxic than the paracetamol itself. Photocatalytic degradation of paracetamol in water was studied using TiO_2 as the catalyst with light sources of UVA or UVC. With UVA radiation, no obvious degradation of paracetamol was found in the absence of TiO_2, although a significant reduction in the paracetamol concentration was observed during irradiation with UVC radiation only. A much faster degradation and effective mineralization of paracetamol took place under UVC irradiation in the presence of TiO_2. Experimental results showed that the rate constants decreased upon increasing the initial concentration of paracetamol, but increased upon increasing in light

intensity and additional oxygen. It was also found that although total conversion of the PCA may be achieved during the photocatalytic process, mineralization itself may not be complete owing to the formation of PCA degradation products. As in the case of ozonation and UV radiation, mainly phenolic products and aliphatic organic acids are involved [20].

The direct comparison of the efficiency and limitations of different oxidative processes is often complicated by their various demands concerning pH, concentrations of auxiliary oxidants or catalysts, particularities of the photoreactor systems, the UV irradiation parameters in the case of photoinitiated AOPs, and a number of other parameters. Thus, the comparative studies of different AOPs must be interpreted with necessary caution with respect to their generality.

The aim of this study was to evaluate both the limitations and effectiveness of ozonation, photolysis, and heterogeneous photocatalysis during the removal of PCA and IBP from synthetic solutions of water samples. The initial drug concentration, pH and temperature were similar in all experiments. A relatively high drug concentration in solution was selected to better understand the oxidation power of each method. Preliminary experiments were also carried out to select appropriate experimental conditions of individual processes (i.e., volumes, flow rates, irradiation intensity, and concentrations of reagents and the catalyst). The influence of hydrogen peroxide addition on the mineralization process was also explored. Additionally, as the efficiency of the UV processes is closely related to the used UV light, different irradiation sources were used at laboratory scale: UVC lamp (emitting monochromatic radiation with a maximum at 254 nm) and broad-spectrum UV lamp (emitting radiation wavelengths between 200 and 700 nm, with a maximum at 254 nm. In addition, the mineralization grade, the chemical oxygen demand, and the biodegradability were evaluated.

2. EXPERIMENTAL

Chemicals. All solutions were prepared using demineralized water (reverse osmosis water purification system, University of Pardubice, 4 μS/cm). Concentrations of both IBP (Sigma Aldrich. U.S.) and PCA (Penta, Czech Republic) used in all experimental systems were 20 mg/dm^3. NaOH and HCl (Penta) were used for pH adjustment. Acetonitrile (Penta) and phosphoric acid (Penta) were used for HPLC analysis. The concentration of H_2O_2 (30%, Lach-Ner, Czech Republic) used in ozonation, UV photolysis, and photocatalysis reactions was 0.5 g/dm^3. Commercially available titanium dioxide of anatase type (AV-01, Precheza, Czech Republic) was used as the catalyst in heterogeneous photocatalysis.

Analytical and test procedures. Particle size distribution of the catalyst was measured with a Zetasizer Nano ZS (Malvern, UK). Particle diameter (at pH 7) was in the

range of 0.08–3.30 μm with a mean value of 0.301 μm. pH corresponding to the isoelectric point was 3.9.

Absorbance spectra of aqueous solutions of IBP and PCA were determined using a HP 8453 UV-visible spectrophotometer (Agilent Technologies, U.S.). The IBP spectrum was determined for the soluble sodium salt whilst the PCA spectrum was measured for the base form of the phenolic substance. Absorbance maxima were at 225 nm for IBP and at 245 nm for PCA.

The HPLC analysis was performed using a DeltaChrom 1000 LC chromatograph (Watrex) with photodiode array detection on a reverse phase Nucleosil C18 analytical column (250 mm×4 mm).The mobile phase consisted of a mixture of acetonitrile and water (1:1) adjusted with 750 μl of orthophosphoric acid with an isocratic flow of 1.0 cm^3/min at room temperature. The injection volume was 20 μl. Detection was accomplished at 245 nm for PCA and at 225 nm for IBP.

Retention times of 2.5 min for PCA and 12 min for IBP were determined. Data analysis was performed using the software Clarity® (DataApex). The degradation efficiency (%) was calculated as sample peak area reduction at a given time from the peak area of the initial solution. Here the conversion (%) of the ibuprofen and paracetamol is expressed as 100 – degradation efficiency.

The oxygen equivalent of the organic matter of the drug samples was analyzed using a chemical oxygen demand (COD) cuvette method LCI 500 (Hach). Cuvettes were analyzed with a spectrophotometer DR6000 (Hach). Determination of the biochemical oxygen demand in 5 days (BOD_5) was done by using the cuvette tests LCK 555 (Hach). Total organic carbon (TOC) was determined using a TOC/TN analyzer (Skalar Formacs, Netherland). A digital pH meter l HI 9124 (Hanna) was used to measure the pH and conductivity.

