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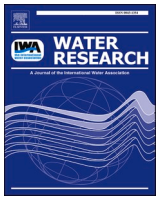

Degradation of 75 organic micropollutants in fresh human urine and water by UV advanced oxidation process

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ABSTRACT

In household wastewater, a large proportion of organic micropollutants (OMPs) load is attributed to human urine. OMPs could pose a risk to human and environmental health when urine collected in source-separating sanitation systems is recycled as crop fertiliser. This study evaluated degradation of 75 OMPs in human urine treated by a UV-based advanced oxidation process. Fresh urine and water samples were spiked with a broad range of OMPs and fed into a photoreactor equipped with a UV lamp (185 and 254 nm) that generated free radicals *in situ*. Degradation rate constant and the energy required to degrade 90% of all the OMPs in both matrices were determined. At a UV dose of 2060 J m^{-2}, average ΣOMP degradation of 99% (±4%) in water and 55% (±36%) in fresh urine was achieved. The energy demand for removal of OMPs in water was <1500 J m^{-2}, but for removal of OMPs in urine at least 10-fold more energy was needed. A combination of photolysis and photo-oxidation can explain the degradation of OMPs during UV treatment. Organic substances (*e.g.* urea, creatinine) likely inhibited degradation of OMPs in urine by competitively absorbing UV-light and scavenging free radicals. There was no reduction in the nitrogen content of urine during treatment. In summary, UV treatment can reduce the load of OMPs to urine recycling sanitation systems.

1. Introduction

Domestic wastewater is a valuable resource since it contains water, nutrients and energy that can be recovered (Vinnerås et al., 2006), but it also contains organic micropollutants (OMPs) such as pharmaceuticals, personal care products and hormones. These pollutants are potentially (semi-)persistent, bioaccumulative and toxic to aquatic organisms (Zenker et al., 2014).

Around 80% of the wastewater produced worldwide is discharged directly to the environment without any treatment (Connor et al., 2017). Even when wastewater is processed by a municipal treatment plant (WWTP), OMPs are typically not efficiently removed by conventional treatment processes. For instance, Golovko et al. (2021) analysed the fate of 164 OMPs at 15 WWTPs in Sweden and found that ΣOMP concentration declined on average by only 60% during wastewater treatment, while several OMPs, including metoprolol, carbamazepine, diclofenac and most antibiotics, were not removed at all during WWTP treatment. Around 103 OMPs were detected in sewage sludge and 122 OMPs were detected in recipient waters in that study, with the concentrations of OMPs being 50% higher in samples taken downstream compared with upstream of the WWTPs (Golovko et al. (2021). Following subsequent transport, OMPs end up in reservoirs where drinking water is sourced. In a study by Malnes et al. (2022), OMPs were detected in more than half of river water samples (n = 60) and lake water (n = 33) samples from three of Sweden's largest lakes, which are used as a drinking water source. That study estimated that several tons of OMPs are released to the lakes every year (Malnes et al. (2022). Tröger et al. (2021) found average removal of OMPs of around 65% for drinking water treatment plants in Europe and Asia.

An alternative approach to manage nutrients (nitrogen (N) and phosphorus (P)) and OMPs in wastewater is to target the upstream source, by source-separating wastewater into different fractions (urine, faeces, greywater) (Simha et al., 2020). One fraction that has received much research attention is human urine, because it contributes just 1%

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of the volume but 80% of the N and 50% of the P and potassium (K) load to WWTPs (Vinnerås et al., 2006). Human urine can be recycled back to farmland and used as a crop fertiliser (Heinonen-Tanski et al., 2007), but there are concerns about this practice since it is estimated that urine contributes ≈64% (±27%) of the pharmaceuticals in wastewater (Lienert et al., 2007). Thus closing the loop by using urine as a fertiliser may introduce a new pathway for OMPs to circulate, posing a risk to human health and the environment (Larsen et al., 2021; Simha et al., 2018). Several attempts have been made to develop treatment techniques for removing or degrading OMPs in urine. For example, Pronk et al. (2006) achieved 92% removal of propranolol, ethinylestradiol, ibuprofen, diclofenac and carbamazepine from fresh urine by nanofiltration, but found that the treatment also removed phosphate and sulphate. Duygan et al. (2021) found that two months of storage was insufficient to degrade OMPs in hydrolysed urine, while biological nitrification efficiently degraded atazanavir, ritonavir and clarithromycin. Köpping et al. (2020) demonstrated that >90% of 11 OMPs could be removed from biologically nitrified and stored urine by adsorption onto activated carbon. Few other techniques to degrade pharmaceuticals in fresh human urine at source and at bathroom scale have been researched, but use of the ultraviolet (UV) radiation could be promising.

Treatment with UV radiation is widely applied for disinfection purposes in many drinking water treatment plants, but in advanced form it can also be used to degrade micropollutants through photolysis and photo-oxidation (Wols et al., 2013). Compared with conventional UV treatment, UV-based advanced oxidation involves addition of photocatalysts such as ozone, hydrogen peroxide (H_2O_2) and peroxydisulphate ($S_2O_8^{2-}$), which propagate a chain reaction involving free radicals and enhance the degradation of OMPs (Zhang et al., 2015). Free hydroxyl radicals can also be generated *in situ* during vacuum UV irradiation (VUV) (light wavelength <190 nm) (Krakkó et al., 2022; Zhang et al., 2015; Zoschke et al., 2014). Although many studies have evaluated use of UV-based advanced oxidation processes to degrade OMPs, they have limited the evaluation to treated water or mixed wastewater samples (Giri et al., 2015). Therefore, this study fills this gap by evaluating the degradation of OMPs in freshly excreted urine. Furthermore, our study provides knowledge on the degradation of micropollutants that was not reported previously (*e.g.* carazolol, budenoside, cetirizine, fexofenadine, encazamene, mirtazapine, oxycodone, pyrimethamine, simvastatin and sulindac).

