

## Removal of emerging contaminants from domestic sewage using advanced technologies

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### Highlights:

- Nearly 99% removal of paracetamol, naproxen, and caffeine, highlighting the efficacy of the treatment system in addressing diverse emerging contaminants.

**Keywords:** Advanced Treatment Technologies; Emerging Contaminants Removal; Domestic Wastewater Treatment

## INTRODUCTION

In recent decades, certain classes of organic compounds have garnered attention from researchers worldwide and are referred to as emerging contaminants. These contaminants exist in the environment at various concentrations, posing adverse effects on both human health and the ecosystem. Notably, they are not covered by current regulatory frameworks<sup>1</sup>.

Conventional wastewater treatment methods were not originally designed to address the removal of these organic compounds. Consequently, their effectiveness in eliminating emerging contaminants is limited and may require additional treatment steps or adjustments to operational parameters<sup>2</sup>.

Recognizing the gravity of these contaminants and their impact on the environment, it becomes imperative to conduct studies assessing their presence and devising strategies for their removal within wastewater treatment plants (WWTPs). This includes exploring alternative treatment approaches beyond conventional methods.

Additionally, it is crucial to emphasize areas without proper wastewater collection and treatment facilities, besides center commercials, and industrials. In those locations, technological solutions must be implemented to achieve the same quality standards as centralized system, even within reduced spatial constraints.

The present study focused on assessing the removal of eight emerging contaminants—namely, bisphenol A, caffeine, fipronil, fipronil sulfide, fipronil sulfone, imidacloprid, naproxen, and paracetamol—from domestic wastewater using advanced treatment technologies.

## METHODOLOGY

The samples were collected from a treatment plant receiving effluent from a shopping. This plant features a treatment system combining a membrane bioreactor (MBR) with reverse osmosis, operating at a recirculation rate of 50%. Preliminary treatment involves screening with a 2mm opening. The influent sources include grease traps and other devices for solid and grease retention.

The samples were collected in 6 campaigns spanning from December 2023 to March 2024, and at four successive stages: influent wastewater (I), post-MBR treatment (II), post-RO (III) and RO concentrated (IV). The samples were characterized concerning turbidity, conductivity, pH, organic matter in terms of total and soluble chemical oxygen demand (COD), as well as suspended solids series, following the Standard Methods for the Examination of Water and Wastewater<sup>3</sup>.

The extraction of emerging contaminants was performed by solid phase extraction (SPE), using a 500 mL aliquot of the sample. HLB Oasis cartridges were used containing a solid phase of 500 mg according to the method previously described by Montagner et al. (2014)<sup>4</sup>. The identification and quantification of compounds were performed by liquid chromatography tandem mass spectrometry (LC-MS/MS) with electrospray ionization (ESI), operating in positive and negative ion modes. Chromatographic separation was carried out using a Zorbax SB-C18 column (2.1 x 30 mm, 3.5 µm) at 25 °C, with a flow rate of 0.3 mL min<sup>-1</sup> and an injection volume of 10 µL. The mobile phase consisted of ultrapure water and methanol containing 0.01% (v/v) formic acid and ammonium hydroxide for compounds ionizing in positive and negative modes, respectively. The eluent gradients for the positive and negative modes and the mass spectrometry parameters were described by Santos et al. (2022)<sup>5</sup>. The compounds were monitored in Multiple Reaction Monitoring (MRM) mode. The limit of quantification was 1 ng L<sup>-1</sup> for most compounds, except for bisphenol A (10 ng L<sup>-1</sup>) and paracetamol (5 ng L<sup>-1</sup>).

## RESULTS AND CONCLUSIONS

The findings depicted in Figure 1 illustrate the effectiveness of the treatment system in addressing various contaminants. Bisphenol A, initially present in raw sewage across multiple sampling campaigns, was undetectable following all treatment processes, indicating complete removal at each stage. Caffeine exhibited a substantial reduction post-membrane bioreactor, with removal estimated at approximately 99%. Fipronil demonstrated partial removal, persisting through all treatment stages, including the reverse osmosis concentrate. Furthermore, two fipronil by-products, fipronil sulfone and fipronil sulfide, displayed varying concentrations throughout the treatment stages, emphasizing their persistence and potential environmental impact from raw sewage to reverse osmosis concentrate. Imidacloprid also underwent reduction, particularly after reverse osmosis, although traces were still present in the concentrate. Paracetamol and naproxen showed high removal percentage, approximately 99%. Despite this, their detection in the osmosis concentrate, alongside other contaminants, underscores the necessity of considering not just the efficacy of the primary treatment but also the rejects produced during the process.