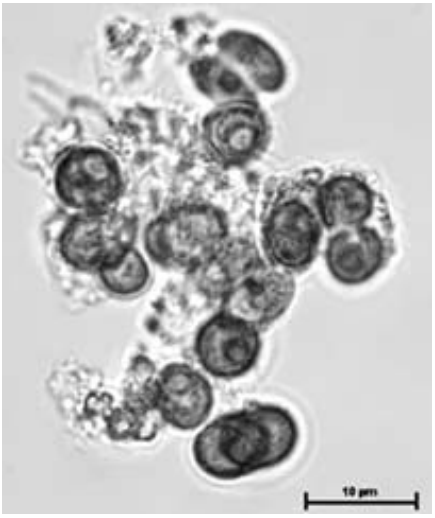

Fig. 1. *Parachlorella kessleri* algae (CCALA 253, LARG/1) in growth medium, magnification 1000×, phase contrast, 22 °C

Ecotoxicity test was performed on *Parachlorella kessleri* algae (Fig. 1) obtained from the Culture Collection of Autotrophic Organisms (CCALA, Czech Republic). The initial cell concentration was 1×10^5 cells/cm^3. Algae were incubated at 22±1 °C under continuous white (5000 lux) light illumination. The cell concentration was determined 72 h after the start of the test. Inhibition of algae growth (%) was evaluated in terms of growth rates of the suspension calculated from cell numbers compared to the blank sample. To evaluate the cell number, a Nikon Eclipse 80i microscope with a Bürker chamber and DSFI-1 digital camera was used.

To determine the amount of radiation emitted by the UV lamp and transferred into the reactor, chemical feroxioxalate actinometric experiments were performed. The method is based on the photochemical decomposition of potassium ferrioxalate. The ferrioxalate solution was prepared just before irradiation by mixing ferric sulfate and potassium oxalate. At the end of the irradiation, buffered phenanthroline solution was added and the absorbance at 510 nm was measured immediately.

Experimental systems. Three experimental systems were used for the degradation of IBP and PCA in aqueous solutions. They were: (a) ozonation in a batch recirculation reactor, (b) photolysis in a batch recirculation reactor, and (c) UV photocatalytic reactor with heterogeneous TiO_2 catalyst. The ozonation experiments were carried out at neutral solution. Additional runs were performed while adding a solution of hydrogen peroxide into the reactor. A dose of 0.5 g/dm^3 was used.

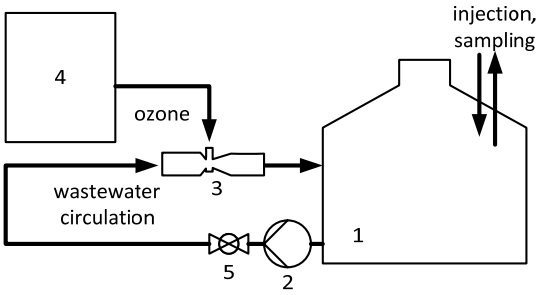

Fig. 2. Schematic diagram of the ozonator experimental setup:
1 – storage tank, 2 – pump, 3 – ozone injection, 4 – ozone generator, 5 – flow control valve

The apparatus shown in Fig. 2 consists of a storage tank for contaminated water (45 dm^3), an ozone injection reactor, an ozone generator control, and a regulation unit. Water was transported into the reactor by a centrifugal pump (Ebara, Japan). A venturi injector was used, which creates a vacuum inside the injector body and initiates ozone suction through the suction port. Ozone was generated from atmospheric oxygen using Ozonstar 100 high-voltage ozonation equipment (Ozon Moravia, Czech Republic) with an output of 1 g of O_3/h. Throughout the runs, samples were taken for analysis at 15 min

intervals. The total time of the standard experiment was 1 h although in some cases the experiment duration was 3 h. The wastewater flow circulation rate was maintained at 45 dm^3/min.

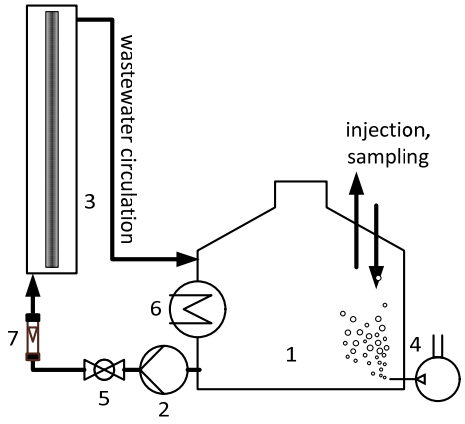

Fig. 3. Schematic diagram of the UV photolysis experimental setup:
1 – storage tank, 2 – pump, 3 – irradiation unit with UV lamp,
4 – air blower, 5 – flow control valve, 6 – thermostat, 7 – flow meter

The photolysis apparatus is shown in Fig. 3. It consists of a storage tank (20 dm^3), a circulation pump (Aquacup, Czech Republic), a Wedeco Aquada 35 W NLR WS 1825 UV photoreactor (Xylem Inc., USA), an air blower, and a control and regulation unit. The UV lamp being extensively used in the field of UV disinfection was arranged centrally in a watertight quartz tube placed in the high-grade steel chamber (7 cm in diameter and 35 cm long). For this irradiation unit arrangement, the thickness of the irradiated water layer was 2.25 cm with an irradiated volume of 1.18 dm^3. The wastewater flow circulation rate was maintained at 2.5 dm^3/min.