The aim of this study was to evaluate degradation of OMPs in fresh source-separated human urine during UV treatment. Specific objectives were to: (i) determine the degradation behaviour and degradation rate constants for 75 OMPs in batch UV treatments of water and fresh human urine; (ii) estimate the UV dose required to degrade 90% of each OMP in water and fresh urine; and (iii) analyse the influence of the matrix (water *vs.* fresh urine) and the photochemical properties of the OMPs on their degradation during UV treatment.

2. Materials and method

2.1. Urine collection

Fresh urine donations ($n = 27$) were collected from volunteers (male and female, aged 20–65 years) one day before the experiment, using high-density polyethylene (HDPE) bottles with plug cap and lid, and refrigerated at 4 °C. Prior to use, the urine donations were pooled, mixed and allowed to reach room temperature (20 ± 2 °C).

2.2. Organic micropollutants

A total of 75 OMPs were analysed, including antibiotics, antidepressants, antihypertensives, non-steroidal anti-inflammatory drugs (NSAIDs), beta-blockers, anti-epileptics, antifungals, antihistamines, opioids and opiates, anthelminthics, anaesthetics, antidiabetics, sedatives, medications for treating cancer and Alzheimer's disease, an antilipidaemic, an antiplatelet, an antineoplastic and an antipsychotic, and personal care products, stimulants, vitamins, X-ray contrast agents, diuretics, a laxative, a diagnostic agent and an insect repellent (see Table S1 in Supplementary Information (SI)). A full list of the OMPs analysed, including their CAS registry number and photochemical properties (*i.e.* molar absorption coefficient (ε), quantum yield (Φ), and rate constant of hydroxyl radical (K_{OH^*}) is provided in Table S2 in SI. The 75 OMPs were selected based on environmental relevance (Howard et al., 2011), previous studies (Lienert et al., 2007; Wols et al., 2013; Yu et al., 2019) availability of analytical standards and analytical performance of the substances.

2.3. Photoreactor set-up

The study was carried out in a cylindrical photoreactor that consisted of the UV lamp surrounded by a quartz sleeve. A 15 W tubular low pressure (LP) mercury lamp (Heraeus, Hanau, Germany) with a fluence rate of 43 μW cm^{-2} as the UV light source was used in the experiments. According to the manufacturer (Heraeus, 2022), emission of light by the lamp at a relative output at 185 nm is an estimated 8% of the output at 254 nm. The lamp was fitted with a quartz sleeve and placed in a cylindrical reactor chamber with dimensions, 40 cm length and 3.7 cm diameter with a total volume of 430 mL. The reactor was connected to a peristaltic pump (Masterflex, Fisher Scientific, USA) using UV-resistant Tygon® tubing (internal diameter 4.8 mm). The pump circulated urine within the photoreactor at a rate of 40 mL min^{-1}. Samples of the treated urine were collected via a shut-off valve at the bottom of the column.

2.4. Degradation experiments

Two sets of experiments were performed, in which degradation of OMPs was evaluated in triplicate in spiked fresh human urine and Milli-Q water. Before each experiment, the UV lamp was switched on and operated for 10 min to ensure constant light emission. Then 300 mL of fresh urine or Milli-Q water were spiked with a standard solution (1800 μL of 10 ng $μL^{-1}$) containing a mixture of 75 OMPs (see Section 2.2), and thoroughly mixed over a magnetic stirrer for 5 min. This represented a concentration of 60 μg L^{-1} (*i.e.* 0.076 to 0.465 μM or 18 μg absolute mass) for each OMP, with an estimated total organic carbon (TOC) of 6 mg L^{-1} added becasue of spiking which is less than 5% of the TOC concentration (4 g L^{-1}) in fresh urine. A 15 mL sample of the spiked solution (time zero min) was sampled, while the rest was added to the photoreactor and the peristaltic pump was switched on. The photoreactor was operated for 80 min and 15 mL samples were collected after 1, 2.5, 5, 10, 20, 40 and 80 min of operation. When sampling, the first 2 mL were discarded as they were estimated to represent dead volume trapped in the valve. The 15 mL samples were divided into three equal portions by volume and transferred to 7 mL amber vials, among the three, 2 vials were used for analysis while the rest is kept as a backup. A mixture of mass-labelled chemicals (each 10 ng absolute mass; Table S3 in SI) as internal standards was added to two vials (each 5 mL). These samples were subjected to analyses of OMPs (Section 2.5) and other standard parameters (UV–vis, ammonium, chemical oxygen demand) (Section 2.6) (Figure S1 and Table S4 in SI).

Two control experiments were conducted in duplicate in dark conditions, where fresh urine and Milli-Q water spiked with OMPs were added to the photoreactor, but the UV lamp was not switched on. To block light irradiation, the reactor and the tubing were covered with aluminium foil. Samples were collected after 1, 10 and 80 min of residence time inside the reactor. As blank controls, in two duplicate experiments fresh urine and Milli-Q water without spiking with OMPs were added to the reactor and sampled only once, after 80 min of operation.

2.5. Extraction and analysis of OMPs

All urine and water samples were extracted using solid phase extraction (SPE) with Oasis HLB cartridges (6 mL, 150 mg sorbent, 60 μm). The cartridges were first conditioned with 5 mL methanol and 5 mL Milli-Q water, after which the samples (5 mL with internal standard chemicals, see Section 2.4) were loaded. The cartridges were then washed with 5 mL Milli-Q water, dried under vacuum for 30 min and eluted with 4 mL methanol. The eluted samples were concentrated to 200 μL extracts under a stream of nitrogen gas and reconstituted with 800 μL Milli-Q water to give a final volume of 1 mL.

