Performance of a University Wastewater Treatment Plant (UASB–CBR–Ozonation) in the Removal of Ibuprofen, Diclofenac Sodium and Metoprolol from Domestic Sewage

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Abstract

The presence of emerging contaminants (ECs) at trace concentrations (µg to ng/L) is a challenge for WWTPs not designed for their removal and, therefore, not controlled by Brazilian water law. In this study, the efficiency of a UASB reactor, cyclic biological reactor (CBR) and ozonation, analysed over six sampling campaigns at four measuring points of UNISINOS WWTP (Sao Leopoldo, RS, Brazil), was evaluated for the reduction of Ibuprofen, Diclofenac Sodium and Metoprolol and also for chemical oxygen demand (COD), total organic carbon (TOC), pH and residual ozone. The results from the two analytical methods (UV254 absorbance and liquid chromatography) were compared for monitoring micropollutants. The mean COD removal was above 75%, and the plant complied with Res. 355/2017 from CONSEMA for the COD and pH parameters. Ibuprofen levels in raw sewage ranged from 21.10 to 950.66 ng/L, with an Efficiency of 51.43% in the UASB reactor and 65.03% in ozonation. Diclofenac Sodium was present from 24.58 to 4,464.99 ng/L and showed high persistence in the UASB (4.83%), increasing by 35.47% after ozonation. Only one sample contained metoprolol. The removal of pharmaceuticals was correlated with organic-load reduction (high negative Diclofenac-TOC correlation) and the removal of ibuprofen might be indicated indirectly by UV254, but not the removal of diclofenac. The results suggest that biological treatment would be more effective for PFBs than for persistent compounds, stressing the importance of optimizing ozone dosage and maintaining continuous monitoring in university-scale WWTPs.

Keywords: Micropollutants, Pharmaceuticals, Domestic Sewage, Wastewater Treatment Plant, Ibuprofen, Diclofenac Sodium, Ozonation.

1. Introduction

In addition to regulated pollutants governed by the environmental law, emerging contaminants (ECs), in particular pharmaceuticals, have been an increasing focus of scientific and regulatory efforts around the world. They are generally measured at micro or Nano gram per litre concentrations, and currently, there are no specific limits in Brazilian environmental legislation. Exposure to the domestic sewage stream, their pharmacological specificity and persistence in the environment creates a real challenge for water and wastewater treatment plants (WTPs and WWTPs) which were built decades ago to remove organic matter, nutrients and pathogens rather than trace organic micropollutants.

Pharmaceuticals commonly detected in domestic effluents include non-steroidal anti-inflammatory drugs (NSAIDs) like Ibuprofen and Diclofenac Sodium, and the beta-blocker Metoprolol. Ibuprofen is generally considered as highly degraded species, while Diclofenac sodium shows moderate biodegradability and higher survival rates even in systems with high level of biological degradation. In the environment, after discharge, these compounds may end up in surface waters, and chronic exposure, even at very low concentrations, has been linked to ecotoxicological effects on aquatic organisms.

At the federal level, CONAMA Resolution No. 430/2011 sets effluent discharge standards in Brazil, and at the state level, CONSEMA Resolution No. 355/2017 (state of Rio Grande do Sul). Although both instruments set a control limit for conventional organic and inorganic parameters, neither considers pharmaceuticals or other micropollutants. This means that there are important gaps in the regulations. Ozonation is proposed as a promising tertiary treatment, since ozone is a strong oxidant and can produce hydroxyl radicals that could attack complex organic molecules, including pharmaceuticals, which are difficult to treat by biological processes.