The maximum of the emitted radiation of the lamp used was at 254 nm (90% of emitted energy). The density of photon flow in the system investigated was determined by ferrioxalate actinometry as 2.5±0.7 μEs/(dm^3·s). Samples of the reaction mixture were taken for analysis at 1 h intervals. During photolysis with oxygen as an oxidizer, the system was aerated to ensure constant oxygen concentration in the storage tank. Additional runs were also carried out for photolysis in the presence of hydrogen peroxide with the same initial concentration as in the previous case of ozonation, i.e., 0.5 g/dm^3.

A submersible photoreactor in batch recirculation mode (see Fig. 4) with a mercury-doped low-pressure UV lamp was used. The reactor consists of a storage vessel (1 dm^3), a peristaltic pump (Heidolph), a cooling system, and a low-pressure Creator CUH 11 W lamp (Creator UV & IR Lighting, P.R.C.). The lamp was centered vertically in the quartz tube. Water with PCA or IBP circulated in the spiral quartz tube (total inner vol-

ume of 0.17 dm^3) around the UV lamp in the quartz cylinder. The wastewater flow circulation rate was maintained at 2.5 dm^3/min. The density of photon flow of 13±0.4 μEs/(dm^3·s) in the interval 200–700 nm was measured by the ferrioxalate actinometry.

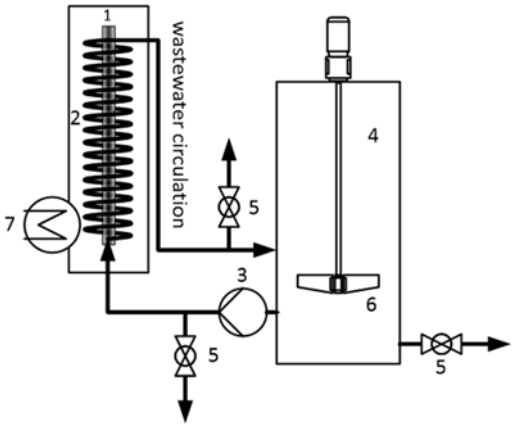

Fig. 4. Schematic diagram of the catalytic submersible UV photoreactor:
1 – source of UV radiation in a quartz cylinder, 2 – spiral quartz tube,
3 – peristaltic pump, 4 – storage vessel, 5 – sampling valve, 6 – stirrer, 7 – thermostat

The volume of the treated solution was 0.5 dm^3. The TiO_2 catalyst concentration was 0.5 g/dm^3. A concentrated dispersion of the catalyst particles was prepared by sonication of an aqueous slurry of titanium dioxide for 30 min. As an oxidizing agent O_2 or hydrogen peroxide H_2O_2 were used. A constant oxygen concentration of 37 mg/dm^3 (measured by the oximeter WTW Oxi 330i at 21 °C) was maintained by aeration in the reaction mixture. The concentration of hydrogen peroxide at the beginning of the reaction was 0.5 g/dm^3. The wastewater flow circulation rate was maintained at 1.3 dm^3/min.

Samples of the reaction mixtures were withdrawn from the reactor regularly for HPLC, COD, BOD_5 and TOC analysis as well as for the toxicity test. Immediately, samples were centrifuged for 5 min at a speed of 6400 rpm on a centrifuge Fisher Scientific Model S67601A, followed by filtration through a Sartorius 0.2-μm Minisart® membrane to remove the suspended TiO_2 particles before analysis.

3. RESULTS AND DISCUSSION

3.1. PRIMARY DEGRADATION OF PHARMACEUTICALS IN VARIOUS PROCESSES

In order to check the feasibility of oxidative treatment for the degradation of both PCA and IBP, the following control experiments were performed: ozonation, UV photolysis, and photocatalysis. The experiments with addition of hydrogen peroxide were also carried out. H_2O_2 may act as an alternative electron acceptor and it could result in

enhanced rates of pollutant destruction. The results of the experiments are presented in Fig. 5a (for PCA) and 5b (for IBP conversion).