Concentration of OMPs ($n = 75$) was analysed using a DIONEX UltiMate 3000 ultra-high pressure liquid chromatography system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (TSQ QUANTIVA, Thermo Scientific, Waltham, MA, USA). Eight calibration standards in the range 0–400 ng mL^{-1} were analysed together with the samples. Chromatographic separation of OMPs was conducted using a Kinetex® biphenyl analytical column (100 × 2.1 mm, 2.6 μm) at 40 °C with a flow rate of 0.5 mL min^{-1} and mobile phases of Milli-Q water and methanol, each with 0.1% formic acid. The injection volume was 10 μL. Multiple reaction monitoring with two transitions for each chemical was used for data acquisition. This extraction and analytical methodology was also applied in previous studies by our research group (Golovko et al., 2021; Sörengård et al., 2019).

Over the eight-point calibration range, linearity of 0.9614–0.9998 was observed for the OMPs (Table S5 in SI). Limit of quantification (LOQ) ranged between 0.01 and 5.5 μg L^{-1} (0.03 to 40 nM) (Table S6 in SI). No contamination was observed during analysis of blanks with Milli-Q water in the same extraction batches, but sebacic acid, sertraline, caffeine, sulisobenzone, nicotine, methylparaben and budesonide were present in the fresh urine samples (Table S7 in SI). The initial concentration of sebacic acid and caffeine in urine was about 3-fold and 37-fold higher, respectively, than the concentration spiked in the sample. Average recovery of OMPs was 90±16% (Table S8 in SI).

2.6. Analysis of standard parameters

The pH was measured using an electrode (Fisher Scientific Accumet, 13–620-AE6, USA) attached to an Accumet AE150 pH metre (Fisher Scientific, USA). Electrical conductivity (EC) was measured using a probe (TetraCon 325, WTW, Germany) connected to a handheld EC metre (Cond 340i, WTW, Germany). UV absorbence measurements were made using a Lambda 365 UV–vis spectrophotometer (Perkin-Elmer, USA) within a scan window of 190–400 nm and a scanning rate of 480 nm min^{-1}. Urine samples were diluted 10-fold before the measurements, but Milli-Q water samples were not diluted.

To determine total solids (TS) content, 100 mL of fresh urine were dried in an oven at 105 °C for 24 h. To determine volatile solids (VS) content, the dried urine was combusted in a furnace (LH30/12, Nabertherm GmBH, Germany) at 650 °C for 6 h. A balance (Kern KB 2000–2NM, Germany; 0.01 g precision) was used to monitor the change in weight.

Concentrations of total nitrogen, total ammonium-nitrogen and chemical oxygen demand (COD) were analysed colorimetrically using Spectroquant® test kits (Merck KGaA, Darmstadt, Germany) and a photometer (NOVA 60 A, Merck KgaA, Germany). For measurements of COD and ammonium-nitrogen, urine was diluted 100-fold and analysed using, respectively, a Spectroquant® COD test kit (109,772) in the concentration range 10–150 mg L^{-1} and Spectroquant® ammonium test kit (100,683) in the concentration range 2–150 mg L^{-1}. For total nitrogen analysis, urine was diluted 1000-fold, digested using a Spectroquant® Crack-Set 20 test kit (114,963) and analysed for concentration of nitrate in the range 1–25 mg L^{-1} using a Spectroquant® nitrate test kit (109,713). The initial concentration of P, K, calcium (Ca) and magnesium (Mg) in fresh urine was determined by inductively coupled plasma-optical emission spectroscopy (Optima Avio 200, PerkinElmer, USA), prior to which samples were digested with 65% HNO_3 and diluted with Milli-Q water.

2.7. Kinetic modelling

Degradation (%) of OMPs was calculated as:

$$Degradation\ (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times\ 100 \quad (1)$$

where C_0 and C_t represent the concentration of OMPs initially (time zero min) and at the time of sampling, respectively.

The experimentally determined degradation of each OMP was plotted against treatment time and fitted to the pseudo first-order rate equation:

$$\ln\left(\frac{Ct}{C0}\right) = -kt \quad (2)$$

where t(min) is treatment time and k is the degradation rate constant (min^{-1}).

The time required to degrade the OMPs by 50% (t_{50}) (Eq. (3)) and 90% (t_{90}) (Eq. (4)) of their initial concentration was also calculated. The UV dose equivalent to the treatment time was calculated using the lamp fluence rate (Eq. (5)).

$$t_{50} = \frac{ln2}{k} \quad (3)$$

$$t_{90} = \frac{\ln(0.1)}{k} \quad (4)$$

$$UV\ dose\ \left(Jcm^{-2}\right) = fluence\ rate\ \left(Jcm^{-2}s^{-1}\right) * treatment\ time\ (s) \quad (5)$$

2.8. Statistical analysis

For the OMPs with concentrations below LOQ, half the LOQ value was used in statistical analysis of the data. The data on degradation of OMPs were tested for normality and homogeneity of variance. Analysis of variance (ANOVA) at 95% confidence interval was performed to compare degradation of the OMPs in water and in urine at different treatment times, with and without UV treatment. The degradation efficiency values were normalised so that the initial concentration difference in OMPs was not reflected in the variance. Major functional groups for OMPs studied were compiled using an online platform and the presence and absence of these functional groups were artificially coded to a dichotomous variables (zero and one) during analysis (Kentucky, 2023). Principal component analysis (PCA) was conducted using R software to evaluate whether predictor variables (functional groups properties of OMPs) could explain the variance in degradation of the OMPs in fresh urine due to UV treatment. Additionally, Point-biserial correlation was conducted using R software find significant correlation between functional groups and photocehmical properties with degradation of OMPs in urine. Linear regression analysis at 95% confidence interval was performed on the variables of interest. In the PCA and correlation analysis, the data for all OMPs were analysed together and as subsets for different therapeutic groups.