Given this background, the main research question that was addressed in the present work was that of whether or not ozonation – as it is applied on a university-scale WWTP – is effective for the partial removal of pharmaceuticals Ibuprofen, Diclofenac Sodium and Metoprolol in domestic sewage. The overall goal of this work was therefore to determine the performance of the sequential treatment stages of the UNISINOS WWTP, comprising an up flow anaerobic sludge blanket (UASB) reactor, a cyclic biological reactor (CBR), and an ozonation unit, with the aim of minimizing the concentrations of these three pharmaceuticals. Specific objectives were: (a) to determine the respective concentrations of the three pharmaceuticals in raw sewage; (b) to determine the efficiency of removal of each pharmaceutical after undergoing biological treatment; (c) to quantify the performance associated with the ozonation stage; (d) to correlate the concentration of pharmaceuticals with COD and TOC; and (e) to compare the effectiveness of liquid chromatography and UV254 absorbance as complementary techniques. The results are expected to improve understanding of the removal characteristics of these compounds at a small-to-medium-sized BWTF that is piped to a low-cost tertiary ozonation step and to help guide future operational and monitoring improvements to the plant.

2. Materials and Methods

2.1 Case study

The study was performed in the Wastewater Treatment Plant of the University of Vale do Rio dos Sinos (Unisinos WWTP), in the campus of São Leopoldo, Rio Grande do Sul, Brazil. The plant operates under Operating Licence: No. 154/2024-DLA and has design capacity of 600 m^3/d of its plant effluent generated by the institution is treated. The facilities were originally installed in 1986 to supply water to about 18,000 people, but have been expanded in 2009 to provide water for about 27,000 people, with post-UASB treatment stages added at the time (CBR, settling tanks, and ozonation).

This treatment train consists of primary screening which removes bulky solids, dewatering to remove particles greater than 0.2 mm using a grit removal unit, flow equalisation tanks, an up flow anaerobic sludge blanket (UASB) reactor, a cyclic (rotating) biological reactor (CBR) (an aerobic fixed-bed process), two settling tanks, and then a final dewatering stage of ozonation. At the time of this study, only one of three sets worked full time yielding an estimated dose of 0.27 g O3/h, four times less than the nominal design.

2.2 Sample collection

The monitoring points selected for the treatment train were: P1 at the plant inlet after screening (raw sewage); P2 at the outlet of the UASB reactor; P3 at the outlet of the CBR and settling tanks (final of biological treatment); and P4 at the outlet of the ozonation unit (final effluent). Sampling was conducted at six campaigns from 4.0 to 7.3 L/s (deliveries of plant flows) for each of these duties from October 2024 to January 2025 (7th and 21st October, 4th November and 18th November, 9th December 2024 and 23rd January 2025). In all campaigns samples were taken simultaneously at all four stations between 11:30 a.m. and 1:00 p.m. in 1-L amber glass bottles, which allow little photodegradation, and then shipped to the laboratory in insulating containers. Physicochemical parameters (COD, pH, TOC, residual ozone and UV254) were analysed on the collection day; the samples to be used for pharmaceutical analysis were subjected to solid-phase extraction (SPE) on the collection day and stored accordingly for subsequent chromatographic analysis.

2.3 Analytical methods

The measurement of chemical oxygen demand in the effluent (COD) was carried out using the closed reflux colorimetric method (potassium dichromate range 10-150mg/l), using absorbance measurements at 446 nm with a calibration curve of R^2=0.9991. Measures were taken for total organic carbon (TOC) by catalytic oxidation method with Multi N/C 2100S Analyser and calculated by subtracting the inorganic carbon levels. A benchtop digital pH meter was used to measure the pH. Residual ozone concentration at P4 was measured by indigo colorimetric method (SM 4500-O3 B) after adding glycine to inhibit the effect of manganese and measuring absorbance at 600 nm.

Ibuprofen, Diclofenac Sodium and Metoprolol have been identified and quantified using Ultra-High-Performance Liquid Chromatography (UHPLC, Shimadzu) with a quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI, Bruker Impact HD). Samples were previously concentrated using solid phase extraction (SPE) columns (C18-E, 500 mg/3 mL) and injected into the UPLC system, which was validated at Nutrifor Technological Institute of Unisinos. Following the method of Altmann et al. (2016) and Knopp et al. (2016), pre-filtered samples (M0.47 glass fibre membrane) were subsequently analysed for UV absorbance at 254 nm on a spectrophotometer, which also served as an indirect estimation for the monitoring of organic micropollutants.