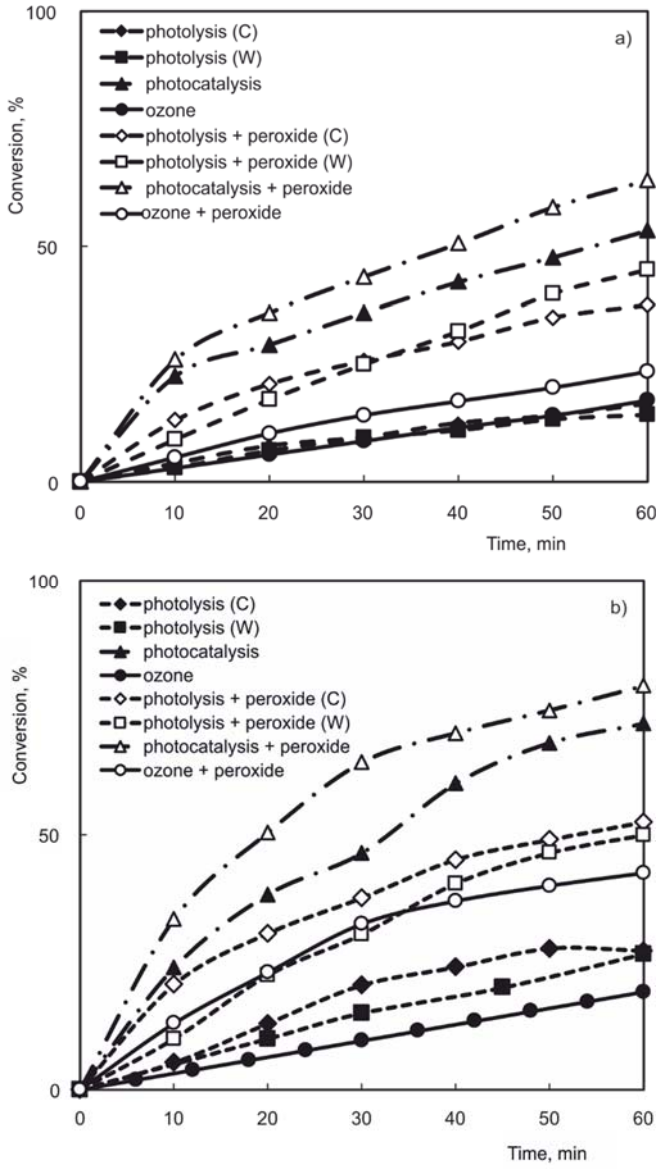

Fig. 5. Time dependences of a) paracetamol, b) ibuprofen conversion during photolysis, ozonation, and heterogeneous photocatalysis; initial concentration of drugs solutions was 20 mg/dm^3, air saturation, pH ca. 7.2, temperature 20 °C, irradiation with Creator CUH 11 (C) and Wedeco Aquada (W), ozone concentration 1 g/dm^3; H_2O_2 dose 0.5 g/dm^3

Various degrees of PCA degradation were achieved for the systems studied. After 60 min of operation, the PCA conversion varied from 14.3% for photolysis to 64% for photocatalysis with H_2O_2 addition. The lowest conversions were detected in ozonation and photolysis systems without the presence of peroxide. In the case of ozonation, the PCA conversion was only 17.5% after 60 min. Comparable values were observed in both photolysis systems, i.e., 14.3% for the Wedeco UV lamp and 16.5% for the Creator UV lamp. Nevertheless, the PCA 50% conversion was achieved after 3 h of ozonation while photolysis with the Wedeco lamp reached only 35% conversion at the same time (not shown in the paper). The addition of H_2O_2 into the ozonation system at pH 7 improved the ozonation slightly. In this combined process without photolytic initiation, the direct reactions of ozone dominated. However during the UV photolysis, the degradation rate increased considerably when H_2O_2 was used. It was most likely due by photo initiated disruption of peroxide HO–OH bond and subsequent formation of highly reactive nonselective hydroxyl radicals.

The conversion of IBP over time during the ozonation, photolysis, and heterogeneous photocatalysis (Fig. 5b) is qualitatively similar as that of PCA but the conversion values are higher for all studied systems. The photolysis systems show slightly higher efficiency in comparison with that of ozonation.

Although a fall in the concentration of a drug usually involves very complex schemes of reactions, the observed reaction kinetics can often be described phenomenologically by simple rate expressions. Therefore, to find the parameters which include kinetic influence and reactor design effects on the global reaction, the experimental time evolution of pharmaceutical concentration was fitted with a pseudo-first order reaction:

$$c = c_0 \exp(-kt) \tag{1}$$

here c and c_0 (mg/dm^3) are the initial and instantaneous drug concentrations at time t (min), and k (min^{-1}) is the pseudo-first order transformation rate constant.

This exponential decay model, describing the time dependence of the drug concentration for extremely diluted systems, is in good agreement with the experimental data presented under the entire range of experimental conditions. The coefficients of determination (R^2) are in the range of 0.96–0.99 for all processes tested. The rate constants of individual processes are summarized in Table 1 together with the half-lives, $t_{1/2}$ of the examined drugs. The process exhibiting the highest value of k is peroxide-enhanced photocatalysis of IBP, where k is 10 times higher than that of the UV photolysis of PCA and 9 times higher than that of its ozonation. In terms of the half-life, this means that only 24 min is needed to decrease the concentration of IBP to 10 mg/dm^3 during peroxide-enhanced photocatalysis, while 217 min are needed to achieve the same drug concentration during PCA ozonation.