3. Results

3.1. Degradation of OMPs without UV treatment

In the dark controls (*i.e.* no UV irradiation) for water, after 80 min of treatment there was <20% degradation for 56 out of 75 OMPs, of which 47 OMPs exhibited <10% degradation, while there was <5% degradation for 39 OMPs. There was >90% degradation for atorvastatin, clopidogrel, encazamene, tamoxifen and simvastatin, while the degradation for ioperamide, meclofenamic acid, mefenamic acid and

valsartan varied between 50 and 70% (Figure S2A in SI).

In the dark controls for urine, after 80 min of treatment there was <20% degradation for 63 out of 75 OMPs, of which 52 OMPs exhibited <10% degradation. There was <5% degradation of 39 OMPs, including atenolol, azithromycin, carbamazepine and metformin. Clopidogrel, encazamene and tamoxifen were the only OMPs which exhibited >90% degradation (Figure S2B in SI).

3.2. Degradation of OMPs with UV treatment

In experiments treating water spiked with OMPs in the photoreactor with UV, >90% degradation of almost all OMPs (n = 73 of 75) was observed after 80 min of UV treatment (2100 J m^{-2}). The remaining two OMPs, memantine and sebacic acid, exhibited 71% and 83% degradation, respectively (Fig. 1).

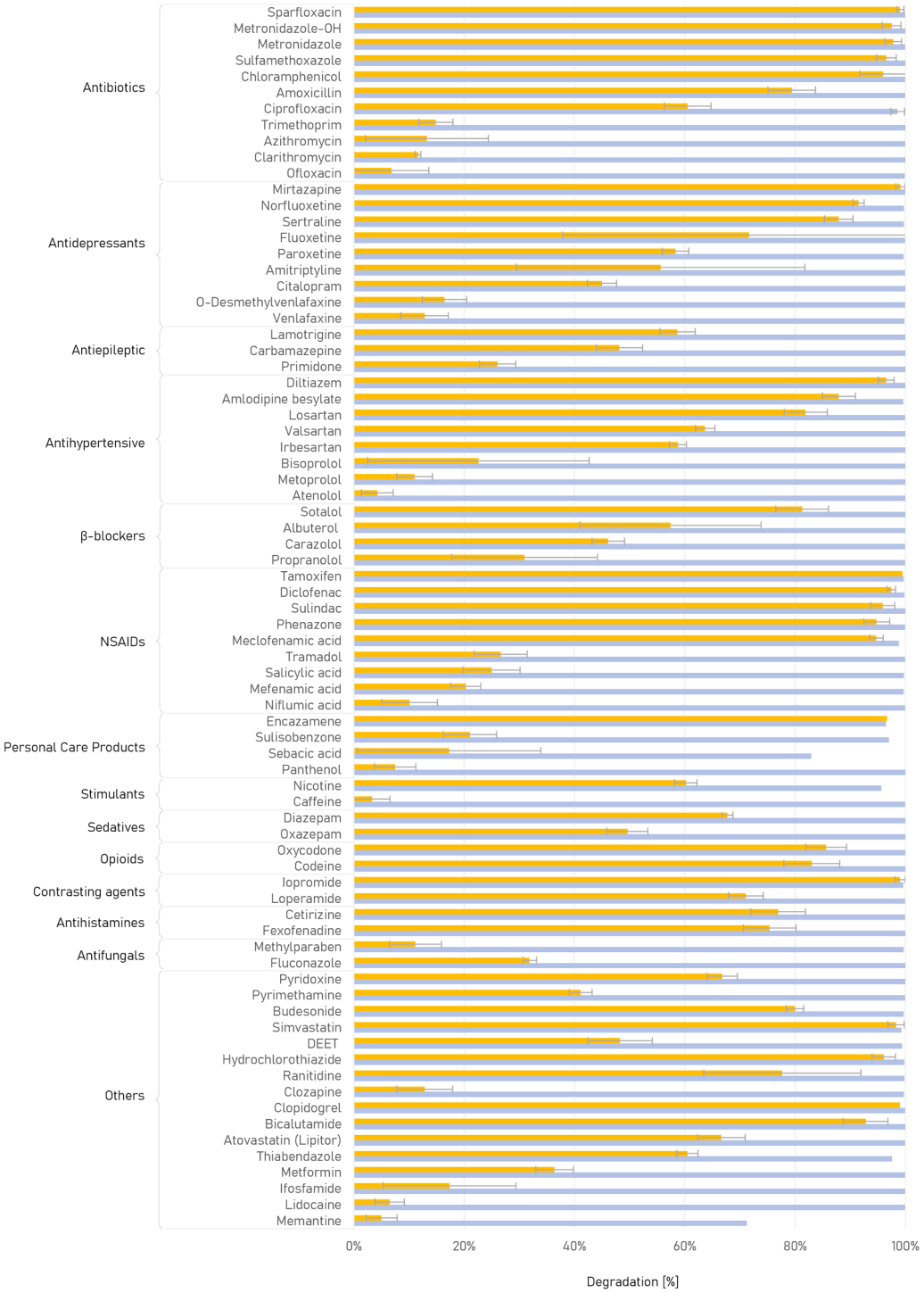

Fig. 1. Degradation (%) of 75 target OMPs after 80 min of UV treatment (UV dose 2060 J m^{-2}) of water (blue) and fresh urine (yellow). Average values are shown, error bars indicate standard deviation (n = 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