2.4 Statistical analysis

Each parameter and sampling location has been calculated descriptive statistics such as minimum, maximum, coefficient of variance, standard deviation and mean. To compare the concentrations between the sampling points a Kruskal-Wallis test was applied, and for the diclofenac dataset one-way ANOVA was applied. Pearson and Kendall's tau-b coefficients calculated between the concentrations of Ibuprofen, Diclofenac Sodium, COD, TOC, UV254 and pH, and the significance levels were set to 0.05 and 0.01.The Pearson and Kendall's tau-b statistic values were computed between Ibuprofen, Diclofenac Sodium, COD, TOC, UV254 and pH at significance level 0.05 and 0.01.

3. Results

3.1 Conventional parameters

The average removal efficiency was 77% for P1, 72% for P2, 73 % for P3 and 73 % for P4 which shows that there is a reduction in mean COD concentrations from P1 raw sewage to P2 after UASB, P3 after CBR and P4 after ozonation. The plant had a campaign average close to or in all cases, the removal efficiency was near or exceeded 75% and the discharge limit imposed by CONSEMA (355/2017) was 120 mg/L. The Kruskal-Wallis test included only P1 and the other points ($p < 0.05$) were not significantly different.

The range of pH documented at all sampling locations and campaigns was: 6.91–7.76, which is within the tolerance limit for CONSEMA 355/2017. Essentially there was no residual ozone in the final effluent as the residual ozone measured ranged from 0.012 to 0.021 mg O3/L, within the analytical uncertainty of the method.

Two campaigns were conducted (P1, P2), for the other four campaigns, TOC was measured, with the mean removals at P3, P4, respectively, of 95% and 95%.Two campaigns were conducted (P1, P2) while the other four were conducted, where TOC was measured for the removals of 97%, 95% and 95%, respectively. In the same manner as with COD the Kruskal-Wallis test detected that only significant differences can be found between P1 and following points.

3.2 Pharmaceuticals

Ibuprofen was detected in 4 of 6 samples at P1 (222.24–950.66 ng/L), 4 of 6 at P2 (23.33–482.13 ng/L), 5 of 6 at P3 (21.10–446.19 ng/L) and in all 6 samples at P4 (35.64–256.36 ng/L). Mean concentrations decreased progressively from 399.27 ng/L (P1) to 193.94 ng/L (P2), 153.97 ng/L (P3) and 139.63 ng/L (P4). The cumulative removal was found to be 51.43% after UASB reactor, 61.44% after CBR/settling tanks and 65.03% after ozonation. The single-stage removal achieved by the UASB reactor was the highest, about 51%, followed by the CBR/settling tanks (about 10%) and the ozonation (about 4%).
Diclofenac Sodium was detected in all samples at all four points, with mean concentrations of 2,472.33 ng/L (P1), 2,352.97 ng/L (P2), 1,722.16 ng/L (P3) and 1,595.48 ng/L (P4). After the UASB, 4.83% of the removal was cumulated relative to P1; after the CBR/settling tanks, 30.34% and after the ozonation stage, 35.47% relative to P1. The single-stage reduction due to the CBR/settling-tank stage was the highest at around 26%, whereas the single-stage reduction due to the UASB reactor and due to ozonation were around 5% and 6% respectively. Concentrations of diclofenac did not significantly differ in the treatment stages [One-way ANOVA, $p = 0.195$].

Metoprolol was only detected at one point (P1) during the first campaign, with a concentration of 94.495 ng/L, and was not detected at any of the other points or the second campaign.