In the ozonation, two possible oxidizing processes may be considered: the direct one, because of the reaction between the ozone and the dissolved drug, and the radical

way owing to the reactions between the generated radicals produced in the ozone decomposition (hydroxyl radicals) and the dissolved compounds. For the almost neutral solutions in the experiments performed, the slow direct reaction mechanism is much more likely. Especially in the case of PCA ozonation, this conclusion can be supported by an insignificant degradation rate improvement (up to 10%) after addition of peroxide to the reaction mixture. On the other hand, after addition of hydrogen peroxide, the conversion during ozonation of IBP increased by more than 40% and after 3 h of ozonation 92% conversion was achieved. It indicates a probable participation of both reaction mechanisms in the case of peroxide-enhanced ozonation of IBP.

Table 1

Pseudo-first order kinetic rate constants k and half-lives $t_{1/2}$ for the processes studied

Process	Paracetamol		Ibuprofen	
	k (10^{-2} min^{-1})	$t_{1/2}$ (min)	k (10^{-2} min^{-1})	$t_{1/2}$ (min)
Photocatalysis	1.35	51	2.20	32
Photolysis (C)	0.31	224	0.62	112
Photolysis (W)	0.28	248	0.51	136
Ozonation	0.32	217	0.35	198
Photocatalysis + peroxide	1.78	39	2.85	24
Photolysis + peroxide (C)	0.87	80	1.38	50
Photolysis + peroxide (W)	0.99	70	1.22	57
Ozonation + peroxide	0.46	151	1.05	66

In photo-initiated AOP applications, it is obvious that the appropriate selection of the lamp type often determines the effectiveness of the desired process. The evaluation has to take into account both technical and economic considerations. Apart from the experimental set up geometry and sample volume, the only difference between the photolysis experiments performed was the type and amount of light irradiating the system. The maximum of the emitted radiation of the Wedeco (W) lamp was at 254 nm (90% of emitted energy) with total energy input of 35 W and a density of photon flow of 2.5±0.7 μEs/(dm^{3}s). The spectrum created by Creator (C) lamp (with total power input of 11 W) was wider and richer in longer wavelengths. The system exhibited higher cumulative density of photon flow, i.e., 13±0.4 μEs/(dm^{3}s) in the interval from 200 to 700 nm. Actually, in the considered spectrum range, some of the photons (40%) were in the 400–700 nm stretch and only 60% of photons were below 400 nm. The maximum of the emitted radiation of the lamp was at 230 nm, as can be seen from Fig. 6.

To evaluate the efficiency of an individual lamp, the energies that are carried by UV radiation were examined and compared with the energies required for chemical bond dissociation in the system investigated. Theoretically, any radiation with a wavelength lower than the bond threshold wavelength can break the given chemical bond. It means

that radiation with a wavelength over 300 nm is not absorbed by drug reactants and thus it cannot contribute to the generation of electronically excited states, which are needed as the first step of the reaction mechanism in direct photolysis.

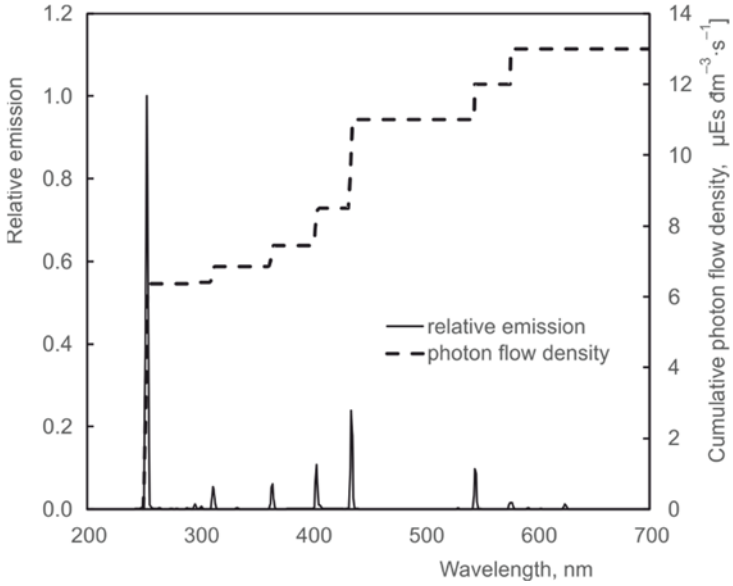

Fig. 6. Relative emission spectra of CUH 11 W lamp and cumulative photon flow density in a Creator submersible photoreactor measured by the ferrioxalate actinometry