When fresh urine spiked with OMPs was treated with UV, >90% degradation was observed for 19 out of 75 OMPs after 80 min of treatment. The degradation varied from <1% (±0%) (azithromycin) to >99% (±1.0%) (chloramphenicol) for antibiotics, <1% (±0%) (atenolol) to 97% (±1.0%) (diltiazem) for antihypertensives, <13% (±4%) (venlafaxine) to 99% (±1%) (mirtazapine) for antidepressants, <1% (±0%) (niflumic acid) to 97% (±1%) (diclofenac) for NSAIDs, 26% (±3%) (primidone) to 59% (±4) (lamotrigine) for antiepileptics, 31% (±13%) (propranolol) to 81% (±5%) (sotalol) for β-blockers, and 1% (±0%) (sebacic acid) to 99% (±5%) (encazamene) for personal care products (Fig. 1). There was <1% degradation of atenolol, azithromycin, bisoprolol, caffeine, clozapine, ifosfamide, lidocaine, memantine, mefenamic acid, niflumic acid, ofloxacin, sebacic acid, sulisobenzone and trimethoprim (Fig. 1).

The average ΣOMP degradation during UV treatment was 99% (±4%, standard deviation) in water, which was significantly higher than the average degradation in urine (55% ±36%) ($p<0.0001$, $n = 75$). In comparison to the dark controls, UV treatment significantly enhanced the degradation of OMPs in both water and urine ($p<0.0001$, $n = 75$).

For some OMPs, degradation was highly variable (standard deviation >20%). These OMPs included metformin and cetirizine in the dark control for water, metformin and diclofenac in the dark control for urine, and fluoxetine, amitriptyline, albuterol, ranitidine and propranolol in UV-treated urine. Thus the results on degradation of these OMPs should be interpreted with caution. Apart from these compounds, the variability in degradation of OMPs during UV treatment was low (average standard deviation 6% in water and <5% in urine).

3.3. Degradation trends and kinetics

To illustrate the major trends observed in the experiments, degradation of four representative OMPs (clopidogrel, memantine, sulphamethoxazole, venlafaxine) was plotted against time for water and urine, with and without UV treatment (Fig. 2).

Clopidogrel was among the OMPs that was degraded in the dark controls. Tamoxifen and encazamene showed similar degradation behaviour to clopidogrel, with >90% degradation after 80 min in the dark control of both water and urine (Figures S1A and S1B in SI). Degradation of memantine in the dark controls (<5% after 80 min) was similar to that of 47 OMPs in water and 52 OMPs in urine (Figures S2A and S2B in SI).

During UV treatment of water, 18 OMPs showed >99% degradation after 1 min of treatment, which was similar to degradation of sulphamethoxazole (Fig. 3B). The half-life of 73 OMPs was less than 20 min (at ≈500 J m^{-2}) in water, with average OMP degradation of 75% (±30%), 82% (±27%) and 93% (±17%) after 1, 2.5 and 5 min of UV treatment, respectively (Table S9 in SI).

During UV treatment of urine, most OMPs showed degradation behaviour in between that of clopidogrel and venlafaxine (Figs. 2C and 2D). Of the 75 OMPs analysed, 18 OMPs had half-life of <20 min (≈500 mJ m^{-2}). The average degradation of OMPs was <15% (±15%), <30% (±24%) and 55% (±36%) after 5, 20 and 80 min of UV treatment, respectively (Table S9). The different starting concentrations for sulfamethoxazole and clopidogrel can be explained by degradation of the compounds and sorption effects before starting the experiment.