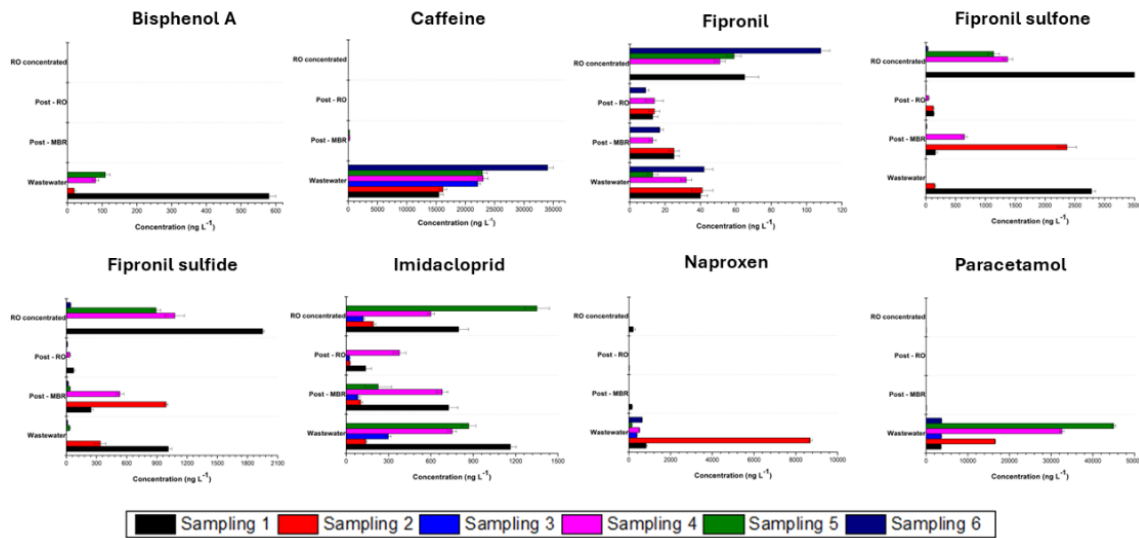


Figure 1. Concentration ( $\text{ng L}^{-1}$ ) of emerging contaminants in wastewater, post-MBR, post-RO and RO concentrated.

Furthermore, Table 1 provides a characterization of the samples concerning turbidity, conductivity, pH, organic matter in terms of total and soluble chemical oxygen demand (COD), as well as suspended solids series. Detailed characterization of samples provides insights into treatment performance and environmental impact.

Parameter	Wastewater	Post-MBR	Post-RO	RO concentrated
Turbidity [NTU]	183 ± 46	1 ± 0	0 ± 0	1 ± 0
Conductivity [ $\mu\text{S/cm}$ ]	1270 ± 262.3	1079.7 ± 62.6	457 ± 445.5	2066 ± 237.4
pH	7 ± 0.4	7 ± 0,3	5 ± 1.3	7 ± 0.6
Total COD [mg/L]	849 ± 33	<LQ*	0 ± 0	<LQ*
Soluble COD [mg/L]	316 ± 283	0 ± 0	25 ± 44	<LQ*
Total Suspended Solids [mgTSS/L]	81 ± 141	0 ± 1	6 ± 10	10 ± 17
Fixed Suspend Solids [mgFSS/L]	59 ± 103	0 ± 0	6 ± 10	9 ± 16
Volatile Suspend Solids [mgVSS/L]	22 ± 38	0 ± 1	0 ± 0	1 ± 1

\*LOQ: Limit of quantification – 48  $\text{mg L}^{-1}$  for COD (total or soluble)

Table 1. Characterization of wastewater, post-MBR, post-RO and RO concentrated.

## ACKNOWLEDGMENTS



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