The situation is much more complex for systems with hydrogen peroxide addition. This substance has an absorption onset at 310 nm and a threshold wavelength at 562 nm. As a result of this high energetic absorption onset, hydroxyl radicals can be created by the direct photolysis of H_2O_2 with a quantum yield close to unity for shorter wavelengths. This increased the drug conversion considerably (see Fig. 5). Wavelength limitation can also be seen in the case of photocatalytic degradation of the drugs investigated. The band gap energy of anatase catalyst is about 3.2 eV (corresponding to 387.5 nm). The radiation in the wavelength range exceeding 387.5 nm is inefficient in the titania photocatalytic systems. As shown previously, a considerable part of the Creator lamp radiation is useless, decreasing the overall yield of the processes studied.

Nevertheless, for example, Fig. 5a shows that irradiation with both (W) and (C) lamps leads nearly to the same conversion after 1 h of direct photolysis of PCA in two different batch recirculation reactors used. To explain this phenomenon, all the parameters affecting the photolysis must be taken into account, including the quantum efficiency φ of the photoreaction, the irradiation time, the radiant power, both the irradiated and the total sample volume, and the wavelength of the UV radiation applied. The results of the analysis of both systems are summarized in Table 2.

Table 2

Direct photolysis decomposition parameters

Process	Volume [dm^3]		Lamp power input [W]	Paracetamol		Ibuprofen	
	Total	Directly irradiated		φ	EE/O [kWh/dm^3]	φ	EE/O [kWh/dm^3]
Photolysis (W)	20	1.18	35	0.00213	24.0	0.00286	13.2
Photolysis (C)	0.5	0.16	11	0.00054	272.4	0.00102	136.2
Photolysis + peroxide (W)	20	1.18	35	0.00485	6.8	0.00539	5.5
Photolysis + peroxide (C)	0.5	0.16	11	0.00129	97.0	0.00221	61.2

φ is the reactor quantum efficiency, EE/O – electrical energy per order, Wedeco (W) and Creator (C) batch recirculation reactors.

The reaction quantum efficiency φ was defined as the ratio of the number of drug moles decomposed to the number of photons absorbed in the spectral region used (from 200 to 400 nm) during the reaction. The quantum efficiencies for direct photolysis of both PCA and IBP were very low (from 5.4×10^{-4} to 5.39×10^{-3}). Because the experimental drug conversions were independent of irradiation source as well of the reactor set up and volume (for the constant initial drug concentration), it can be concluded that the systems were operated in the regime of excess radiation and the limiting reagent was the drug concentration. These findings on the one hand confirm the former assumption that the pseudo-first order reaction of Eq. (1) can be used to describe the reaction systems investigated, and on the other hand suggests that we can use a lower radiation intensity for optimal photolysis operation.

Since photodegradation of aqueous solutions of pharmaceutical pollutants is an electric energy-intensive process, the electric energy can represent a major fraction of the operating costs. In the case of low pollutant concentrations, which applies here, the appropriate figure-of-merit is the electrical energy per order (EE/O), defined as the number of kWh of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90%) in 1 m^3 of contaminated water [21].

Low EE/O leads to low power cost during the reactor lifetime. Generally, an EE/O value <10 kWh/dm^3 per order is regarded an economically acceptable for the most organic micro pollutants. Table 3 also gives the values of EE/O for the photolysis systems investigated. It can be seen that EE/O is both a contaminant- and reactor-specific parameter. It is evident that the values determined from laboratory testing of direct photolysis are rather high and thus it is questionable whether these methods are competitive with other AOPs and conventional treatment technologies. Nevertheless, the results with photocatalysis show that an optimum balance between UV light applied, catalyst dose, and peroxide dose probably exists giving higher effectiveness of the process studied. The EE/O values in this case were reduced to 25% of the EE/O determined for the direct photolysis and to 48% of the value for photolysis with peroxide addition.

3.2. EVALUATION OF TOC, COD, AND BOD_5 PARAMETERS

It has been reported that some of the intermediate products of a degradation process are more stable than the parent pharmaceutical compounds. Thus, the composition changes in the reaction mixture were monitored not only by HPLC but also by total organic carbon (TOC), chemical oxygen demand (COD), and biodegradability (BOD_5) parameters. According to the HPLC results, the drugs were oxidized into other organic compounds. However, the TOC, COD, and BOD_5 given in Tables 3 and 4 show that some intermediate organic species remain in the solution for long periods.