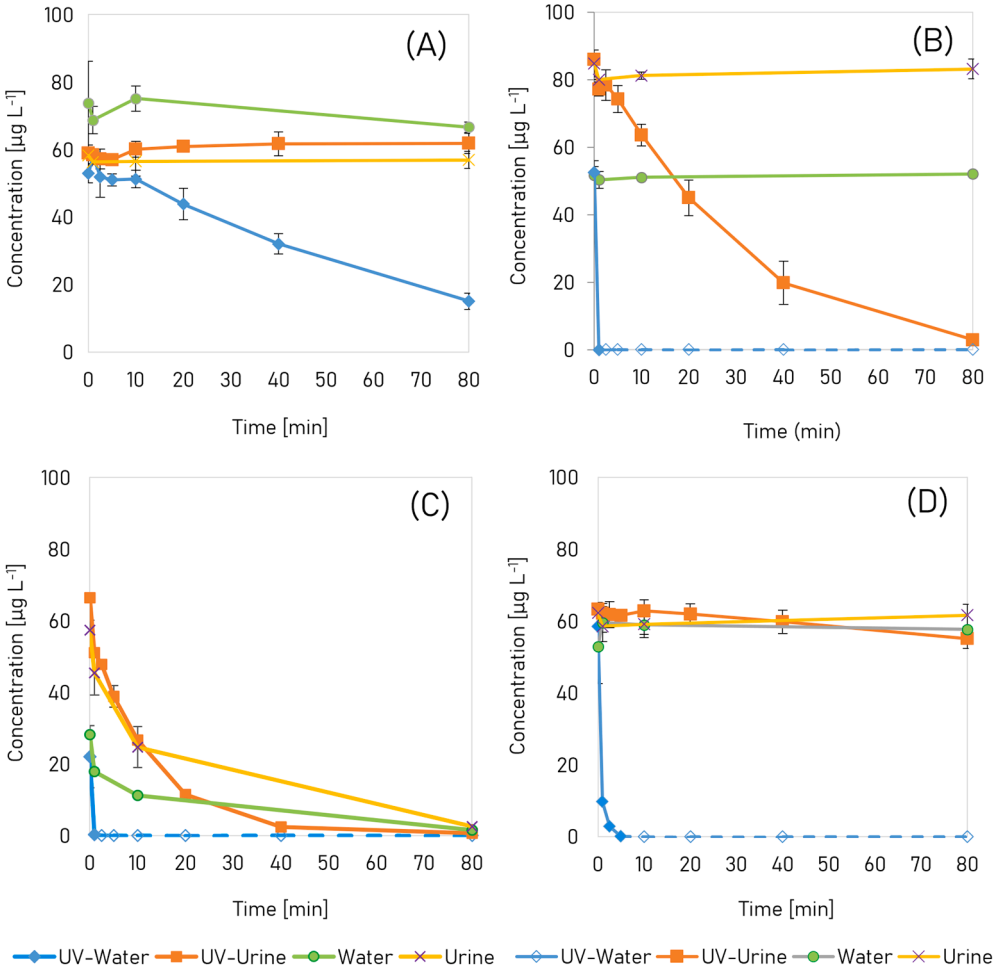

Fig.. 2. Degradation kinetics of (A) memantine, (B) sulfamethoxazole, (C) clopidogrel and (D) venlafaxine in water and fresh urine, with and without UV treatment. The open diamonds in B, C and D represent detection of the OMPs below their LOQ.

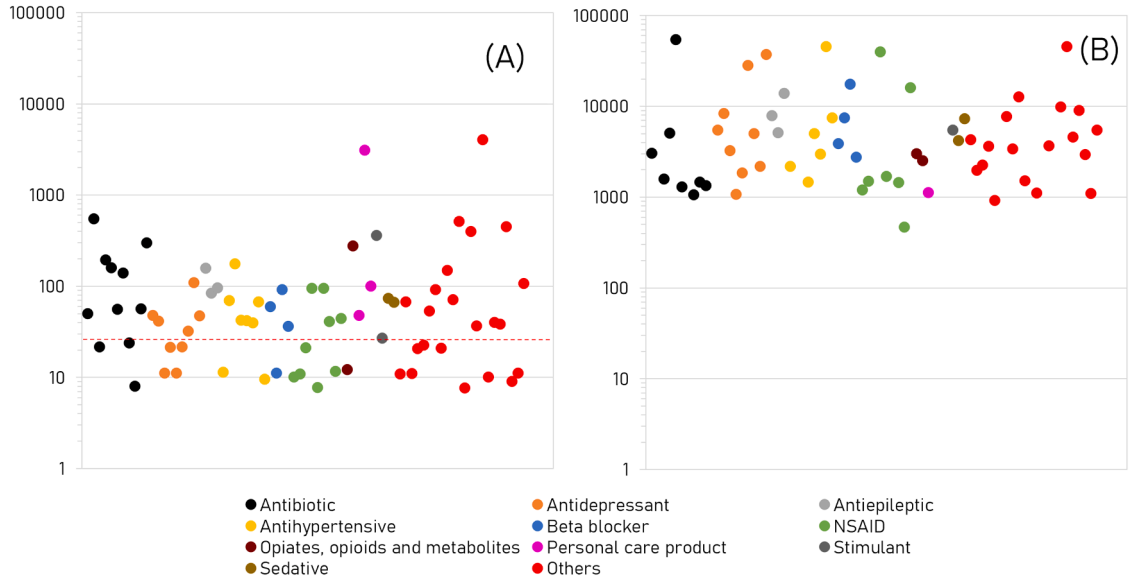

Fig. 3. Ultraviolet (UV) dose required to degrade 90% (UVe_{90}, J m^{-2}) of the 75 target OMPs in (A) water and (B) fresh urine. The y-axis shows UVe_{90} on a log_{10} scale and the x-axis a list of OMPs, arranged alphabetically. OMPs below the red dotted line have conservative E_{90} values as the concentration fell below LOQ within 1 min of UV treatment (at 26 J m^{-2}). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To estimate the amount of energy required to degrade the OMPs by more than 90%, t_{90} for each compound was calculated according to Eq. (4) and the value was used to calculate the equivalent energy according to Eq. (5). To degrade the OMPs to more than 90% of their initial concentration in water, a UV dose of <1000 J m^{-2} was required, except for memantine and sebacic acid. Hydrochlorothiazide, a diuretic pharmaceutical, was not included in the energy demand calculations, as its degradation in UV-treated water could not be explained by pseudo first-order kinetics. In comparison, the UV dose required to degrade the OMPs to 90% of their initial concentration in urine was at least 10-fold higher and varied between 1000 and 20,000 J m^{-2} for most OMPs (Fig. 3). The exceptions, with even higher UV dose requirement, were clarithromycin, metoprolol, methylparaben, niflumic acid, *O*-desmethylvenlafaxine and venlafaxine (Table S9). The UV dose required for degrading 14 other OMPs in urine could not be estimated, as they were not degraded (highly persistent) during the treatment (Table S10 in SI). Since any loss of energy in the system was not considered, the energy requirement shown is an estimate based on the treatment time to degrade the OMPs, and actual energy requirement might differ in other set-ups or settings.

4. Discussion

This study evaluated degradation of 75 OMPs in water and fresh human urine during UV treatment. With UV treatment for up to 80 min (at 2100 J m^{-2}), more than 99% and 55% degradation of OMPs was observed in water and urine, respectively. However, degradation of OMPs in urine required 10-fold higher treatment time/energy input than degradation in water. In a previous study, Wols et al. (2013) reported >90% degradation of atenelol, proranolol, carbamazepine, sulfamethoxazole, venlafaxine, sotalol, fluoxetine and diclofenac following treatment with 5 mg L^{-1} H_2O_2 and a UV dose of 2000 J m^{-2} generated with a 60 W monochromatic (254 nm) LP lamp.