3.3 UV254 absorbance and correlations

Mean UV254 absorbance decreased from 0.419 (P1) to 0.243 (P2), 0.208 (P3) and 0.210 (P4), corresponding to relative reductions of 42.0%, 50.4% and 49.9%. The reduction profile of UV254 was similar to that of Ibuprofen while contrasting to that of Diclofenac Sodium because it was a relatively poorer reduction compared to the absorbance drop.
Pearson analysis showed a moderate positive correlation between Ibuprofen and Diclofenac ($r = 0.331$; $p = 0.023$), confirmed by Kendall's tau-b ($\tau = 0.293$; $p = 0.004$) and Spearman's rho ($\rho = 0.431$; $p = 0.002$). TOC correlated strongly with COD (Pearson $r = 0.749$–0.989 depending on the test; $p < 0.01$) and with UV254 ($r = 0.585$–0.945; $p < 0.01$). Furthermore, both statistical tests found significant negative correlations and diclofenac was removing significantly with the reduction in the organic load for all of them as suggested by the Pearson correlation ($r = -0.931$; Kendall $\tau = -0.857$; Spearman $\rho = -0.929$, $p < 0.01$). There was a low to moderate positive correlation between ibuprofen or Diclofenac with UV254 (Pearson's $r = 0.349$ and $r = -0.146$ respectively). The other parameters of the Pearson analysis or Kendall correlation did not show statistically significant correlation with pH.

4. Discussion

The Unisinos WWTP performed well with respect to the discharge of the conventional parameters regulated under CONSEMA Resolution No. 355/2017 the excellent performance of the WWTP with respect to this parameter came as no surprise, particularly in terms of compliance with the 70–78.5 pH limit and COD discharge requirement, meeting these criteria in more than 97% of campaigns with efficiencies comparable to those reported by other case studies from Brazil (e.g., 71–91% for COD removal in UASB and UASB–SAF configurations). Although the COD, TOC and UV254 values are statistically similar among P2, P3 and P4, this similarity coupled with the absence of significant differences among the P4 stages indicates that most of the bulk organic matter removal was occurring at the anaerobic reactor treating stage and that COD, TOC and UV254 were being removed from similar amounts at the post-UASB stages (conventional pollutant removal, CBR, and ozonation).

The pharmaceutical results show that there is a significant difference in the removal behaviour for each of the two NSAIDs investigated. Since Ibuprofen's removal reached as high as 60% even during the anaerobic stage, as reported in previous studies with removal efficiencies ranging between 43% and 64% for UASB and conventional biological treatment, and near-complete elimination of Ibuprofen in lab-scale ozonation studies, its relative high biodegradability and low sorption to solids resulted in such high removal. In contrast, recent literature shows that the removal of Diclofenac Sodium is very poor (usually <30-40%) even in advanced biological treatment systems, a result consistently observed in the present study, except when the drug concentration is high with ozonation, at much higher dosage, or when it is used in combination with activated-carbon adsorption. The low removal rate observed here despite ozonation, is largely due to the comparatively low ozone dosage provided by the plant (approx. 0.27 g/h, only one of 3 ozone-generating units was operating during the monitoring period), and, indeed, the very low residual ozone measured at P4 was representative of a high ozone consumption, probably by the residual organic matrix, rather than by the target pharmaceuticals. The current study results are in line with published ones that report high removal efficiencies (90–practically 100%) only when ozone doses and contact times were much higher than used at the Unisinos WWTP.

The single occurrence of Metoprolol is probably attributable to the population demographics of the university campus, as older people are more likely to use hypertension medications, which would have much higher rates of occurrence than within the general municipal sewer shed to which the University campus is related, where mean concentrations approaching 1,000 ng/L have been reported.

Diclofenac was strongly correlated with TOC in all three correlation methods tested, indicating that its removal is well correlated with the overall removal of the organic pollutant rather than with a particular removal mechanism like only removal of UV254. The moderate correlation between Ibuprofen and UV254 is potentially relevant for indirect monitoring of readily degradable pharmaceuticals using this surrogate parameter. However, the weak association found between diclofenac and UV254 indicates that the optical properties of these compounds are not the optimal method to qualify persistent micropollutants and that direct chromatographic quantification is still necessary to effectively characterize them.

The overall results suggest that the biological treatment of the Unisinos WWTP improves the removal of the pharmaceuticals Ibuprofen and Diclofenac Sodium, especially for the compound that can be easily degraded in the biological reactor, Ibuprofen, and that the present design of dose is not enough to efficiently reduce Diclofenac Sodium among more persistent products. An interactive recovery of the ozone-generation system and potentially for a longer contact time would be required to achieve the higher removal efficiencies that have been reported from other researchers in the literature when removing pharmaceuticals as tertiary treatment using the ozonation method.

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