Table 3

HPLC, COD, BOD_5, and TOC values for paracetamol after 1 h photolysis, ozonation, and heterogeneous photocatalysis

Process	COD [mg O_2/dm^3]		BOD_5 [mg O_2/dm^3]		TOC [mg C/dm^3]		HPLC [mg/dm^3]	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Ozonation	53.5	48	4.5	5	20.5	18.5	20	16.5
Photolysis (W)		47.5		6		17.9		17.1
Photolysis (C)		46.8		6		17.7		17.7
Photocatalysis		34.5		8		16.2		10

Table 4

HPLC, COD, BOD_5, and TOC values for ibuprofen after 1 h photolysis, ozonation, and heterogeneous photocatalysis

Process	COD [mg O_2/dm^3]		BOD_5 [mg O_2/dm^3]		TOC [mg C/dm^3]		HPLC [mg/dm^3]	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Ozonation	61.5	47.5	4.56	7.0	21.6	19.4	20	16.1
Photolysis (W)		48.0		11.0		17.2		14.7
Photolysis (C)		48.0		11.0		18.2		14.1
Photocatalysis		33.0		11.0		15.1		6.0

Based on the data obtained, the following conclusions can be drawn: (i) both the TOC and COD removal were much less than that of the drug degradation process under the same experimental conditions. The results show that after oxidative processes TOC decreased by 8–20% for PCA and by 10–30% for IBP; (ii) photocatalysis reactions were quite efficient for the degradation of IBP as well PCA, but complete mineralization was not achieved even after a 3 h process duration; (iii) photocatalysis showed higher selectivity for the mineralization of IBP than for PCA; and (iv) the initial values of BOD_5/COD ratio

(all lower than 0.1) indicated that both drugs are persistent, non-biodegradable, organic pollutants.

Similar results in TOC removal were also reached by Brillas et al. [22]. However, 53% of TOC was removed by UV-C irradiation (253.7 nm) and 9% by UV/H_2O_2 photolysis [23]. After using all processes studied, the ratio became higher, mainly owing to lower COD and higher BOD_5 values. The maximum biodegradability index was reached for heterogeneous photocatalysis, in which a ratio of 0.23 was obtained for PCA and 0.33 for IBP. These results, which are close to the biodegradability of the municipal wastewater, already indicate a partially biodegradable system. In general, the results show that it is quite uneconomic to use the processes studied to complete the mineralization of PCA and IBP. It is more appropriate to use advanced oxidative processes as a pretreatment process for water containing pharmaceuticals, especially when the biodegradability is too low and toxicity effects may be expected.

3.3. ECOTOXICITY MEASUREMENTS

Besides biodegradability, the toxicity of wastewater is an important parameter for the evaluation of the effectiveness of an AOP treatment. In most cases, the toxic potential of intermediates is not known and often compounds can be created that are more toxic to the water ecosystems than to the original organic compounds. To analyze this issue, samples were taken prior to and after the treatment process and tested using the toxicity test on *Parachlorella kessleri* algae. For both PCA and IBP solutions with an initial concentration of 20 mg/dm^3, the measured inhibition of the algae growth was 31% and 25%, respectively. Thus, *Parachlorella kessleri* algae was a highly sensitive species for the tested substances. However, the amounts of PCA and IBP used in our experiments were 1000 times higher than those found in the output of WWTP or waterways. Hence, the results of PCA and IBP ecotoxicity tests do not reflect the real conditions in water ecosystems, but can be used as one of the parameters for evaluation of water treatment efficiency. The toxicity of the treated samples shows that the oxidation of both drugs promoted the overall toxicity reduction. The toxicity decrease correlates with the conversion of pharmaceuticals determined by HPLC. The best results for PCA were achieved for heterogeneous photocatalysis with growth inhibition of only 11%. Similarly, in the case of IBP the lowest inhibition appears after heterogeneous photocatalysis (9%).

4. CONCLUSIONS

The presented results indicate that pharmaceuticals such as ibuprofen and paracetamol can be effectively removed from model water samples by ozonation, photolysis, and heterogeneous photocatalysis using oxygen or hydrogen peroxide as oxidizing agents. The systems tested allowed efficient drug decomposition, but they did not assure total mineralization of contaminants. The rate of drug removal was dependent on the

drug type, the experimental set up and UV lamp characteristics. In general, ibuprofen was decomposed more efficiently than paracetamol. Direct ozonation was marginally effective, no H_2O_2 addition lead to significant improvement of the process. The best degradation was achieved in the process of heterogeneous photocatalysis with the addition of hydrogen peroxide (conversion of 64% and 80% for PCA and IBP, respectively).

Although complete mineralization was not observed, all processes improved the biodegradability of the products obtained. To find the parameters which include kinetic influence and reactor design effects on the global reaction, the experimental time evolution of the pharmaceutical concentration was fitted with a pseudo-first order reaction equation. The results also show that an appropriate figure-of-merit is the electrical energy per order (EE/O). Based on experimental reaction rate constants, electric energy consumption was mainly beneficial for IBP removal (for example 136.2 kWh/dm^3 for IPB compared with 272.4 kWh/dm^3 for PCA). The efficiency of the UV processes was closely related to the used UV source and experimental set up. The results, together with the expected relatively low capital, operating, and maintenance costs, indicate the potential of the optimized AOP processes for photooxidative degradation of waters contaminated by paracetamol and ibuprofen.