During UV treatment, OMPs can be degraded due to photolysis, photo-oxidation or a combination of both (Zhang et al., 2016). The type of UV lamp (185 nm and 254 nm) used in this study could generate hydroxyl free radicals in the treatment solution (Gonçalves et al., 2021). Therefore, degradation of OMPs during UV treatment was due to a combination of photolysis and photo-oxidation occurring simultaneously in the photoreactor.

The OMPs evaluated in this study absorbed light predominantly within the range 190–300 nm (Figure S1A in SI). According to Hokanson et al. (2016), OMPs with larger photolysis/molar absorption coefficient (ε) are more susceptible to UV photolysis. Since UV radiation at 185 nm and 254 nm was used in the present study, photodegradation of OMPs by direct photolysis likely occurred. For instance, high overall degradation rate constants in water were observed for photo-susceptible OMPs such as diclofenac (>5.9 min^{-1}), iopromide (>7.73 min^{-1}) and sulfamethoxazole (> 7.39 min^{-1}), presumably due to their high molar absorption coefficient (ε_{254} 6–23× 10^3 M^{-1} cm^{-1}) and high quantum yield (Φ_{254} 2.8–22 × 10^{-2} mol^{-1} E^{-1}) (Yu et al., 2019). Our results for the degradation rate constants are comparable to that of Kim et al. (2009) for carbamazepine (0.36 min^{-1}), diclofenac (1.8 min^{-1}), metoprolol (0.42 min^{-1}) and propranolol (0.3min^{-1}), even though they used an 8 W LP monochromatic UV lamp and 6 mg L^{-1} H_2O_2. This is because we used a UV lamp that emitted light at 185 nm, which allowed fast degradation without the addition of H_2O_2. For example, the degradation rate constant of venlafaxine in our study was 1.25 min^{-1}, whereas the degradation rate constant of venlafaxine was only 0.37 min^{-1} in a study by Giannakis et al. (2017) despite the addition of 100 mg L^{-1} of H_2O_2 during UV treatment using a 11 W LP lamp. Kim et al. (2015) have also observed a higher degradation rate constant for trimethoprim when using a UV lamp emitting at 185 nm and 254 nm (0.013 min^{-1}) compared to a monochromatic LP UV lamp emitting light only at 254 nm (0.0017 min^{-1}). In contrast, caffeine is photoresistant even though it absorbs photons (ε_{254} 4.2 × 10^3 M^{-1} cm^{-1}), and its quantum yield ($\Phi\varepsilon_{254}$ 0.003 mol^{-1} E^{-1}) is around 100-fold lower than that of diclofenac (Yu et al., 2019). Therefore, the degradation rate constant for caffeine (0.16 min^{-1}) was among the lowest observed in our study (Table S10 in SI).

In addition to photolysis, OMPs can be degraded by photo-oxidation by free radicals (Vogna et al., 2004). During vacuum UV irradiation, hydroxyl radicals (OH*) can be generated due to: i) homolysis and photochemical ionisation of water and ii) decomposition of ozone generated photochemically from oxygen in the gas phase (Zoschke et al., 2014). The reaction rate constants for photo-resistant OMPs such as caffeine, carbamazepine, atenolol, propranolol, primidone and trimethoprim with hydroxyl radicals are high (10–28 × 10^9 M^{-1} s^{-1}), in contrast to that of photo-susceptible OMPs such as iopromide (3 × 10^9 M^{-1} s^{-1}) (Yu et al., 2019). Degradation of the photo-resistant OMPs (caffeine, carbamazepine, atenolol, propranolol, primidone and

trimethoprim) in water (>99%) during UV treatment was dominated by photo-oxidation, since their reaction rate constant with OH* was high. Kim et al. (2009) investigated the contribution of direct and indirect oxidation to degradation of pharmaceuticals during UV treatment and found that indirect oxidation was responsible for up to 90% of the degradation for photoresistant compounds such as DEET, carbamazepine and metoprolol.

Unlike water, fresh urine is a complex solution. The urine used in the present study had an organic matter content of 10 g COD L^{-1} (Table S4 in SI). Urine can contain hundreds of organic substances and metabolic breakdown products (Bouatra et al. (2013) and some of these organic substances, such as creatinine and amino acids, have high UV absorbence (Yokoyama et al., 2005). The major organic compound in urine is urea, which absorbs UV light between 190 nm and 220 nm. The concentration of urea measured in the fresh urine used in this study was 4.5 g L^{-1}, which is 750-fold higher than the concentration of ΣOMP added to the urine at the start of the treatment (Table S4 in SI).

Organic and inorganic substances in urine can influence UV oxidation of OMPs in several ways. First, they can competitively absorb incident photon flux (inner filter effect) (Doll et al., 2003) and reduce the degradation of OMPs due to direct photolysis (*e.g.* urea and creatinine) (Figure S1B in SI). Second, they can scavenge reactive species and free radicals like OH* and O_3, and thus reduce the photo-oxidative degradation rate of OMPs. Third, hydroxyl radicals can react with organic compounds in urine to form intermediate radicals that propagate the advanced oxidation process (Pignatello et al., 2006).

Two of the major scavengers in fresh urine are urea and ammonia (Giannakis et al., 2018; Zhang et al., 2015). After 80 min of UV treatment, there was no change in total nitrogen concentration in the urine samples in this study, but the concentration of urea decreased by 18% and the concentration of ammonium decreased by 20% (Table S4 in SI). Long et al. (2019) reported comparable urea photooxidation (22%) during 2 h treatment in swimming pool water using a low pressure UV lamp emiting at both 185 and 254 nm. Furthermore, Yang et al. (Yang, 1998) reported photooxidation of ammonia to nitrate and nitrite. In the present study, we observed a 46% increase in nitrate-nitrogen, but this increase did not correspond directly to the decrease in both ammonia-nitrogen or urea-nitrogen (Table S4).

After 80 min of UV treatment, the concentration of COD in urine decreased from 10 g L^{-1} to 8.2 g L^{-1}(19%), which is in line with the decrease in light absorbence at 254 nm (Figure S1B). COD is used as a surrogate for removal of organic pollutants in wastewater treatment (Altmann et al., 2014). A 20% reduction in COD was observed by Giannakis et al. (2017) after 4 h of UV treatment of real urine using a 35 W monochromatic (254 nm) UV lamp. In our study, average ΣOMP degradation in urine was only 55% (±36%) and some UV-resistant OMPs such as atenolol and caffeine could not be degraded by UV treatment (Table S9 in SI). For further degradation of ΣOMP, considerably higher energy input is required (Table S10 in SI), and could be supplied either by increasing the treatment time or by using higher wattage UV lamps (Wols et al., 2013). In addition, improved degradation of the OMPs in fresh urine could be achieved by supplementing the UV treatment with photocatalysts such as H_2O_2 (Wols et al., 2013), peroxydisulphate (Wang et al., 2020), titanium oxide and ozone (Vogna et al., 2004).

To predict the degradation of OMPs, principal component analyses were done to test the influence of presence or absence of major functional groups (arene, amine, benzene, etc.) of OMPs on their degradation in fresh urine. However, the presence or absence of these functional groups could only explain 14.19% (PC1) and 14.92% (PC2) of the degradation. Additionally, a significant correlation between functional groups of OMPs and their degradation could not be found, irrespective of whether the original dataset including all 75 OMPs was used or a subset of the data dividing the OMPs into different therapeutic groups was used (Table S11 and Table S12-A). Furthermore, OMPs degradation in urine was correlated against OMPs photochemical properties (molar absorption coefficient (ε), quantum yield (Φ) and rate constant for hydroxyl radical (K_{OH^*}), but no significant correlation could be found with either of the photochemical properties (Table S2 and Table S12-B). However, when we use the subset of OMPs (therapeutic groups), a strong positive correlation was observed between degradation of antihypertensives in urine with K_{OH^*}, ε and Φ, which suggests that these groups of OMPs can be degraded by both photolysis and photo-oxidation (Table S12-B). However, a strong positive correlation with Φ of beta-blockers and a negative correlation with K_{OH^*} points out that this group of OMPs are degraded by photolysis rather than photo-oxidation (Table S12-B).

Although no significant correlation ($p > 0.05$) could be found for all of the OMPs degradation with either of the photochemical properties or major functional groups, the OMPs could be degraded through the following major photodegradation routes suggested by Ahmad et al. (2016): (i) Photoaddition, (ii) Photoaquation, (iii) Photocyclization, (iv) Photodealkylation, (v) Photodecarboxylation, (vi) Photodehalogenation, (vii) Photodehydrogenation, (viii) Photodimerization, (ix) Photoelimination, (x) Photoinduced hydrolysis, (xi) Photoisomerization, (xii) Photooxidation, (xiii) Photoinduced rearrangement, (xiv) Photoreduction, and, (xv) Photoinduced ring cleavage.

Among the 75 OMPs evaluated in this study, information on degradation pathways is available for meclofenamic acid (photocyclisation), norfloxacin (photodehalogenation), (Ahmad et al., 2016), diclofenac (decarboxyllation), atenelol (hydroxylation) (Salgado et al., 2013), sulphamethoxazole (desulphonamidation, photoelimination, hydroxylation), amitryptiline (photohydration) (Nassar et al., 2017), tamoxifen (hydroxylation) (Ferrando-Climent et al., 2017), sertraline (dechlorination and dehydration) (Calza et al., 2021), salicyclic acid (hydroxylation) (Milovac et al., 2014), rantidine (denitration) (Dong et al., 2017), oxazepam (hydroxylation) (Kosjek et al., 2012), diazepam (hydroxylation and demethylation) (Mitsika et al., 2021), cetirizine (dechlorination and dehydroxylation) and fexofenadine (deamination and dehydroxylation) (Liu et al., 2022). Additionally, Lin et al. (2022) reported transformation pathways for antidepressants including citalopram, fluoxetine, sertraline and venlafaxine. For a full understanding of the effects of UV treatment prior to implementation, further evaluation of the photodegradation products and their degradation rate is required, since photodegradation products can have longer half-lives and can potentially be more toxic than the parent compounds (Voigt et al., 2017; Zhang et al., 2016).

5. Conclusions

Degradation behaviour and degradation rate constants were determined for 75 OMPs in water and fresh human urine during UV treatment using a dichromatic lamp (185 nm and 254 nm). A UV treatment duration of 1 min (26 J m^{-2}) gave ΣOMP degradation of 75% in water and 11% in urine. Increasing the UV treatment time to 80 min (2100 J m^{-2}) increased ΣOMP degradation to 99% in water and 55% in urine. The degradation rate constant of the OMPs ranged in value from 0.01 to 7.7 min^{-1} in water, whereas the maximum value observed in fresh urine was 0.13 min^{-1} (for tamoxifen). Compared with degradation of OMPs in water, the energy demand for degrading OMPs to <10% of their initial concentration in fresh urine was at least 10-fold higher. Of the 75 OMPs analysed, 16 OMPs were not degraded in urine by UV treatment. Scavenging of free radicals by urea and ammonia, combined with high initial organic matter content of urine (10 g COD L^{-1}), might be responsible for the slow degradation kinetics of OMPs in urine. However, the UV treatment resulted in no notable change in total nitrogen concentration, which is an advantage in the case of fresh urine intended for use as concentrated fertiliser. Overall, the results show that UV treatment can be a promising on-site process to reduce the load of OMPs to urine recycling sanitation systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120221.

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