ACKNOWLEDGMENTS

This work was supported by University of Pardubice, project SGS_2017_002.

REFERENCES

[1] BARCELÓ D., PETROVIC M., *The Handbook of Environmental Chemistry. Emerging contaminants from industrial and municipal waste: Occurrence, analysis and effects*, Springer, Heilderberg 2008.

[2] PIGNATELLO J.J., OLIVEROS E., MACKAY A., *Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry*, Crit. Rev. Environ. Sci. Technol., 2006, 36, 1.

[3] CHELLIAPAN S., SALLIS P.J., *Removal of organic compound from pharmaceutical wastewater using advanced oxidation processes*, J. Sci. Ind. Res., 2013, 72, 248.

[4] ESCHER B.I., BRAMAZ N., MAUER M., RICHTER M., SUTTER D., VON KÄNEL C., ZSCHOKKE M., *Screening test battery for pharmaceuticals in urine and wastewater*, Environ. Toxicol. Chem., 2005, 42, 750.

[5] CLEUVERS M., *Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects*, Toxicol. Lett., 2003, 142, 185.

[6] LEE H., KIM J.Y., KOO E.J., LEE J., LEE E.H., OH K.S., YUK S.H., *Nanoencapsulation of drug-loaded lipid by temperature-induced phase transition*, Chem. Biochem. Eng., 2012, 26, 385.

[7] SANTOS L.H., ARAÚJO A.N., FACHINI A., PENA A., DELERUE-MATOS C., MONTENEGRO M.C., *Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment*, J. Hazard. Mater., 2010, 175, 45.

[8] CARBALLA M., OMIL F., ALDER A.C., LEMA J.M., *Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pretreatment concerning the removal of pharmaceuticals and personal care products*, Water Sci. Technol., 2006, 53, 109.

[9] ROBERTS P.H., THOMAS K.V., *The occurrence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment*, Sci. Total. Environ., 2006, 356, 143.

[10] KIM I., TANAKA H., *Use of ozone-based processes for the removal of pharmaceuticals detected in a wastewater treatment plant*, Water Environ. Res., 2010, 82, 294.
[11] PEREIRA V.J., WEINBERG H.S., LINDEN K.G., SINGER P.C., *UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm*, Environ. Sci. Technol., 2007, 41, 1682.
[12] WEIMIN X., GEISSEN S.U., *Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration*, Water Res., 2001, 35, 1256.
[13] MENDEZ-ARRIAGA F., ESPLUGAS S., GIMÉNEZ J., *Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO_2 and simulated solar irradiation*, Water Res., 2008, 42, 585.
[14] PRESCOTT L.F., *Kinetics and metabolism of paracetamol and phenacetin*, Br. J. Pharmacol., 2012, 10, 291.
[15] BOTTONI P., CAROLI S., CARACCIAOLO A.B., *Pharmaceuticals as priority water contaminants*, Toxicol. Environ. Chem., 2010, 92, 549.
[16] HAN G.H., HUR H.G., KIM S.D., *Ecotoxicological risk of pharmaceuticals from wastewater treatment plants in Korea. Occurrence and toxicity to Daphnia magna*, Environ. Toxicol. Chem., 2006, 25, 265.
[17] JJEMBA P.K., *Pharmaecology. The occurence and fate of pharmaceuticals and personal care products in the environment*, Wiley, Hoboken 2008.
[18] ANDREOZZI R., CAPRIO V., MAROTTA R., VOGNA D., *Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system*, Water Res., 2003, 37, 993.
[19] SKOUMAL M., CANOT P.L., CENTELLAS F., ARIAS C., RODRÍGUEZ R.M., GARRIDO J.A., BRILLAS E., *Mineralization of paracetamol by ozonation catalyzed with Fe^{2+}, Cu^{2+}, and UVA light*, Appl. Catal. B: Environ., 2006, 66, 228.
[20] CENTI G., PERATHONER S., *Advanced oxidation processes in water treatment*, [In:] D. Duprez, F. Cavani, *Handbook of advanced methods and progress in oxidation catalysis*, Imperial College Press, London 2014, 251–320.
[21] BOLTON J.R., BIRCHNER K.G., TUMAS W., TOLMAN C.A., *Figures-of-merit for technical development and application of advanced oxidation processes*, J. Adv. Oxid. Technol., 1995, 1 (1), 1.
[22] BRILLAS E., SIRÉS I., ARIAS C., CABOT P.L., CENTELLAS F., RODRIGUEZ R.M., GARRIDO J.A., *Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode*, Chemosphere, 2005, 58, 399.
[23] LOAIZA-AMBULUDI S., PANIZZA M., OTURAN M., OTURAN M.A., *Removal of the anti-inflammatory drug ibuprofen from water using homogeneous photocatalysis*, Catal. Today, 2014, 224, 29.